International Symposium on

New Frontiers in Fiber Materials Science

October 11–13, 2011

Conference Proceedings

Conference Co-Chairs
Dr. Konstantin Kornev, Clemson University
Dr. Philip Brown, Clemson University

Francis Marion Hotel
Charleston, South Carolina, USA
Tuesday, October 11, 2011

CAROLINA A and B
7:00    Registration Desk Opens
7:45    Welcome and Opening Remarks
        Konstantin Kornev (FS, Co-chair)
        Philip Brown (AATCC, Co-chair)
        Martin Jacobs (NTC)
        Ian R. Hardin, Fiber Society President
        Fred L. Cook, AATCC Past President
8:00–8:45 Plenary Talk: Julian Vincent, University of Bath, United Kingdom
        Plant Fibre Structures Inspire Novel Materials and Mechanisms

CAROLINA A
Session: Fibers from Carbon Nanotubes and Applications
Session Chair: Philippe Poulin, CNRS, France
9:15    Composite Wet Spun Polymer—Nanotube Fibers - Philippe Poulin, CNRS, France
9:45    Direct Formation of Carbon Nanotube Fibers During Carbonization Process - Teddy M. Keller, Naval Research Laboratory
10:15   Break
10:30   Recent Advances in Carbon Nanotube Fibres - Juan J. Vilatela, University of Cambridge, United Kingdom
11:00   Nanotailored Carbon Fibers via Ultralong Carbon Nanotubes: Scale-up and Post Processing - Jay B. Gaillard, Savannah River National Laboratory
11:30   Surface Tension Analysis for Characterization of Carbon Nanotube Dispersion - Vijaya Sa, Clemson University
12:00   Lunch On Your Own; Poster Setup, 2:00–4:00, Carolina AB
1:30–5:00 Student Paper Competitions, Gold Ballroom
5:15–7:00 Poster Session, Table Tops, and Reception, Carolina AB

CAROLINA B
Session: Fiber Spinning
Session Chair: Philip J. Brown, Clemson University
9:15    Structure of Porous, High-modulus Polypropylene Fibers - David R. Salem, South Dakota School of Mines & Technology
9:45    Temperature-responsive Fibers for "Smart" Thermal Insulation - Stephen A. Fossey, U.S. Army Natick Soldier RDE Center
10:15   Break
10:30   From Centrifugal Spraying to Nanofiber Spinning - Tao Huang, DuPont
11:00   Free-surface Electrospinning from a Wire Electrode - Keith M. Forward, MIT
11:30   Properties of Nanoclay-added Composite Polypropylene Monofilaments Using Twin and Single Screw Extruders - Sabit Adanur, Auburn University
12:00   Lunch On Your Own; Poster Setup, 2:00–4:00, Carolina AB
1:30–5:00 Student Paper Competitions, Gold Ballroom
5:15–7:00 Poster Session, Table Tops, and Reception, Carolina AB

GOLD BALLROOM
Session: Multifunctional Fibers
Session Chair: Rudolf Hufenus, Empa, Switzerland
9:15    Design and Development of Fibers with Flexure Rate-dependent Viscoelastic Properties - Rudolf Hufenus, Empa, Switzerland
9:45    A Study on the Photostability of Photochromic Fabrics from Hybrid Organosilica Coatings - Marzieh Parhizkar, Deakin University, Australia
10:15   Break
10:30   Piezoelectric Sensor Fibers Based on Meltspun Poly(vinylidene fluoride) and Electrically Conductive Polymer Nanocomposites - Stephan Walter, RWTH Aachen University, Germany
11:00   Bamboo: A Multifunctional "Green" Fibre - Taranunn Afrin, Deakin University, Australia
11:30   Self-decontaminating Multifunctional Nano/Submicrofibers and Nanofibrous Membranes - Gang Sun, University of California, Davis
12:00   Lunch On Your Own; Poster Setup, 2:00–4:00, Carolina AB
1:30 Fiber Society Student Paper Competition
2:45 Break
3:00 NTC Student Paper Competition
5:00 Session Concludes
5:15–7:00 Poster Session, Table Tops, and Reception, Carolina AB

Wednesday, October 12, 2011

CAROLINA A
Session: Electrospun Nanofibers for Composites
Session Chair: Yuris Dzenis, University of Nebraska, Lincoln
8:00 The History of the Science and Technology of Electrospinning from 1600 to 1995 - Kathleen Hofman, NZ Institute for Plant & Food Research, New Zealand
8:30 Mechanical and Morphological Properties of Polymer Nanofibers - Darrell H. Reneker, University of Akron
9:00 Polymer Dynamics During Solution Electrospinning: Experimental Observations of the Structure of the Jet - Eyal Zussman, Technicon, Israel
9:30 Production and Characterization of Electrospun Polyanyline Fibers with High Electrical Conductivity - Yuxi Zhang, MIT
10:00 Break
10:15 Onset of Electrospinning - David Lukáš, Technical University of Liberec, Czech Republic
10:45 Electrospun Nanofibrous Mats for Composite Membranes - Benjamin Chu, Stony Brook University
11:15 Open
11:45 Lunch On Your Own

Session: Electrospun Nanofibers for Composites (continued)
Session Chair: Yuris Dzenis, University of Nebraska, Lincoln
1:30 Needleless Electrospinning and Direct Electrospinning of Nanofiber Yarns - Tong Lin, Deakin University, Australia
2:00 Open
2:30 Biomineralized, Highly Aligned, Nanofiber Array-based Building Unit for Bone Regeneration - Eleni Katsanevakis, Clemson University
3:00 Continuous Nanofiber: Reinforced Structural Nanocomposites - Yuris Dzenis, University of Nebraska, Lincoln
3:30 Break

Session: Advances in Fiber-based Materials
Session Chair: Sergey Lopatnikov, University of Delaware
3:45 Optimizing Conditions for Creating Graphene Coatings to Create Unique Textile Materials - Ian R. Hardin, University of Georgia
4:15 Effect of Cotton Fiber Properties on Properties of Hydroentangled Nonwoven Fabrics - Paul Sawhney, USDA-ARS-SRRC
4:45 Tunable Capillary Pore Membranes - Glen E. Simmonds, DuPont
5:15 Effects of Abrasion on Tenacity of Synthetic Fibers - A. Abu Obaid, University of Delaware
5:45 Session Concludes

6:00–6:45 Fiber Society Annual Business Meeting, Gold Ballroom: Open to Fiber Society Members Only
7:00 Reception, Hotel Lobby
7:30 Awards Banquet, Colonial Ballroom
Speaker: Dr. Adrian Freed, CNMAT, UC Berkeley, and Fine Arts, Concordia University, Montreal
Building Interactivity in Textiles and Related Fibers

CAROLINA B
Session: Advanced Textile Materials
Session Chair: Martin I. Jacobs, National Textile Center
8:00 Photovoltaic Fiber Having Zinc Oxide-Nanoparticles (ZnO-np) and Inverted Layer Sequence - İsmail Borazan, Istanbul Technical University, Turkey
8:30 Textile Heartvalve Prosthesis: Assessment of In Vivo Performances - Frederic Heim, ENSISA, France
9:00 De Novo Assembly of Extracellular Matrix Proteins - Mohammad R. Badrossamay, Harvard University
9:30  Breathable Liquid Repellent Polypropylene Nonwovens for Surgical Gowns - Seshadri Ramkumar, Texas Tech University

10:00  Break

Session: Fiber Science Theory and Computer Simulations
Session Chair: Alejandro Rey, McGill University, Canada
10:15  A Model for Mesophase Wetting of Sheets, Fiber, and Fiber Bundles - Alejandro D. Rey, McGill University, Canada
10:45  Nonclassical Scaling for Forced Wetting of a Nematic Fluid on a Polymeric Fiber - Mohan Srinivasarao, Georgia Institute of Technology
11:15  Textile Composite Structures for Sensor Data Transport from Ocean Depths to Internet - Walter Paul, Woods Hole Oceanographic Institution
11:45  Lunch On Your Own

Session: Fiber Science Theory and Computer Simulations (continued)
Session Chair: Alejandro Rey, McGill University, Canada
1:30  Bending and Position Hysteresis of Magnetic Microfibers in Nonuniform Magnetic Fields - Richard E. Groff, Clemson University
2:00  Structure and Mechanics of Fiber-reinforced Cylindrical Membranes - Yogesh Kumar Murugesan, McGill University, Canada
2:30  Chains of Superparamagnetic Nanoparticles as Biomedical Sensing and Diagnostic Tools - Gary Friedman, Drexel University
3:00  Characterization of Interfiber Capillary Distance for C-CP Polymer Fiber Separations Columns - Christopher L. Cox, Clemson University
3:30  Break
3:45  Dynamics of Rotational Film Fibrillation and Nanofiber Formation - Tao Huang, DuPont

Session: Control of Fiber Structures
Session Chair: Takeshi Kikutani, Tokyo Institute of Technology, Japan
4:15  Effect of the Blending of High-tacticity Component on the Structure and Properties of Elastomeric Fibers of Low-tacticity Polypropylene - Takeshi Kikutani, Tokyo Institute of Technology, Japan
4:45  Polymer Fiber-based Field Effect Transistors: Advances and Opportunities - Richard Gregory, Old Dominion University
5:15  A Process for Noncircular, High-luster Acrylic Fiber - Anasuya Sahoo, Aditya Birla Science & Technology, India
5:45  Session Concludes

6:00–6:45  Fiber Society Annual Business Meeting, Gold Ballroom: Open to Fiber Society Members Only
7:00  Reception, Hotel Bar
7:30  Awards Banquet, Colonial Ballroom
Speaker: Dr. Adrian Freed, CNMAT, UC Berkeley, and Fine Arts, Concordia University, Montreal
Building Interactivity in Textiles and Related Fibers

GOLD BALLROOM
Session: Carbon Fibers and Composites
Session Chair: Amod Ogale, Clemson University
8:00  Crystalline and Tensile Properties of Carbon Nanotube-filled Polyamide-12 Fibers Meltspun by Industry-related Processes - Sanjukta Chatterjee, Empa, Switzerland
8:30  Electromagnetic Shielding Mechanisms of Ultrahigh Thermally Treated Carbon Nanofibers-LLDPE Nanocomposites - Byron Villacorta, Clemson University
9:00  Open
9:30  Mechanical Properties of Composite Plates Produced from 1x1 Rib Knit Fabrics with Carbon Fibers - Mehmet Emin Yuksek, Usak University, Turkey
10:00  Break
10:15  High Thermal Conductivity Carbon Fibers and Fabrics: Low-cost Petroleum Pitch Precursors - Young-Pyo Jeon, Clemson University
10:45  Rapid Manufacture of Carbon Fiber from Organosolv Lignins - Darren A. Baker, University of Tennessee
11:15  Open
11:45  Lunch On Your Own
Session: Fiber-based Probes and Sensors
Session Chair: Margaret Frey, Cornell University
1:30 Electrospun Nanofibers for Microfluidic Analytical Systems - Margaret W. Frey, Cornell University
2:00 Micro- and Nanofiber Bundles as a Platform for Sensitive Detection of Biomacromolecules - Kenneth A. Christensen, Clemson University
2:30 Fabrication and Characterization of Electrospun Semiconductor Nanoparticle-Polyelectrolyte Ultrafine Fiber Composites - Caroline L. Schauer, Drexel University
3:00 Development of a Rapid Fiber-based Immunoassay - Ryan Waddell, Clemson University
3:30 Break
3:45 Fiber-based Biosensors for mRNA Extraction from Cells - Victor Maximov, Clemson University
4:15 Self-assembly of Optically Responsive Nematic Liquid Crystal/Polymer Core-Shell Fibers - Ebru A. Buyuktanir, Kent State University

Session: Functionalization of Fiber Surfaces
Session Chair: Igor Luzinov, Clemson University
4:45 Microwave-promoted Deposition of Functionalized Nanoscopic Silica Coatings for Protective Textile Applications - Jeffery Owens, AFRL
5:15 Surface-tethered (Bio)Macromolecular Nanostructures Synthesis and Characterization - Stefan Zauscher, Duke University
5:45 Session Concludes

6:00–6:45 Fiber Society Annual Business Meeting, Gold Ballroom: Open to Fiber Society Members Only
7:00 Reception, Hotel Bar
7:30 Awards Banquet, Colonial Ballroom
Speaker: Dr. Adrian Freed, CNMAT, UC Berkeley, and Fine Arts, Concordia University, Montreal
Building Interactivity in Textiles and Related Fibers

Thursday, October 13, 2011

CAROLINA A
Session: Protective Clothing and Wetting of Textiles
Session Chair: Jeffery Owens, AFRL
8:00 Dynamics of a Drop on Elastic Fibers - Camille Duprat, Princeton University
8:30 Open
9:00 Textiles for the Next Generation of Military Clothing - Eugene Wilusz, U.S. Army Natick Soldier RDE Center
9:30 Toward Self-cooling Gradient Shell for Body Armor - Ruslan Burtovyy, Clemson University
10:00 Break
10:15 Oleophobic Coating for Self-cleaning, Fluid-resistant Textiles - Laura Habersack, Luna Innovations Inc.
10:45 Observations on the Behaviour of Chemical Warfare Agents and Other Liquids on Super-repellent Textiles - Corrine Stone, Dstl, United Kingdom
11:15 Moisture Transport and Reaction Enhancements in Fabrics - Heidi Schreuder-Gibson, U.S. Army Natick Soldier RDE Center
11:45 Wettability Gradient-driven Directional Water Transport Across Thin Fibrous Materials - Tong Lin, Deakin University, Australia
12:15 Generation of Short Hypersonic Water Jet for Testing of a Material's Rain Erosion Resistivity - Sergey Lopatnikov, University of Delaware
12:45 Conference Concludes

CAROLINA B
Session: Biomimetics for Fiber Science
Session Chair: You-Lo Hsieh, University of California, Davis
8:00 Artificial Proboscises - Konstantin G. Kornev, Clemson University
8:30 Botanical Hydroscopic Shape Change Mechanisms for Composite Textile Systems - Veronika Kapsali, MMT Textiles, United Kingdom
9:00 Ant-Tex: 3-D Visualization of the Water-repellent Network of Fire Ants - Nathan Mlot, Georgia Institute of Technology
9:30  Structure-Function Relationships in Synthetic Spider Silk Fibers Made from Chimeric Proteins - Florence Teulé, Utah State University
10:00  Break
10:15  Biopolymer-assembled Nanofibers - You-Lo Hsieh, University of California, Davis
10:45  Biochemical Characterization of Spidroin Self-assembly - William Marcotte, Clemson University

Session: Polymer Synthesis and Recycling
Session Chair: Fred Cook, Georgia Institute of Technology
11:15  Removal of Spandex from Polyamide/Spandex-blended Fabrics by Selective Depolymerization - Youjiang Wang, Georgia Institute of Technology
11:45  Polymer Waste Streams for Synthetic Turf Infill - Richard E. Harper, Georgia Institute of Technology
12:15  Comparative Study of Characteristics of Knitted Fabrics Made of Recycled Fibres - Karina Takamune, University of São Paulo, Brazil
12:45  Conference Concludes

GOLD BALLROOM
Session: Functionalization of Fiber Surfaces (continued from Wednesday)
Session Chair: Igor Luzinov, Clemson University
8:00  Surface Functionalization of Fibers by Grafting to Method - Igor Luzinov, Clemson University
8:30  Inkjet Printing Equipment for Narrow Fabrics - Bertram Wendisch, ENSISA, France
9:00  Formation and Application of Functional Coatings on Synthetic Fibers - Jan Genzer, North Carolina State University
9:30  Stimuli-responsive Alginate Fibers - Sergiy Minko, Clarkson University
10:00  Break

Session: Optical Fibers
Session Chair: Sylvain Danto, Clemson University
10:15  Investigation of Subcritical Crack Growth in Glass Fibers Using Load Relaxation Tests on Bundles - Jacques Lamon, CNRS/National Institute of Applied Science, France
10:45  Advances in Semiconductor Core Optical Fibers - Stephanie Morris, Clemson University
11:15  A Phototherapy Device Prototype for Neonatal Jaundice Based on POF Fabric - Jing Shen, Hong Kong Polytechnic University, China
11:45  Low-loss, High-strength Fibers from Improved Chalcogenide Glasses - Sylvain Danto, Clemson University
12:15  Optically Active Polymeric-based Fibers - Philip Brown, Clemson University
12:45  Conference Concludes

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Poster Session: Tuesday, October 11, 5:15–7:00, Carolina AB
Session Chair: Konstantin Kornev

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Chen-Chih Tsai  Highly Aligned Electrospun Nanofiber Yarns
Maryana Kovalchuk  Fiber-based Probes for Cell Analyses
Tieling Xing  Structure and Properties of Silk Grafted with N,N-Dimethylaminoethyl Methacrylate via ARGET ATRP Method
Austin Beachler  Spreading of Liquids on Porous Surfaces
Mahmut O. Kesimci  Development of Surface Differential Scanning Calorimeter for Evaluation of Evaporative Cooling Efficiency
Taras Andrukh  Imbibition of Liquids into Capillaries
Nancy Elizabeth Allen  Incorporation and Performance of Molecular Polyoxometalates in Cellulose Substrates
Xiao-Shi Xu  Mechanism of Surface Roughness Development in Melt Spinning of Blend Fibers for Artificial Hair
Michael S. Ellison  The Challenges of Material Selection for Compliant Robotic Surfaces
Sam Lukubira  Melt Spinning of Soy Flour-based Fibers
Martin W. King  The Effect of Silver Antimicrobials on the Physical and Thermophysiological Properties of Burn Pressure Garments
Mustafa E. Üreyen  Imparting Multifunctional Properties to PES/Cotton Woven Fabrics by Fluorocarbon and Silver-based Finishing Agents
Laura E. Lange  Effects of Plasma Etching on Self-decontaminating Properties of Magnesium Oxide Nanoparticles in Polypropylene Fibers
Zarife Doğan  A Novel Silver Sulfadiazine-loaded Electrospun Nanofiber Wound Dressing
Usha Sayed  Biomimicking of Enzymes for Textile Processing
Chen-Chih Tsai  Microwave Heating Study of Carbon Nanofiber Nanocomposites no hyphen
Shinjung Yoo  Upper Body Sweat Rate, Skin Temperature, and Clothing Microclimate Distribution During Winter Cycling with Air Flow
Kaiyan Qiu  “Green” Composites Using Soy Protein Resin and Novel Low-cost Carbon Source-based Bacterial Cellulose
Yinan Lin  Mechanical Properties of Polymer Nanofibers Revealed by Interaction with Streams of Air
Daria Monaenkova  Bernoulli Catenary and Elasto-capillary and –wetting Effects of Fibrous Materials
Usha Sayed  Anti-soiling Finish of Polyester Fabrics
Lin Shu  Intelligent Footwear System for Continuous Dynamic Foot Monitoring in Daily Activities Based on Fabric Pressure Sensors
Nyssa Thongthai  The Effect of Annealing and Doping on Crystallinity and Conductivity in Polyaniline for Processable Films and Fiber
Kathleen Hofman  A History of Electrospinning 1600–1995
NTC Posters

Title

Blue Light Curable Ink Chemistry for Textile Digital Printing
Active Nanocoatings for Textiles
Novel Polymerizable Bifunctional Flame Retardants
Polymer Flow in Confined Elastic Boundaries: Stronger Continuous Nanofibers
Engineered Reinforced Structures from Short Fibers
Fiber-based Bioreactor Media for Air Pollution Control
Challenges in Advanced Nanofiber Wound Dressings
Fluids in Fabrics
Melt Spinning of Cellulose-based Fibers
3D Textile Architecture for Tissue Engineering Scaffold
Fiber-based Biohazard Sensor Assemblies
Electroluminescence
Nanoscale Surface Embrittlement of Fibers
Electrospun Composite Nanofibers for Lithium-Ion Batteries
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Functional Fibers via Biomimetics and Inorganic-Organic Hybrids
Feasible Fiber-Nanoparticle Systems for Commercial Applications
Nanofibrous Materials as Sensors for Heavy Metals
Light Emitting Nanocomposite Fibers (LENFs)
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Masculine Style(s): Shifting Identities and Textile/Apparel Industry Opportunities
National Research Network on Multifunctional Protective Clothing
Effective Thermal Conductivity of Fibrous Materials
Development of Visual Fit Assessment Tool for Apparel Firms
Integrated System to Design and Produce Engineered Knit Garments
Logistics of Closed Loop Textile Recycling
Sustainability Checklist Manifesto for New Textile Products
Fibers from Carbon Nanotubes and Applications
Composite Wet Spun Polymer—Nanotube Fibers

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OBJECTIVE
This paper deals with the development of fiber wet spinning processes for the production of polymer composite fibers loaded with a large fraction of carbon nanotubes. Kinetics of fiber coagulation, fiber properties and potential applications will be discussed.

INTRODUCTION
Carbon nanotubes offer novel opportunities for the development of composite polymer fibers with improved properties or new functionalities. In particular, conductive fibers and textiles could find applications in heating structures, functional composites with sensing or actuating capabilities. Nevertheless, the inclusion of large fractions of carbon nanotubes in polymer fibers is not straightforward. Direct addition of nanotubes to polymers induces a strong increase in viscosity which makes extrusion and melt spinning difficult. By contrast, wet spinning from nanotube dispersions in aqueous or non-aqueous solvents allows fibers with greater fractions of carbon nanotubes to be produced. Optimization of such processes requires a good knowledge of the coagulation mechanisms when the dope is injected in coagulating media. We present in this paper an approach to measure the kinetics of solidification of composite fibers in liquid media. The systems under study are made of polyvinyl alcohol (PVA) – carbon nanotube composite fibers (1, 2). The mechanical and electrical properties of the fibers will be discussed. In particular it will be shown that fiber drawing has positive effects on the mechanical properties whereas it tends to lower the electrical conductivity. It will also be shown how hot drawing leads to storage of mechanical stress in the fibers (3). The residual stress can be assessed by Raman spectroscopy and its manifestation can be used for novel shape and temperature memory phenomena (4).

APPROACH
The kinetics of fiber solidification of PVA-CNT fibers in liquid media is investigated in millifluidic devices (5). The fibers are circulated in cylindrical pipes with diameter constrictions as sketched in Figure 1.

FIGURE 1. Sketch of a diameter constriction in a glass pipe used to create an elongationnal stress capable of breaking fiber materials.

An elongational flow field develops at the constriction. This leads to viscous frictional forces on the fibers. Depending on its state of solidification the fiber can sustain the resultant stress or break if it is not yet sufficiently solidified. Examples of these limiting cases are shown in Figure 2. This approach allows measurements of the evolution of strength of the fiber with increasing its residence time in the coagulating medium. The results are particularly helpful for the optimization of the fiber spinning process. The mechanical and electrical properties are characterized using conventional equipments for fiber characterizations. The fibers are drawn at high temperature in order to improve the degree of alignment of the polymer chains and of the carbon nanotubes along the fiber axis. It is observed that hot drawing at a temperature $T_d$ (with $T_d$ in between the glass transition and melting temperatures of the neat PVA) leads to a substantial storage of stress. Mechanical energy is restored by re-heating the fibers; giving rise to shape memory phenomena. These shape memory phenomena are associated to a large generation of mechanical stress and to a surprising temperature memory effect. The level of stored mechanical energy can be assessed by Raman spectroscopy.

RESULTS AND DISCUSSION
Examples of the evolution of the strength of fibers as a function of the residence time $t$ in a coagulating media are shown in Figure 3 for PVA of different molecular weight. It is observed that the strength evolves as $t^{1/2}$. This suggests that the solidification is limited by diffusion mechanisms.
FIGURE 3. Strength of composite PVA-nanotube fibers as a function of the square root of their residence time in a coagulating medium. The obtained fibers are electrical conductive. Their conductivity as a function of strain exhibits a quadratic decrease at large strain. This behavior is explained by considering the relative translation of the nanotubes with respect to each other as the fiber is stretched. Fibers drawn at high temperature \( T_d \) and subsequently frozen below \( T_g \), the glass transition temperature of the neat PVA, store a significant amount of mechanical energy. The latter is restored by re-heating the fibers above \( T_g \). As shown in Figure 4, a peak of generated stress at fixed strain is observed when the fibers are reheated. Surprisingly, the peak temperature is observed at \( T_d \); reflecting thereby an actual temperature memory of the fiber materials. The origin of this temperature memory is still unclear but possible consequences of gradients of \( T_g \) at the interface of the nanotubes are proposed to explain the observed phenomena.

Lastly it will be shown how the storage of stress in nanotube-polymer fibers can be assessed using polarized Raman spectroscopy. We have indeed found that the Raman response of nanotubes exhibits a distinct sensitivity to strain when embedded in polymers which have experienced different thermal and mechanical treatments. While structural characterizations achieved by X-ray scattering do not allow materials to be differentiated, large changes of Raman bands sensitivity to strain are observed as a function of the stored mechanical energy.

CONCLUSIONS
Carbon nanotube-PVA fibers exhibit original features which can be of potential uses in future applications from heating textiles to mechanical sensors through shape memory structures. The results shown in this work provide guidance for the optimization of the processing of such fibers and the main features of their mechanical, electrical and thermal properties.

REFERENCES

FIGURE 4. Stress generated by a nanocomposite fiber when it is reheated. The strain is fixed and the temperature is increased from deformed. A peak of generated stress is observed in each case for a temperature roughly equal to \( T_d \).
Direct Formation of Carbon Nanotube Fibers During Carbonization Process

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PURPOSE/OBJECTIVE: Direct formation of carbon nanotube fibers from common carbon/graphitic precursor materials such as polyacrylonitrile.

INTRODUCTION
Carbon nanotubes (CNTs) are currently the object of intense research efforts due to their unique mechanical, magnetic, electrical, and optical properties and have been proposed as building blocks for future nanotechnologies. Many applications have been proposed ranging from polymeric structural composites to nanoelectronic devices, which would benefit from the availability of CNTs of varying diameters in large quantities. These potential applications depend on the development of a low-cost and readily scalable route to CNTs.

The NRL has developed a unique method for the synthesis and formation of multi-walled carbon nanotubes (MWNTs) in shaped, porous carbonaceous solids based on the thermal decomposition of melt-processible organometallic compounds and/or metal salts in the presence of an excess amount of a carbon precursor, ultimately forming MWNTs during the carbonization process in shaped solids, films, and fibers [1,2]. Carbon nanotube fibers can be produced from polyacrylonitrile (structural fibers) and petroleum pitch (thermal control fibers) in the presence of a minute quantity of a metal salt or an organometallic compound. The growth of the CNTs proceeds in the solid phase during the carbonization process. In the synthesis, only a minute quantity of metal nanoparticles is required to initiate the formation of CNTs in the developing carbonaceous solid. Shaped CNT-containing compositions can be readily fabricated by our novel method.

Today, there is currently an intense effort throughout the scientific community to efficiently disperse CNTs into polymeric fibers to take advantage of the exceptional mechanical properties of carbon nanotubes [3-5]. Moreover, various research groups have used aerogels and fuming sulfuric acid to utilize the CNTs grown by chemical vapor deposition (CVD) in the formation of CNT-containing fibers. Carbon fibers derived from polyacrylonitrile (PAN) have been the dominant reinforcement in advanced composites since their commercialization in the late 1960s. By using a liner polymer such as PAN, which can be spun into a fiber, stabilized, and then carbonized, the formation of CNT fibers has been exploited using the NRL breakthrough method for the formation of CNTs.

APPROACH
Carbon nanotube-containing fibers can be fabricated by drawing from the melt of a B-staged thermoset resin at elevated temperatures or by conventional spinning techniques of a carbon precursor followed by carbonization. In an effort to develop a method for the fabrication of CNT-containing fibers formulated directly from the precursor carbon material, experiments have been conducted at the NRL, whereby fibers were drawn from the melt of a Fe_2(CO)_9/phthalonitrile precursor composition and by the deposition of a fiber into water from a solution of Fe_2(CO)_9/polyacrylonitrile (PAN) or Co_2(CO)_8/PAN in a dipolar aprotic solvent. The fibers are stabilized in air at 250-300°C. The polymeric stabilized fibers were used in the direct formation of the carbon nanotube (MWNT) fibers by slowly heating to temperatures above 1000°C under inert conditions. Our studies show that any materials that can be spun or drawn into a fiber and carbonized by the NRL breakthrough method can be converted into carbon nanotube-containing fibers. We are able to achieve the direct formation of CNT fibers using a simple carbonization process from precursor materials such as PAN and petroleum pitches that are currently used to form carbon and graphitic fibers.

RESULTS AND DISCUSSION
Since we have demonstrated by our method that the formation of CNTs can occur directly from a mixture of a metal salt such as Fe_2(CO)_9 and PAN, pitches, or phthalonitriles in a shaped composition including large diameter fibers and rods, these precursor compositions are ideal candidates to spin polymeric fibers that can be directly converted into MWNT-fibers during the
carbonization process. Upon cure and carbonization of the polymeric fiber, x-ray diffraction (XRD) and TEM studies confirmed the presence of copious amounts of MWNTs in the carbonized fibers. SEM images (Figure 1) show that the CNTs can be potentially aligned within small diameter sized fibers (micron-and nanometer-sized fibers).

Both polymeric nanofiber sheets and micron-sized unidirectional fibers were spun from a dipolar aprotic solvent-metal salt/PAN mixture by electrospinning and conventional spinneret techniques. The polymeric sheets and fibers were stabilized in air by heating at 250 °C for 3-5 hr and at 300°C for 5 min. The stabilized sheets were then heated at 1000°C for 2 hr whereas the polymeric fibers were heated at 1300°C and 2700°C to afford CNT-containing carbon fibers. The small metal nanoparticles that form below 350°C catalyzed the in situ formation of the CNTs within the fibers during the carbonization process under atmospheric inert conditions. Figures 2 and 3 show SEMs of a CNT nanofiber carbon sheet and CNT-containing carbon fibers, respectively.

CONCLUSION
We have demonstrated that CNTs can be grown in situ from an embedded metal nanoparticle within a fiber during thermal treatment to elevated temperatures. A simple carbonization process, which is currently used by industry to produce carbon and graphite fibers, is being utilized to form the CNTs within the carbon fibers. The growth of the CNTs is catalyzed by the metal nanoparticles embedded within the fibers. Only a small quantity of the nanoparticles is needed to initiate the formation of the CNTs. Potential payoffs and impact areas of the CNT fibers include structural, energy, membrane, nanoelectronic, air filtration, and various catalytic applications.

FUTURE WORK
Follow-on programs are planned to optimize the processing procedure and selected physical properties of the CNT-containing fibers for possible transition to industry. Selected physical property determinations will be performed on the CNT nanofiber sheets/fibers and the CNT-containing fibrous materials will be evaluated for specific applications.

ACKNOWLEDGMENT
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Recent Advances in Carbon Nanotube Fibres

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ABSTRACT REQUIREMENTS
There is an ever increasing need of reducing the weight of materials used in many applications in order to decrease energy consumption throughout the manufacturing, service and disposal/recycling stages of their lifecycle. A clear opportunity to achieve this goal is through the use of novel nanostructured materials that can provide additional functionality. As a consequence of their size and atomic structure, nanomaterials have a range of unique properties often not found or difficult to realise in the bulk. Examples of these are: boron nitride (BN) nanotubes with stiffness of ~ 1TPa [1], carbon nanotubes (CNTs) with thermal conductivity of ~ 3000 W/mK [2] and an electrical conductivity close to that of copper [3], graphene layers with an estimated specific surface area of 2630 m²/g. These properties are exceptional; however, the challenge is to produce macroscopic materials that exploit the outstanding properties of these individual ‘molecules’. For nanotubes, their elongated shape and axial properties suggest that the optimal arrangement is a fibre, with the nanotubes aligned parallel to each other and to the fibre axis. This route is consistent with traditional methods for making strong/stiff fibres based on long backbones of carbon-carbon bonds extended along the fibre axis and parallel to each other, as proposed some eight decades ago [4].

Carbon nanotube fibres can be spun directly from the reactor by drawing them out of the hot-zone during CNT growth by chemical vapour deposition (CVD) [5]. This process is continuous and allows production of CNT fibres at rates of 10 – 100 m/min. The fibres have typical tensile strength and stiffness of 1.5GPa and 100GPa, respectively; although values as high as 9GPa and 360GPa have been observed [6]. The material is also thermally and electrically conductive, with present values at 100W/mK and 8x10⁻⁵ S/m [7]; has similar chemical and thermal resistance like graphite; and shows high resistance to cutting and exceptional tolerance to bending [8].

The structure of CNTs fibres is unusual for a high-performance fibre. Rather than solid, its structure resembles that of a yarn like cotton [9], with the small subfilaments being the nanotube bundles (Figure 1). This network structure means that the internal surface is orders of magnitude higher than the surface area of a traditional reinforcing fibre. Indeed, BET measurements give values in the range of 200m²/g. In the context of polymer composites, this structure results in polymer chains penetration into the fibres, which enhances the adhesion and thereby, the mechanical performance of the CNT fibre composites [10].

ACKNOWLEDGMENT
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REFERENCES
Nanotailored Carbon Fibers via Ultralong Carbon Nanotubes: Scale-up and Post Processing

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INTRODUCTION
The goal of the proposed work is to refine and scale-up the production of high strength continuous threads prepared from ultra-long (>3mm) carbon nanotubes (CNTs). Beginning shortly after their discovery in 1991, carbon nanotubes were used as additives to polymer materials in an attempt to impart strength and electrical conductivity to the composites. Due to the large difference in properties (particularly strength and strain-to-failure) between nanotubes and traditional reinforcing fibers, CNTs have the potential to outperform these other reinforcing fibers. Preliminary efforts to produce carbon nanotube threads have shown the potential to achieve similar strength and modulus to standard carbon fibers, such as PAN-based AS4 fiber, but with a higher strain to failure [1]. If these properties could be maintained in a scaled-up process, the production of composite threads with the same strength and stiffness of carbon fibers, but at a much higher toughness, would be possible.

To develop effective CNT fibers and production methods capable of leveraging the potential benefits of employing carbon nanotubes as a replacement material for carbon fibers, the mechanics controlling the final tensile properties of the fiber bundle should be understood. Harele’s classic approximation [2] is a useful guide for elucidating what role the properties of various component fiber play in determining the final strength properties of twisted threads:

$$\frac{\sigma_v}{\sigma_f} \approx (1 - k \sin^{-1} \alpha) \cos^2 \alpha$$  \hspace{1cm} (1)

$$\sigma_v/\sigma_f$$ - ratio of thread strength to component fiber strength

$$\alpha$$ - helix angle that component fibers make with the thread’s principal axis

$$k = \frac{1}{3} \left( \frac{d}{\mu L} \right)^{\frac{1}{2}}$$

$$d$$ - component fiber diameter

$$L$$ - component fiber length

$$\mu$$ - coefficient of friction between component fibers

$$Q$$ - fiber migration length (distance along thread over which the fiber migrates from the outer surface to deep interior and back again)

Generally speaking, the tensile strength of twisted fiber-bundle threads increase as the component fibers get longer (L↑) and smaller in diameter (d↓). This motivates the inclusion of ultra-long CNTs as the fiber component. In addition, as might be expected, increasing the friction (μ↑) between the component fibers by improving the inter-fiber contact forces and increasing the intertwining of the component fibers (Q↑) both act to increase the overall thread strength. The effect the helix angle has on fiber strength is not immediately obvious. On the one hand decreasing this angle aligns the strong fibers with the thread axis, which has a positive effect on the strength (cos²α↑). However, as the helix angle decreases the compressional effect on the fiber bundle decreases, which reduces the effects of fiber-fiber interactions (sin¹α↑).

APPROACH
Millimeter long CNT arrays have been grown by various academic groups over the past few years. For example, Geoghegan et al. [3] grew millimeter long multi-wall nanotube (MWNT) arrays on Si using a multi-layered catalyst system of Al₂O₃/Fe/Mo. Recently, Yun et al. [4] at the University of Cincinnati used a similar multi-layered system of Al₂O₃/Fe with the addition of water vapor to grow aligned arrays of CNTs exceeding 1 cm in length. Dry spinning of nanotubes from forests have been demonstrated [5], but for the most part, these prepreg methods limit the spinnability of the CNT forest to ~1.2mm forest heights. Our growth methods are not limited by length due to a continuous catalyst feedstock.

We have employed a floating catalyst Chemical Vapor Deposition (CVD) method (Fig. 1) using xylene/ferrocene as the precursor for CNT growth. The floating catalyst method is an in-situ method which eliminates the step of pre-preparing the catalyst on substrates, a method that requires metal evaporation steps. Based on specific control of the process parameters, ultralong carbon nanotubes are grown at atmospheric pressure in the reactor zone on cleaned quartz or silicon substrates. The nanotubes were found to grow at 30mm in diameter and up to 11 mm long. Figure 2 shows an SEM image of the ultralong MWNTs.

RESULTS AND DISCUSSION
Figure 1 shows a CNT fiber being spun using our ultralong nanotubes. The sample was handspun and placed across two pieces of conductive carbon tape. The ultralongs have been spun into 20 m spools using a mechanical spinning apparatus.

![Figure 1. Schematic of CVD growth for ultralong CNTs.](image-url)
We have spun yarns using the ultralong nanotubes and embedded them with Epon 862 and curative W. Using a 10% Epon solution in acetone, yarns were mechanically spun at 2500 rpm, soaked in the Epon solution, and then post-spun before the curing cycle. The strengths were measured up to 3 GPa with a modulus of 180 GPa using a 5 mm gauge length and 1 mm/s pull rate. These results are based on using a 0.04 g/km TEX value of the yarn after epoxy infiltration. The values calculated according the cross-sectional diameter were almost an order of magnitude less in strength. However, the yarns were found to double in strength using Epon 862 in the yarns.

Two additional methods were investigated for producing yarns from ultralong CNT forests including baling (wet spinning) and directional double rolling the forests into sheets and subsequent spinning. These methods can be used to spin yarns from forests that are not pullable from the dry state. For the baling method, the yarn strengths were lower, but they were found to be defect free since their strengths were independent of gauge length.

Several properties of the epoxy/nanotube yarns will be presented including the effect of cure time. For instance, we found that the shape of the curves shows that a fully cured epoxy is brittle while the partially cured yarn has plastic properties. An additional characterization method includes the failure modes of the yarns. SEM images revealed that the yarns can fail catastrophically, by separation of twisted segments, and by necking. The results will be presented.

CONCLUSIONS

We have successfully demonstrated that ultralong nanotubes up to 11 mm in length can be continuously dry spun into yarns. The infiltration of Epon 862 and curative has the potential to substantially improve, in this case double, the CNT yarns strength and modulus. Future efforts will include increasing the nanotube to nanotube friction, decrease their diameters, and improve densification to eliminate the yarns porous structure.

ACKNOWLEDGMENT

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Surface Tension Analysis for Characterization of Carbon Nanotube Dispersion

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OBJECTIVE
This work aims to develop an effective tool for the characterization of highly loaded dispersions of carbon nanotubes. These dispersions are black and cannot be analyzed by the existing optical methods.

INTRODUCTION
For effective use of carbon nanotubes in polymeric composites, it is important to have a uniform dispersion in the dispersant. Surfactants are widely used to disperse and stabilize the nanotubes against clustering. Sodium dodecyl sulfate (SDS) is a common surfactant used for nanotube dispersing in water [1-3]. The advantage of using SDS-stabilized nanotubes in aqueous solutions of polyelectrolytes was discussed in Ref. [4].

, The characterization methods used for the analyses of carbon nanotube dispersions include UV-vis, atomic force microscopy, scanning electron microscopy, transmission electron microscopy, and dynamic light scattering -11]. As the concentration of nanotubes in water increases these methods fail to characterize the dispersions. All available methods assume that the dispersion is very dilute, in the range of 0.01 wt % nanotubes or lower [5-11]. At higher nanotube loadings, the blackness and opacity of the dispersion makes it extremely difficult to characterize the structure of the nanotubes in the solution. We explored the surface tension analysis as a possible way to characterize the surfactant enabled nanotube dispersion with any level of nanotube loading.

APPROACH
To prepare the aqueous single-walled carbon nanotube dispersions, SDS was dissolved in water in the range concentrations varied between 0.347 mM to 85 mM. These solutions were loaded with 0.30 wt % nanotubes and sonicated for 15 min using a horn sonicator. Surface tension of the solutions before after nanotube adding was measured using Kruss DSA10 instrument. A typical critical drop that is about to fall is shown in Figure 1. Average of three measurements was taken to obtain the final surface tension for each solution.

RESULTS AND DISCUSSION
The change of surface tension with the variation of surfactant concentration and nanotube loading is shown is Figure 2. As shown in this Figure, the surface tension decreases with SDS concentration and then it becomes almost constant after crossing the critical micelle concentration (CMC). Aqueous solution of SDS reaches the CMC at around 8 mM.

FIGURE 1. A typical critical drop for surface tension measurements

FIGURE 2. Variation of surface tension with surfactant and nanotube loading fitted with sigmoidal fitting

For the 0.30 wt % nanotube dispersion, the CMC was shifted to the right and it was estimated to be 10 mM. This analysis has been conducted for different SDS-nanotube dispersions and the CMC was obtained for all dispersions.

We also studied the SDS adsorption on nanotubes with the variation of concentration of SDS in the dispersion.

The developed analysis was applied to optimize the polymer-nanotube composition in the dope that we used to spin carbon nanotube-alginate fibers. In Figure 3 we show the pictures of the produced fibers [4].

CONCLUSIONS
We have proved the idea of characterization of nanotube dispersions using surface tension measurements.
A significant amount of information was extracted from the surface tension analyses. We studied the CMC dependence on nanotube loading, adsorption of SDS on nanotube surface, and SDS-nanotube phase diagram. This method becomes more useful for high level of nanotube loading where other typical nanotube dispersion characterization methods do not work.

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Fiber Spinning
Structure of Porous, High-modulus Polypropylene Fibers

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INTRODUCTION
A new class of polypropylene multifilament yarn has been developed by Innegrity LLC [1] which combines a high modulus (> 40% of the theoretical value for a perfect iPP crystal lattice), a toughness equivalent to gel-spun UHMWPE fibers, and a density lower than that of amorphous polypropylene. These properties are obtained from polymers of standard molecular weight via a high-output, melt-spin/hot-draw process that imparts unusual structural characteristics to the fiber. This study explores these structural features in detail with the goal of revealing the physical mechanisms by which the advantageous combination of fiber properties are achieved.

APPROACH
A key aspect of the fiber-forming process used to make the high modulus polypropylene (HMPP) fibers in the present study is that the melt-spinning conditions are designed to crystallize the filaments while the polymer is in a highly relaxed, highly disoriented state [1]. Despite the high crystallinity of the resulting (as-spun) precursor filaments, high draw ratios and efficient chain orientation are achieved in the subsequent high temperature drawing operation.

The structure and properties of three HMPP multifilament yarns (IN1, IN2 and IN3), produced by the method outlined in US Patent 7,074,483 [1], were studied. In each case the molten isotactic polypropylene was extruded through a spinneret and then quenched into a liquid bath at room temperature, just below the spinneret orifice. After exiting the quench bath, the filaments entered a heated draw zone comprising a set of drawing rolls enclosed in an oven set to 160°C. For all three samples, the roller speeds were set to impose a draw ratio of 16. After exiting the oven, samples IN1 and IN2 were wound up on a take-up roll whereas the IN3 filaments passed, under tension, through a second heating zone at about 162°C before being wound up.

For the purposes of comparison, the following samples were also included in the investigation:

IN0: As-spun (quenched, undrawn) Innegrity filaments (MFI 1.3)
ST: Commercial standard tenacity fiber
CHT: Commercial high tenacity fiber

RESULTS AND DISCUSSION
Crystallinity and Orientation
WAXS and SAXS patterns indicate that the quenched, undrawn, filaments (IN0) contain spherulitic α-form crystals. Since rapid quenching has generally been observed to result in the formation of a predominantly mesophase structure, the well-developed α phase of the IN0 filaments mostly likely results from the presence of nucleating agent in the molten polymer. The subsequent high temperature drawing operation causes the crystals, which remain and/or recrystallize in the α form, to become highly oriented in the fiber axis direction (fc = 0.99). This is accompanied by a significant increase in crystallinity. Results from WAXS, FTIR and DSC methods concur that the crystalline fraction of the HMPP fibers lies between about 0.75 (IN1) and 0.8 (IN3), compared with about 0.5 for the undrawn filaments (IN0). The degree of crystallinity of the standard tenacity fiber (ST) and the conventional high-tenacity fiber (CHT) is about 0.5 and 0.65 respectively.

An absence of SAXS meridional reflections indicates that the Innegrity HMPP fibers, unlike the ST and CHT fibers, do not contain a significant fraction of chain-folded crystals and do not comprise alternating crystalline-amorphous regions along the fiber axis, although highly oriented noncrystalline regions are likely to be present.

Void Formation and Fiber Density
Despite having a high level of crystallinity and crystalline orientation, the density of the HMPP fibers is about 0.84 g/cm³; somewhat below the density of iPP in the amorphous state (0.85 g/cm³). The reason for the low fiber density is the presence of extensive crack formation, which results in a void volume of about 10%. High void volume and surface roughness results in a surface area of 1.5 m²/g, measured by BET, which is about eighteen times higher than would be expected from a void-free fiber of equal diameter. This level of void formation does not appear to have been observed previously in highly drawn polyethylene and polypropylene fibers, except after etching the fiber surface [2]. It appears that the voids develop from density deficient regions between fibrils, which arise from transverse stresses accompanying fibril formation during uniaxial drawing.

A major advantage of the HMPP fibers of the present study is their combination of high modulus (up to ~19GPa), high tenacity (~0.7GPa), high energy of absorption or toughness (~50MPa) and low fiber density (~0.84 g/cm³), and it is of interest to understand how the...
superior mechanical properties of these fibers are maintained despite the existence of a high void volume.

**Striations and Crack-Stopping Mechanism**

A significant factor that may mitigate the effects of extensive crack propagation on mechanical properties is the transverse bands or striations evident in SEM images of the HMPP fibers (Figure 1). These features must evolve during the drawing process since they are absent in the as-spun fibers. Similar striated structures have been observed in highly drawn polyolefin fibers and films by others [2, 3]. In the SEM image of Figure 1 (left), the transverse bands are manifested as quasi-periodic microscale fluctuations in SEM intensity, with the shorter, higher intensity bands (striations) having a fiber-axis dimension of the order of 0.5 - 1 μm and a quasi-periodicity along the fiber length of the order of several micrometers. The longitudinal cross-sectional view of Figure 1 (right) confirms that the striations are not merely ring-like surface features, but extend into the fiber core, often spanning the entire fiber diameter (~50 μm) and usually exceeding 10 μm in width. Atomic Force Microscopy studies reveal that the striations protrude significantly from the fiber surface (Figure 2a), and a 2D surface profile along the axial center line of the sampled section shows peak maxima in the approximate range 100 – 300 nm (Figure 2b).

![Figure 1: SEM images of Innegra™ HMPP fibers. RHS is a longitudinal cross-section view.](image1)

The extensive void formation occurs only in the inter-striation regions (of lower SEM intensity) and it appears from Figure 1 (right), and other images not shown, that cracks cease to propagate when they reach a striation, despite the high levels of strain in the drawing process. Thus, the striations appear to be disk-like strata comprising a structure that resists crack propagation and initiation.

We propose that the striations arise from a bistability in the drawing process involving two different routes to structure development which have similar energy barriers.

**Voids with Nanofilament Bridges**

A closer examination of the HMPP fibers by field emission SEM, reveals that the cracks are frequently bridged by ‘nanofilaments’ which appear to be highly strained and may be highly ordered (Figure 3). These nanofilament bridges appear in views of cracks taken along the fiber surface and, although prone to destruction by microtoming, they are also found in fiber cross-sections. The nanofilaments typically have diameters in the range 30 – 100 nm and often populate the full length of the cracks, which usually extend to several micrometers. They are most likely formed as fibrils are pulled apart by the transverse stresses, and they presumably reflect the drawing-out of a relatively sparse distribution of material that interconnects the fibrils in the inter-striation regions. It is possible that the cross-linking structure of the nanofilaments help to stabilize the cracks in the lateral direction, which would provide another mechanism for reducing the impact of the voids on mechanical properties.

![Figure 2: AFM contour map of an HMPP fiber surface, with z-axis expanded relative to the x and y axes to enhance visibility of protrusions; (b) profile taken along the axial center line of the map.](image2)

![Figure 3: SEM image of cracks spanned by nanofilaments in an HMPP fiber.](image3)

**ACKNOWLEDGMENT**

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**REFERENCES**

Temperature-responsive Fibers for “Smart” Thermal Insulation

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OBJECTIVE
We are developing thermal insulation that responds to temperature changes based on fibers that bend and straighten with changes in temperature. This work investigated the effects on bending response of fiber cross section and composition in bi- and tri-component fibers.

INTRODUCTION
So-called “self-crimping” fibers based on stress relaxation have been known for some time. Typically these fibers would be of circular cross section with one hemisphere made of one polymer and the other made of a second polymer. Using this design with bi-component fibers where the polymers have different coefficients of thermal expansion (CTE) results in a fiber that bends in response to temperature changes. This approach has been used to create a thermal insulation batting that responds to decreasing temperature by becoming thicker.[1]

This earlier work demonstrated for the first time that bi-component polymeric fibers could be used to create a batting that changed thickness with temperature. Unfortunately, the response of these battings was limited to about 1% per degree C (~0.5% change in thickness and ~0.5% change in “inherent” combined conduction and radiation).[2] The ability to spin (almost) arbitrary cross-section tri-component fibers using a newly acquired pilot scale spinning apparatus allows us to investigate new specialized fibers not originally available.

APPROACH
Fiber bending theory. Two materials having sufficiently different coefficients of thermal expansion (CTE), when bonded together, will bend as their temperature changes. This happens because the one with the greater CTE is constrained from elongating linearly by the other material which does not expand (or contract) to the same degree.

An analysis of the forces and bending moments acting on a section of such a system results in an equation that allows the fiber designer to tailor the amount of bending if the elastic moduli of the two components are known or can be reasonably estimated. Regardless of the geometry of the fiber cross-section, this relationship for the curvature of the fiber takes the form,

\[
\frac{1}{\rho} \propto \left( A + Bn + \frac{C}{n} \right)^{-1}
\]  

(1)

The parameters A, B, and C are unique to the cross-sectional shape of the fiber and the ratio of the two components and n is the ratio of the moduli of the components. Thus for a given n and cross-sectional shape, the amount of bending can be controlled by adjusting the ratio of the materials (m). The trade-space of curvature as a function of n and m has a saddle shape as seen in Figure 1.[3]

\[
E = \rho c^2 
\]

(2)

\[
n = \frac{E_1}{E_2} \approx \left( \frac{c_1}{c_2} \right)^2 = nc 
\]

(3)

In (3) we are making an assumption that the densities of the two components are approximately equal to one another.

Polymer selection. Polymers that are readily compatible and spun were chosen. In this case, the high CTE polymer was syndiotactic polypropylene (s-PP) and the low CTE polymer was isotactic polypropylene (i-PP). s-PP crystallizes slowly and was expected to remain primarily amorphous with a high CTE and low modulus while the i-PP crystallizes readily and was expected to be low CTE and relatively high modulus. A compatibilizing layer of a random ethylene-propylene copolymer was chosen. It has very low modulus and is expected to have a high CTE similar to s-PP.
Table 1. Properties of polymers studied.

<table>
<thead>
<tr>
<th>Polymer Properties</th>
<th>Syndiotactic (s-PP)</th>
<th>Co-EP</th>
<th>Isotactic (i-PP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Flow (g/10 min.)</td>
<td>20</td>
<td>11</td>
<td>23</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.87</td>
<td>0.89</td>
<td>0.90</td>
</tr>
<tr>
<td>Melt Point (C)</td>
<td>130</td>
<td>134</td>
<td>151</td>
</tr>
</tbody>
</table>

**Fiber spinning.** Fibers were spun using a tri-component fiber spinning machine manufactured by Hills Inc. This machine has three thermally isolated melt pumps that were used to control the cross sectional area of the three components. Thirty six filaments of triangular cross section were spun with draw ratios between 2:1 and 3:1.

**Batting thickness measurements.** Batting thickness measurements were carried out using an Instron tensile tester in a temperature controlled chamber. Circular samples of 20 square inches (129 cm²) were die cut and placed in the environmental chamber at room temperature. Samples were then compressed with a 20 in² circular platen starting well above the sample and continuing to a fixed testing load of 1.1 lb. The platen was then raised and the test repeated. Thickness measurements were based on the second compression since earlier testing had shown a third compression measurement was essentially the same as the second measurement. The chamber was then cooled to a lower temperature and the batting and chamber allowed to equilibrate for 15 minutes. By measuring higher temperatures first any error caused by “compression set” would serve to diminish the change in thickness with temperature.

**RESULTS AND DISCUSSION**

**Batting thickness measurements.** Figure 2 shows a typical set of compression tests. It can be clearly seen that the batting thickness increases as the temperature is decreased. The thickness values at 0.4 lb load correspond to 0.02 psi. Thicknesses measured at 0.02 psi were used to calculate the thickness change due to temperature.

**Comparison of Batting Response with Fiber Bending Theory.** Figure 3 shows the batting thickness changes measured as a function of the area fraction of the i-PP (high modulus and low CTE) component. For comparison the curvature from theory of a bi-component fiber with a ratio of moduli based on sonic modulus measurements is also plotted. It can be seen that the measured batting thickness change and the curvature of fibers from the theory behave in a similar manner each varying linearly with area fraction.

The sonic moduli were measured on a separate set of bi-component fibers spun under the same conditions. Figure 4 shows the measured moduli as a function of the composition.

**CONCLUSIONS**

We have demonstrated a fiber with a strong bending response to temperature change and successfully demonstrated battings based on these fibers, in the best case with a thickness change of 1.8% per degree C between approximately 27 C and 0 C.

**FUTURE WORK**

The effect of repeated temperature cycling needs to be explored and batting properties will also be optimized.

**REFERENCES**

ABSTRACT
DuPont has developed commercial scale nanofiber technologies. DuPont centrifugal spun fiber process is one developed from centrifugal spraying to nanofiber spinning based on DuPont Nonwoven and Automotive Performance Coating technology. In this presentation, we report the nanofiber formation from the centrifugal shear-spinning process. High-speed imaging and the Laser LaVison have been used in real-time in-situ observation and measurement. Results have been also reported in terms of the morphological phase diagram of fiber/droplets selection, the nanofiber size distribution and molecular chain orientation versus polymer properties and process parameters.

INTRODUCTION
Nanofibers can be made and collected into a fibrous web useful for selective barrier end uses such as in the fields of air and liquid filtration, flame retardancy, biomedical, battery and capacitor separators, biofuel membranes, cosmetic facial masks, biomedical applications, such as, hemostasis, wound dressings and healing, vascular grafts, tissue scaffolds, synthetic ECM (extra cellular matrix), and sensing applications, electronic/optical textiles, EMI Shielding, and antischemio protective coatings.

Generally, polymeric nanofibers are produced by an electrospinning process, other very fine fibers can be made from melt spun “islands in the sea” cross section fibers [1] and meltblown nanofiber processes. What is needed is a high throughput process to make very fine fibers and uniform fibrous webs.

A DuPont new nanofiber process [1] employs a rotary sprayer that leverages a strong process understanding obtained through its utility in modern automotive paint processes. In this new centrifugal nanofiber process, polymer solution or melt is issued to the center of a rotary bell-cup or spinning disk to form a polymer thin film on rotating surface, then the thin film fibrillated at the bell-cup edge resulting in sub-micron or nanofibers.

DuPont centrifugal nanofiber spinning process provides a number of critical process advantages: e.g., higher productivity (lower processing cost) due to the higher flow rate (up to 500germ/min), rotary bell speed (up to 75,000 rpm), and commercial availability of necessary production equipment which includes precise process control system. It strives to provide new areas of impact and provide fundamental capability outside the realm of other nanofiber technologies.

EXPERIMENTAL
Rotary sprayers used in conjunction with a feeding fluid and an electrical field are useful in atomizing paint for coating a target device. The centrifugal force supplied by the rotary sprayers produces enough shear to cause the paint to become atomized and the feeding fluid and electrical field draw the atomized paint to the target device. This process has been optimized for the production of polymer nanofibers. Figure 1 shows a automotive paint sprayer, bell-cup and the configuration to spin nanofibers and to collect nanoweb. Figure 2 shows the high-speed video images of spraying and nanofiber spinning. Figure 3 shows the typical SEM of centrifugal spun nanofiber from 10wt% PEO/H2O solution.

FIGURE 1. Rotary sprayer used for nanofiber spinning

FIGURE 2. High-speed images of spraying and nanofiber spinning

FIGURE 3. Typical SEM of centrifugal spun nanofiber from 10wt% PEO/H2O solution.
RESULTS AND DISCUSSION

Figure 4 to Figure 8 show the results of the flow field analysis of nanofiber spinning, droplets and nanofiber formation, the nanofiber size distribution and molecular chain orientation versus polymer properties and process parameters.

FIGURE 3. SEM image of Nanofibers from 10wt% PEO/H2O solution

FIGURE 4. Flow field analysis of Nanofiber spinning

FIGURE 5. Laser LaVision images on droplets formation in spraying and fiber formation in spinning

FIGURE 6. Experimental results on operational regime and droplets and nanofiber morphology selection.

FIGURE 7. The average nanofiber diameter as function of Beery number (the dynamic viscosity times concentration).

FIGURE 8. The molecular chain orientation measured by polarized Raman and FTIR.

CONCLUSIONS

In this study, we have reported a high throughput centrifugal spun nanofiber process using automotive paint sprayer. The formation of droplets and nanofibers has been studied by using high-speed video and Laser LaVision imaging system. Results have been also reported in terms of the morphological phase diagram of fiber/droplets selection, the nanofiber size distribution and molecular chain orientation versus polymer properties and process parameters.

ACKNOWLEDGMENT

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Free-surface Electrospinning from a Wire Electrode

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The needle based electrospinning process has long been investigated for its ability to produce materials with high surface area and high porosity while being able to operate at relatively low cost compared to other techniques for the manufacture of nano-materials. These materials have applications in a wide range of fields such as textiles, filtration, tissue engineering, drug delivery systems, nanocomposites, and alternative-energy generation systems such as solar cells, fuel cells, and energy storage devices. However, the productivity from needle based electrospinning is rather low (0.1-1 g/hr/spinneret), which limits its ability to be scaled up and applied to industrial manufacturing. For this reason, new techniques are being investigated to increase the throughput where electrohydynamic jets self-organize along a free liquid surface. We refer to this process as “free surface electrospinning” (also known as “needleless electrospinning”). The major upside to this process is that the production rate is several orders of magnitude greater than needle-base systems while requiring a relatively small footprint.

In this report, we consider the system where a wire electrode is rotated horizontally in a polymer solution bath. As the electrode is dragged through and exits the bath, polymer solution is entrained and uniformly coats the wire. Due to Rayleigh instabilities, the thin film breaks up into droplets. We present a correlation for solution entrainment and droplet break-up in the presence of an applied electric field perpendicular to the wire electrode. As the local electric field increases, the individual droplets deform and jetting occurs. High speed photography in association with electrical current measurements was used to study the initiation individual jets. The solution charge density was calculated from the electrical current measurements and productivity of the system. The fiber size distribution was determined for different operating properties and solution properties.
Properties of Nanoclay-added Composite Polypropylene Monofilaments Using Twin and Single Screw Extruders

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STATEMENT OF PURPOSE
The purpose of this study is to combine the traditional polymeric materials with nanoclays to form high performance monofilaments for industrial applications using extrusion process.

INTRODUCTION
Polymer-layered silicate (PLS) nanocomposites have been investigated in recent years because the final composites often provide a desired enhancement of mechanical, molecular barrier, thermal, flame retardant, corrosion protection and other properties relative to the original polymer matrix, even at very low clay contents [1-8]. Polypropylene and nanoclays have advantages in nanocomposite structures. Nanoclays have high aspect ratios and plate morphology. Their low cost and environmental friendly characteristics make them very attractive. On the other hand, polypropylene is one of the most widely used polyolefin because of the low cost, low density, and easy processibility. Twin and single screw extrusion machines are mainly used for filament and film manufacturing. Nanocomposite structures can be produced using extrusion machines because of their good mixing characteristic and processing efficiency compared to other methods. The features of the extruder and screw configuration are important to obtain good dispersion. Clay plates can be broken into small pieces under high shearing effect. Interlayer spacing increases during the processing, and the increase in interlayer space helps for better dispersion and distribution of the nanoclays in polymer matrix.

APPROACH
Polypropylene copolymer 30 Melt 2 Izod Natural with melt flow index (MFI) of 30 g/10 min, was purchased from Premier Plastic Resins, Inc. (USA). Cloisite 15A and 30B, which were already modified with a quaternary ammonium salt, was purchased from Southern Clay Products, Inc. Polybond 3200 (PP grafted with malefic anhydride; 1.0 weight % maleic anhydride level) was donated by Chemtura Corporation (USA). Twin and single screw extruders were used to produce composite monofilaments with different weight percentage (0.5, 1, and 1.5 %) and types of nanoclays (Cloisite 15A and 30B) and compatibilizer (Polybond 3200). The sample codes are listed in Table I. One sample (P1-C10) which was produced with only single screw extruder was compared with twin and single screw extruder samples.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>% Cloisite 15A</th>
<th>% Cloisite 30B</th>
<th>% Compatibilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-A-5</td>
<td>0.5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>P-A-10</td>
<td>1.0</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>P-A-15</td>
<td>1.5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>P-A</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-B</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>P-B-5</td>
<td>-</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>P-B-10</td>
<td>-</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>P-B-15</td>
<td>-</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>P1-C10</td>
<td>1.0</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

The structure and properties of the new monofilaments were characterized using scanning electron microscopy (SEM), thermal gravimetric analyzer (TGA), differential scanning calorimeter (DSC), and Instron universal testing machine.

RESULTS AND DISCUSSION
The results were listed in Table II. It is seen that melting temperature of the samples decreased slightly by addition of nanoclay particles.
TABLE II. Thermal and mechanical properties of the composite monofilaments

<table>
<thead>
<tr>
<th>Samples</th>
<th>Melting temperature (°C)</th>
<th>Decomposition temperature (°C)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PP</td>
<td>166.79</td>
<td>358.86</td>
<td>308.8</td>
</tr>
<tr>
<td>P-A-5</td>
<td>163.72</td>
<td>398.88</td>
<td>296.8</td>
</tr>
<tr>
<td>P-A-10</td>
<td>164.45</td>
<td>406.86</td>
<td>281.8</td>
</tr>
<tr>
<td>P-A-15</td>
<td>164.80</td>
<td>425.73</td>
<td>272.5</td>
</tr>
<tr>
<td>P-A</td>
<td>165.29</td>
<td>397.61</td>
<td>275.4</td>
</tr>
<tr>
<td>P-B</td>
<td>165.42</td>
<td>394.12</td>
<td>258.4</td>
</tr>
<tr>
<td>P-B-5</td>
<td>164.70</td>
<td>399.66</td>
<td>283.2</td>
</tr>
<tr>
<td>P-B-10</td>
<td>165.18</td>
<td>404.15</td>
<td>272.4</td>
</tr>
<tr>
<td>P-B-15</td>
<td>164.43</td>
<td>417.94</td>
<td>261.8</td>
</tr>
<tr>
<td>P1-C10</td>
<td>166.60</td>
<td>368.32</td>
<td>289.1</td>
</tr>
</tbody>
</table>

Decomposition temperatures of the monofilaments were increased between 10 to 18% by addition of nanoclay compared to pure polypropylene monofilaments. Figure 1 shows decomposition behavior of the samples.

![FIGURE 1. Decomposition behavior of pure polypropylene and nano clay (Cloisite 15A) added monofilaments](image)

The tensile stress values decreased compared to the pure polypropylene monofilaments for all composite samples. This is probably due to interfacial debonding and incoherence between nanoclay particles and polymer matrix. Addition of more nanoclay caused more decrease as seen in Table II.

ACKNOWLEDGEMENT
This research is supported by U.S. Department of Commerce (DOC-ITA-08-TBD-E), which is appreciated.

CONCLUSIONS
Composite PP monofilament structures were successfully produced using twin and single screw extruder machines. The amount of the nanoclay affected the monofilament processing. Higher % nanoclay content caused more difficult processing due to lower interaction between nanoclay and polymer matrix. Decomposition temperature increased compared to pure polypropylenes. Tensile strength decreased with the addition of nanoclays due to some agglomerated and large particles in the polymer matrix. Nanoclay layers may be separated better by increasing shear during processing, and better dispersion could be obtained. Monofilament production using both twin and single screw extruders was easier than only using single screw extruder. Less breakage occurred during processing because of having smaller nanoclay particles in the system.

REFERENCES
Multifunctional Fibers
Design and Development of Fibers with Flexure Rate-dependent Viscoelastic Properties

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2Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, USA
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INTRODUCTION

We are investigating how to produce polymeric fibers with an internal liquid phase. Our aim is to design a multicomponent melt-spinning pack enabling the combination of a molten polymer and a liquid, and to develop a method to control and tailor the morphology of the liquid phase inside the fiber. Choosing a liquid with appropriate rheological properties, we expect to achieve fibers with a wide range of novel properties.

As an example such fibers can be used as replacement of existing hard shell components used to dissipate the energy on an impact [1-3]. A structure suitable for this purpose is depicted in Figure 1.

FIGURE 1. Example of proposed structures of liquid filled fiber. Two geometries are shown: large reservoirs interconnected through thin channels (left) and small side reservoirs connected to an inner channel (right).

During fiber bending or deformation, a liquid confined in large compartments, linked to each other through thin constriction, can be squeezed from one container to the other. The constrictions will create an elevated shear rate. If the liquid is a shear thickening fluid (STF), i.e. its viscosity increases with increasing shear rate, we hope to obtain fibers with rate dependent viscoelastic properties.

Due to their low vapor pressure and high thermal and suspension stability [4, 5], ionic liquid based nanoparticle dispersions [6, 7] are examples of STF candidates that can withstand melt-spinning processes.

Up to now, investigations were performed, aiming at understanding how a molten polymer and a liquid react when injected together in a structure similar to a spin pack. We will present the initial study and discuss first results.

APPROACH

To understand and to analyze the flow of molten polymer and liquid within the spin pack, we built a macroscale analogon where co-flow of polymer and liquid is investigated systematically. The macroscale analogon is composed of a glass cylinder with a finite length and a coaxial capillary. The inner fluid flows in the capillary and at its outlet meets the outer fluid flowing inside the glass cylinder. The fluids are pumped into the setup using pressurized bottles with controlled flow rates. A high-speed camera is placed in front of the glass cylinder to record the transient and the steady flow of the two phases and the morphology of their interface during co-flow. These experiments are done to understand and analyze what happens inside a spin pack during melt-spinning of a polymer as outer flow and a liquid as inner flow.

As a first step we performed various model experiments at room temperature using a) oil or liquid polymer substituting a molten polymer, and b) water or oil replacing a shear thickening liquid. This allows us to understand and isolate the driving forces that may lead to the desired interfacial morphology between the two phases. Considering theoretical knowledge developed in the fields of jet physics [8, 9] and core-annular flow physics [8, 9], we performed complete fluid dynamics investigations.

Based on these results we also studied the influence of fluid viscosity ratio [10], variation of the inner and outer flow rate [11, 12] and surface tension [13] on development and stability of the morphology. Dimensionless groups such as Reynolds, Capillary, Weber, and Bond numbers were calculated for the experiments in order to compare our results with the real spin pack geometry, existing theories, and with computational fluid dynamics (CFD) simulations.

The resulting morphology of the core can be tuned by changing the geometry of our setup, in particular by using an inner capillary with apertures at the side, varying in dimension and distribution. Another possibility to tune the inner flow and the interfacial morphology is achieved by fixing a perforated screen at the capillary outlet that divides the inner flow into several streams.
RESULTS AND DISCUSSION
Our experiments yielded a variety of morphologies. We consider the inner fluid as a jet penetrating into a flowing outer phase. Droplets developed with different size and frequency and flowed with varying speed along the observation region. We also noted the presence of stable jets or jets showing a surface wave propagating along their length (see fiber morphology on the left in Figure 1).

For all these morphologies we evaluated characteristic fluid parameters and flow geometry characteristics. These quantities can be related to those of similar experiments done with different materials and geometries by appropriate scaling of the dimensionless parameters listed above. It is possible, e.g., to tune the thickness of the core by changing the flow rate ratio. Furthermore, to avoid the formation of droplets, the interfacial tension between inner and outer phase can be decreased. Finally, perforated screens with different opening widths at the capillary will lead to the coexistence of a continuous jet and droplets, a morphology that is similar to the one shown at the right hand side of the fiber in Figure 1.

FUTURE WORK
The results obtained from our model experiments, and the future data coming from CFD simulations, will enable us to design a spin pack geometry that yields the desired fiber core morphologies.

ACKNOWLEDGMENT
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REFERENCES
A Study on the Photostability of Photochromic Fabrics from Hybrid Organosilica Coatings

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ABSTRACT
Photochromic fabrics were prepared using a coating solution containing photochromic dyes and silica sol-gel. The photochromic effect was rapid. The effect of three different post treatments on the optical and durability of the photochromic fabrics was evaluated. These included incorporating a UV stabilizer, increasing the surface hydrophobicity by fluorinating the pores, and blockading the dye-containing pores with additional silica coating. All the treatments improved photostability, without significantly affecting response/fading speeds.

INTRODUCTION
Photochromism is a color changing response to light stimulus, resultant from structural transformation in the dye molecule. It has been used in developing optical devices such as sensors, shutters, and switches. It could have novel applications in UV protecting, environment-sensing, and fashionable color-changing clothing. We previously produced a hybrid organosilica coating with encapsulated photochromic dye via the sol-gel method [1]. Although the optical performance response was very fast, the photochromic fabric showed low photostability. The following processes were assessed for this purpose: adding UV stabilizer, increasing surface hydrophobicity by incorporation of fluorine, and blockading the dye-encapsulating pores with addition coating layer.

APPROACH
Silica sols were prepared by mixing tetraacetoxy silane (TAS), alkyltriethoxysilane (RSi) and ethanol, stirring vigorously until TAS was dissolved. Water was subsequently added at a 1 ml/h rate and the mixture was stirred for 24 hours. The molar ratio of TAS: R Si: H2O: EtOH was 1:32:100:320. Alkyltriethoxysilanes included octyltriethoxysilane (OTES) and phenyltriethoxysilane (PhTES), used in a 1:2 (mol/mol) combination, respectively. To incorporate photo stabilizers, a photochromic dye-ethanol solution containing stabilizer was mixed with the synthesized sol-gel solution. Wool fabric was dip-coated with the coating solution, air-dried and cured at 110 °C. To adjust the wettability of the coating, FAS was added to the silane combination at the beginning of synthesis (before adding water). To seal off the dye-containing pores, a second layer of sol containing no dyes was applied after air-drying the first layer.

RESULTS AND DISCUSSION
The typical structure of the Spirooxazine class of photochromic dyes and its ring-opening reaction with UV stimulation are shown in Figure I.

Figure II (a) shows the absorption spectra of the control sample in the presence and absence of UV radiation. Figure II (b) illustrates the ascent and descent of absorption with time as UV light was turned on and off. The time required for absorbance to rise and subsequently fall to half of its maxima, indicated as t1/2 and t′1/2, were calculated to signify the response and fading speeds of photochromic coatings.

![FIGURE I. Structure and photochromic reaction of spirooxazine](image)

![FIGURE II. a) Absorption spectra and, (b) colouration-decolouration curve of the control sample.](image)

<table>
<thead>
<tr>
<th>Name</th>
<th>Constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>OTES:PhTES 1:2 sol + dye</td>
</tr>
<tr>
<td>Adding UV stabilizer</td>
<td>UV-1084: O.P 1:2 sol + UV-1084 + dye</td>
</tr>
<tr>
<td></td>
<td>HALS-622: O.P 1:2 sol + HALS-622 + dye</td>
</tr>
<tr>
<td></td>
<td>Tinuvin 329: O.P 1:2 sol + Tinuvin 329 + dye</td>
</tr>
<tr>
<td></td>
<td>HMBP: O.P 1:2 sol + HMBP + dye</td>
</tr>
<tr>
<td>Fluorination</td>
<td>FAS: O.P 1:2 + FAS sol + dye</td>
</tr>
<tr>
<td>Dbl. coating with extra silica</td>
<td>APS: 1st layer O.P 1:2 sol + dye</td>
</tr>
<tr>
<td></td>
<td>2nd layer APS sol only</td>
</tr>
<tr>
<td></td>
<td>MPS: 1st layer O.P 1:2 sol + dye</td>
</tr>
<tr>
<td></td>
<td>2nd layer MPS sol only</td>
</tr>
<tr>
<td>Same silica</td>
<td>1st layer O.P 1:2 sol + dye</td>
</tr>
<tr>
<td></td>
<td>2nd layer O.P 1:2 sol only</td>
</tr>
</tbody>
</table>

UV-1084: 2,2′-thiobis(4-tert-octylphenolato)-N-butylamine nickel (II), HMBP: 2-hydroxy-4-methoxy-benzophenone, Tinuvin 329: 2-(2Hbenzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol, HALS-622: poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol-alt-1,4-butanedioic acid), FAS: Tridecafluorooctyltriethoxysilane, APS: (3-Aminopropyl)triethoxysilane; MPS: 3-(Trimethoxysilyl)propyl methacrylate

Coating descriptions are given in Table I, and full names of additives are listed below the table. The optical
properties of the coatings, namely, differential absorption at maximum (\( \lambda \approx 620 \text{ nm} \)) or \( \Delta A_{\text{max}} = A_{\text{light}} - A_{\text{dark}} \), photostability, and response/fading half-life times, \( t_{1/2} \) and \( t'_{1/2} \) are presented in Table II.

**TABLE II. Optical properties**

<table>
<thead>
<tr>
<th>Coating</th>
<th>( \Delta A_{\text{max}} )</th>
<th>Photo-stability (h)</th>
<th>Response/Fading (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.32±0.01</td>
<td>9.5</td>
<td>1.6±0.1  3.3±0.1</td>
</tr>
<tr>
<td>UV-1084</td>
<td>0.32</td>
<td>47.5</td>
<td>1.7               3.9</td>
</tr>
<tr>
<td>HALS-622</td>
<td>0.24±0.09</td>
<td>13.5±3</td>
<td>2.1±0.1  3.7±0.5</td>
</tr>
<tr>
<td>Tinuvin-329</td>
<td>0.13±0.05</td>
<td>23±1.5</td>
<td>2.1±0.3  3.5±0.3</td>
</tr>
<tr>
<td>HMBP</td>
<td>0.19±0.02</td>
<td>12.7±2.6</td>
<td>2.1±0.4  3.7±0.2</td>
</tr>
<tr>
<td>FAS</td>
<td>0.34±0.02</td>
<td>11.9±1.6</td>
<td>2±0.2    3.9±0.2</td>
</tr>
<tr>
<td>APS</td>
<td>0.19±0.01</td>
<td>44.3</td>
<td>1.1±0.3  2.1±0.2</td>
</tr>
<tr>
<td>MPS</td>
<td>0.3±0.02</td>
<td>19±2.6</td>
<td>1.6±0.3  2.5±0.2</td>
</tr>
<tr>
<td>Dbl. SS*</td>
<td>0.42±0.003</td>
<td>12.7±1.5</td>
<td>2.1±0.2  4.3±0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coating</th>
<th>G (weft)</th>
<th>G (warp)</th>
<th>Q (warp)</th>
<th>Q (weft)</th>
<th>C.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>83.5±5</td>
<td>60.8±1.6</td>
<td>85.01</td>
<td>21.4</td>
<td>2.03</td>
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<tr>
<td>UV1084</td>
<td>87.8</td>
<td>75.1</td>
<td>106.5</td>
<td>16.7</td>
<td>2.3</td>
</tr>
<tr>
<td>HALS622</td>
<td>88.1±2</td>
<td>58.5±8.3</td>
<td>148.6</td>
<td>29.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Tin.329</td>
<td>81.7±3.9</td>
<td>62.8±9.2</td>
<td>106.6</td>
<td>21.01</td>
<td>2.7</td>
</tr>
<tr>
<td>HMBP</td>
<td>81.3±4.7</td>
<td>53.6±6.8</td>
<td>102.0</td>
<td>19.1</td>
<td>2.2</td>
</tr>
<tr>
<td>FAS</td>
<td>74±3.4</td>
<td>53.3±8.8</td>
<td>97.6</td>
<td>20.5</td>
<td>2.9</td>
</tr>
<tr>
<td>APS</td>
<td>93.8±4.5</td>
<td>55.3±5.9</td>
<td>12421</td>
<td>1618</td>
<td>444</td>
</tr>
<tr>
<td>MPS</td>
<td>75.5±15</td>
<td>44.7±11</td>
<td>168.2</td>
<td>27.7</td>
<td>4.7</td>
</tr>
<tr>
<td>2x SS</td>
<td>92.1±19</td>
<td>58.7±4.3</td>
<td>287.8</td>
<td>31.5</td>
<td>12.6</td>
</tr>
</tbody>
</table>

**REFERENCES**

OBJECTIVE
The presented results are taken from on-going research at the Institut für Textiltechnik der RWTH Aachen University (ITA) which strives to develop a novel sensory fiber based on the piezo-electricity of melt-spun poly(vinylidene fluoride). The characteristic of the forming piezo-electricity requires linear electroding along the fiber axis. This is realized either by an outside electrically conducting coating, ready melt-spun electrodes within the fiber cross section or a combination thereof. The latest advances in research are presented.

INTRODUCTION
Poly(vinylidene-fluoride)
Melt spinning of poly(vinylidene-fluoride) (PVDF) has been a research focus for decades. The polymorphic character has ever since raised elevated attention since PVDF exhibits piezo-electric properties when predominantly present in the crystalline polar β-phase. The formation of this β-phase during the melt spinning process has been described in numerous reports. [1,2] In commerce until today, the piezo-electric effect has only been utilized in films. These commercially available products are used for e.g. underwater microphones [3]. In fiber form these amongst potential piezo-electric polymers outstanding properties have not been able to use efficiently. This is due to the characteristic of the forming piezo-electric behavior of PVDF fibers. As the molecular chains are oriented along the fiber axis the dipoles formed by hydrogen and fluorine side chain ends orient perpendicular to the fiber axis. Thus a linear electroding along the entire fiber is required in order to access, measure and utilize the charge separation.

Electrically conductive fibres
For the production of electrically conductive fibers, several approaches exist. One of them is to use polymer nano-composites, which has been only realized in slowly spun monofilaments [4]. Another possibility in the coating of insulating materials with intrinsically conducting polymers (ICP) like PEDOT:PSS [5]. Today, mostly silver coated polyamide fibers are used for textile applications.

Polymer nanocomposites
Nanoparticles based on graphite / carbon, like carbon nanotubes (CNT), have a good performance in electrical and thermal conductivity as well as mechanical properties at low densities. Several authors have proved the enhancement of the electrical conductivity of insulating polymers with the help of carbon nanotubes. The electrical conductivity can be described by percolation models [6] and mainly depends on the amount of particles as well as the particle geometry. For CNTs with high aspect ratios, low amounts are sufficient for achieving electrical conductivity.

Bicomponent fiber spinning
Bicomponent fiber spinning technology is based on the co-extrusion of two thermoplastic polymers, which form multi-layered fibers. With the bicomponent spinning technology, core/sheath, side by side, segmented pie or islands in the sea-fibers can be produced [7]. Through separation of core and sheath material also the concept of insulating the outside from the core and utilizing the sheath between the inside electrode and an outside environment becomes possible.

APPROACH
In this study, a bicomponent fiber is melt spun with an electrically conductive core consisting either of multiwalled carbon-nano-tube modified polyamide 6 or an ethylene-vinyl acetate and a sheath of PVDF (see figure 1). Thus different melting points of the core, and its resulting influence on the β-phase formation and evolving of electric conductivity can be studied.

RESULTS AND DISCUSSION
Determination of spinning conditions
Temperatures for melt spinning are determined from thermal analysis and rheometry. The polymers are then spun to fine bicomofilaments. The as spun fibres are characterized regarding their polymer structure and their electrical conductivity.

FIGURE 1. Principle of electrically conductive bicomponent fiber

Spinning conditions are determined from thermal analysis and rheometry. The polymers are then spun to fine bicomofilaments. The as spun fibres are characterized regarding their polymer structure and their electrical conductivity.
221 °C, EVA: 73 °C) the temperature level for extrusion is chosen to be 265 °C for (PVDF & PA6/CNT) and 245 °C for (PVDF & EVA/CNT). Especially for the EVA material the final extrusion temperature is chosen only for the spin pack.

Microscopy
After melt spinning the cross section and diameter of the filaments is analyzed by optical microscopy. The diameter of the fibres is not regular and in the range of 100 μm. For the lower core / sheath ratios (e.g. 1:3) nearly round cross sections are achieved (see figure 2).

Electrical conductivity
No DC electrical signal could be measured. Possible reasons could be too much orientation of the CNTs due to shearing or melt drawing. The AC conductivity is analyzed by using impedance spectroscopy. The AC conductivity is measured to be in the range of $10^9 \Omega \cdot \text{cm}$.  

<table>
<thead>
<tr>
<th>Property</th>
<th>Reference</th>
<th>Masterbatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation factor f</td>
<td>0.58 ($\alpha$ phase)</td>
<td>0.43 ($\alpha$ phase)</td>
</tr>
<tr>
<td>Crystallinity $X_c$</td>
<td>29.3 %</td>
<td>29.8 %</td>
</tr>
<tr>
<td>Relative phase content $X_{\beta}$</td>
<td>13.1 %</td>
<td>0 %</td>
</tr>
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CONCLUSIONS
It was demonstrated, that the bicomponent spinning process can be used to produce fibers with high nanoparticle amounts in the core. These masterbatches would normally not be processable to filaments. The CNT-doped core is fully covered by the sheath, so that the outer material acts as an insulating layer. Due to viscosity differences, the structure of the sheath material (PVDF) changes. Since the reference material is drawn more in the melt state, the crystalline $\beta$ form of PVDF can be found. Ideal electrical conductivity is not yet achieved.

FUTURE WORK
In the future the dependencies of different melting points of the core material are further investigated. The influence on the $\beta$-phase formation in the shear PVDF will be studied. With melting points of the core below the curie temperature of the PVDF a second step annealing for enhancing the conductivity of the core can be examined. If a bicomponent fiber with PVDF sheath, crystallized in the $\beta$ phase, can be produced, the piezoelectric effect of PVDF could be used.

REFERENCES
Bamboo: A Multifunctional “Green” Fibre

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OBJECTIVE
This study explores the scope of bamboo as an emerging “green” multifunctional natural fibre in the textile sector.

INTRODUCTION
Bamboo plant is well recognized for its multifunctionality as food, medicine, constructions material and so on, serving the daily needs of billions of people over centuries [1-2]. Bamboo has amazingly fast growth rates with no or very little needs for pesticides and irrigation. The carbon sequestration activity of each acre of bamboo is much higher than trees [3]. As such, bamboo is recognized as one of the most eco-friendly crops and the ‘green’ properties of bamboo have started to attract consumers in the textile market.

However, most of the manufacturers are currently using regenerated viscose production method to process bamboo plants into fibres, using a large amount of toxic chemicals. Therefore, it is questionable to use the term “green” on the current bamboo textile products [4]. Hence, there is a great need for developing an eco-friendly method to produce bamboo fibres. In this research, an Australian grown bamboo plant (*phyllostachys pubescens*) is processed into fibres in a natural and eco-friendly manufacturing method without losing the unique properties of bamboo plants. This research also describes the origin of the ultra violet (UV) absorbing and antibacterial activity of bamboo.

APPROACH
Several characterization methods are used to explore the morphology and chemical components of raw bamboo and processed fibres such as scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. For investigating the origin of UV blocking property, several extractions of raw bamboo were carried out using polar and non polar solvents. Raw bamboo was crushed into powder with sizes of around 5-6 µm by using mechanical milling. The extraction was performed with 10g of powder in 300 ml of solvents for 72 hours at room temperature with continuous stirring. A mixture of non polar and polar solvents (dioxane: water= 9:1), which is the Björkman solvent for lignin extraction, was also used [5].

The antibacterial study was carried out against gram negative bacteria *E. coli* with bamboo extracts in three solvents, namely, water, Dimethyl Sulfoxide, DMSO (a typical plant solvent) and 90% aqueous dioxane. After extraction in 90% aqueous dioxane, dioxane was removed from the solution by evaporation in order to eliminate the effect of dioxane on the antimicrobial activity. The extract in DMSO was diluted down to 20% to optimize the observation conditions of E-coli colonies on agar plates.

Bamboo plant is processed into fibres with the aid of mechanical (such as ultra sonication) and mild chemical treatment (such as enzymes and hydrogen peroxide).

RESULTS AND DISCUSSION
Under SEM, raw bamboo showed a highly porous structure with grooves like capillaries in its cross section (*Figure 1a*). XRD confirmed the cellulose I crystalline structure. FT-IR spectroscopy revealed the presence of aromatic and carbonyl groups in the raw bamboo. The lignin content in the raw bamboo was identified to be 28 wt% by using GB5889-86 standard method (*Figure 1b*).

Raw bamboo extracts in protic solvents such as water and ethanol (*Figure 2a*) showed UV absorbing ability, but the extracts in polar aprotic solvents did not. Interestingly, a non polar solvent, hexane, extracted the UV absorbing chemical compound out from raw bamboo (*Figure 2a*).

The fact that bamboo extracts in both polar and non polar solvents showed UV absorption properties indicates that bamboo has more than one UV responsible chemical components. Since polar protic solvents normally solvate...
negatively charged ions, the UV absorbing components of bamboo are thought to be positively charged. The extract in the mixture of the non polar and polar solvents (dioxane:water= 9:1) showed a similar UV absorbance spectrum (Figure 2b). As this Björkman solvent is a typical lignin extraction solvent, the results indicate that the UV absorption property of raw bamboo lies in the chemical components of lignin.

Bamboo extracts in water showed no antibacterial activity (Figure 3a, b). The extract in 90% aqueous dioxin after removal of dioxane showed 100% antibacterial activity even after diluted 20 times (Figure 3c, d). The DMSO extracts did not show significant antibacterial activity, but the colony size was smaller compared to the control samples (Figure 3e, f), indicating that the bamboo extracts in DMSO inhibited bacterial growth but could not kill them thoroughly. Since DMSO is considered as an extraction solvent for hemicellulose [6], that the results suggest that the chemical components in hemicellulose are not strongly antibacterial. The above results of antibacterial test confirm that the antibacterial activity of bamboo mainly stems from the water insoluble chemical components in lignin.

Bamboo plants were processed into fibres according to the flow diagram in Figure 4. Figure 5(a) shows a typical SEM image of the processed fibre. It was found that the raw bamboo and processed bamboo fibres had much higher UV absorption property than cotton that is another cellulose-based common natural fibre (Figure 5b). FT-IR spectroscopy revealed the presence of aromatic and non conjugated carbonyl stretching (1400 -1750 cm⁻¹) in raw bamboo and processed bamboo fibre, indicative of the presence of lignin. On the other hand, the FT-IR spectrum of cotton did not suggest the presence of lignin. The results therefore suggest that the UV blocking ability originates from those aromatic and carbonyl groups in lignin.

![FIGURE 3. The antibacterial characteristics of raw bamboo against E.coli in agar plates.](image)

![FIGURE 4. Process flow graph of natural bamboo fibre from bamboo plants.](image)

![FIGURE 5. (a) SEM micrograph of processed natural bamboo fibre; (b) comparison of the UV absorbance among raw bamboo, cotton and processed natural bamboo fibre.](image)

### CONCLUSIONS

The unique multifunctional properties of bamboo, such as UV absorption and antibacterial properties stem from lignin in *Phyllostachys pubescens*. The new method to process raw bamboo into fibre successfully retained those unique properties in the fibre. The future works involve the spinning and knitting/weaving of the processed fibres.

### REFERENCES

Self-decontaminating Multifunctional Nano/Submicrofibers and Nanofibrous Membranes

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Introduction

Chemical modifications of polyolefins with several halamine precursors were conducted in either a mixer or a twin-screw extruder by a radical polymerization. The chemically modified polymers were then prepared into nano- and submicro sized fibers by a high-throughput melt extrusion process invented by this group. The fibers were dispersed in various solvent systems according to fiber chemical structures, and the fiber dispersions were coated onto meltblown nonwoven or polyester monofilament woven screen fabric as supporting materials to become uniform membranes with varied air permeability and barrier properties. SEM images demonstrated the dense and even fiber distributions in membranes. Air permeability, water vapor penetration performance, particle filtration efficiency properties of the membranes were evaluated. Water vapor penetration properties of the membranes were outstanding, while air permeability was relatively low. A simple chlorination process could convert the modified fibers to biocidal halamine structures, and biological and chemical protective functions were evaluated as well. The products exhibited powerful antimicrobial properties against both Escherichia coli and Staphylococcus aureus, and the functions are durable and refreshable. In addition, chemical detoxification functions were evaluated as well. The fibers are suitable for biocidal filters and respirators for biological protection.

Experimental

Commercial grades of polypropylene (PP) and poly vinyl alcohol-co-polyethylene (PVA-co-PE) were employed in the study. Modification of PP was carried out in a 3-PC mixer on a Brabender Plasti-Corder ATR (C.W. Brabender, USA) at 185°C and 50 rpm for 5min or in a Leistritz co-rotating twin-screw extruder (Model MIC 18/GL 30D, Nurnberg, Germany)[1-2]. Nitrogen gas was purged above the mixing chamber to reduce oxidation during reaction. The initial concentration of monomers was 300mpm (mole per million part of PP), while the peroxide was 4mpm. All 40g reactants (PP, monomer and peroxide) were dry mixed together for 5min before their fast (< 0.5 min) introduction into the preheated chamber.

The modified polymers were further processed into nano/submicro-sized fibers through an immiscible blending (a mixer of chemical modified polymer/cellulose acetate butyrate) extrusion based on previously reported method[3]. Then, the chemically modified nanofibers were produced.

The nanofibers were dispersed in different solvent systems to make a uniform dispersion, and the dispersion was applied onto a supporting material, either a meltblown PP nonwoven or a fine polyester screen fabric.

Air and moisture vapor transport properties of the membranes were evaluated following industry standards.

Results and Discussion

1. Nanofibrous membranes

The SEM images of nanofibrous membranes are shown in Figure 1. The size of the fibers was in a range of 100-200 nanometers. The pore size is in a range of 100-2000 nm. Since there are many layers of the nanofibers, the overall pore size could be smaller than 100 nm.
Figure 1 SEM images of PVA-co-PET on PET screen fabric membranes in different magnification scales

2. Air and water vapor transport properties

Due to the very fine pores existing the air permeability of the nanofibrous membranes was low, even using PET screen fabric as a support material. Table 1 shows the air permeability values of the samples, which is consistently decreased as the thickness of nanofibers was increased.

Table 1 Air permeability of samples

<table>
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<tr>
<th>Samples</th>
<th>Thickness</th>
<th>Air permeability</th>
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<tbody>
<tr>
<td>PP meltblown control</td>
<td></td>
<td>86.5</td>
</tr>
<tr>
<td>PET screen control</td>
<td></td>
<td>614.7</td>
</tr>
<tr>
<td>PVA-co-PE Coated on PET screen Fabric</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 mils</td>
<td></td>
<td>4.98</td>
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<tr>
<td>4 mils</td>
<td></td>
<td>1.25</td>
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<tr>
<td>8 mils</td>
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<td>0.82</td>
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<tr>
<td>10 mils</td>
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<td>0.23</td>
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<tr>
<td>12 mils</td>
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But, the water vapor transport properties of the membranes were very much close to the base materials, indicating super moisture vapor transport properties. It is even more exciting to find that even more hydrophobic nanofibers such PTT also resulted acceptable moisture transport performance.

3. Antibacterial functions

The thus prepared membranes were chlorinated in a diluted chlorine bleach to convert to biocidal halamine structures. The active chlorine contents on the membranes were in a range of 200 to 2000ppm depending on different chemical structures. The biocidal properties were confirmed by using both gram negative and gram positive bacteria. The testing results will be discussed at the conference.

Conclusion

N-halamine nanofibers and membranes were prepared by using novel processes. The membranes demonstrated proper water vapor transport property by reduced air permeability. The chlorine activated samples provide powerful antimicrobial properties against both Gram-negative and Gram-positive bacterium based on active chlorine content.

Acknowledgments

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References

Electrospun Nanofibers for Composites
The History of the Science and Technology of Electrospinning
from 1600 to 1995

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INTRODUCTION

The science behind the technology of electrospinning has a history that stretches back to the earliest days of scientific investigation. Whilst it is incorrect to say that these early investigators were working directly towards the process of electrospinning, the work undertaken by these savants provides the theoretical framework for the process. Workers from a number of disciplines have investigated electrospinning including physicists, chemists, mathematicians, medics and meteorologists.

In parallel with the efforts of the scientific community, the work of industry is recorded in the number of patents, of varying levels of practicality, filed since the beginning of the last century. The process requires the simultaneous availability of high voltage power, spinnable raw materials, enabling technologies, and a commercial end-use.

Current interest in the process is due to the ease with which nano-scale fibres can be produced in the laboratory. The benign processing conditions – room temperature and no coagulation chemistry mean that chemically or biochemically complex materials can be processed without damage.

The history of the prior art in the process should be of great interest to the research and development community as it provides a rich vein of ingenious mechanisms to solve the problems of the manufacturer, and access to the theoretical considerations of several generations of scientists.

The first record of the electrostatic attraction of a liquid observed in the time of Queen Elizabeth 1 of England by William Gilbert. Observing that amber exerts an attractive force that is not transmitted by movements in the air, Gilbert said:

“indeed it plainly does draw the body itself in the case of a spherical drop of water standing on a dry surface; for a piece of amber applied to it at a suitable distance pulls the nearest parts out of their position and draws it up into a cone; otherwise, if it were drawn by means of the air rushing along, the whole drop would have moved”[1]

This is the first record of the deformation of a drop of liquid into what would become known as the Taylor cone. In 1665 Robert Hooke suggested that it might be possible to duplicate silk artificially using an unspecified “artificial glutinous composition” if only “very quick ways of drawing it out into small wires for use could be found”.

George Mathias Bose (1710-1761) professor of natural philosophy at Wittenberg, Germany and a probable co-inventor of the Leyden jar described aerosols generated by the application of high electric potentials to drops of fluid [2]. Bose demonstrated his apparatus by standing a female subject on an insulated pitch platform, charging her up and inviting a man from the audience to kiss her, and consequently both parties received a static shock through the lips. An inventive publicist, he held electrical feasts with static discharges flickering across the table and published his results as poems [3]. He also managed to convey a charge through a six foot jet of water, determining the presence of the charge by shocking one of his assistants with it [4].

Manchester silk manufacturer Louis Schwabe (he made the silk for Queen Victoria’s wedding dress) invented the extrusion spinneret. His test material was glass, and he spun the fibres to make demonstration pieces of Williams and Sowerby’s glass damask which was exhibited at the Manchester Mechanics Institute in 1840 [5].

In June 1842, Schwabe was reported in the Manchester Courier as asking for the assistance of the British Association in:

“ carrying out experiments which would lead to the discovery of a substance which would form a homogeneous mass possessing the quality of ductility and susceptible of being drawn out through fine holes, or otherwise, into filaments or fibres possessing suitable strength and other properties to adapt it for manufacturing purposes.”[6]

Schwabe’s effort to produce artificial fibres ended unhappily with his protracted suicide via a draught of sulfuric acid in 1845.

It is unfortunate that a suitable candidate material, nitrocellulose was discovered only a year later by Christian Friedrich Schönbein. It is said [7] that whilst distilling nitric and sulfuric acids in his kitchen he spilt his reaction mixture, and mopped it up with a cotton apron. He washed the apron, and hung it up to dry above the stove. The result was that the apron exploded, leaving negligible solid residue or smoke. Schönbein, realising the potential of this material rushed to patent rather than publish, and was able to demonstrate his new explosive schießbaumwolle (“guncotton”) by rock blasting at Istein, Germany in July 1846.

In 1855 George Audemars of Lausanne, Switzerland patented a method for spinning Collodion – extracted from cellulose from mulberry (Morus alba) trees. This wood
was perhaps selected because it forms the foodstuff for the mulberry silkworm, *Bombyx mori*. At this time silk was an expensive luxury, and as now, there was a clear market for cheaper substitute materials. Audemars’ first experiments simply dipped a needle into his solution, and drew it out, pulling a long thread of rapidly hardening Collodion behind it [8]. This method was time consuming and produced a product that being essentially guncotton, was really was far too inflammable for use in clothing.

John Francis Cooley originally of Penn Yan New York, was a professional inventor and an electrician. His inventions included a rotary steam engine or pump, and a very ambitious attempt to build a flying machine at Rochester New York. Cooley filed the first electrospinning patent [9] in which he proposed three types of indirectly charged spinning heads – a conventional head, a coaxial head, an air assisted model, and a spinneret featuring a rotating emitter. He also proposed the recovery of solvent and the use of a dielectric liquid instead of a gas as the medium.

William James Morton (1845-6 - 1920) was a professor of electrotherapeutics who used, as part of his electrical arsenal, X-rays to both diagnose and treat ailments such as alopecia and cancer. His high voltage source was described (Anon 1896) as "a Crocker-Wheeler quarter horse power motor with a make-and-break attachment connected with the street arc light wires, a Rhumkorff coil with a four-and-a-half inch spark, a cabinet for tests in opacity and Crookes tubes of various patterns". The length of the spark indicates that this induction coil apparatus was capable of producing about 110kV. His 1902 patent (no. 705691) is very light on practical details, describing a sort of separating funnel allowing a stream of liquid to fall in front of a ball shaped anode and variously a chain, or a reel to collect the fibre as a “cobweb-like mass” which ultimately “may be put to any industrial use”.

In 1914 John Zeleny, published work on the behaviour of fluid droplets at the end of metal capillaries. His effort began the attempt to mathematically model the behaviour of fluids under electrostatic forces. Dipl. Ing Ludwig Rudolph Anton Formhals was born in Mainz on 24 Aug 1877. He worked for the Verein fur Chemische Industrie AG. His contribution to electrospinning is marked by at least 18 patents. In 1938 N.D Rozenblum and I.V Petryanov-Sokolov at the Aerosol Laboratory of the L. Ya Karpov Institute in the USSR, generated electrospun fibres, which they developed into filter materials that became known as "Petryanov filters". By 1939, this work had led to the establishment of a factory in Tver’ for the manufacture of electrospun smoke filter elements for gas masks. The material, dubbed BF (Battlefield Filter) was spun from cellulose acetate in a solvent mixture of dichloroethane and ethanol. By the 1960s output of spun filtration material was claimed as 20 million m² per annum [10].

Between 1964 and 1969 Sir Geoffrey Ingram Taylor produced the beginnings of a theoretical underpinning of electrospinning. Taylor’s work contributed to electrospinning by mathematically modelling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone. He further worked with J. R. Melcher to develop the “leaky dielectric model” for conducting fluids. In the early 1990s several research groups (notably that of Reneker who popularised the name electrospinning for the process) demonstrated that many organic polymers could be electrospun into nanofibers. Since then, the number of publications about electrospinning has been increasing exponentially every year.

ACKNOWLEDGMENT
The authors acknowledge the support of the NZ Institute for Plant and Food Research and wish to thank Dr. Sander De Vrieze now of Centexbel, Mr Jack Cooley Clifford, The Lord Mayor of Mainz and Dr Frank Teske of the Landeshauptstadt Mainz Stadtarchiv for their help and efforts completing this research.

REFERENCES
[9] Cooley, J. F, 1900, Patent GB 06385 “Improved methods of and apparatus for electrically separating the relatively volatile liquid component from the component of relatively fixed substances of composite fluids.”
The design of composites containing nanofibers is aided by knowledge of the mechanical stress-strain curve for individual fibers. It is not unusual for the stress-strain relationship of an electrospun nanofiber to change during the initial elongation, so that the incremental modulus is a function of the strain history.

A nanofiber segment, captured between movable grips, and deflected by a transverse air stream, assumes the shape of a catenary curve. With proper illumination, the shape of the nanofiber at a measured air speed was photographed with a video camera. The observed shape, combined with scanning electron microscopy measurements of the diameter of fiber ends at the grip after the deformation, provides stress-strain information. Control of the air speed and grip separation rate enable mechanical hysteresis of the fibers to be measured. Direct comparisons were made among polymers with mechanical properties having a wide range of values. This information is helpful for selecting polymers and developing useful intuition for the design of composites, filters and bandages.

The internal morphology of nanofibers was observed in interesting detail by transmission electron microscopy. Enough electrons to produce useful images passed through the thin fibers without causing changes in many morphological features.
Polymer Dynamics During Solution Electrospinning:
Experimental Observations of the Structure of the Jet

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ABSTRACT
There is a growing demand in surfaces specialized in the collection (separation), retention, and release of various kinds of particles. Initially, such surfaces can be applied for medical/hygiene, security, and high-tech areas. However, in general, they can be potentially interesting for the housekeeping area of application. In the medicine, selective collection of bacteria of different sizes from different surfaces might be a promising approach for further increase of sterility monitoring in operation rooms. Selective pollen collection might be an extremely promising way to build specialized anti-allergic filter systems. In the high-tech areas, cleaning of sensitive optics (especially large-scale telescope mirrors) cannot be achieved by conventional methods of application of solvents or/and microfiber wipes. Recent security regulations and defense operational requirements demand on-site analysis of explosives residues or post-blast debris to enable rapid identification such that swift action may be taken, hence convenient methods for particles collection are desired. The majority of the current collection and cleaning methods rely on traditional textile fabrication technologies. In these methods, in general, a wipe is used which is made of commercialized woven micro-fibers. Usually several post-processes are followed to increase the adhesion and the durability of the wipe, such as plasma treatment and impregnation, where is some cases liquids are added during the particle collection process to increase the adhesion.

A promising fabrication method is electrospinning, which is a common method to produce fibers with a diameter in the range of a few micrometers to less than 100 nm. The electrospun fibers form nonwoven mats with a large surface area per unit mass and very small pore size.

The aim of this study is to develop surfaces for selective particle collection of different sizes and shapes for a variety of applications. One major difference between commercial swabs to electro-spun ones, as can easily be seen, is the individual fiber size within the mats, where electro-spun (ES) fibers display significantly smaller fiber size, less than 1µm in comparison to 10-20µm of the commercial swabs fibers. Additionally, the apparent porosity of ES mats is larger than commercial ones (see Figures 1-2). Surface area quantification of the chosen swabs, through BET; have revealed that the specific surface area of the commercial swabs was no more than 0.3 m²/gr, while nylon swabs have demonstrated a specific area of ca. 17 m²/gr. Thus, emphasizing the observed difference in porosity of these swabs.

In this work, ES nylon 6,6 swabs were fabricated using two distinct solutions of 25 and 20 wt.% nylon. Nylon pelts were dissolved in 70/30 wt.% solution of formic acid (FA) and trifluoroethanol (TFE). Each of the resulting solutions was electro-spun to form both oriented and non-oriented mats consequently yielding four different types of mats – oriented and non-oriented nylon 6,6 spun from 25% solution and denote here as nylon25Or and nylon25NO and similarly nylon20Or and nylon20NO for mats spun from 20% solution. The selected test surface was a computer 3.5" diskette made of Poly (Acrylonitrile, Butadiene, Styrene, ABS). The investigation of the
swabs’ collection efficiency was carried out through series of steps that included contamination of the surface by ca. 1 μg of Tinopal to the test surface using a normal force of 1.5 kg and 10 iterations and was subsequently collected from the surface using the investigated swab. Typical series of pictures for Muslin and nylon20NO can be viewed in Figure 3.

Figure 3: Typical collection pictures for (top to bottom): Muslin and nylon20NO. Pictures were taken for (left to right): neat swab, contaminated surface, post-collection surface and post-collection swab.

In Figure 3, the superior collection efficiency of the nylon is easily visible to the naked eye. The image-processing analysis was performed by comparing the two ABS pictures (contaminated and post collection). Due to high dissimilarities between swabs and some erosion of its surface during collection data analysis could not be carried out using the swabs. Thus, analysis was performed on ABS surfaces.

SEM micrographs of the post-collection swabs presented here for the nylon25NO swabs in Figure 4. The micrographs indicate that Tinopal was collected on the entire swab surface. Furthermore, some Tinopal particles have been shown to be immobilized between several nylon fibers. This phenomenon is attributed to the higher elasticity of the nylon fibers, enabling certain fibers to retract and recoil during surface wiping, thus lifting and engulfing particles.

Further improvement of collection efficiency of the nano-fibered swab was primarily approached by manufacturing a complex-hierarchy single fiber and on-line detection capabilities.

Figure 1: SEM micrographs of a post-sampling nylon20NO swab.
Production and Characterization of Electrospun Polyaniline Fibers with High Electrical Conductivity

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INTRODUCTION

Electrospinning is a convenient method [1] to produce polymer nanofibers with controlled diameters on the order of tens of nanometers to microns [2]. The resulting nonwoven fiber mats have large surface-area-to-weight ratios, around 1 to 100 m²/g. Combined with the high electrical conductivity of intrinsically conductive polymers, conductive electrospun fiber mats are promising for a variety of applications, such as multifunctional textiles, resistance-based sensors, flexible reversibly hydrophobic surfaces, organic photovoltaics, scaffolds for tissue engineering, and to provide a conductive substrate for surface functionalization and modifications [3].

Polyaniline (PAni) is one of the most studied yet hard-to-process electrically conductive polymers. As with other conductive polymers, it has rigid backbones, and exists in relatively low molecular weight forms, so that the elasticity of its solutions is generally insufficient to be directly electrospun into fibers.

One way to solve the problem is to blend high-molecular-weight non-conducting polymers with the conductive polymers to make the solution electrospinnable [4], but the resulting fibers have much lower conductivity due to the blending.

Core-shell electrospinning technique can be employed to make fibers with conductive polymers in the core and non-conducting polymers in the shell as processing aids [5]. With the selective removal of the shell component of the resulting fibers, we have produced pure polyaniline electrospun fibers with high electrical conductivity.

APPROACH

Polyaniline (Sigma-Aldrich, M_w = 65,000) with equimolar amount of (+)-camphor-10-sulfonic acid (Fluka) were dissolved in chloroform and dimethylformamide (DMF), ranging from 0.5 to 2 wt%, and blended with either poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMMA) to form a blended solution. The weight percentage of polyaniline in the resultant blended fibers ranged from 5% to 67%.

For core-shell electrospinning, the core fluid was 2 wt% polyaniline with equimolar amount of (+)-camphor-10-sulfonic acid in 5:1 weight ratio of Chloroform/DMF; the shell fluid was 15 wt% PMMA (Scientific Polymer, M_w = 540,000) in DMF. The shell component of the resultant fiber mats were dissolved using isopropyl alcohol to achieve purely polyaniline fibers.

We have used a reliable and sensitive characterization method to accurately determine the electrical conductivity of single electrospun polyaniline fibers, instead of an averaged value with all tortuous conducting pathways in a highly porous network of fibers. Interdigitated Pt electrodes (IDE) with finger spacings ranging from 5 to 20 μm were purchased from ABTech. For accurate characterization, aligned electrospun fibers were deposited directly on the electrodes and hot-pressed at 200°C afterwards to ensure contact. Solartron 1260/1287A high-impedance analyzers were used to measure the resistance between the two electrodes on the IDE. The number of parallel pathways was estimated from optical microscope images, and fiber diameters from SEM images. The finger spacings were varied to extrapolate the contribution of the contact resistances.

Polarized infrared spectra, dynamic scanning calorimetry, and X-ray photoelectron spectrometry were used for structural characterization of the electrospun fibers.

RESULTS AND DISCUSSION

PAni blended with PEO (M_w = 1,000,000 and 2,000,000) was readily electrospun from a mixed 5:1 chloroform/DMF solution into fibers in the range of 11 to 67 wt% PAni in the final fibers. PAni blended with PMMA (M_w = 540,000 and 960,000) was electrospun from its chloroform solution to form fibers with 3 to 25 wt% PAni in the fibers. Higher weight percentage of PAni in the fibers was not achievable through the blended solutions because of insufficient elasticity of the solutions to have continuous fibers drawn under the electric fields available.

The core-shell PAni-PMMA fibers were electrospun under various core and shell fluid flow rates to achieve smooth and continuous fibers. After dissolution of the mats and fibers by isopropyl alcohol, the fiber diameters decreased, but the fiber surfaces were still mostly smooth, as shown in representative SEM images in Figure 1.
The electrical conductivity of the single fibers were calculated based on Equation (1), where $R$ is the overall IDE resistance measured, $N$ is the number of parallel pathways, $d$ is the average fiber diameter, and $\delta$ the finger spacing.

$$\sigma = \frac{1}{\rho} = \left[\frac{(R \times N) \times (\pi d^2 / 4)}{\delta}\right]^{-1} = \frac{4\delta}{\pi d^2 RN}$$

The contact-resistance correction was done by depositing the same fibers on IDEs with different finger spacings (5, 10, 15, and 20 $\mu$m), and plotting the single-fiber resistances ($R \times N$) against the finger spacings to project to the contribution of the contact resistance at zero finger spacing, which was then subtracted from the resistances measured.

The electrical conductivities of the electrospun polyaniline fibers, both blended with processing-aid polymer and core-shell electrospun, are summarized in Figure 2.

The single-fiber electrical conductivities are found to be increasing exponentially with the weight percent of doped polyaniline in the fibers. The electrical conductivities of the PAni-PEO systems are order of magnitude higher than the PAni-PMMA systems at the same weight percent of PAni, indicating that the processing-aid polymers act more than just a non-conducting filler in the fibers and behave differently, possibly due to different intrinsic conductivity and degree of phase separation with the conducting PAni.

The highest electrical conductivity achieved is from the 100% PAni fibers after the shell PMMA components were removed, and the calculated single-fiber conductivity is found to be $50 \pm 30$ S/cm.

Further stretching of the aligned 100% PAni fibers in the fiber direction up to 100% strain increases the conductivity to $130 \pm 40$ S/cm. The most likely cause of this increase is the enhanced molecular orientation in the electrospun fibers along the fiber direction, supported by the polarized FTIR measurements.

CONCLUSIONS

We have successfully produced electrospun polyaniline fibers over a range of compositions in blended fibers. For the first time, pure conductive polyaniline fibers have been produced by core-shell electrospinning and subsequent removal of the shell processing-aid polymer. The conductivities are found to increase exponentially with the weight percent of doped polyaniline in the fibers, to as high as $50 \pm 30$ S/cm when all processing-aid polymers are removed, and to $130 \pm 40$ S/cm upon further stretching. Enhanced molecular orientation during the extensional deformation in the electrospinning process and afterwards during further stretching is the main cause of these high conductivities obtained.

ACKNOWLEDGMENT

We wish to thank Prof. H.L. Tuller, Prof. K.K. Gleason, and Prof. V. Bulovic for helpful discussions. This research was supported by the U.S. Army through the Institute for Soldier Nanotechnologies (ISN), under contract ARO W911NF-07-D-0004.

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Onset of Electrospinning

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STATEMENT OF OBJECTIVE
The work deals with the electrically driven instability of polymeric solutions that gives rise to electrospinning from a free liquid surface. A characteristic hydrodynamic time for electrospinning is investigated and analyzed both theoretically and experimentally. Low and high-viscose Polyvinyl Alcohol (PVA) solutions are used for this analysis. Oscilloscope readings of electric current immediately after the field switching are compared with theoretical prediction of relaxation times.

INTRODUCTION
The Tonks–Frenkel instability of a charged liquid surface plays a critical role in various scientific, technical, and technological applications, such as electrospraying and atomization of liquids and metals, and electrospinning of nanofibers from polymer solutions and melts. In many cases, polymer solutions and melts are difficult to electrospin. It is therefore important to understand the mechanisms of jet formation and causes of instability. We investigate the onset of electrospinning of a viscose polymer solution, PVA, and develop experimental methods for the analysis of jetting at the microsecond scale.

APPROACH
We start with the linearized Navier–Stokes Equation to describe the behavior of surface waves. The liquid in question is assumed incompressible and the amplitude of capillary waves from which the Taylor cones evolve is considered small compared to the wavelength.

Following Levich’s approach [1], we obtained a relaxation time needed for the Taylor cone formation. Theoretically predicted relaxation times for various polymer solutions and applied voltages were compared with the measured values to confirm the applicability of the proposed theory.

The experimental setup used for the analysis is shown in Figure 1 and it consists of a rod with a drop of polymer solution and a counter electrode. The rod of the electrospinner was connected to the positive pole of the high voltage source while the collector was grounded.

A device for the measurements of characteristic hydrodynamic times measures two voltaic signals at canal no. 1 and canal no. 2 of the oscilloscope. The canal no. 1 records the switch on state of the spinner that is realized by the quick-acting switcher. The oscilloscope canal no. 2 controls the voltage in the applied to the drop of the electric circuits. The time difference between these two signals is the measured experimental characteristic hydrodynamic time.

FIGURE 1. Electrospinning device consisting of a rod with a polymeric droplet on its tip and a disc collector.

FIGURE 2. Oscilloscope records from canal no. 1 and canal no. 2. The time difference between the peaks represents the experimentally measured characteristic hydrodynamic time $T$. 

FIGURE 2. Oscilloscope records from canal no. 1 and canal no. 2. The time difference between the peaks represents the experimentally measured characteristic hydrodynamic time $T$. 

FIGURE 1. Electrospinning device consisting of a rod with a polymeric droplet on its tip and a disc collector.
RESULTS AND DISCUSSION

*Figure 3* illustrates an example of the theoretical relaxation time, the continuous curve, together with the experimental one, dots, representing the average values obtained from 10 experimental trials.

![Graph showing dimensionless relaxation time τ as a function of Electrospinning number Γ][2] for PVA 8% wt aqueous solution having an Ohnesorge number of 0.048.

CONCLUSION

This study shows that the analysis based on the linearized Navier-Stokes equation is able to predict the characteristic hydrodynamic times of jet formation. The developed experimental method is very helpful for the analysis of spinability of various polymer solutions and melts.

ACKNOWLEDGMENT

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Electrospun Nanofibrous Mats for Composite Membranes

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STATEMENT OF OBJECTIVE
The main objective is to use fibers of different diameters, composition, and morphology as a new format for the fabrication of composite membranes in applications suitable for water purification.

INTRODUCTION
The importance of water will soon follow as one of the new challenges of the 21st century. With global warming and a population reaching about 9 billion by 2050, there is simply not enough usable water for many parts of the world, partly because the distribution of usable water on earth is extremely uneven and people often live in regions where there is a limited amount of accessible usable water. The key sources of water, aside from rivers and lakes, are from oceans and from ground water, although the rate of replenishment for ground water needs to be taken into account if we were to increase its usage substantially.

APPROACH
Two breakthroughs based on the use of nanofibers have been developed as a platform technology for separation applications to water and air purification. Due to its broad implications associated with specific targets, functions and formats, the current presentation deals with water purification. In particular, a few examples are discussed for water purification using micro-filtration (MF) and ultra-filtration (UF) [1, 2].

The key features of our approach are illustrated schematically in Figure 1. In the present configuration, the nanofibrous filter is composed of 2-3 integrated layers of non-woven mats, fabricated from fibers of different fiber diameters. We take advantage of the fact that with comparable porosity, non-woven structures from smaller diameter fibers yield smaller effective pore sizes. Over a reasonable range of layer thickness and for the same fiber diameter, the effective pore size depends on the porosity. Thus, the effective pore size and pore size distribution can be controlled for a range of materials by using different processing techniques. Moreover, we can fill the empty space among the fibers with porous materials that form molecular cavities for permeation of water with the interphase between the porous materials and nanofiber surface as directed water (or fluid) channels, and thereby increase the water (or fluid) permeability.

In Figure 1, the mid-layer nonwoven mat is typically fabricated by electro-spinning, which can produce nanofibers with average diameters ranging from microns down to about 100 nm. Based on experimental results from electro-spin non-woven mats, we can take advantage of an interesting relationship between the average fiber diameter and the effective pore size at a reasonable layer thickness, as shown in Figure 2. The finding implies that if we use a combination of a non-woven support layer (for mechanical strength) and an electro-spin non-woven layer with an average fiber diameter of about 100 nm, bacteria cannot pass through such a 2-layer filter by size exclusion.

![Fig. 2 Relationship between Pore Size and Fiber Diameter](Image)

Fig. 2 Relationship between Pore Size and Fiber Diameter

One of the crucial developments in electro-spinning technology is its scale-up advances. While there are companies that have facilities capable of producing quantities at an industrial level, the technical know-how is often proprietary. In addition, for liquid filtration, the requirement on pore size and pore size distribution is often more stringent than applications related to air purification. For these reasons, we have spent considerable effort to establish our own multi-jet electro-spinning technology [3]. Figure 3 shows a computer-controlled 100-jet electro-spinning unit with environmental control for continuous production of electro-spun mats. We have used a range of polymers, including the current standard polymers used in the water
purification industry, such as poly acrylonitrile (PAN) and poly ether sulfone (PES).

RESULTS AND DISCUSSION
We have carried out microfiltration (MF) and ultrafiltration (UF) studies, using the non-woven fibrous mat concept, as illustrated in Figure 2. Table 1 shows some of our findings, in comparison with commercial Millipore filters, having comparable pore size characteristics.

Our MF filters are of the 2-layer format. Based on their mean pore size and maximum pore size, they are suitable for elimination of bacteria by means of pore size exclusion.

Figure 4 shows cross-flow ultrafiltration measurements using a cellulose ultra-thin nanofiber mat, as illustrated in Figure 1, for separation of oil/water emulsion. In comparison with a commercial PAN UF (Sepro) membrane with comparable rejection ratio, our improvement in permeation flux is of the order of 10.

The use of electro-spun nanofibrous mats would only be a laboratory demonstration if we could not scale-up the electro-spinning process. Figure 5 shows that we have succeeded in fabricating spiral wound cartridges that can be tested in an industrial environment.

CONCLUSIONS
We have scaled up the electro-spinning process and have demonstrated the use of fiber concept for MF and UF.

FUTURE WORK
We plan to introduce directed water channels onto the top barrier layer by using ultra-thin fibers whose surfaces could promote pure water flow. Although initial tests using modified multi-wall carbon nanotubes showed the feasibility, further investigation is in progress.

ACKNOWLEDGMENT
We gratefully acknowledge support of the water project by the Office of Naval Research (N000140310932) and an EAger grant from the National Science Foundation (DMR-1019370). The experimental work was performed by members of the Chu-Hsiao team, especially Drs. Hongyang Ma, Christian Burger and Dufei Fang, as well as Ran Wang and Yan Liu.

REFERENCES
Needleless Electrospinning and Direct Electrospinning of Nanofiber Yarns

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Electrospinning is a simple, but efficient and versatile, technology to produce polymeric nanofibers for widely diverse applications in both textile and non-textile areas [1]. This technique has been shown many advantages such as universality in processing polymeric materials, easiness of controlling the fiber diameter and functionalizing nanofibers through adjusting solution composition for electrospinning, and flexibility to generate fibrous membranes of various geometries. Although the novel applications of electrospun nanofibers have been extensively explored [2], the technology development for mass electrospinning of nanofibers has been hampered.

In most cases, nanofibers are electrospun in the form of nonwoven webs. Nanofiber bundles that have long continuous length and interlocked fibrous structure, or nanofiber yarns, are expected to create new opportunities to develop more complicated nano fibrous structures with well-defined three-dimensional architectures and better mechanical performance, which will lead to many new applications. It remains a challenge to produce nanofiber yarns that have continuous length and controlled twist structure directly from an electrospinning process.

In this report, our recent works on needleless electrospinning for mass production of nanofibers and direct electrospinning of highly-twisted continuous nanofiber yarns are introduced.

NEEDLELESS ELECTROSPINNING

In an effort to increase the productivity of electrospinning, we have recently developed new needleless electrospinning systems (Fig 1). Disc was initially chosen as fiber generator and compared with cylinder [3]. The disc fiber generator needed a relatively low applied voltage to initiate the fiber formation, and the fibers were mainly formed on the disc edges. By comparison, nanofibers electrospun from the cylinder showed a higher dependence on polymer concentration and the applied voltage. The fibers were initiated from the cylinder ends first, and then from the entire cylinder surface only if the applied voltage was increased to a certain level. With the same polymer solution, the critical voltage to generate nanofibers from the disc was lower than that from the cylinder. Both electrospinning systems could produce uniform nanofibers, but the fibers produced from the disc were finer than those from the cylinder when the same voltage was applied to both. More recently, a spiral coil was used as fiber generator, which showed finer fibers with narrower diameter distribution, but much higher productivity than the disc system [4].

As listed in Table 1, nanofibers produced by the disc are finer with narrower diameter distribution (better quality). A thin disc (diameter 8 cm and thickness 2 mm) could produce nanofibers at a similar rate to a cylinder of the same diameter but 100 times wider (i.e. 20 cm long). However, the coil that has the same length and the diameter to the cylinder are double in the production rate, but the produced fibers are finer with narrow diameter distribution.

In comparison with the conventional needle electrospinning, the cylinder or the disc electrospinning system produced coarser nanofibers, but the dependency of fiber diameter on the polymer concentration showed a
similar. However, for the coil system, it produced even finer nanofibers with narrower diameter distribution than the conventional electrospinning system. In addition, the crystallinity of polymer in needleless electrospun nanofibers was higher than that of nanofibers produced by conventional needle electrospinning.

CONTINUOUS ELECTROSPINNING OF NANOFIBER YARNS

Figure 2 schematically illustrates the basic setup for electrospinning of nanofiber yarns, which consists of two needle nozzles, a rotating funnel collector, a cross winder, and a high-voltage DC power supply. Two nozzles were placed in front of either side of the funnel collector, and a yarn-winding system was set between the nozzles with a distance further than that between nozzle and funnel collector. During electrospinning, two needle nozzles were connected separately with positive and negative polarities of the DC power supply. Nanofibers electrospun from the oppositely charged nozzles were deposited onto the rotating funnel collector to form a fibrous membrane covering the funnel surface.

To form a nanofiber yarn, the nanofibers deposited were pulled off the funnel surface, while at the same time maintaining the funnel rotating constantly (Fig 3a). This led to the formation of a “cone” shaped fibrous membrane attaching to the funnel edge (Fig 3b). With continuously rotating and drawing the fibrous cone, a twisted fiber bundle was formed at the fibrous cone tip, which can be wound to form a continuous nanofiber yarn. Figure 3c shows the appearance of a nanofiber yarn produced by this process, which looks similar to that of conventional yarns, except that the fibers are on nanometer scales (with an average diameter of 486 nm in this study). In addition, most of the nanofibers within the yarn aligned in certain angles along the yarn length direction (Fig 3d).

Kilometers of a continuous nanofiber yarn can be directly withdrawn from the “cone” apex, with up to 7400 turns-per-meter of twists inserted through the rotation of the funnel. The maximum yarn production rate is 5 m/min, and the yarn twist level and fiber orientation can be controlled by the funnel rotating speed and yarn withdrawal rate. The nanofiber and yarn morphologies, yarn dimension, twist level and production rate are determined by both the operating parameters (e.g. applied voltage, electrospinning distance, flow-rate of polymer solution, funnel dimension and rotating speed, the distance between funnel and winder, and winding speed) and material properties (e.g. polymer, polymer concentration).

The tensile properties of nanofiber yarns were found to depend on the twist level. With increasing the twist level, both the tensile strength and the elongation at break increased. However, when the twist reached certain level, the tensile strength started decreasing, while the elongation at break maintained the increase trend. The maximum average tensile strength of the PVDF-HFP nanofiber yarn produced from this work was 60.4 MPa. Also, these yarns were further processed into braids and fabrics. The braided nanofiber yarns showed considerable improvement in tensile strength.

In conclusion, we have demonstrated the potential of using needleless setups to large-scale electrospin nanofiber nonwovens and dual-nozzle electrospinning setup to directly electrospin highly-twisted continuous nanofiber yarns. These nanofiber processing techniques may be useful for producing quality nanofibrous materials for various applications.

REFERENCES

Biomineralized, Highly Aligned, Nanofiber Array-based Building Unit for Bone Regeneration

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Statement of Purpose: The purpose of this study is to examine the ability of using mineralized nanofibrous scaffolds to replace current strategies for bone defect repair, in order to actually regenerate the injured tissue.

Introduction: Bone’s microstructure is composed of highly aligned collagen nanofibers embedded with hydroxyapatite (HAp) crystals that form between and elongate on these collagen fibers. This refined structure allows for enhanced mechanical properties that give bone its necessary high strength and fracture toughness, which maintain its load-bearing function, as well as elasticity, which allows it to absorb shock. Current treatment methods, such as bone autografts and allografts, for critical sized defects in bone do not suffice due to numerous issues associated with these methods. The field of bone tissue engineering focuses on mimicking the structural and mechanical properties of bone by creating a scaffold that closely resembles bone’s microstructure. In the present study, highly aligned biomineralized polymer nanofibrous scaffolds were created as the fundamental building unit for bone regeneration. By combining the use of our novel electrospinning apparatus, which creates highly aligned electrospun fibers, along with SBF immersion, which provides biomimetic ceramic coating on the fibers, we were able to create a scaffold which mimics the microstructure of the natural extracellular matrix of bone, as well as possesses enhanced mechanical properties, which are necessary for this application.

Approach: A novel electrospinning device (Figure 1A) was used to create highly aligned polycaprolactone (PCL) nanofibrous scaffolds (Figure 1B).

The surface of these scaffolds were then functionalized and mineralized using a biomimetic technique in order to create an even coating of hydroxyapatite nanoparticles on the surface. The parameters of this mineralization process (surface hydrolysis time and 5X simulated body fluid (SBF) immersion time) were altered in order to produce an optimal coating which demonstrated similar chemical and structural properties to that of natural bone. The mechanical properties of these optimized scaffolds were also assessed in order to test their ability to serve as a bone tissue engineering scaffolds. Cell studies were also conducted in order to assess attachment, alignment, proliferation, and alkaline phosphatase (ALP) activity of human embryonic palatal mesenchymal (HEPM) stem cells on the mineralized. After these preliminary studies were completed, these aligned scaffolds were stacked on top of each other in a parallel orientation in order to create 3D structures. The morphology of these 3D structures was then assessed using a microCT.

Results and Discussion: It was determined that scaffolds hydrolyzed for 30 min. and soaked in 5X SBF for 24 hr. created an optimal coating on the scaffolds (Figure 2).

Average fiber diameters (Figure 3) of the mineralized and unmineralized scaffolds, as well as angular deviation (Figure 4), was assessed using image analysis software and SEM images.
Initial mechanical testing data indicates significantly higher ultimate tensile strength, elastic modulus, and toughness of mineralized scaffolds as compared to the unmineralized controls. Further, the ultimate strain of the samples was comparable for both groups, indicating that the mineralized samples exhibited both strength and elasticity, which is very important for bone tissue engineering scaffolds (Figure 5).

![Mechanical Properties of Nanofibrous Scaffolds](image)

**Figure 5.** Mechanical properties of unmineralized and mineralized PCL nanofibrous scaffolds

Preliminary cell studies indicate similar cell attachment and alignment for both mineralized and unmineralized samples (Figure 6).

![Cell Alignment](image)

**Figure 6.** Cell alignment on mineralized (A) and unmineralized (B) PCL nanofibrous scaffolds

An alamar blue assay was conducted in order to assess the cytotoxicity of the mineralized scaffolds as well as compare these scaffolds to the unmineralized controls. Data indicates no cytotoxicity of mineralized scaffolds as well as similar proliferation as compared to unmineralized controls (Figure 7).

![ALP Activity](image)

**Figure 8.** An ALP activity assay assessing differentiation of HEPM cells on mineralized and unmineralized scaffolds. N=2, significance not tested.

40 aligned, mineralized nanofibrous scaffolds were then stacked on top of each other in a parallel orientation in order to create a 3D scaffold. MicroCT images were then taken to observe the structure of the bone tissue engineering scaffold.

![MicroCT Images](image)

**Figure 9.** MicroCT images illustrating mineralized 3D scaffold.

The ALP activity of HEPM cells seeded onto mineralized and unmineralized scaffolds was assessed. Data indicates higher ALP activity of HEPM cells on mineralized scaffolds at days 10 and 14 (Figure 8).

![HEPM Proliferation](image)

**Figure 7.** Alamar Blue assay assessing cytotoxicity and proliferation of mineralized and unmineralized scaffolds. n=2, significance not tested.

Conclusions: This study has been successful in determining the optimal parameters that created a bioceramic coating on polymer nanofibers, both in composition and structure. Further, this coating created a scaffold that has significantly enhanced mechanical properties, which is very important for bone tissue engineering. HEPM cells exhibited no cytotoxicity and demonstrated excellent cell attachment, alignment, and proliferation on these scaffolds.

Future work: Future *in vitro* studies include conducting mechanical testing on 3D structures as well as cell studies, including viability, proliferation, migration, ALP activity, and Collagen I production. Future *in vivo* studies include implantation of these structures into mice in order to assess immune rejection and new bone formation.

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Continuous Nanofiber: Reinforced Structural Nanocomposites

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ABSTRACT
Continuous nanofibers possess considerable advantages to discontinuous nanomaterials, such as nanoparticles, nanorods, and nanotubes. Continuous nanofibers with diameters several orders of magnitude smaller than the diameters of conventional advanced fibers can revolutionize existing and create entirely new applications. Progress on nanofiber applications in advanced nanocomposites will be reviewed in this lecture. Relevant nanomanufacturing issues will be discussed. Examples of novel high-performance continuous polymer, carbon, and ceramic nanofibers will be presented. Several new ways to utilize nanofibers in advanced structural nanocomposites will be introduced and discussed. Pioneering designs of advanced composites with nanofiber-reinforced interfaces developed by the author’s group will be presented and analyzed. Prospects of structural supernanocomposites defined as composites exceeding mechanical performance of existing advanced composites such as carbon-epoxy will also be discussed.
Advances in Fiber-based Materials
Optimizing Conditions for Creating Graphene Coatings to Create Unique Textile Materials

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Carbon fibers, carbon nanotubes have been used to create unique textile materials. We survey that work in this paper, and describe innovative work done in the UGA laboratories. In this work, we used cotton fabric as a template to create macro sheets of graphene. The cotton fabric was dipped into a graphene derivative suspension. The graphene-coated cotton textile was then annealed in a quartz tube furnace under an Argon flow. During the annealing process, the gaps between separated graphene sheets were “soldered” by the “glue” molecules (aromatic molecular surfactants) to form graphene-coated pyrolytic carbon. Because the graphene “skin” was created on the pyrolytic carbon by annealing, a flexible graphene coat was created that can contribute relatively high capacity to a lithium battery sandwich. This occurs because of porous structure of graphene sheets and the high surface area of the pyrolyzed carbon with a shell-core structure. This novel, facile, and low-cost method can be expanded to applications of other carbon-rich materials such as peanut shells, wood waste and other cellulosic waste materials.

Recently, great interest has been focused on graphene nanocomposites for various applications. Graphene is a one atom-thick material made up of sp²-bonded carbon atoms. Its unique properties include high electrical and thermal conductivity, the quantum Hall effect, massless transportation properties, and strong mechanical properties [1-11]. Among several possible applications, the use of graphene as an electrode in lithium batteries is very promising because of graphene’s relatively low-cost and accessibility. However, a graphene anode alone provides relatively low lithium storage capacity and has an unstable charge and discharge cycle performance, which is a problem to overcome before the commercialization of graphene electrodes is feasible. Recently, several different nano-materials, including various carbonaceous materials and nanometal/oxides have been tested as templates to enhance the lithium storage capacity and the cycling performance of the graphene. However, because of the high cost, inaccessibility, and the potential nano-toxicity of these template materials, it has proved difficult to produce graphene-based electrode materials on a large scale.

Cotton is almost pure cellulose. It is a carbon-rich, cheap, and available on a large scale. Recently, there have been reports of highly electro-conductive cotton/carbon nanotube composites prepared by dipping a cotton fleece (pile) fabric into a carbon nanotube solution. This was successful because of the flexibility of the nanotubes and the strong binding between the carbon nano-tubes and the cotton fibers. Graphene also exhibits the good flexibility and electro-conductivity that carbon nano-tubes do, but with the added advantage of being potentially much less expensive.

Little research has been done on the fabrication of graphene-coated textiles, probably due to the difficulty of preparing stable graphene solutions, wrapping the seamless graphene layer on the fibers, and reaggregation of graphene sheets, as well as the complications of pre- and post-
treatments. In the present work (as shown in Scheme 1), we use cotton fibers as templates where the graphene sheets are created and wrapped the fibers. The result is a graphene coated pyrolytic carbon material. Because of the core-shell structure of the graphene-coated pyrolytic carbon, we believe that the graphene-coated pyrolytic carbon can exhibit excellent charge/discharge performance, as well as mechanical flexibility.

In the present work, the chemical nature, morphology, and thermal and electrical properties of the graphene-coated textile nanocomposites have been studied by atomic force microscopy (AFM), UV-Vis spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and Galvanostatic charge-discharge experiments. The primary goal of this work is to produce a facile, low-cost method to prepare graphene-coated pyrolytic carbon materials for potential applications in energy-storage, electronics, and other uses. In the present work, the emphasis has been on optimizing the conditions of heat treatment to maintain maximum possible strength of the materials while keeping the unique electrical properties.
INTRODUCTION
Based on the consumer interests in sustainability and the communications with nonwovens manufacturers, a strong demand now exists for nonwoven products that contain a certain percentage of cotton - a natural, likable, renewable and, hence, sustainable fiber.

However, the bleached cotton and cotton byproducts, which are presently used in a few nonwoven products, are considered somewhat less economical compared to other competing fibers. Aside from certain other factors, this lack of fiber (raw material) cost competitiveness appears to be a major factor that, so far, has inhibited the expected growth in use of cotton in today’s rapidly growing nonwovens markets.

To increase value-added use of cotton in nonwoven products, the Agricultural Research Service of the U. S. Department of Agriculture has directed an expanded and more comprehensive research program on the development of cotton-based nonwovens at SRRC in New Orleans.

New, state-of-the-art equipment for the pilot-scale production, finishing and testing of cotton-based nonwovens has been added to the existing, extensive cotton research facilities at the Center\textsuperscript{1,2}. New researchers and support personnel have also been added to ensure efficient utilization of the expanded research resources and facilities.

In the last two years or so, most of the cotton-based nonwovens research efforts were devoted to the identification and processing of cotton(s) that is cost competitive and also compatible with the existing nonwovens production/ manufacturing processes, and practices. And that will also have to fit in with the conditions for certain high-volume markets.

Today, I am pleased to let you know that we, so far, have been fortunate in successfully accomplishing most of our research objectives of the assigned time period. In short, after a lot of multiple testing and processing studies, we now have identified mechanically cleaned greige/virgin (non-bleached) cotton that is cost competitive and seemingly compatible in processing with man-made fibers that are commonly used in modern nonwovens manufacturing. This pre-cleaned cotton (UltraClean\textsuperscript{®} Cotton)\textsuperscript{3} is now commercially available in several different quality versions. Some of its advantages are as follows: it does not need the traditional (mill) cleaning of its non-lint contaminants; it reportedly sells for much less than a bleached cotton of an equivalent quality; in its hydroentangled fabric form, this cotton fiber does not require the traditional process of chemical scouring and may not even require bleaching for certain nonwovens end-uses; and, above all, when hydroentangled under certain processing conditions, the fabric is absorbent (hydrophilic w/o scouring). Although the filtration for recycling of effluent of the hydroentangling process for this cotton has not yet been fully studied, it seems that this very clean cotton should not present any unsolvable difficulties or problems in a real world scenario.

At any rate, in a collaborative research project with the supplier of UltraClean\textsuperscript{®} cottons, we have separately processed, under similar conditions, seven pre-cleaned cottons of different quality measurements (the fiber length, length uniformity, and micronaire were the predominant variants) and uniformly converted them all into hydroentangled nonwoven fabrics. This presentation today will give you a bird’s eye view of the entire processes involved in the research with a special emphasis on the effects of cotton fiber properties on properties of the nonwoven fabrics made thereof.

RESULTS
All cottons processed reasonably well, i.e., without encountering any unsolvable difficulties or problems. Figure 1, showing fabric rolls of the various cottons processed, is a testimony.
Figure - 1 Rolls of H-E cotton nonwoven fabrics.

Table I shows properties of the selected greige cottons. As seen, they primarily and predominantly differ mainly in their fiber length, length uniformity (index), and micronaire. All of them have negligible non-lint content. Indeed, they are very clean raw materials.

Table I – HVI properties of the various cottons.

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Micron -air</th>
<th>UFML [in]</th>
<th>Ul [%]</th>
<th>SF [%]</th>
<th>Str [gm/ tex]</th>
<th>Elong. [%]</th>
<th>Trash Count [ / gm]</th>
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<td>SBIR#1</td>
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<tr>
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<td>21.1</td>
<td>26.0</td>
<td>3.5</td>
<td>2.8</td>
</tr>
<tr>
<td>SBIR#7</td>
<td>4.82</td>
<td>1.05</td>
<td>81.5</td>
<td>13.2</td>
<td>29.0</td>
<td>5.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table II shows properties of the fabrics made with the seven cottons. As seen, they all have satisfactory properties of a good-quality cotton nonwoven fabric. In other words, it appears that, unlike the traditional textiles, the cotton properties considered in the study did not have significant effects on the fabric properties.

Table II. Tested properties of the various greige (unwashed) cotton fabrics.

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>SBIR # 1</th>
<th>SBIR # 2</th>
<th>SBIR # 3</th>
<th>SBIR # 4</th>
<th>SBIR # 5</th>
<th>SBIR # 6</th>
<th>SBIR # 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (g/m²)</td>
<td>70.3</td>
<td>61.4</td>
<td>71.1</td>
<td>68.9</td>
<td>70.3</td>
<td>66.3</td>
<td>73.3</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>Std. Dev.</td>
<td>0.63</td>
<td>0.59</td>
<td>0.62</td>
<td>0.59</td>
<td>0.65</td>
<td>0.61</td>
</tr>
<tr>
<td>Drop Absorbency Test (sec)</td>
<td>Std. Dev.</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Tongue Tear MD (Newtons)</td>
<td></td>
<td>9.61</td>
<td>8.86</td>
<td>11.26</td>
<td>9.52</td>
<td>10.41</td>
<td>8.41</td>
</tr>
<tr>
<td>Tongue Tear CD (Newtons)</td>
<td></td>
<td>12.06</td>
<td>12.24</td>
<td>14.60</td>
<td>12.59</td>
<td>11.97</td>
<td>10.95</td>
</tr>
<tr>
<td>MD Tensile Strength (N/2&quot;)</td>
<td>Std. Dev.</td>
<td>103.14</td>
<td>88.82</td>
<td>111.70</td>
<td>94.44</td>
<td>102.31</td>
<td>106.91</td>
</tr>
<tr>
<td>MD Elongation (%)</td>
<td>Std. Dev.</td>
<td>5.90</td>
<td>6.67</td>
<td>5.89</td>
<td>5.09</td>
<td>5.57</td>
<td>8.99</td>
</tr>
<tr>
<td>MD Tensile Strength (N/2&quot;)</td>
<td>Std. Dev.</td>
<td>38.60</td>
<td>38.60</td>
<td>47.53</td>
<td>34.13</td>
<td>40.07</td>
<td>35.20</td>
</tr>
<tr>
<td>MD Elongation (%)</td>
<td>Std. Dev.</td>
<td>2.86</td>
<td>3.16</td>
<td>2.46</td>
<td>2.70</td>
<td>2.33</td>
<td>2.75</td>
</tr>
<tr>
<td>CD Tensile Strength (N/2&quot;)</td>
<td>Std. Dev.</td>
<td>129.45</td>
<td>100.21</td>
<td>147.00</td>
<td>137.06</td>
<td>117.14</td>
<td>113.35</td>
</tr>
<tr>
<td>CD Elongation (%)</td>
<td>Std. Dev.</td>
<td>16.30</td>
<td>11.88</td>
<td>24.23</td>
<td>9.19</td>
<td>10.39</td>
<td>7.11</td>
</tr>
<tr>
<td>CD Elongation (%)</td>
<td>Std. Dev.</td>
<td>39.11</td>
<td>38.75</td>
<td>45.12</td>
<td>44.79</td>
<td>42.98</td>
<td>40.65</td>
</tr>
<tr>
<td>Diaphragm Burst</td>
<td>Std. Dev.</td>
<td>3.71</td>
<td>2.64</td>
<td>4.32</td>
<td>3.10</td>
<td>2.84</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Notes: “Mention of trade names or commercial products in this presentation is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.”
Tunable Capillary Pore Membranes

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OBJECTIVE
Microporous membranes are prevalent in the chemical, food, pharmaceutical and medical industries where they are used to separate desired and undesired components of process streams. In many applications, performance is greatly limited by the largest pores in the membrane because the largest pore controls the size of the particulate that can be excluded and the majority of flow is relegated to the larger pores, such that the smaller pores may give a higher porosity number to the membrane but contribute little to overall flux. Thus, it is desirable to produce membranes with little or no variation in pore size.

APPROACH
Membranes and sheet structures can be created from a “fiber-on-end” (FOE) process wherein multicomponent fibers with microfeatures, such as sheath-core or islands-in-the-sea (INTS) fibers, are assembled in a preferred direction and then consolidated or sintered together to create a defect-free structure. When this solid structure is cut or sectioned in a direction that is perpendicular to the orientation of the fibers, membranes and sheets with microfeatures are created. The membrane can then be treated to remove the sacrificial polymer to create uniform pores. DuPont has created commercially viable routes to manufacture such structures. The basic steps of this process are shown in Figure 1.

RESULTS AND DISCUSSION – CUSTOMIZATION OF PORES
Bicomponent fibers, such as sheath-core and INTS, have become common in modern fiber manufacturing. The typical use of these technologies, especially INTS, is to use a sacrificial sea polymer to create micron or sub-micron fibers in the final product. See Figure 2.

FIGURE 1: Sequence of basic steps to create a membrane from multicomponent fibers.

FIGURE 2: Nonwoven fabric from INTS fibers

Alternatively, membranes with highly uniform and customizable pores can be made by sacrificing the islands instead of the sea. Customization of the capillary pores is possible by manipulating the ratio of islands to sea polymers, filament denier, and number of islands to “tune” the pores in terms of diameter and overall porosity. Capillary length is determined by the thickness of the membrane. See Figure 3 for an example of a Surlyn® 8150 ethylene/methacrylic acid copolymer membrane.

FIGURE 3. Capillary pore membrane, shown at different magnifications, from sheath-core filaments of 70/30 weight ratio of sheath to core polymer at 3.6 dpf resulting in a mean flow pore diameter of 11.4 microns as measured by capillary porometry.
A typical nonwoven exhibits a log-normal pore size distribution. See Figure 4. By contrast, the pore size distribution of a FOE membrane is extremely narrow. See Figure 5.

![Figure 4: Theoretical cumulative distribution function F(x) and distribution density function f(x) for pore size for a nonwoven fabric.](image)

**FIGURE 4:** Theoretical cumulative distribution function $F(x)$ and distribution density function $f(x)$ for pore size for a nonwoven fabric.

Further customization is possible to achieve unique membrane properties. For example, a bicomponent or tricomponent fiber can be used to create a membrane where an inner sheath contributes a special functionality to the capillary walls, such as hydrophilicity, hydrophobicity, or conductivity. Furthermore, the capillary walls can contain active or reactive chemical moieties such as carboxylic acid groups, hydroxyl groups, epoxy groups, etc. Another example of customization is shown in Figure 6 and Figure 7.

![Figure 6: Bicomponent fibers with a hollow center, a rigid inner sheath of polycaprolactam and an outer sheath of Nucrel® 0411HS ethylene methacrylic acid copolymer](image)

**Figure 6:** Bicomponent fibers with a hollow center, a rigid inner sheath of polycaprolactam and an outer sheath of Nucrel® 0411HS ethylene methacrylic acid copolymer

![Figure 7: Porous membrane made from fibers shown in Figure 3. Pores retain size and shape even as the elastic membrane is stretched.](image)

**Figure 7:** Porous membrane made from fibers shown in Figure 3. Pores retain size and shape even as the elastic membrane is stretched.

**CONCLUSIONS**

It is now possible to make highly customized porous membranes with very uniform pore sizes and with functionalities tailored to specific applications. Customer trials of membranes are currently in progress.

**REFERENCES**


Effects of Abrasion on Tenacity of Synthetic Fibers

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Abrasion of fibers against metal surfaces (steel rollers used in a standard 2D and 3D weaving process) is one of the key parameters that can affect tenacity degradation (abrasion factor) of the fibers during the weaving process. The tenacity degradation mechanism is dependent on tow tension and velocity, radius of curvature of the rollers and the cumulative frictional contact length between the fiber tow and the metal surfaces. In this effort, master curves of tenacity-frictional contact length were developed for aramid (Dupont KM2) and S glass tows (AGY S2 and OCV Shieldstrand S). Abrasion tests were conducted at tension level of 8% of failure load and 24 in/min using a specially developed abrasion test machine. Results indicated the abrasion resistance is highest for KM2, intermediate for ShieldStrand S and lowest for AGY S2. Degradation mechanism due to mass loss, micro-structure damage and fibers breakage is discussed for the three types of fibers. SEM measurements showed that the fibers after abrasion test experienced different types and levels of surface damages depending on the fiber type and contact length. Glass fibers exhibited surface damages (micro-cracks and sizing removal). KM2 fibers showed surface damage where fibril pull-out and splitting are observed.

*Presented by Sergey Lopatnokiv, University of Delaware, on behalf of A. Abu Obaid
Advanced Textile Materials
Photovoltaic Fiber Having Zinc Oxide-Nanoparticles (ZnO-np) and Inverted Layer Sequence

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STATEMENT OF PURPOSE/OBJECTIVE
In this study, designing and producing a textile fibre which can generate electricity from sun light by using polymers and inverted type of solar cells model. Photovoltaic effect is developed on polyester filaments. The photovoltaic fibres, which are produced using easier techniques and materials compared to silicon based solar cells, are used to produce yarns and fabrics. The photovoltaic fibres can be also integrated into fabrics or clothes.

INTRODUCTION
Recently, with the increasing world population and progress in technology, exhaustion of energy resources is a critic issue. Consequently, renewable energy sources and their improvement are very most popular topics which are studied on, recently [1,2]. Out of renewable energy technologies, photovoltaic cells have a great attraction related to their admirable properties [3]. Over the last decade, organic solar cells attracted attention due to their unique properties such as flexibility, cost-effectiveness, graded transparency, light, easy processing techniques, being environmental friendly, and applicability to both large and small areas. People, far from the electric grids, will be able to get electricity by photovoltaic textile structures for small electrical devices, such as music player, mobile phone charger etc. Preliminary studies on developing a fibre showing photovoltaic effect were done previously [4-11] by different groups.

Conventional and inverted organic solar cell structures were shown Figure 1.

![Figure 1. The conventional and inverted organic solar cell structures](image1)

APPROACH
There are several types of photovoltaics. In this study, inverted type of solar cells are employed. In such devices electrons, which in the conventional forward mode are transported to the reflective electrode, are instead extracted to the transparent electrode. This reversal of normal behavior is generally achieved by coating the electrodes with an inorganic or surface-functionalized inorganic material and thus modifying the electrode work function. Buffer layers (PeO, ZnO, TiOₓ etc.) are empirically used to enhance \(V_{OC}\).

![Figure 2. Schematic diagram showing the organic photovoltaic fiber](image2)

RESULTS AND DISCUSSION
Following device structures were developed in order to obtain photovoltaic fiber based device (Figure 2). An active photovoltaic fiber using polymer based solar cell materials and a buffer layer was developed successfully. Moderate efficiency was obtained from preliminary studies.
CONCLUSIONS
A photovoltaic fiber generating electricity using inverted layer sequence was developed. From these preliminary studies, moderate efficiency was obtained. After further optimization, this photovoltaic structure may be a candidate for electricity generating textiles.

FUTURE WORK
Produced photovoltaic fibres/filaments will be coated with a corresponding polymer to protect photovoltaic structure from oxygen and humidity.

Keywords: Inverted organic solar cell, Nano-materials, Photovoltaic fiber, Zinc Oxide-Nano particles (ZnO-np)

REFERENCES
Textile Heartvalve Prosthesis: Assessment of In Vivo Performances

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INTRODUCTION
Percutaneous (non invasive) aortic valve implantation has become an alternative technique to surgical valve replacement in patients with high risk for open chest surgery [1,2]. Today, the valves used in non invasive valve surgery are made up with biological tissue. The tissue associated with metallic stents is however fragile material and risks to be degraded during the crimping process. Heim et al showed that textile polyester is less fragile material and could be an alternative solution to replace valve leaflets [3]. The authors report about the good performances obtained in vitro with the textile valve. Results are in the range of what is obtained with other commercially available valves. In vivo behavior of textile, used as vascular replacement material, has already been widely reported. However, no information is available in literature about how textile material, when used in valve position, behaves in contact with living tissues. The purpose of the present work is to give the first histopathological assessment results obtained for a textile valve after 8 weeks implantation in a sheep model.

APPROACH

Valve manufacturing
The valve is obtained from a tubular textile polyester (PET) membrane (plain weave, 60 yarns/cm, yarn count 60dtex). The manufacturing process consists in performing air suction across the valve leaflet material thickness in order to press the textile membrane against a cylindrical counter-mold designed with the expected valve cusp semi-lunar geometry. The fabric being porous, a plastic membrane is wrapped and sealed around the whole shaping device before sheathing. The system is then heated over polyester vitreous transition temperature in order to fix the obtained shape. The shaped textile membrane was assembled with a ring taken from a Mitroflow bioprosthesis (Sorin, Milano, Italy) from which the biological valve was removed and replaced by the textile valve (Fig. 1).

Implantation
After cardiopulmonary bypass, the textile valve prototype was implanted in mitral position in a sheep model (Institut Mutualiste Montsouris Paris, France). The animal received humane care in compliance with the guidelines established by the French government. After 60 days of implantation, the animal was sacrificed for valve material analysis purpose.

Histological evaluation
The tissue and histological evaluation consisted of Ca and P dosage, evaluation of cuspal damage, evaluation of pannus growth, evaluation of thrombus deposition. The Ca and P dosage on the cusps was performed by Atomic Absorption Spectroscopy method. Additionally scoring of calcium deposit using Faxitron analysis along with pannus and cuspal damage were performed using scoring system available for biological valves in order to draw comprehensive data for the final interpretation of the study.

RESULTS AND DISCUSSION

Cuspal tear analysis
The valve was evaluated for cuspal damage macroscopically. Damages were observed on the free edge of the cusps, mainly consisting of “tear” like damage; it seemed that the textile fibres were very mildly “disentangled”. Figure 2 is a representative picture of the cuspal damage, due to the free edge cutting process. In further implantations, replacing the cutting with the edge of the fabric should prevent this effect.

Pannus growth analysis
The overall pannus growth evaluation on the valve showed that it was mild. Almost absent on the inflow surface were it was located exclusively on the stent and mild on the outflow surface (Fig. 3).
Macroscopic thrombus evaluation
The macroscopic evaluation of the thrombus deposit on the cusps of the valve showed that small fibrine like deposits were visible at the commissures of the cusps (Fig. 4). With better adjustment of the fabric valve height to the stent, turbulence related thrombus could be avoided in the future.

Calcium analysis
The results obtained with Atomic Absorption Spectroscopy showed that there was around 4.5% of calcium deposit and 2.5% of phosphorus deposit on the valve. These values are significant, but the Faxitron analysis showed that calcium deposits occurred mainly at the level of the valve commissures (Fig. 5). One can assume that with less turbulence at the commissure level, the (Ca) rate should decrease.

Histological evaluation
Histological evaluation of cross and longitudinal profiles of the woven fabric material were performed in resin (Fig. 6) and paraffin (Fig. 7) sections. The cusp analysis showed a pannus growth (not exaggerated) mainly on the valve inflow side (thickness ranges between 0.114 and 0.300 mm) consisting in collagen and fibroblasts. Other observations could be made: (1) only few inflammatory cells, (2) non thrombus, (3) locally concentrated mineral deposits (Ca), (4) no sign of infection.
These first results show that the porosity of the fabric doesn’t lead to exaggerated tissue ingrowth after 2 months. Mineral deposition occurs however on the fibrous structure. Future change in the fabric structure (using monofilament yarns for instance) should allow reducing the mineralization of the structure.

CONCLUSIONS
In this study, the quality and quantity of morphological changes observed resemble those of currently available bioprosthetic valves; however, these changes are usually observed after 3 to 5 months implant duration whereas in the present study these changes were observed early, after 2 months implant. The early degeneration of the valve (valve calcification and stiffening of the leaflets) was not compatible with the survival of the animal after 2 months. The first experimental evaluation of the performance of the textile valve did not exhibit satisfactory durability and haemodynamic results in this feasibility phase. However, there’s huge potential to optimize the fabric structure in order to improve the in vivo behavior of the device.

REFERENCES
De Novo Assembly of Extracellular Matrix Proteins

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INTRODUCTION
Extracellular matrix (ECM) proteins (ECM) are dynamic nanoscale fibrillar textiles to provide strength and elasticity to multicellular organisms under mechanical load and motion, and to facilitate tissue morphogenesis [1]. An in-depth understanding formation of these networks will shed light on design and development of engineering scaffolds for studying development and assembly of cells within the vasculature and tissue regeneration. Cells are expert bio-manufacturing facilities reading the instructive signals from their microenvironment to assemble and build supportive matrix blocks [2]. But, engineering the complex topology and composition of ECM networks in cell-free systems is a remaining challenging. Here we describe multiple biologically inspired approaches to mimic the ECM constructs under cell-free fashions.

APPROACH
Proteins forming ECM has different structures and functions but is similar in some common features such as their giant size, asymmetric shape, and multi-domain structures [3]. ECM molecules due to their built-in self-associate properties form order assemblies with other ECM proteins as a result of multi-modular structures in which domains of different binding potential are arranged in defined patterns [4]. Although self-assembly process drives by interaction potential between domains, it is highly regulated by cellular surrounding [2]. For instance, fibronectin (FN) is secreted as a disulfide-bonded dimer with three types of repeating modules (type I, II, and III repeats) that mediate interactions with cells, ECM components and other FN molecules, Figure1A [5]. FN in a globular state binds to cell surface receptors, unfolds and extends to assemble insoluble fibrillar structure in a process called fibrillogenesis. While the in vivo production of ECM fibrous matrix is well studied, in vitro manufacturing of FN fibrils remains a challenge. So far, random matrices without structural organization have been assembled by exposing ECM proteins to denaturants or reducing agents [2].

We developed two interface-driven techniques to engineer matrix architecture and composition at the nanoscale with multiple ECM proteins. The first method is a surface initiated assembly event and the second one is based off of a rotary jet spinning technology to synthesize free standing ECM constructs.

RESULTS AND DISCUSSION
1. Surface-Initiated Assembly
Protein nanoFabrics composed of unfolded ECM proteins patterned onto sacrificial surfaces were synthesized using a surface initiated assembly event [2]. The process consists of (i) adsorption of nanometer-thick layers of ECM proteins onto hydrophobic surface of patterned stamps to partially unfold and expose cryptic binding domains (ii) transferring the ECM proteins in the unfolded state to a relatively hydrophilic, dissolvable surface, and (iii) thermally triggering surface dissolution to release the matrix assembly (Figure 1B).

FIGURE 1. (A) Diagram of the modular structure of fibronectin as a dimer composed of two monomers linked at the C-terminus by a pair of disulfide bonds. (B) Schematic of surface-initiated assembly process (i) Solublar FN proteins adsorb onto PDMS stamp. (ii) The stamp transferred to PIPAAm film. (iii) The FN-FN interaction happens as the PIPPAm dissolves at cold water and FN nanostructure is released. Fluorescent images of stamped FN (iv) before release and (v) after released. (vi) SEM image of FN weaves post-release from the substrate, scale bar = 100 µm.

We engineered 1 to 10 nm thick multi-geometry protein nanofabrics micrometer to centimeter wide from a range of ECM proteins including FN, LAM, FIB, COL I , COL IV, and their combinations using different stamp
geometries (Figure 1B). Fabric thickness may be customized by controlling the density of protein molecules adsorbed to the surface via the concentration of the initial ECM solution used to ink the stamp. Dry FN nanofabrics on PIPAAm were 1-5 nm thick which increased to ∼8 nm when hydrated, significantly less than the FN dimer diameter in solution [2].

Fluorescence resonance energy transfer (FRET) and Raman signals suggested that the secondary structure of FN within released nanoFabrics is in a compact conformation and upon release oriented nanoFabrics contract up to 65% which provide a 6-fold extension without failure, likely due to protein extension under high strain.

2. Rotary-jet Spinning process
The synthesis of synthetic nanofibers with specific protein domains provides a basis from which to manipulate material properties, with particular control over conformational changes and mechanical properties. We have developed a novel, and facile technique for generation of continuous nano-scale non-woven textiles based on high-speed mechanical rotation of polymeric solution. This process, termed rotary-jet spinning (RJS) allows for the rapid synthesis of anisotropic nanofibers in the absence of an applied external voltage, as is necessary for other techniques [6]. The system is composed of a rotating motor, a perforated reservoir, and a stationary or rotating collector (Figure 2). Protein or polymer solutions are loaded into the reservoir either continuously or in measured allotments. Due to centrifugal forces (at speeds from 0 to 64,000 rpm) on the solution, polymer or protein jets are forced out of the reservoir through the perforated side wall and through subsequent je-extension and solvent evaporation, nanofibers are formed.

While ECM protein solution passes through the reservoir orifices (orifice channels may be as long as a few microns to a few millimeters), shear forces on the proteins in addition to following jet extension cause protein chain unfolding, exposing binding domains. To test this hypothesis, protein unfolding was first modeled using the Poiseuille equation, and then studied as a function of rotational speed, shear forces, and protein concentration. Insolubility of the produced FN nanofibrils in physiological media is the direct evidence of shear force-induced fibrillogenesis through RJS process resembling the in-vivo fibrillar formation process observed in beta sheet containing proteins (Figure 2). Cryptic binding domains are exposed by to extensional flow within the capillary channel and jet necking process, specific domains responsible for FN-FN binding come in contact forming irreversible bond. Insoluble, aligned and continuous FN fibers hundreds of nanometers in diameter with a smooth morphology and intact secondary structure are easily fabricated by RJS.

CONCLUSIONS
In summary, we have developed several ECM self-assembly techniques taking advantage of interfacial molecular forces such as surface interaction and shear-force induction. These free-standing biopolymer constructs are spatially organized from the nanometer to millimeter length scales with sufficient mechanical stability, extensibility, biofunctionality and cellular activities.

ACKNOWLEDGMENT
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REFERENCES
Breathable Liquid Repellent Polypropylene Nonwovens for Surgical Gowns

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ABSTRACT

Polypropylene (PP) nonwovens are being restrained in the next-to-skin applications such as surgical gowns due to its lack of comfort properties. The attribute requirements of surgical gowns are breathability for the comfort characteristics and liquid (blood) repellency for viral protection. Even though, the hydrophobic nature of PP nonwovens is an advantageous one for enhancing the liquid repellency property, the breathability issue remains to be a constraint. Our preliminary research has shown that the breathability of PP nonwoven can be enhanced by 95% by using the latest Atmospheric Pressure Plasma treatment (APT). It is also very well known that the liquid repellency property could be imparted to PP nonwoven through the APT treatment by employing various reactive gases. This project has been targeted to achieve the combination of attributes such as the breathability and liquid (blood) repellency required by surgical gowns through the APT treatment. The breathability of APT treated PP nonwovens will be evaluated by following the BS-7209 standard and the liquid (blood) repellency results by AATCC Test Methods 42-2007 and 118-2007 in this project.
Fiber Science Theory and Computer Simulations
A Model for Mesophase Wetting of Sheets, Fiber, and Fiber Bundles

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ABSTRACT
This paper presents a model based on the Landau-de Gennes (LdG) liquid crystal theory that leads to carbonaceous mesophases’ wetting thresholds of carbon sheets, fibers, and fiber bundles under strong anchoring and uniaxial equilibrium nematic order. It is found that for typical material properties and fiber radii, from nano to micron ranges, the ability of carbonaceous mesophases to wet carbon substrates decreases from fiber bundles to sheets to single fibers. The critical Harkinson spreading parameter or wetting threshold for each geometry is expressed in terms of the isotropic wetting threshold times an amplification factor that encapsulates the resistance of LC long range elasticity to wetting. It is shown that the amplification factor is close to one for both fiber bundles and single fibers of micron size and hence the isotropic fluid inequality rules should be reliable when considering mesophases for this micron fiber size [1].

OBJECTIVE
The specific objective of this work is to determine whether a generic type of nematic mesophase, such as a CM, displays the same wetting threshold sensitivity with respect to geometry and arrangement as reported for isotropic liquids on a chemically similar substrate [1].

INTRODUCTION
Understanding fundamental wetting physics of fibers and fiber bundles is required in many applications, including textile fibers and fiber composites [1]. Most of the previous studies on wetting of fiber bundles have focused on the wetting properties of isotropic liquids on fibrous substrates [1]. For typical substrates and liquids, it has been shown that it is more difficult to wet a single fiber than a flat substrate, and it is always easier to wet a fiber bundle than a flat substrate [1]. In practical applications, the wetting fluid or wetting material is a soft matter material such as a mesophase. Here, we seek to develop a fundamental understanding of wetting thresholds for mesophases [1-2].

THEORY
Wetting Thresholds for Isotropic Fluids
We consider the Harkincon spreading S parameter defined by [1].

\[ S = \gamma_S - (\gamma_{SL} + \gamma_L) \]  

(1)

where \( \{\gamma_i: i=S, SL, L\} \) denote the surface tension of the substrate (S), the interfacial tension of the substrate-liquid interface (SL), and the surface tension of the liquid (L), respectively. According to previous results [1], for isotropic liquids, the critical wetting thresholds for fiber bundles \( S_{bi}^c \), planar sheets \( S_{pi}^c \), and single fibers \( S_{fi}^c \) obey the following ordering [1]:

\[ S_{bi}^c > S_{pi}^c > S_{fi}^c > 0 \]  

(2a-c)

where \( R \) is the outer radius of the fiber bundle, \( n_f \) is the total number of fibers, \( r_f \) is the fiber radius, and \( H \) is the film thickness and \( \gamma_L \) is the surface tension.

RESULTS AND DISCUSSIONS
Relative Mesophase Wetting Thresholds
Using the Landau de Gennes Q-tensor order parameter in terms of the homogeneous free energy density \( f_h \) and a gradient free energy \( f_g \) which are given by:

\[ F_e = \int (f_h + f_g) dV \]

\[ f_h = \frac{1}{2} a_o (T - T^*) \mathbf{Q} : \mathbf{Q} - \frac{b}{3} (\mathbf{Q} : \mathbf{Q})^2 + \frac{c}{4} (\mathbf{Q} : \mathbf{Q})^2 \]

\[ f_g = \frac{L}{2} \nabla : (\nabla \mathbf{Q})^T \mathbf{Q} = \Psi \left( \mathbf{n} \mathbf{n} - \frac{1}{3} \mathbf{I} \right) + \frac{P}{3} \left( \mathbf{mm} - \mathbf{I} \right) \]

(3a-d)

where \( a_o, b, c \) are the Landau parameters, \( L \) is the Frank elastic constant, and \( T^* \) is the super-cooling temperature, \( \mathbf{Q} \) is the quadrupolar tensor order parameter, and \( \Psi \) and \( P \) are the uniaxial and biaxial scalar order parameters and \( \{\mathbf{n}, \mathbf{m}, \mathbf{l}\} \) the orientation triad [1].

LIQUID CRYSTAL CRITICAL PARAMETER
a) Single fiber
Using the free energy difference per unit area for the single fiber configuration [1], the critical wetting threshold \( S_{flc}^c \) for a fiber/LC system is:

\[ S_{flc}^c = \Lambda_f S_{fi}^c ; \Lambda_f = 1 + 0.5 \left( 1 + H^{-1} r_f \right) \ln \left( 1 + H^{-1} r_f \right) \]

(4a,b)

b) Fiber bundle
Whereas for a fiber bundle, it becomes:

\[ S^{c}_{bLC} = \Lambda_b S^{c}_{bi} \]

\[ \Lambda_b = 1 - 8^3 \left[ \frac{6n^2}{3n^2 + n} \right] \left[ 2^{-1} + \ln \left( \frac{0.228 r_c^{-1}}{r_e} \right) \right] \]  

(5a,b)

In equations (4a,b-5a,b), \( \{ S^{c}_{bLC}, S^{c}_{bLCS} \} \) and \( \{ S^{c}_{fi}, S^{c}_{bi} \} \) are the critical spreading parameters for liquid crystals on single and fiber bundles and for isotropic fluids on single and bundles fibers respectively. \( \{ \Lambda_f, \Lambda_b \} \) are the amplification factor for fibers and bundle due to LC gradient elasticity respectively and \( \Box \) is the length scale ratio for shape.

**RELATIVE MESOPHASE WETTING THRESHOLDS**

Follows Rey’s work, the nematic critical wetting ratio of fiber and bundle \( S^{c}_{fLC} \left| S^{c}_{bLC} \right|^{-1} \) and the isotropic fluid \( S^{c}_{fi} \left| S^{c}_{bi} \right|^{-1} \) ratio by the ratio of amplification factors \( \Lambda_f \Lambda_b^{-1} \) [1]:

\[ S^{c}_{fLC} \left| S^{c}_{bLC} \right|^{-1} = \frac{S^{c}_{fi} \left| S^{c}_{bi} \right|^{-1}}{\Lambda_f \Lambda_b^{-1}} \]

(6)

\[ \left( \frac{\Lambda_f}{\Lambda_b} \right) = \frac{1 + 0.5 \Box \left( 1 + r_c H^{-1} \right) \ln \left( 1 + r_c H^{-1} \right)}{1 - 0.125 \Box \left( 1 + 2 \ln \left( \frac{0.228 r_c^{-1}}{r_e} \right) \right)} \]

(7)

The brackets in the numerator and denominator of eqn. (7) contain the purely geometric effect. For typical values \( H<r_c, r_c<r_e \) the amplification ratio is a function of \( \Box \):

\[ \Lambda_f \Lambda_b^{-1} \approx \frac{1 + 0.5 \Box}{1 - \Box} = \frac{r_c \gamma_{LC} + 0.5 L \Psi^2}{r_c \gamma_{LC} - L \Psi^2} \]

(8)

The asymptotic limits of eqn.(8) are (i) \( \Box \ll 1 \), (ii) \( \Box \approx 1 \), and can be summarized as follows: (i) Weak bulk elasticity/tension regime \( \Box \ll 1 \): for micron-sized fibers and typical values of the Frank elasticity and surface tension the amplification ratio is close to one, and the critical ratios are given by:

\[ \Lambda_f \Lambda_b^{-1} \approx 1 + 1.5 \Box, S^{c}_{fLC} \left| S^{c}_{bLC} \right|^{-1} \approx S^{c}_{fi} \left| S^{c}_{bi} \right|^{-1} \]

(9)

In this regime, mesophase wetting is close to isotropic fluid wetting. (ii) Equivalent bulk elasticity/tension regime \( \Box \approx 1 \): for nano-sized fibers (retaining strong anchoring) and/or vanishing surface tension and large Frank elasticity, the shape ratio may be close to unity: \( \Box \approx 1 \) with

\[ S^{c}_{fLC} \left| S^{c}_{bLC} \right|^{-1} \approx 2^{-1} S^{c}_{fi} \left| S^{c}_{bi} \right|^{-1} \left( 1 - \Box \right)^{-1} \gg S^{c}_{fi} \left| S^{c}_{bi} \right|^{-1} \]

(10)

**CONCLUSIONS**

In this work, a model for mesophase wetting thresholds of sheets, fibers and fiber bundles is presented. It is found that for typical material properties and fiber radii, from submicron to micron ranges, the ability of carbonaceous mesophases to wet carbon substrates decreases from fiber bundles to sheets to single fibers. The complex system is analyzed with a model based on the Landau-de Gennes (LdG) liquid crystal theory. The main conclusions of the analysis are: (1) The liquid crystal critical Harking spreading parameter or wetting thresholds for each geometry can be expressed in terms of the isotropic wetting threshold times an amplification factor that expresses the resistance of LC long range elasticity to wetting. It is found that the amplification factor is close to one for both fiber bundles and singles fibers of micron size and typical nematics and hence the isotropic fluid rules should be reliable when considering mesophase for micron fibers and typical nematics. In order to significantly decrease the wetting abilities of mesophase under strong anchoring, the fiber radius has to be in the nano range and/or the ratio of the Frank elastic constant \( L \) to the surface tension has to be significantly larger, which may be obtained by using novel chemistry compounds.

**FUTURE WORK**

At the nanoscale dimensions of a disclination core, the current version of the model maybe incomplete, as biaxiality may be present and the homogeneous free energy contributions has to be included. Further experimental work may guide the modeling of wetting thresholds at the scale of nematic disclination cores [2].

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**REFERENCES**


Nonclassical Scaling for Forced Wetting of a Nematic Fluid on a Polymeric Fiber

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In many industrial applications it is necessary to coat a solid substrate with a fluid for a variety of reasons [1-3]. This is usually accomplished by dragging the solid object through the fluid of interest. Here we refer to such processes as forced wetting of the solid substrate, irrespective of whether the fluid is a wetting or a nonwetting fluid for the substrate. In such a process, it is obvious that the thickness of the fluid coating will depend on the velocity at which the solid substrate is withdrawn. At zero velocity the film thickness is zero (where we ignore the possibility of a thin wetting film), and at infinite velocity it will be zero as well since the fluid does not have enough time to form a coating and/or the air is entrapped in the interface. Thus a maximum wetting speed naturally enters the problem of forced wetting [4-7].

We are interested in gaining an understanding of how the fluid film thickness varies with an increase in velocity. In particular, we confine our attention to the special case of the solid substrate having a cylindrical geometry and where the fluid is an anisotropic fluid with long range orientational order. The wetting and spreading characteristics of nematic fluids on planar substrates have been extensively studied [8-13], while the behavior on cylindrical objects has hardly been studied. In this presentation, we report on the forced spreading of a nematic fluid on a polypropylene fiber, both in its ordered nematic and disordered isotropic phase.

Wetting of cylindrical substrates, or fibers, by viscous fluids differs from that of planar substrates of the same material. This is due to the fact that the curvature of the fiber causes capillary pressure imbalance at two interfaces of the annular fluid film, namely the substrate/fluid and the air/fluid. An important consequence is that fiber wetting occurs only when the spreading parameter $S$ is greater than a critical positive value, $S_c$, while wetting on planar substrates occurs when $S > 0$. In many cases, this annular film is quickly broken into droplets due to Rayleigh instability. Under the same conditions, the film thickness before breakup is greater for fibers than for planar substrates.

In our forced wetting experiments, a polypropylene fiber of diameter 200 $\mu$m is dragged through a Teflon tube reservoir (inner radius = 0.24cm, length = 1.5cm) containing the fluid of interest. The fiber passes through the tube in horizontal direction at a constant velocity, $V$, and the mass of this fluid reservoir is continuously recorded as a function of time, $t$. As the fiber moves through the reservoir, the mass of the fluid uptake by the fiber, $\Delta W$, increases linearly with time. As mentioned above, the annular liquid film forced-wet breaks up, but the initial film thickness, $h$, can be easily computed using the mass balance equation:

$$h = -r + \left[ r^2 + \frac{(\Delta W/\Delta t) (\pi \rho V)}{\Delta W} \right]^{1/2}$$

where $r$ and $\rho$ are the fiber radius and fluid density.

Nonslip boundary conditions coupled with the finite viscosity of the fluid lead to the result that the fluid elements near the solid must move at the same velocity as that of the solid, forming a thin coating on the fiber. However, this motion results in a deformation of the fluid-air interface, which is opposed by surface tension forces. Hence, viscous and capillary forces oppose each other, thereby naturally introducing a force balance defined by the ratio between the two, the so-called capillary number, $Ca$ ($Ca = \eta V / \gamma$), where $\eta$ is the fluid viscosity. It is expected that the initial film thickness, $h$, can be expressed as $h \sim l \sqrt{Ca}$, where $l$ is some static length which will depend on the geometry of the solid. Landau, Levich and Derjaguin were the first to correctly predict that the film thickness at low withdrawal velocity will scale as $h \sim Ca^{2/3}$ for Newtonian fluid. This is the well-known LLD law for free meniscus coating.

Nematic liquid crystals have long range orientational order without positional order, and the average molecular orientation is given by a unit vector, the director $\mathbf{n}$. The fiber wetting by nematics involves the determination of director orientation in annular spaces [14]. For nematic liquid crystals, the Frank elasticity due to orientation gradients may have to be taken into account, depending on their significance in comparison to the viscous stress.

In this work, we have used a liquid crystal mixture E7 in the nematic phase (room temperature) as well as in the isotropic phase (100°C). Figure 1 shows...
fluid pickup by the fiber at several velocities. The forced wetting quickly reaches the steady state and the weight pickup is linear in time. We stress here that the thickness, calculated using aforementioned mass balance, is just the initial thickness, largely because the annular fluid is unstable and breaks up by the surface tension driven “Rayleigh Instability”. Figure 2 is a bilogarithmic plot of the reduced thickness, $h/r$, of the nematic E7 fluid as a function of capillary number both in the nematic and the isotropic phases. It is clear that the LLD law is obeyed for the fluid in the isotropic phase while it is not in the nematic phase.

By considering the Ericksen-Leslie expressions for the nematic hydrodynamics, we provide an explanation for the deviation from the LLD law for the forced wetting of nematic fluids on fibers.

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REFERENCES
TEXTILE COMPOSITE STRUCTURES FOR SENSOR DATA TRANSPORT FROM OCEAN DEPTH TO INTERNET

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Introduction: Oceanographic Data Buoys perform near real-time and real-time communication to shore stations via satellite or shore radio links from a variety of sensors. The sensors are positioned on a surface buoy, in the water column, and at the sea floor. Data from an ocean site like weather, ocean currents, and sea-water temperatures, underwater sound and seismic activities as well as bio-productivity and ocean chemical data (salinity, pollution) are valuable tools to monitor ocean health and climate change. As example there are 39 US data buoys in deep ocean stations monitoring tsunami waves in the Pacific and Atlantic, series of buoys track hurricane paths, and several 100 weather buoys along coastal waters of the US, Canada, and other countries deliver continuous updates of wind, waves and water currents from their positions.¹

In the last decade the capabilities of data buoys were improved or enabled through the development of highly compliant elements to absorb the heave and surge motions caused by the wave following surface buoys like a large bungee cord. These elements are rubber stretch hoses with nylon tire-cord reinforcement, typically connected to the bottom of a surface buoy. The hoses can stretch up to 175 percent and are designed to absorb the heave motions of the surface buoy from the lower mooring.²

The surface wave following buoys constantly raise and lower any instrumentation assembled as part of the mooring connection to the anchor. Acoustic and other measurements were compromised or impossible with conventional buoy moorings, because of flushing flow noises of the sea water streaming around the acoustic sensors arranged in the buoy mooring. This makes monitoring of whale vocalization, noise from fish swarms or ships impossible except when the sea state is near zero.¹

These stretch or “Gumby” hoses allow an additional capability, the ability to contain electrical conductors, embedded in “comfort geometry” inside the stretch hose rubber wall and transfer to buoys and sensors. The stretch hoses and embedded conductor links have been deployed up to 5 years without failure. The surface buoy is able to communicate underwater signals to a shore station via satellite or radio-telephone link. The stretch hoses made it possible to put underwater events on the internet.

Summary: This abstract describes the stretch hoses as composite tire-cord reinforced rubber hose structure with the inclusion of suitable copper conductor assemblies.

¹ In the last 50 years the development of such buoy systems was expanded from all chain buoy moorings in shallow waters, wire rope moorings for medium water depths to deepwater moorings using ropes from synthetic fibers (nylon, polyester, and polypropylene). More recently ropes high-performance fibers (Aramid, Vectran, UHMWPE and others). Chain moorings are used up to 800 ft water depth due to their low breaking length of 3 to 4 kilometer. Wire rope moorings can be used in deeper water but are subject to destructive kinks and hocking due to their twisted construction. The kinking and hocking occurs at sudden load relaxation when a surface buoy in storm seas plunges into a deep wave trough faster than the wire rope mooring can fall. (The max. ocean depth is almost 11 kilometers or 6.8 miles.)

² There are typically 6-12 million relentless ocean wave cycles per year.

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Figure 1: A Stretch hose buoy mooring. The hose connects a surface buoy to a subsurface buoy, to which a hydrophone further below connects with a cable. A wire rope link below to an acoustic release and a chain link to the anchor form the bottom portion of the mooring.

The Stretch Hose Design: Reinforced rubber stretch hoses with molded-in couplings are of rugged and flexible
design which can stretch up to 175%. Unreinforced rubber can elongate over 500% but has low mechanical strength. Nylon tire-cord strength members embedded as thin rubber sheets in the hose wall, counter-helically applied along the hose axis, control and limit the hose stretch and add significant mechanical strength needed to support typical buoy mooring tensions. The nylon strength members are sliced into ribbons of specified widths, which when but-wrapped around and along the hose body deliver specified wrap angles, see Figure 4. The wrap angles greatly influence the required load-extension behavior of the hose under tension and allow to develop hoses with known load stretch behavior, see Figure 5. The completed hose is filled with water.

**Figure 4:** Spiraled reinforcement member or conductor in relaxed and stretched condition of a hose. Legend: \( \alpha \) = wrap angle of spiraled member with hose axis; \( l_s \) = length of spiraled path; \( p \) = pitch length of spiraled member; \( d_w \) = wrap diameter. Subscript \(_0\) indicates relaxed status, no subscript indicated stretched status.

**Figure 5:** Elongation of stretch hose versus elongation of reinforcing cords spiraled inside hose wall under constant volume (isochoric) stretch

**Design Background:** The stretch hose mechanics has evolved from the textile structural calculation methods developed mostly at the University of Manchester and at MIT and the Fiber Research Lab in Boston a few decades ago. Details will be presented at the Symposium.

**Conductor Designs for Stretch Hoses:** The high stretch and retraction response of the hose to the buoy’s wave following motions causes much smaller but unavoidable contractions and extensions of the spiraled conductor path in the hose wall. In order to accommodate the large hose stretch, the conductors need to be assembled in small compliant cable designs, which can both contract by up to 20% and slightly extend their cable axes\(^3\). This is needed to accommodate the up to 175% elongation of the stretch hoses in taut moorings. The conductor lengths need to be almost 5 times (!) longer than the hose itself for an assumed isochoric hose extension, and arranged in tightly specified multi-spiraled patterns in the hose wall [4]. The resulting copper conductor arrangements keep them within the maximum \( \frac{1}{2}\% \) elastic copper stretch to survive.

**Future Work:** Currently fiber-optic compliant small cable assemblies are developed, which are needed to download video files from Autonomous Underwater Vehicles. The bending sensitivity and brittleness of glass fibers present a particular survival challenge.

**References:** For a list of references contact <wpaul@whoi.edu>

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\[^3\] Based on isochoric deformation (non-linear Poisson Ratio) of the stretch hose, for given Poisson Ratios the results differ.
Bending and Position Hysteresis of Magnetic Microfibers in Nonuniform Magnetic Fields

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STATEMENT OF PURPOSE
Magnetic microfibers bend in response to an applied nonuniform magnetic field and display position hysteresis as the field varies. The objective is to demonstrate the hysteresis behavior experimentally and to derive a model which captures the hysteresis behavior.

INTRODUCTION
The magnetic microfibers used in this paper are hollow polymer fibers with a layer of superparamagnetic nanoparticles on the inner surface of the fiber, causing the fibers to behave as flexible paramagnetic materials. Recall that paramagnetic materials respond to magnetic fields but, unlike ferromagnetic materials, they cannot be permanently magnetized.

Magnetic microfibers will serve as the basis for electromagnetically actuated, fiber-based manipulators for microfluidic applications. The manipulators consist of a cantilevered fiber, typically 1-5cm in length, which is positioned between electromagnets with axes orthogonal to the fiber.

Paramagnetic chains and fibers have been examined previously, including formation of colloidal paramagnetic particles into chains under the influence of an external field[1,2], and dynamic behavior of chains of paramagnetic particles linked permanently using polymers [3-8]. Several approaches have been taken to derive the dynamics, including dipole models [6] and energy methods [3,7-8]. In general, these assume a uniform applied field and an unconstrained fiber. In contrast, the present work involves nonuniform fields and a cantilevered fiber.

FIBER MODEL
The model presented here predicts the stable shape or shapes of a paramagnetic microfiber in the presence of a nonuniform magnetostatic field. A stable shape corresponds to a local minimum of the potential energy of the fiber. The fiber potential energy has two components, \( U = U_s + U_m \), where \( U_s \) is the strain potential energy and \( U_m \) is the mechanical potential associated with position of the fiber in an externally applied magnetic field. Both of these potentials depend on \( \theta(s) \), the configuration or “shape” of the fiber, where \( s \in [0, L] \) is the distance along the fiber measured from the cantilevered end and \( \theta(s) \) is the angle of the fiber at distance \( s \) along the fiber, measured relative to the world coordinate frame. The shape parameterization as well as the strain energy term

\[
U_s = \frac{1}{2} \int_0^L E I \left( \frac{d\theta}{ds} \right)^2 ds.
\]  

are taken from Euler’s elastic.

The magnetic energy term is derived under the assumption that the fiber is a very slender body. Also, the magnetic field is approximated as locally constant across the fiber. The mechanical potential due to an externally applied field is then given by

\[
U_m = \frac{1}{2} A \mu_0 \int_0^L \left[ H_s^2((\theta(s)) + \frac{1}{\mu_s} H_s^2(\theta(s)) \right] ds.
\]  

where

\[
H_s((\theta(s)) = H_s \cos \theta(s) + H_t \sin \theta(s)
\]

\[
H_t((\theta(s)) = -H_s \sin \theta(s) + H_t \cos \theta(s)
\]

are the components of the externally applied magnetic field at the point in space occupied by the fiber element at \( s \), and \( A \) is the cross sectional area of the fiber, \( \chi_f \) is the magnetic susceptibility of the fiber, and \( \mu_0 = 4\pi \times 10^{-7} \) H/m is the permeability of free space.

In the case of a uniform magnetic field, the Euler-Lagrange necessary conditions from the calculus of variations can be applied to generate a differential equation whose solution \( \theta(s) \) minimizes potential energy \( U \). A different approach is required when the field depends on spatial location. In the present case, a Rayleigh-Ritz method is employed. The fiber shape is approximated as a linear combination of basis functions plus a constant:

\[
\theta(s) = \theta_0 + \sum_{i=1}^n \alpha_i \phi_i(s).
\]

The basis functions are chosen so that any linear combination will automatically satisfy the boundary conditions \( \theta(0) = \theta_0 \) and \( \theta(L) = 0 \). A family of polynomials was chosen:

\[
\phi_n = s^{n+1} - (n + 1)Ls \text{ for } n = 1, 2, 3, \ldots
\]

When (4) is substituted into the expression for \( U \), the minimization over the infinite dimensional \( \theta(s) \) becomes a minimization over the finite dimensional coefficients \([\alpha_1, \alpha_2, \ldots, \alpha_n]^T\). In practice, three to five basis functions are sufficient to capture the fiber behavior accurately.
**APPROACH**

The experimental platform consists of a magnetic microfiber fiber hanging from an acrylic plate with an electromagnet (1350 turns, 0.95cm ferrite core, 3.0cm length, 100mT at 1A current) positioned orthogonal to the fiber. A control system implemented using Matlab controls the current through the magnets and measures the fiber tip displacement using computer vision.

The fiber properties are: length $L = 3.5\text{cm}$, radius $a = 23\mu\text{m}$, Young’s modulus $E = 1\text{GPa}$, magnetic susceptibility $\chi_f = 0.028$, and relative offsets from center of the magnet surface to the base of the fiber are $x_0 = -14.0\text{mm}$ and $y_0 = -7.1\text{mm}$.

To simulate the fiber under various magnetic fields, the applied magnetic field was first computed numerically using FEMM (Finite Element Method Magnetics), a free software package. The field was imported into Matlab using the OctaveFEMM toolbox, and Matlab was used to perform numerically minimize the energy over the parameters.

**RESULTS AND DISCUSSION**

The experimental data relating fiber tip position to electromagnet current is shown in Figure 1. Recall that the magnetic field is proportional to the current. The experimental data is plotted against the simulation data for comparison.

The hysteresis loop is clearly visible in the plot. As current increases from 0A up until about 1.15A, the fiber moves smoothly within the “low-current stable region,” displaying an approximately parabolic relationship between tip position and current. At just above 1.15A, the fiber “jumps” to an equilibrium shape close to the magnet surface remains there until current falls below 0.34A. The model correctly predicts the fiber behavior for small deflections as well as the location and extent of the hysteresis. From the simulations, it is clear that the hysteresis is caused by a pair of bifurcation in the stable shapes of the fiber.

Figure 2 shows how the experimental hysteresis curves vary as the distance between the electromagnet and fiber is adjusted. As the magnet is moved farther away from the fiber, the size of the low-current stable region increases slowly, at the cost of much high current required from the electromagnet.

**CONCLUSIONS AND FUTURE WORK**

The hysteresis behavior has been demonstrated and the model predicts the position of the fiber under varying magnetic fields as well as the hysteresis behavior. The model is useful for predicting the range of motion within the low-current stable region while designing and analyzing electromagnet-fiber configurations for use as actuators. The empirical or simulated curves can be used for open-loop position control within this region.

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Structure and Mechanics of Fiber-reinforced Cylindrical Membranes

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ABSTRACT
We present a mechanical model for fiber reinforced cylindrical membranes, where a dilute dispersion of rigid fibers of variable orientations is uniformly distributed on a deformable viscoelastic membrane. The model integrates the elastic energy of the membrane, the nematic Landau-de Gennes fiber orientation energy, and competing curvophilic and curvophobic interactions mediated by the membrane geometry and the fibrils’ orientation. Applications of the model to cylindrical membranes, relevant to the plant cell wall, a model biological fiber reinforced membrane system indicate that due to curvature-orientation couplings, the fiber orientation display three modes: (i) along the cylinder axis (line), (ii) oblique to the axis (helical), and (iii) normal to the axis (ring), where the former arises under large curvature and the latter under weak one [1]. The model is then extended to cylinders of variable cross-section, whose shape varies from a circle to a sharp cornered super-ellipse as in many plant cell specimens, and whose size increases as in plant cell growth. The structure-properties relations for super-elliptical membranes with gradient curvature are established and its role in cell growth shape is predicted. The principal mechanisms are the role of fiber orientation and order on bending stiffness: (a) orientation along the axis has no stiffening effect, (b) orientation along the azimuthal direction produces maximal stiffening, and (c) fiber randomization softens the membrane. It is found that super-elliptical shape invariant growth and expansion is preferred for cells with sharp/soft corners and straight/stiff sides. Otherwise growth promotes shape changes.

INTRODUCTION
Fiber reinforced cylindrical membranes are widespread in nature and understanding the coupling between in-plane fiber orientation and order and the curvature of the membranes demonstrated by these systems has the potential to open up a novel venue to design two dimensional anisotropic soft matter with tailored functionalities. In this work, a planar self assembly mechanism that imparts fiber orientation and order through a delicate interplay between membrane curvature and embedded fiber order in the plant cell wall, a model biological fiber-reinforced cylindrical membrane system, is explored using a mathematical model that integrates membrane elasticity and liquid crystal fiber ordering [1]. In plant cell walls the membrane shape and the fiber orientation are coupled and hence adapt to each other dynamically by simultaneously varying fiber structure and membrane shape. Fig. 1 shows a schematic that defines one of the main issues of planar microfibril self-assembly on a soft deformable membrane, considered in this paper.

Fig 1. Schematic of curvature-induced 2D planar self-assembly on membranes. At sufficiently low fiber packing density, the isotropic state observed on a flat membrane (left) may lead to a nematic state (right) due to curvature-mediated interactions. Adapted from [1]

The objective of this work is to investigate the curvature-induced microfibril orientation in plant cell walls by solving an integrated micromechanical model developed for fiber-laden membranes. To understand the structure-properties relations in fiber-reinforced membranes, the bending mechanics of cylindrical membranes of super-elliptical cross-section (relevant to plant cell walls) in which the membrane curvature varies around the circumference of the membrane resulting in spatially graded elastic properties are investigated.

The fiber structure is described by a 2x2 symmetric traceless quadrupolar tensor order parameter Q:

$$Q = S (n n - I/2)$$

where S is the scalar order parameter that measures the microfibril alignment along the director n. The membrane geometry is defined by the curvature tensor: $b = H_{i} + Dq$, where H is the average curvature, and D is the deviatoric curvature. For the cylindrical membrane, $D = H = -(1/2R)$ where R is the radius of curvature of the membrane. In this work, the cross-sectional shape of the cylindrical membranes is represented by a family of super-ellipses. The cross-sectional shape of the cylindrical membranes deviates from that of a circle to an ellipse or a super-ellipse, the curvature varies smoothly around the circumference and is a function of polar angle $\theta$. This family of curves is mathematically described by Lame’ curves [2]:

$$\left(\frac{x}{a}\right)^{n} + \left(\frac{y}{b}\right)^{n} = 1$$

(1)

where the shape parameter $\eta$ is any rational number. The size parameters a and b correspond to the intersections of the curves with x and y axes respectively. In this work, the subset of Lame’ curves, $\eta \geq 2$ and $a = b$ is considered.

FREE ENERGIES AND ORIENTATION MODES
The total free energy per unit area $\rho \hat{A}$ is posited to be:

$$\rho \hat{A} = \rho \hat{A}_{membrane} + \rho \hat{A}_{fiber} + \rho \hat{A}_{coupling}$$

(2)

where $\rho$ is the fiber density. The Helfrich free energy used to describe the elasticity of membranes reads [1]:

$$\rho \hat{A}_{membrane} = \gamma_{s} + 2k_{s} (H - H_{s})^{2} + \tilde{k} (H^{2} - D^{2})$$

(3)

where $k_{s}$ is the membrane bending elastic moduli, $H_{s}$ is the spontaneous curvature of the membrane, $\tilde{k}$ is the torsion elastic moduli of the membrane. The fiber contribution is given by the Landau-de Gennes expansion:
where $a_1$ is a function of microfibril concentration and $a_1 > 0, a_4 > 0$ indicating that if fiber ordering arises at all, it is only through the fiber order-membrane curvature coupling; The fiber order-membrane curvature coupling contribution up to second order terms is given by [1]:

$$\rho \dot{A}_{\text{fiber}} = (a_1 / 2)Q : Q + (a_4 / 4)(Q : Q)^2 \quad (4)$$

$$\rho \dot{A}_{\text{coupling}} = b : (a_2 S + a_3 s \cdot s) + (a_5 / 2)(b : s)^2 \quad (5)$$

where $S = Q + (I_1 / 2)$ and $I_1$ is the unit surface dyadic. For $a_2 > 0, a_5 > 0$ the first term in Eq. 5 promotes fiber alignment along the principal $e_1$ direction (curvophilic). For $a_3 > 0$, the second term in Eq. 5 promotes fiber orientation away from the principal axis (curvophobic).

When the free energy is minimized, there are three equilibria states in terms of fiber director [1]: (a) ring mode: orientation along major curvature, $\alpha = 0$; (b) line mode: orientation along the minor curvature, $\alpha = \pi / 2$; and (c) Helical or oblique mode, $cos^2 \alpha = -\beta_2 / 2\beta_1$, where $\alpha$ is the fiber orientation angle with respect to $e_1$. At small (large) radius, the fibers align along the minor (major) curvature direction. At intermediate curvatures, the oblique state minimizes the free energy. As the membrane radius increases, the fiber order $S$ decreases until a local minimum (cusp) is reached, due to the cancellation of free energy contributions from curvophobic and curvophilic interactions. At the onset of the ring mode, the fiber order $S$ starts increasing until a local maximum is reached promoted by curvophilic interactions. At high membranes radii, the fiber order vanishes asymptotically as the membrane curvature vanishes resulting in random fiber orientation (fig. 2).

For membranes with circular cross-section, fibers have the strongest effect in increasing bending stiffness of the cross section when they are strongly mutually aligned (high $S$) and with an average orientation in the azimuthal direction (region ii in fig 2). When the fibers are disordered they promote elastic softening (region iii in fig 2), and when they are axially oriented they have essentially no effect. The largest fiber stiffening effect is found when the membrane length scale (radius of curvature) and fiber length scale (curvophobic/curvophilic energy ratio) are equal. During cell growth, the variation of bending stiffness can serve as a shape lock-in mechanism (hardening regime) or conversely allow shape change through the softening effect.

In super-elliptical membranes, spatially varying curvatures results is membranes with soft sections with low bending elastic modulus that deform easily and stiffened sections with high bending elastic modulus remains intact resulting in characteristic membrane deformation under stress. For $\eta = 2.5$ and $b = 0.5$ in Eq. 1, soft sections of low bending modulus are in the corners of the super-elliptical membrane and stiffened sections of high bending modulus are on the sides resulting in shape invariant growth. For $\eta = 6$ and $b = 3.5$ soft sections of low bending modulus are in the sides and stiffened sections of high bending

ACKNOWLEDGMENT

This research was funded in part through a grant by FQRNT and the Department of Chemical Engineering of McGill University modulus are in the corners. This bending stiffness variation can only grow through shape distortions of the membrane.

REFERENCES

Chains of Superparamagnetic Nanoparticles as Biomedical Sensing and Diagnostic Tools

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MOTIVATION AND SUMMARY

Magnetic nanoparticles are being widely employed for separation and detection of various biological targets including bacteria, mammalian cells, viruses and molecules. The advantage of magnetic detection over fluorescence based methods is the absence of scattering, screening or interference for magnetic fields in typical biological media. However, fluorescence based detection does have one important advantage: it offers the possibility of multiplexing (detecting multiple targets in parallel), which has not been implemented with magnetic based assays. Here we propose that chains of magnetic nanoparticles could be fabricated to have different rates of magnetization relaxation (so-called Neel relaxation) and that different magnetic relaxation rates could be used to distinguish different chains and, therefore, enable their use in detection and separation of multiple biological targets in parallel. We report on the initial modeling result of Neel relaxation in magnetic nanoparticle chains.

BACKGROUND

Magnetic moment dynamics in a single-domain magnetic nanoparticle is subject to thermal fluctuation and can be viewed as a form of Brownian motion in a potential energy landscape that has at least two local minima separated by a barrier. This barrier is related to crystalline or shape anisotropy. In a simplified model, instead of Gilbert equation driven by noise \[1\], the magnetization can be viewed as a binary random variable (corresponding to magnetic moment having two opposite directions) whose probability is governed by the Master’s equation \[2\]:

\[
\frac{dp_+}{dt} = -v_+p_+ + v_-p_- = -v_+p_+ + v_- (1 - p_+)
\]

where \(p_+\) and \(p_-\) are probabilities of positive and negative values of the magnetic moment and

\[
v_+ = v_0 \exp\left(\frac{U_+}{kT}\right)
\]

and

\[
v_- = v_0 \exp\left(\frac{U_-}{kT}\right)
\]

are transition rates which depend on potential barriers \(U_+\) and \(U_-\) associated positive and negative magnetic moment directions and characteristic transition frequency \(v_0\). These potential barriers, in turn, depend on the crystalline anisotropy \(A\), particle volume \(V\), saturation magnetization \(M\) and magnetic field \(H\) as follows:

\[
U_+ = (A + MH)V
\]

\[
U_- = (A - MH)V
\]

If initially \(p_+ = 1\), for a single-domain particle subject to a constant external field the above Master’s equation can be solved analytically to yield exponential decay of the probability. The characteristic time of this decay is typically referred to as the Neel relaxation time.

SIMPLE ANALYTICAL MODEL RESULTS

The situation can be more complicated for a chain of single-domain particles that interact with each other through the magnetic field. In this case, using the mean-field approximation,

\[
H = \alpha (m) + H_{ext}
\]

where \(\langle m \rangle\) is the expected value of the average magnetic moment, \(\alpha\) is a dimensionless parameter characterizing the mean strength of magnetic interactions and \(H_{ext}\) is the external magnetic field, one can write a set of coupled Master’s equations and obtain the following differential equation for the expected value of the average magnetic moment:

\[
\frac{d\langle m \rangle}{dt} = -2cosh \left(\frac{MH}{kT}\right)\langle m \rangle + 2M \exp\left(\frac{MH}{kT}\right)
\]

The above model is not hard to solve when the external field is zero. It can be shown that, when the average magnetization of the nanoparticle chain is small, it decays exponentially with the same time constant as the individual particles. In other words, later in the decay process, the decay rate is dominated by the single-domain particles behaving nearly independently since randomization of the nanoparticle’s moments weakens their magnetic interactions. However, early in the decay process, when the average magnetization of the chain is close to saturation and the magnetic interactions are stronger, the decay is logarithmic, i.e.

\[
(M - \langle m \rangle) \approx \frac{kT}{\alpha M V} \ln \left[ C + v_0 \frac{\alpha M^2 V}{kT} \exp\left(\frac{-AV}{kT}\right) t \right]
\]

and the characteristic decay time is:

\[
\tau = \frac{1}{v_0 \alpha M^2 V} \exp\left[\frac{AV}{kT}\right]
\]

It is interesting to note that this early characteristic decay time is inversely related to the mean strength of magnetic interactions \(\alpha\). Intuitively, it seems likely that these interactions can be tuned by the average distance between the particles and by the length of the chain. It is also interesting that the dependence of the early characteristic decay time on the particle’s volume is weaker than exponential for smaller particles, suggesting that chain’s early decay time should be easier to control in the process of chain synthesis than that of a single-domain particle.
NUMERICAL MODEL RESULTS
Simplified mean-field model described above is useful because it reveals qualitative trends in the Neel relaxation of the magnetic nanoparticle chains. In this work we also develop numerical model where coupled Master’s equations are solved for different chain lengths, inter-particle distances and varying particle sizes. Deviations from mean-field model behavior will be discussed, although the numerical model is in general agreement with the mean-field model.

REFERENCES
Characterization of Interfiber Capillary Distance for C-CP Polymer Fiber Separations Columns

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OBJECTIVE
The goal of this work is to provide a useful measure of the average distance between fibers with an irregular cross-section, arranged parallel to one another in a column. In particular, we are interested in columns composed of capillary-channel polymer (C-CP) fibers, having a cross-section shown in Figure 1, [1]. A cross-section of an actual packed column is displayed in Figure 2, [2].

FIGURE 1. SEM image of C-CP fiber cross-section.

FIGURE 2. Packed C-CP fiber column.

Inter-fiber distance is a measure used in determining whether inter-fiber capillaries are of sufficient width for desired fluid fluxes through the medium for applications involving capillary action, [3]. It is also a factor influencing flow characteristics of a separations column, [4], which is the application of primary interest currently. This work is in collaboration with Professor R. Marcus and graduate students J. Pittman and M. Randanu, all in the Department of Chemistry at Clemson University.

INTRODUCTION
The application area motivating this effort is the use of C-CP fibers as stationary phases in high-performance liquid chromatography (HPLC) separations. C-CP fibers are gaining interest in open-tubular liquid chromatography because the fibers have high surface area (approximately 2.5 times the surface area of round fibers with the same cross-sectional area). The polymer fiber serves as both support and stationary phase for HPLC separations. C-CP fiber packed columns hold promise for a variety of separations applications, [5].

Consider the fibers shown in Figure 3. One choice for the distance between the fibers is the minimum distance, which for this case would be near zero. However, the fibers enclose a channel of non-negligible size which would be overlooked if only the shortest distance is used.

FIGURE 3. Neighboring fibers

Rather than using the shortest distance, our strategy is to calculate a series of point-to-point distances between fibers and take the average. The first step, given an arrangement of fibers, is to determine those pairs of fibers which ‘see’ each other, i.e. which are connected by a segment which passes through void space between the fibers. The distance between two fibers is taken as an average value of distances between points on the fiber edges. The distance corresponding to one point on a fiber to another fiber is taken as the shortest of all possible distances between the point and points on the other fiber. Because there is an inherent directionality in this definition, the distances are calculated in both directions, with ‘forward’ referring to distances from fiber i to fiber j with i < j, and ‘backward’ referring to distances from fiber j to fiber i, with i < j. Then the fiber-to-fiber distances are averaged, as summarized in words in Eq. (1).

\[
D_{avg} = \frac{\sum_{\text{over all connected pairs}} \left( \frac{\text{Average of forward distances for one pair}}{2} + \frac{\text{Average of backward distances for one pair}}{2} \right)}{\text{Number of connected pairs}}
\]

Details of how this calculation is carried out are given in the next section, followed by results and a brief discussion of continuing work.
SOLUTION APPROACH
There are four steps in the modeling process used to determine average distance.

Domain Set-Up can be carried out in one of two ways, depending on whether the geometry corresponds to an actual cross-section or one generated computationally. In this write-up we consider virtual columns for which the geometry is generated by a computer program. The image in Figure 1 was digitized using point-and-click digitizing software, resulting in a set of points which define the boundary of the fiber cross-section. A MATLAB program with a graphical user interface was then used to arrange the fibers, resulting in a virtual packed column of 49 fibers having the cross-section shown in Figure 4.

Discretization of the domain, which is the second step, results in the void space partitioned into triangles which facilitates implementation of the final two steps. Figure 5 contains an example of the discretized void space. The Triangle software package was used for this purpose, [6].

Neighbor Identification, the third step, is the process by which connected pairs, i.e. fibers which can be joined by a segment passing through void space, are determined. This is carried out using a C-language code that takes all possible point-to-point combinations and determines which points can be connected by a line segment through void space.

Distance Calculation, the final step, is carried out using a C-language code which calculates the ingredients of Eq. (1).

RESULTS
For comparison, we also constructed a domain consisting of 49 round fibers, each with the same cross-sectional area as the C-CP fibers, so that the void space is identical. Using Eq. (1), the resulting (dimensionless) distances calculated for the round-fiber and C-CP-fiber columns were 0.3175 units and 0.1134 units, respectively. This is not surprising in light of the higher surface area of the C-CP fibers (2.36 times that of the round fibers, for this case). The smaller average distance for the C-CP fibers indicates the potential to capture smaller solute material, and possibly a variety of sizes could be captured if the void space is more uniformly distributed than for round fibers, and the average distance could be ‘tuned’ as needed by modifying fiber size and packing density.

CONTINUING WORK
Next steps in this work include distance calculation for a variety of column geometries, including actual cross-sections and comparison of computed distance values with a heuristic formula used in industry, [3]. Alternatives to Eq. (1) are also under consideration.

REFERENCES
[2] Ibid.
Dynamics of Rotational Film Fibrillation and Nanofiber Formation

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ABSTRACT
DuPont has been developing commercial scale nanofiber technologies based on DuPont Nonwoven and Automotive Performance Coating technology. In this presentation, we report the fundamentals of nanofiber formation from rotational shear thinning polymer thin film fibrillation in a centrifugal nanofiber-spinning process.

A governing equation of rotating thin film flow has been presented including centrifugal, Coriolis and viscous forces. Film thickness, film front velocity and shear rate have been discussed.

INTRODUCTION
Nanofibers can be made and collected into a fibrous web useful for selective barrier end uses. Generally, polymeric nanofibers are produced by an electrospinning process. What is needed is a high throughput process to make very fine fibers and uniform fibrous webs. In Dupont’s centrifugal nanofiber spinning process [1], polymer a solution or melt is issued to the center of a rotary bell-cup or rotational disk to form a thin film on the rotating surface. Then the thin film fibrillates at the edge of the bell-cup or spin disk resulting in sub-micron or nanofibers.

Nanofiber formation in the centrifugal spinning process starts with the wetting and filming of polymer melt or solution on the bell-cup or spin disk surface with shear-thinning, entangled polymer molecular chain oriented in the thin film [1]. Figure 1 shows a bell-cup with varnish film flow on its inner surface and the fingering deflection as evidence of the Coriolis force. Actually, the Coriolis force induced thin film banding, fingering and “shock wave” instability contributes to thin film fibrillation. The threads from the thin film fibrillation will be furthermore stretched into nanofibers by strong centrifugal forces.

RESULTS AND DISCUSSION

Thin Film Formation, Spreading and Shear Rate
In the rotating frame of thin filming, the following forces are acting:

\[ \mathbf{F}_{\text{centr}} = -m\Omega \times (\mathbf{r} \times \mathbf{r}) \]
\[ \mathbf{F}_{\text{cor}} = -2m\Omega \times \mathbf{v} \]
\[ \mathbf{F}_{\text{visc}} = \Delta \mathbf{s} \left[ \frac{d}{ds} \left( \frac{F_{\text{dyn}}}{F_{\text{total}}} \right) \right] \]

The general momentum balance reads:

\[ \mathbf{I}_{\text{in}} - \mathbf{I}_{\text{out}} + \mathbf{F}_{\text{centr}} + \mathbf{F}_{\text{cor}} + \mathbf{F}_{\text{visc}} = 0. \]

Therefore, the governing equation is:

\[ \rho \frac{\partial \mathbf{U}}{\partial t} + \rho \mathbf{U} \cdot \nabla \mathbf{U} = -\nabla p - \rho \mathbf{\Omega} \times (\mathbf{r} \times \mathbf{U}) - 2\rho \mathbf{\Omega} \times \mathbf{U} + \rho v^2 \mathbf{U} \]

Considering a power-law for the flow on flat disk,

\[ \tau = K \left| \mathbf{\dot{e}} \right|^{\gamma-1} \gamma \]

the thin film thickness is:

\[ h = \left[ \frac{2n+1}{2m} \right]^{\frac{1}{2n+1}} Q^{\frac{n+1}{2n+1}} \left( \frac{\rho \mathbf{\Omega}^2}{K} \right)^{1 - \frac{1}{2n+1}} \]

where \( Q \) is fluid feeding rate, \( \mathbf{\Omega} \) is rotational speed.

The result shows in Figure 2 as the shear rate is in the range of 10,000 1/s to 100,000 1/s at rotational speeds of 10,000 rpm.

FIGURE 1. A bell-cup with varnish film flow on inner surface, and the fingering deflection caused by Coriolis force.

FIGURE 2. The shear rate as function of spin disk diameter (under rotational speed of 10,000 rpm).
Film traveling wave and Fingering Instability
When the films are subjected to the action of various mechanical, thermal, or structural factors, they display interesting dynamic phenomena such as wave propagation, wave steepening, see Figure 3, and development of chaotic responses, see Figure 4 as self-excited waves and Figure 5 as “shock wave”. Such films can display rupture phenomena creating holes, spreading of fronts, and the development of fingers. A general nonlinear evolution equation or equations are then derived and only various particular cases can be considered.

FIGURE 3. The traveling waves and fingering instability.

FIGURE 4. the self-excited waves.

FIGURE 5. the “shock wave” as described in [3].

Thin Film Banding Instability and Film Fibrillation
A Coriolis force-induced flow banding instability in a rotating system has been discovered [2]. It has been observed in experiment as shown in Figure 6. This internal banding instability will contribute to thin film fibrillation, and results in the thin thread formation at the bell-cup or spin disk edge. These threads will be furthermore stretched by strong centrifugal force into nanofibers.

Beads-on-String and Nanofibers
The Beads-on-string and nanofiber formation has been studied in terms of centrifugal stretching verses the dynamic extensional viscosity and elasticity, see Figure 7.

CONCLUSIONS
Nanofiber formation in centrifugal spinning processes has been studied in terms of filming instabilities. Coriolis force-induced banding instability inside film ribbons will cause thin film fibrillated into thin threads and stretching by strong centrifugal force into nanofibers.

REFERENCES
Control of Fiber Structures
Effect of the Blending of High-tacticity Component on the Structure and Properties of Elastomeric Fibers of Low-tacticity Polypropylene

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INTRODUCTION
Development of metallocene catalysts enabled us to control the molecular weight distribution and composition distribution of polypropylenes (PP), which may lead to the improved controllability of the higher order structure and properties of end-products [1-3]. Low stereo-regularity PP (L-PP) prepared using metallocene catalysts is expected to be applied for the production of elastomeric nonwoven fabrics through the spunbonding process. Because L-PP essentially has low crystallization rate, the delayed solidification in the spinning process could cause troubles during the fiber formation processes. Extremely low melting temperature also limits the use of spun-bonded nonwoven fabrics at elevated temperatures. Considering the above, effect of the blending of high stereo-regularity PP into L-PP on the processability in the high-speed melt spinning process and the mechanical and thermal properties of resultant fibers were investigated in this study.

APPROACH
Material
Three types of PP, i.e. low stereo-regularity PP (L-PP), LMP blended with 15 wt% of high stereo-regularity/low molecular weight PP (L-PP-LMC) and LMP blended with 15 wt% of high stereo-regularity/high molecular weight PP (L-PP-HMC) were prepared for the melt spinning. Characteristics of the three types of polymer for blending are summarized in TABLE I. Molecular weights of L-PP and LMC were similar.

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>MFR (g/10 min)</th>
<th>Melting Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-PP</td>
<td>60</td>
<td>59.6 °C</td>
</tr>
<tr>
<td>LMC</td>
<td>60</td>
<td>160.4 °C</td>
</tr>
<tr>
<td>HMC</td>
<td>20</td>
<td>161.0 °C</td>
</tr>
</tbody>
</table>

Melt spinning
High-speed melt spinning process was applied for the formation of fibers from the three types of PPs, i.e. L-PP, L-PP-LMC and L-PP-HMC. Polymers were melted at 210 °C and extruded through a spinning nozzle of 0.6 mm diameter at the throughput rate of 2.0 g/min. Take-up velocity was varied from 0.3 km/min to the attainable highest velocity. In the melt spinning process, on-line measurement of the fiber diameter was carried out at various positions to analyze the thinning behavior of fibers along the spinning line.

Characterization of fibers
Tensile tests and elastomeric recovery measurements were conducted to analyze the mechanical properties of prepared fibers. Differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA), and Wide-angle X-ray Diffraction (WAXD) measurements at elevated temperatures were carried out to analyze the thermal property of fibers. In addition, structural changes during the stretching and recovery of prepared fibers were investigated through the in-situ measurements of WAXD and Small-angle X-ray Scattering (SAXS) patterns utilizing X27C beam line at the National Synchrotron Light Source in New York, USA.

RESULTS AND DISCUSSION
Spinning behavior
The attainable highest take-up velocities of L-PP, L-PP-LMC, and L-PP-HMC were 6, 7, and 10 km/min, respectively. This means that the spinnability of L-PP was improved by the blending of high-stereo-regularity PP. It should be noted that the L-PP fibers could not be prepared at take-up velocities lower than 1 km/min because multiple fibers stuck each other on the take-up bobbin. This is due to the low crystallizability of L-PP. On the other hand, the L-PP-LMC and L-PP-HMC fibers were separated each other at the take-up velocities investigated. In other words, processability was improved by the blending of high-stereo-regularity PP. Another interesting feature is that the pure L-PP fibers were also separated each other at higher take-up velocities. This result is attributable to the enhancement of crystallization caused by tensile stress applied in the spinning line.
Structure of as-spun fibers
WAXD and SAXS patterns of as-spun PP fibers are shown in FIGURES 1 and 2. In the WAXD patterns, all fibers showed crystalline reflections of α-form crystals while the starting of crystalline orientation shifted to lower take-up velocities both by the addition of high-tacticity component and higher molecular weight component. In addition, coexistence of c-axis and a*-axis oriented crystals was confirmed while the amount of a*-axis oriented crystals decreased with the increase of take-up velocity. SAXS patterns of the fibers of crystalline orientation showed two-spot patterns, in that fan-like pattern changed to clear two-spot pattern and then width of the spot increased with an increase of take-up velocity. Long period decreased with the increase of take-up velocity, while reduction of long period occurred both by the addition of high-tacticity component and higher molecular weight component.

![FIGURE 1. WAXD patterns of L-PP, L-PP-LMC and L-PP-HMC fibers prepared at various take-up velocities](image)

Mechanical properties of as-spun fibers
Elastic recovery of fibers after 100 % extension was investigated. In the first cycle, elastic recovery took a maximum value at the take-up velocity corresponding to the starting of crystalline orientation, whereas the blending of high tacticity PP leads to the slight reduction of elastic recovery. On the other hand, recovery from the second cycle extension was higher than that from the first cycle extension, and showed high recovery of about 95 % for all the samples.

![FIGURE 2. SAXS patterns of L-PP, L-PP-LMC and L-PP-HMC fibers prepared at various take-up velocities](image)

Thermal properties of as-spun fibers
For the L-PP and L-PP-LMC fibers prepared at 5 km/min, variation of WAXD patterns with the increase of temperature was measured. WAXD patterns obtained at 30, 50, 70 and 100 °C are shown in FIGURE 3. The structure with highly oriented monoclinic crystals was found for the as-spun fibers of both polymers. When the temperature was elevated to 70 °C, crystals in L-PP fibers started to melt, whereas crystalline diffraction of the L-PP-LMC fibers remained intact. At 100 °C, crystalline orientation of L-PP-LMC fibers decreased slightly, whereas disappearance of crystalline diffractions was confirmed for the L-PP fibers. Result of TMA measurement is shown in FIGURE 4. Shrinkage stress showed higher maximum value and remained up to around 200 °C for the fibers prepared from L-PP-LMC and L-PP-HMC. This result is in accordance with the result shown in FIGURE 3. In other words, heat resistance of L-PP fibers, which has extremely low melting temperature, was significantly improved by the blending of high tacticity PP.

![FIGURE 3. Changes of WAXD pattern with increasing temperature for L-PP and L-PP-LMC fibers obtained at 5 km/min.](image)

REFERENCES
Polymer Fiber-based Field Effect Transistors: Advances and Opportunities

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INTRODUCTION

With the advent of all organic inherently conductive polymers (ICPs) over three decades ago new and novel applications of these unique materials have been developed and commercial applications realized. These applications include sensors of various types, organic transistors, organic light emitting diodes, and a whole variety of materials based on either the conducting or semiconducting properties of the polymers. Many new polymers have been synthesized in order to tune desired properties to specific parameters or to apply these to entirely new areas of interest such as all organic lasers, organic display devices, and many other uses where the light weight, flexibility, or other attributes of electrical or electronic polymers can be used in new and novel devices.

Inorganic semiconductor field-effect transistors (FETs) are at the core of most integrated circuit technologies and their formation on n and p type substrates has revolutionized the field of micro-electronics, leading to the miniaturization of today's electronics. Since the middle of the 1980's the potential use of ICPs as all organic field effect transistors (OFETs) has been explored.[1] Many of these early OFETs were based on polyanilines, derivatives of polythiophene, polypyrrole, and other easily synthesized ICP's.[2] By the end of the 1990's, and into the beginning of this century, the field had matured to a point where several excellent review articles had been published on organic thin film transistors used in FET applications.[3]

In most cases the use of OFETs has been applied to flat film architectures and studied in that format. Few articles have looked at OFETs applied to fiber surfaces and normally these have been applications where the fiber is the ICP semiconductor connecting metallic electrodes. Fibers form a particular problem with regard to the positioning of the source and drain electrodes, the gate electrode, and choice of materials with the correct work functions to facilitate device performance. Polymer/polymer interface problems are also of importance such as minimizing contact resistances and insuring good charge mobility across the interfaces. Much of the literature over the past twenty-five years considers the ICP as the semiconductor but still employs metallic source and drain electrodes due to work function considerations. Gold has been quite attractive for use as source/drain electrodes because of its high work function that allows access to many ICP HOMO energy levels where hole charge injection is desired for p type materials. Gold is a noble metal with no oxide formation on its surface. Oxides, once formed, as in the case of lower work function metals, interfere with charge injection across the metal polymer interface. Gold also seems to be a relatively good match for n type materials, where a match with the LUMO is desired, contrary to many theoretical studies. This may be due to the lack of an oxide layer facilitating better injection across the interface. The potential use of polymeric source/drain electrodes is problematic from the standpoint of the interfaces as well as work function considerations. But, if these limitations could be overcome these polymer electrodes would greatly enhance fiber-based OFETs. Studies to overcome many of these difficulties forms the basis of much of our work to date.

The use of fiber-based OFETs is interesting as such devices would be incorporated into or onto the fiber eliminating the need for "gluing" silicon based FETs or other circuit elements onto textile substrates in order to form "electronic textiles". Fiber based OFETs would provide a unique flexible material that has its own logic or other electronic components as constitutive parts of the final structure. Such structures are envisioned for use in conjunction with other ICP fiber-based systems employing all organic lasers, sensors (bio and otherwise) organic photovoltaics, micro-fluidic channeling, etc.
In this presentation we will review our on-going efforts focused on making fiber based FETs a feasible reality. The main goal is to develop fiber based OFET logic circuits contained on individual filaments, yarn bundles, or tightly woven substrates for use in textile panel applications where properties such as flexibility, drape, etc. are desired. We will discuss OFETs placed on fiber surfaces employing similar methods reported from our laboratories for making all organic micro-ring lasers.[4] We will discuss OFET fiber based architectures analogous to the metal insulator semiconductor FET (MISFET), and the thin film transistor (TFT). Particular attention will be given the consequences of the proper selection of ICPs, device parameters, work function considerations, and potential fabrication techniques.

REFERENCES

A Process for Noncircular, High-luster Acrylic Fiber

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OBJECTIVE
This research relates to the development of a modified inorganic solvent based process for manufacturing acrylic fibers having non-circular cross-sections with high luster and softness without use of non-circular spinnerets.

INTRODUCTION
It has become recognized that useful properties can be imparted to synthetic fibers by modifying the cross-sectional configurations which are other than round, such as of dog-bone or dumbbell cross-sectional configuration (e.g. Vinyon™ or Orlon™ from Dimethyl Formamide based process), kidney shaped (e.g. Acrilan™ from Dimethyl acetamide based process). Fibers with non-circular cross-section give fabrics with significantly different appearances and hands as compared to fabrics made of round fibers [1-5]. Non-circular fibers have higher surface area and higher ellipticity index than corresponding fabrics made of round fibers of equal denier, which also affect luster, smoothness, wickability, dyeability, drape and other related properties. [1-5].

The appearance of any product is one of its most important properties which greatly influences a customer’s choice for the product, and the luster or gloss of the surface of the fabric is one of the key attributes which affects the appearance and hence the aesthetic performance of the textile fabric. According to the American Society of Testing and Materials [6], luster is “the appearance characteristic of a surface that reflects more light in some directions than it does in other directions, i.e. it is the amount of specular light the fabric reflects”

The wet spun acrylic fibers with inorganic solvent based systems tend to have circular cross-sections where as non-circular cross-section has been reported in case of acrylic fibers made using organic solvent based systems [1]. Inorganic solvent based acrylic fibers also have lower luster and softness as compared to the organic solvent based acrylic fibers because of the cross section of the fiber. [7]. Various efforts to make non-circular cross-section from an inorganic system primarily focus on use of non-circular spinneret as in US3676540/1972[8] and US 3760053/1973[9]. Such spinnerets tend to be expensive due to high fabrication cost and in some cases, more prone to damage when used under high pressure. The productivity is also low because of the low pressure resistance of these plastic made spinnerets.

In the current paper, we have demonstrated a process to manufacture a non-circular and high luster acrylic fiber using the conventional inorganic solvent based process by modifying the coagulation kinetics of the process. Products developed from such fibers are also expected to have improved smoothness, softness enhanced wickability and drape due to their non-circular cross-section.

APPROACH
The approach here was to impact the coagulation kinetics by modifying the coagulation bath composition and thereby obtaining a non-circular cross-section in the resultant fiber. Fibers were spun, as illustrated in Figure 1, from an aqueous acrylic polymer dope in sodium thiocyanate solvent through circular 80 micron spinnerets into a coagulation bath containing low molecular weight organic solvents and the inorganic solvent in an aqueous solution form.

RESULT AND DISCUSSION
Low molecular weight alcohols were included in coagulation bath to modify the cross-section and luster of the fiber. Of the various alcohols, listed in the table I, isopropanol was selected for further study based on the spinnability and fiber properties.

<table>
<thead>
<tr>
<th>SN</th>
<th>Coagulation Bath</th>
<th>Cross Section</th>
<th>Luster</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Isopropanol-H₂O</td>
<td>Non Circular</td>
<td>Improved</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol-H₂O</td>
<td>Non Circular</td>
<td>Improved</td>
</tr>
<tr>
<td>3</td>
<td>Methanol-H₂O</td>
<td>Non Circular</td>
<td>Improved</td>
</tr>
<tr>
<td>4</td>
<td>DMF-H₂O</td>
<td>Circular</td>
<td>No Improvement</td>
</tr>
<tr>
<td>5</td>
<td>Acetic acid-H₂O</td>
<td>Circular</td>
<td>No Improvement</td>
</tr>
<tr>
<td>6</td>
<td>Glycerol-H₂O</td>
<td>Circular</td>
<td>No Improvement</td>
</tr>
</tbody>
</table>

The isopropanol content in the coagulation bath was optimized to evaluate the optimum solution for getting a non-circular high luster acrylic fiber without any significant effect on the other properties such as tenacity and elongation of the fiber. The phase diagram shown in figure 2 clearly explains the spinnable and non spinnable composition domains in the coagulation bath. Non circular and high luster acrylic fibers were obtained with 40%-90% isopropanol in the coagulation bath. High concentrations of isopropanol in the bath showed poor spinnability, and compositions below 40 %
isopropanol gave circular fibers without any luster improvement. As shown in the phase diagram when the bath composition reached to point where the sodium thiocyanate concentration is 12% in the bath, the fiber cross section was circular without any luster and spinnability was poor.

CONCLUSION

The current approach based on modified coagulation process using IPA water as the coagulating agent successfully produced a non circular high luster acrylic fiber without any significant effect on all other fiber properties. This approach is able to avoid the high fabrication cost of the modified spinneret to achieve the non-circular high luster fiber and hence does not incur the production losses.

FUTURE WORK

The further work will focus on understanding the mechanism of cross-section modification and luster enhancement in the proposed approach with respect to the coagulation kinetics.

REFERENCES


<table>
<thead>
<tr>
<th>Fiber</th>
<th>Denier</th>
<th>Tenacity(gpd)</th>
<th>Elongation (%)</th>
<th>Luster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3.34</td>
<td>3.28</td>
<td>19.31</td>
<td>4.2</td>
</tr>
<tr>
<td>Modified</td>
<td>3.56</td>
<td>3.15</td>
<td>18.93</td>
<td>9.05</td>
</tr>
</tbody>
</table>

The modified fiber and control fiber cross section was shown in Figure 3.

![FIGURE 3. Cross section of (a) modified acrylic fiber (b) control acrylic fiber.](image)

The SEM image of the modified fiber shows thick skin which is absent in control fiber. The thick skin may be responsible for altering the coagulation kinetics by controlling the mass exchange between the fiber and the surrounding medium to produce the non circular cross section of the fiber. The mechanical properties of the modified fiber are comparable to the control fiber as shown in Table II. However, the luster value of the fiber was significantly improved using the modified spinning process which is clearly shown in Table II.
Carbon Fibers and Composites
Crystalline and Tensile Properties of Carbon Nanotube-filled Polyamide-12 Fibers Meltspun by Industry-related Processes

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INTRODUCTION
The tensile strength of carbon nanotube (CNT) filled Polyamide (PA) fibers melt-spun at laboratory scale is usually much lower than the tensile strength of industrial grade PA fibers [1]. Spinning parameters are key factors determining the quality of a fiber [2]. Hence, we used our fiber pilot melt-spinning plant developed for spinning fibers in industrially relevant scales with properties comparable to commercial fibers. Polyamide 12 (PA12) can exhibit domains consisting of one or both of the two polymorphic phases, namely \( \alpha \) and \( \gamma \), as well as amorphous regions [3]. The degree of crystallinity and crystalline orientation act as governing factors to determine the tensile strength of the fibers. We investigated how these important factors are influenced by changes in draw ratio (DR) and by the addition of CNT taking into account a variety of fibers.

EXPERIMENTAL DETAILS
Unfilled PA12 fibers were spun from virgin PA12 at the in-house melt spinning pilot plant with DR 3, 4, and 4.5. PA12 together with the CNT masterbatch was extruded in a twin-screw extruder to obtain compounds with varying CNT concentrations. These compounds were used to spin another set of fibers with varying CNT concentrations (0.003 to 0.15 wt%) and DR. Tensile testing was carried out on a standard Instron apparatus using testing standard ISO 2062:2009. Wide angle x-ray diffraction (WAXD) measurements were done at beamline 1711 at MAX-lab, Sweden. Solid state \(^{13}\)C nuclear magnetic resonance (NMR) was carried out with a Bruker AVANCE-400 MHz NMR Spectrometer.

RESULTS & DISCUSSION
The chemical shifts and line widths of individual resonances were determined by non-linear least-square fits of a sum of Gaussian/Lorentzian curves. When compared to literature [4] the chemical shifts of the as-spun fibers correspond to the \( \gamma' \) phase. For annealed (160°C, 3h) fibers, the chemical shift refers to the \( \gamma \) form. When PA12 is quenched at atmospheric pressure from melt it is prone to crystallize in the \( \gamma' \) phase instead of \( \alpha \) or \( \gamma \) phase, and on annealing above 110°C at atmospheric pressure, a \( \gamma' \to \gamma \) transformation occurs [5].

The meridional and the equatorial reflection in the 2D WAXD pattern of the fibers were attributed to the \( \gamma20 \) and the \( \gamma200 \) planes, respectively [3] (Fig. 1). For the equatorial \( \gamma200 \) peak, the 1D intensity vs. 2\( \Theta \) plot was deduced and de-convoluted to separate the crystalline and the amorphous parts. The equatorial crystallinity index (ECI) and the Herman’s orientation factor (HOF) were calculated using the method described in [6]. For all unfilled and CNT-filled PA12 fibers, the position of the fitted equatorial Lorentzian peaks showed a variation in the 2\( \Theta \) peak position from 14.9° to 15.3° corresponding to d spacings from 4.11 Å to 4.24 Å. Thus, these peaks are attributed to \( \gamma200 \) [3]. From the orientation analysis we observe, as expected, a tendency of higher orientation for higher DR. The ECI of the unfilled fibers vary from 58% to 67%; whereas the ECI of the CNT filled fibers vary in the range of 60% to 68%. The ECI is largely influenced by the DR, but for fibers with the same draw ratio, irrespective of their CNT content, the ECI is very close.

An interesting phenomenon observed is the occurrence of an un-oriented crystalline peak for fibers filled with 0.03 wt% and 0.075 wt% CNT at DR 3 and 4 (Fig. 1). This may be due to the fact that CNTs act as nucleation sites for the formation of new crystallites, as previously reported for PA6 [7]. The CNTs are curved and randomly oriented in the matrix, thus the crystalline domains centered on them are un-oriented. The fact that we do not see an increase in the crystallinity for CNT filled fibers suggests an interchange of crystalline phases (from oriented to un-oriented) instead of the formation of new crystallites. A possible explanation would be that the CNTs inhibit the orienting process of the polymer lamellae. However, at high draw ratios (DR...
4.5), the polymer chains get oriented, no longer exhibiting the un-oriented crystalline peak.

We observe that extrusion has a crucial influence on the mechanical properties of melt-spun fibers, as shearing forces during extrusion cause damage to the polymer chains, diminishing molecular weight. To dilute and mix the CNT masterbatch the polymer had to be twin-screw extruded multiple times. A combination of extrusion and CNT incorporation seems to be detrimental to the tensile strength. We have defined a factor called "extrusion factor" (\(\text{Ext}\)) to quantify this effect. Virgin PA12 was extruded once and twice and the specific tensile strengths of the resulting fibers were measured as 55.3 cN/tex, and 41.6 cN/tex, respectively. The ratio of these two values (1.33) gives us an approximation of the damage. We assume that \(\text{Ext}_1\) of the polymer extruded once is 1 and \(\text{Ext}_2\) of the polymer extruded twice is 1.33. \(\text{Ext}\) of the filled fibers were calculated taking into account the number of extrusion processes the polymer had to sustain (Table 1).

In order to characterize the combined effect of extrusion and CNT incorporation, we introduced a strain factor (\(\text{Str}\)) taking into account the extrusion factor and the CNT concentration. The calculation of extrusion and strain factors will be explained in detail in the presentation. Table 1 summarizes strain factors and specific tensile strengths of the fibers with various CNT concentrations at DR 4.5. The tensile strength is seen to be minimum for the fiber with 0.075 wt% CNT, which has both an elevated value in terms of extrusion factor and CNT concentration. As molecular orientation is crucial for the mechanical strength of fibers, even though new crystallites are born with CNT mixed fibers, their un-oriented nature does not contribute to fiber reinforcement.

**CONCLUSIONS**

The PA12 fibers with and without CNTs crystallize in the \(\gamma\) and \(\gamma'\) phase depending on the pretreatment, without any trace of \(\alpha\) phase. Crystallinity studies show that the DR has a more pronounced effect than the inclusion of the CNTs. However, CNTs seem to act as nucleation sites as un-oriented crystallites are detected by WAXD analysis. Virgin PA12 is a thermoplastic polymer that renders very strong synthetic fibers, but treatments like multiple extrusions or inclusion of nanofillers seem to have detrimental effects on the tensile strength of such fibers.

**ACKNOWLEDGMENTS**

Authors would like to sincerely thank D Rentsch, P Barbadoro, L Gottardo, B Wüst and T Plivelic for their valuable contributions. Financial support from the Swiss National Science Foundation (SNSF) is thankfully acknowledged.

**TABLE & FIGURE**

Table 1: Summary of extrusion factors, strain factors and specific tensile strengths for the fibers with draw ratio 4.5.

<table>
<thead>
<tr>
<th>CNT (wt%)</th>
<th>Extrusion factor ((\text{Ext}))</th>
<th>Strain factor ((\text{Str}))</th>
<th>Specific tensile strength (cN/tex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000</td>
<td>1.000</td>
<td>55.3</td>
</tr>
<tr>
<td>0.150</td>
<td>1.329</td>
<td>1.056</td>
<td>45.0</td>
</tr>
<tr>
<td>0.075</td>
<td>1.164</td>
<td>1.192</td>
<td>35.5</td>
</tr>
<tr>
<td>0.030</td>
<td>1.066</td>
<td>1.077</td>
<td>44.3</td>
</tr>
<tr>
<td>0.015</td>
<td>1.033</td>
<td>1.038</td>
<td>45.1</td>
</tr>
<tr>
<td>0.003</td>
<td>1.007</td>
<td>1.008</td>
<td>51.0</td>
</tr>
<tr>
<td>0.0075</td>
<td>1.016</td>
<td>1.019</td>
<td>49.5</td>
</tr>
</tbody>
</table>

**REFERENCES**

Electromagnetic Shielding Mechanisms of Ultrahigh Thermally Treated Carbon Nanofibers-LLDPE Nanocomposites.

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OBJECTIVE
To investigate the influence of ultra-high thermal treatment of carbon nanofibers (Pyrograf® III PR-19) on the electromagnetic shielding mechanisms of linear low density polyethylene (LLDPE) nanocomposites.

INTRODUCTION
Due to the miniaturization and increased operating frequencies of electronic devices, electromagnetic compatibility (EMC) has become a significant challenge for product design engineers and manufacturers. Steps must be taken to protect electronic circuits from electrostatic discharge (ESD) and radiated electromagnetic interference (EMI). In this regard, conductive carbon-based polymer composites can be used to shield electronic devices from receiving or emitting electromagnetic signals ¹. Nanoforms such as carbon nanofibers (CNF) are suitable modifiers for preparing polymer composites films because of their very small diameter (≈0.5 μm), high aspect ratio and good electrical properties. Thus, the use of nanomodifiers could improve the transport properties of the matrix without deteriorating its mechanical properties ². As a result, carbon-based polymer nanocomposites might be used as EMC materials because of their ease of processing, light weight, corrosion resistance and optimal combination of mechanical and electromagnetic performance ³, ⁴. In this study, the electromagnetic shielding mechanisms of heat-treated to graphitization temperatures carbon nanofiber-LLDPE nanocomposites are evaluated.

APPROACH
Materials: Carbon nanofibers Pyrograf® III PR-19 were used as modifiers. Poly(ethylene-co-1-octene), Dow Dowlex™ 2045 Linear Low Density Polyethylene (LLDPE), which has the following properties: melting point of 122 °C, and Melt Flow Index of 1.00 g/10 min.
Processing: One hour ultra-high thermal treatment in helium at 2500 °C was carried out for PR-19 in a Thermal Technology LCC Furnace prior to compounding ⁵. Then, a DSM Xplore 15 cc twin-screw micro-compounder was used to prepare 20wt% nanocomposites at 190 °C and 20 rpm for 2 min. Compression-molding was used to shape the composites into circular sheets of 2.54 mm (100 mils) in thickness and 133.1 mm in diameter.
Characterization: An Electro-Metrics EM-2107A coaxial transmission line test fixture was used to apply a plane electromagnetic wave to the composite specimens (ASTM D4935). The electromagnetic shielding effectiveness (EM SE) ⁶ was measured based on the incident power, \( P_0 \), and the transmitted power, \( P_T \):

\[
EM \ SE = -10 \log \left( \frac{P_T}{P_0} \right)
\]  

(1)

The EM-2107A test fixture was connected to an Agilent Technologies N5230A PNA Series Network Analyzer. For measuring EM SE, each specimen composite was aligned between the test fixtures and measured at frequencies from 30 MHz to 1.5 GHz.

RESULTS AND DISCUSSION
To establish evidence of the improvement obtained by thermal treatment of the PR-19, the average EM SE values of four replicates as a function of frequency of 20 wt% nanocomposites are displayed in Figure 1. It shows that the EM SE values for PR-19 HT nanocomposites are significantly greater than those for PR-19 nanocomposites. PR-19 HT nanocomposites range 11 to 16 dB of attenuation over most of the frequency range, which means that more than 90 % of the incident power was attenuated. In contrast, untreated nanocomposites only averaged approximately 1 dB of shielding effectiveness.

Electromagnetic shielding theory ⁷ states that there are three basic shielding mechanisms: reflection, \( EM \ SE_R \), absorption, \( EM \ SE_A \), and multiple reflections, \( EM \ SE_M \). The most important ones are the first two when analyzing at high frequencies and working with electrically thick \( t > \text{wavelength} \) materials ¹. In applications where external radiation must be kept from interfering with an electronic circuit, what matters is the actual overall shielding provided by the enclosure, regardless the mechanism. However, when an electronic circuit couples to other circuits in the same enclosure, an absorptive enclosure is preferred. Reflective enclosures can cause large fields to build up internally which can enhance unwanted coupling between circuits inside the enclosure.

For the nanocomposites in this study, an analysis of these two basic shielding mechanisms was carried out by measuring the two main scattering parameters \( S_{11} \) and \( S_{21} \) that define transmittance, \( T \), and reflectance, \( R \):

\[
T = \left| \frac{P_T}{P_0} \right|^2 = |S_{21}|^2
\]

(2)

\[
R = \left| \frac{P_R}{P_0} \right|^2 = |S_{11}|^2
\]

(3)

The measured reflection and transmission (in dB) respectively are:
EM SEₐ = -10 log (1 - R) = -10 log(1 - |S₁₁|²)  \hspace{1cm} (4)
EM SE = -10 log T = -10 log|S₂₁|²  \hspace{1cm} (5)

Thus, absorption can be computed from their difference (energy balance):

EM SEₐ = EM SE - EM SEₐ \hspace{1cm} (6)

The shielding mechanisms in dB for PR-19 and PR-19 HT nanocomposites are shown in Figure 2.

For PR-19 nanocomposites, the EM SE increases with frequency and reflection appears to be the predominant mechanism. In contrast, PR-19 HT nanocomposites show a different behavior: absorption (EM SEₐ) is the predominant mechanism (~10 dB) since reflection (EM SEₐ) is only 4 dB. In addition, both mechanisms are less sensitive to frequency for PR-19 HT nanocomposites than those of untreated nanocomposites.

CONCLUSION

After an ultra-high thermal treatment (2500°C), PR-19 HT carbon nanofibers showed a significant increase in their graphitization level, which led 20 wt% PR-19 HT nanocomposites to exhibit an outstanding improvement in their electromagnetic performance. Over the studied frequency range (30 MHz-1.5 GHz), the EM SE of thermally treated nanocomposites were statistically greater than those of their counterparts (~1 dB), ranging 11-16 dB (>90% of attenuation), which is close to the EM SE target for many electronics applications (20 dB or 99% of attenuation). Furthermore, PR-19 HT nanocomposites turned out to be a predominantly absorptive material, which makes it a promising high-performance alternative for EM shielding.

ACKNOWLEDGMENTS

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REFERENCES

Mechanical Properties of Composite Plates Produced from 1x1 Rib Knit Fabrics with Carbon Fibers

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mehmetemin.yuksekkaya@usak.edu.tr

INTRODUCTION

Composite materials are used to obtain a new type of materials that bring down each other's weaknesses in order to obtain the desired properties and strong structures. Fiber-reinforced composites include a significant section of composites. Significant increases observed especially for tensile, bending and impact strength in fiber-reinforced composite materials.

Carbon fibers are ideal materials for the composite applications due to the excellent mechanical properties of them. Therefore, it is possible to use carbon fiber reinforced composite materials in many areas including aircraft applications.

Shiqiang Deng and Lin Ye [3] investigated the effect of the mechanical properties of fiber-matrix adhesion for graphite/epoxy composites. In their study, they found that interlaminar shear strength significantly increased with the fiber surface treatment. S.M. Elarabi and Yu Weidong[4] studied the effects of cross-lined fiber axial strength. Bilisik [2] used microwave heating and combined with resin transfer molding technique in his experiment and compared the mechanical properties composite 3D structures.

Zhang and Mason [7] studied the effect of pollution on the mechanical properties of carbon fiber-reinforced epoxy composites and measured the tensile strength and the interlayer shear strength. As a result of pollution, they concluded that water pollution and sea water reduces the tensile strength and elasticity modules of composite materials. Selzer and Friedrich [5] have studied the effects of moisture on the mechanical properties of carbon reinforced composite plates. It was found that amount of the moisture reduces the mechanical properties of the composites. Taniguchi et. al. [6] studied the dynamic tensile properties of carbon-fiber composites plates. They have concluded that there was a linear relationship between the tensile strength and strain rate. Baral et. al. [1] examined results of transverse tensile test for unidirectional carbon-epoxy composites for racing yacht construction. They have found that the transverse failure strain decreased with increasing the fiber modulus for PAN fiber-reinforced composites structures. In this study, properties of knitted reinforced fabric composite structures have been studied.

MATERIALS AND METHOD

In the experimental part of this study, 200 tex carbon fiber used and obtained from Aksa Acrylic Chemical Company. Thermoplastic epoxy resin has been used for composite molding. The composition of the knit fabrics was 1x1 rib with two different tightness levels. Then, five fabric layers were used to generate the composite structures with hand lay-up method. Carbon fibers reinforced epoxy composite laminates produced using the hot press located in the laboratory at 100 °C and 80 bar pressure. The processing time was 4 hours at the specified conditions. Before taking out the laminates from press, it was let the composite plates cooled down to the room temperature under the same pressure.

Composite laminates were cut suitable sizes according to the standards for tensile and shear tests by adapting a water jet cutting facility. A picture of samples is given in Figure 1.

![Figure 1. Picture of tensile test sample.](image)

Five layers of fabrics were used in the preparation of samples. The thickness and the sizes of the
samples were identically prepared in order to minimize the sample size variation. The tensile strength tests were made at room temperature. Totally, six samples were prepared and tested for each level of combinations.

RESULTS AND DISCUSSION

After preparation of the samples, tensile strength of the samples was tested for two directions, namely course and wale direction. Based on the test results, modulus and elongation of the composite materials were also calculated. Mean and variance values of each data group were calculated and compared statistically. It was found that the highest value of tensile strength was 1.15 kN/mm² in wale direction for the low tightness level of the samples while the lowest value of tensile strength as 0.51 kN / mm² were found to be in the wale direction for high tightness level of the samples. The difference between the tightness levels was indicated that the carbon fibers are getting damaged each other as the tightness increases. On the other hand, the modulus of the composite materials was found to be dependent to the direction of the tensile test. It was found that the highest value of young modulus was 2.27 MN/mm² in the wale direction for the lower tightness level of the samples while the lowest value of young modulus was 1.87 MN/mm² in the course direction for the lower tightness level of the samples. The highest value of elongation was 23.68 mm in the wale direction for the lower tightness level of the samples while the lowest value of elongation was 8.42 mm in the course direction for the higher tightness level of the samples. Anova test for the tensile strength was indicated that the tightness level and fabric direction had a statistically significant effect on the tensile strength. However, the interaction between the tightness and direction was statistically insignificant.

CONCLUSION

Composite materials are getting more attention from many parts of the industry. The amount of composite material usage is increasing for many applications. The result of this study showed that knitted reinforced fabrics will have an opportunity to be used in composite applications. It has been noticed that damage to the carbon fibers should be reduced by employing the correct set of manufacturing parameters during the knitted fabric production.

5. REFERENCES


FUTURE WORK

Hybrid composite materials could be manufactured by employing carbon and fiber glass materials with woven and knitted fabrics. The mechanical properties of those material could be investigated.

ACKNOWLEDGMENT

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High Thermal Conductivity Carbon Fibers and Fabrics: Low-cost Petroleum Pitch Precursors

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Introduction

Studies on electronic device failure have shown that over half of electronics failures are due to overheating or thermal cycling [1]. Carbon fibers have been used in composite applications due to enhance their strength, modulus, stiffness, and thermal/electrical conductivity [2]. Therefore, the primary goal of this project is to investigate low-cost mesophase pitch precursors that can be used to produce high thermal conductivity carbon fibers for power electronics packaging applications.

Experimental

Two experimental grades of pitches (designated L2 and L3) were used in conjunction with a synthetic Mitsubishi mesophase pitch (AR). Experimental petroleum-based mesophase pitches were prepared by Carbon Fiber Solutions using a proprietary process. The experimental grades contained nominally 100% discotic liquid crystalline content as did the synthetic grade.

The softening points of the samples were measured at a scanning rate of 2°C/min using a Mettler SP unit. L2 showed a high SP of 337°C. A variation of the process led to grade L3, which showed an intermediate SP of 319°C. In contrast, AR has significantly lower SP of about 280°C.

The transient shear viscosity of selected pitches was measured using cone-plate fixtures in an ARES II rheometer at temperatures 20°C to 50°C above the respective softening points. Inert N2 atmosphere was used throughout to prevent oxidation.

The viscosity-temperature results aided in the selection of appropriate temperatures for melt-spinning of various grades of pitches. A constant-throughput, batch machine was used throughout the study for the assessment of fiber spinnability. AR-mesophase pitch (Mitsubishi Gas and Chemicals, Japan) was used as a control sample. A 12-hole spinneret was used throughout the study, which consisted of capillaries with a diameter of 150 μm. Thicker fibers were spun at lower draw-down ratio (DDR), whereas thinner fibers were spun at higher DDRs.

Thermo-oxidative crosslinking kinetics were conducted in a Perkin-Elmer Pyris 1 TGA. The high temperature treatment of the stabilized fibers was conducted in Astro1100 furnace up at temperatures ranging up to about 2400°C in an inert helium environment.

Fiber diameters were measured by optical microscopy and a laser-scattering method. Microstructure was characterized by scanning electron microscopy (SEM Hitachi, S4800 FESEM).

Single filament tensile testing was conducted using MTI Phoenix testing equipment following ASTM Standard D3379-75. Finally, the thermal conductivity of carbon fibers was predicted based on the electrical resistivity data, which was obtained by a 4-probe resistivity measuring method. For thermal conductivity predictions, the following correlation, proposed by Lavin and Issi [3] for mesophase pitch–based carbon fiber was used:

\[ k = \frac{440,000}{(\rho + 258)} - 295 \]

where \( k \) [W/m·K] is thermal conductivity and \( \rho \) [μΩ·cm] is electrical resistivity.

Results and Discussion

The transient viscosity of various grades is displayed in Figure 1. Transient shear viscosity of L2 and L3 showed characteristic maxima and minima observed for discotic liquid crystalline fluids. Such unusual flow behavior has also been observed for various grades of synthetic mesophase pitches in our earlier studies [4,5,6]. At test temperatures ranging from 350 to 380°C, the steady-shear viscosity was found to be in the range 30-300 Pa·s, which is suitable for melt spinning.

To obtain high thermal conductivity, experimental pitches were spun at optimized spinning conditions to maximize the molecular orientation. Estimated thermal conductivity values are listed in Table 1. Thermal conductivity of thin L2 and L3 fiber graphitized at 2400°C were 287 and 450 W/mK, respectively, which are comparable to that of AR (within experimental error). In contrast, thick L2 and L3 fibers showed higher thermal conductivity, with 30~70% of fibers displaying Pac-man splits as captured in Figs. 2 b, 2e, and 2h. TEM micrographs (Figs. 2c, 2f, 2i) showed highly graphitic microstructure at the highest heat treatment temperature, but...
no structural difference was found amongst the three grades (L2, L3, and AR).

**Conclusions**

The shear rheology and fiber spinnability of selected cost-competitive, petroleum pitches are reported. Under suitable processing conditions, electrical resistivity of graphitized fibers was 3 to 6 $\mu\Omega\cdot$m. The Lavin-Issi correlation for thermal conductivity predicts that the experimental mesophase pitch-based carbon fibers would have a thermal conductivity approaching 500 W/m-K for fibers graphitized at modestly low heat treatment temperature of 2,400°C. In contrast, the highest temperatures used for such purpose exceeds 3000°C. SEM micrographs clearly establish that fiber microstructure was line-origin radial, and Pac-man splitting was found for such radial, thick fibers.

**Acknowledgments.** This work was supported by NSF Grant #0823012.

**References**


**Table 1. Tensile and electrical properties of experimental pitch-based carbon fibers heat treated to 2400°C**

<table>
<thead>
<tr>
<th></th>
<th>d$_{fiber}$ [µm]</th>
<th>ER [µΩ·m]</th>
<th>k$_{pred}$ [W/m·K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR_828</td>
<td>10.1 ± 0.8</td>
<td>5.0</td>
<td>287</td>
</tr>
<tr>
<td>L2_828</td>
<td>9.3 ± 0.8</td>
<td>5.0</td>
<td>287</td>
</tr>
<tr>
<td>L3_828</td>
<td>11.7 ± 0.9</td>
<td>3.3</td>
<td>450</td>
</tr>
<tr>
<td>AR_444</td>
<td>16.0 ± 1.0</td>
<td>3.3</td>
<td>455</td>
</tr>
<tr>
<td>L2_444</td>
<td>16.8 ± 2.8</td>
<td>3.6</td>
<td>423</td>
</tr>
<tr>
<td>L3_444</td>
<td>15.6 ± 0.9</td>
<td>3.4</td>
<td>446</td>
</tr>
</tbody>
</table>

**Figure 1. Rheological properties of experimental pitches: in (a) log-normal and (b) log-log planes**

**Figure 2. SEM and TEM micrographs of carbon fibers heat treated at 2400°C: (a-c) L2-based, (d-f) L3-based, and (g-i) AR-based.**
Rapid Manufacture of Carbon Fiber from Organosolv Lignins

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dbaker20@utk.edu

INTRODUCTION
At present, the majority of carbon fiber is manufactured from polyacrylonitrile, while a small amount is derived from mesophase pitch. However, due to the high cost of petroleum-based precursors and their processing costs, carbon fiber remains a specialty product. Emphasis has been placed on lowering the cost of processing through advanced oxidation techniques\(^\text{1,2}\), and also the synthesis of new melt-spinnable PAN precursors\(^3\); the progress in each case provides carbon fiber with strengths of 365KSI\(^2\) and 150KSI\(^1\), respectively. Researchers are also developing a process by which polyolefin fibers can be converted to carbon fiber\(^4\) with a strength of 110KSI. Another program\(^2\), involves the manufacture of carbon fiber from lignin and is directed towards reducing cost through the low cost of the renewable precursor and of processing.

The manufacture of carbon fiber from lignin involves the preparation of a suitable lignin that is melt-spun. The fiber is then oxidatively thermostabilized and carbonized. The integrity of the fiber during stabilization depends on its ability to crosslink, so that the glass transition (T\(_g\)) of the material is maintained above the process temperature, ultimately rendering it infusible. Lignin, which is naturally partially oxidized, demands critical control of the melt-spinning step and has to be prepared to have a low enough melt flow temperature (T\(_{mf}\)) for it to be melt spun without polymerizing during extrusion, and a high enough T\(_g\) for stabilization to proceed at an acceptable rate. Thus a narrow thermal window of opportunity exists for manufacturing carbon fiber from lignin. However, lignin does have advantages: it is very inexpensive, a renewable product, and it can be oxidatively thermostabilized at much higher rates. This allows for substantial cost reduction in carbon fiber manufacture.

The best lignin-based carbon fiber produced to date have strengths of 185KSI and are projected to cost much less than other known methods of carbon fiber production\(^6,7\). Efforts to further increase strength have been historically restricted by the unavailability of suitable lignins. Therefore the objective of this work is to manufacture lignins that are suitable for carbon fiber production.

APPROACH
In previous communications\(^8,9\), Baker described the properties of an organic purified lignin (OP86; i.e. T\(_g\)~86°C). Continuous lignin tow was spun to diameters as low as 10μm and with high speed (1200m/min). However, batch processing of the lignin fiber proceeded slowly with rates of stabilization as low as 0.01°C/min to 250°C being required before carbonization, and the subsequent carbon fiber was of low yield (32%) and had a tensile strength of 75 KSI. Since OP86 was only available in small quantities, attention turned towards Alcell\(^\text{TM}\), where the effect that a thermal pretreatment of the lignin, to alter its T\(_g\) and T\(_{mf}\) properties, would have on the processing of the lignin into carbon fiber was reported\(^10-12\). This gave increased stabilization rates and strength.

It was determined that use of a lignin thermal pretreatment to adjust T\(_g\) and T\(_{mf}\) would be more effective using a lignin with a more narrow molecular weight distribution (MWD)\(^8,9\). Attention returned to OP86. The thermal pretreatment of OP86 gave lignins with varying T\(_g\) and T\(_{mf}\) properties, which were evaluated for melt-spinning. The lignin fiber tows were studied for their stabilization (e.g. Figure 1) and carbonization properties. Ultimately, the best carbon fibers produced had a tensile strength of 185KSI (cf. OP86 lignin at 75KSI) with a carbon yield of 55% (cf. 33% for the OP86 lignin). In addition, the time used for stabilization was reduced to 13 min and for the overall process, less than one hour – many times faster than any other carbon fiber process.

![Figure 1](image-url) - Variation of allowed rate of oxidative thermostabilization against the T\(_g\) of the lignin fiber.

A most notable and undesirable feature of the lignins used in these studies was their wide MWD giving rise to large differences between their T\(_g\)'s and T\(_{mf}\)'s (>50°C), which increased on thermal manipulation (to >80°C). It was clear that the lignin required to manufacture carbon fiber of greater strengths should not only be of high purity, but of narrow MWD, having a T\(_{mf}\) below the anaerobic decomposition temperature, but a T\(_g\) that is sufficiently high to allow the lignin fibers produced to undergo oxidative thermostabilization at an acceptable rate. Our approach for this work is thus to optimize lignin MW and MWD using two methods; the first is by an optimized...
proprietary organosolv biomass separation and the second is by successive solvent extraction – both ultimately designed to give the most appropriate lignins.

**PRELIMINARY RESULTS AND DISCUSSION**

UT has embarked on a bioenergy-based lignin utilization program to enhance the economics of biofuel production via the generation of new products\(^\text{17}\). We are optimizing a novel solvent-based process for use on switchgrass, poplar, and other bioenergy feedstocks, to obtain lignin for chemicals and materials manufacture; and cellulosics for ethanol and advanced fuels production\(^\text{14,15}\). This is an organosolv pretreatment that separates biomass feedstock into its constituents (Figure 2).

![Figure 2 - Organosolv fractionation process.](image)

This solvent separation process offers a number of advantages; of particular importance is the ability to isolate lignin with high yield and purity. Furthermore, the work has revealed that the manipulation of reaction conditions gives rise to a wide gamut of lignin products with differing \(T_g\), \(T_{mf}\) and thus, MW properties (Figure 3). This has afforded the ability to control the process to obtain lignins targeted towards carbon fiber manufacture.

**Figure 3 – Examples of diverse lignins obtained from the UT organosolv process.**

Lignins obtained from alternative processes, e.g. the kraft process, have a wide MWD, and thus a large difference will be observed between their \(T_g\)’s and \(T_{mf}\)’s. It is therefore necessary, to remove the low molecular weight components that may be detrimental. Therefore we have also been examining methods\(^\text{19}\) by which these lignins can be extracted and optimized for carbon fiber manufacture. Most recently we have performed a series of successive solvent extractions which gave a wide variety of lignins with differing properties (Figure 4), with the highest yields (~65%) being obtained using extraction conditions that gave lignin suitable for carbon fiber evaluation (1A, 2B & 2D).

**FURTHER WORK**

The preliminary data from both our organosolv fractionations of biomass and successive solvent extractions of kraft lignins has shown that we can manipulate lignin properties to obtain suitable precursors for carbon fiber manufacture. We will continue to scale up and adjust our organosolv process along with successive extractions to provide fully characterized lignins for high-pressure fiber melt-spinning. A robust melt-spinning line will be installed in 2011 that will allow the high \(T_g\) and \(T_{mf}\) lignins to be fully evaluated. These fibers will be evaluated fully for their oxidative stabilization, carbonization, and graphitization properties. Based on the evidence provided previously, the use of these lignins to manufacture carbon fiber will result in significant increases in strength and reduction in processing cost; and as the required lignin properties are more defined additional improvements will result.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (°C)</th>
<th>(T_{mf}) (°C)</th>
<th>(\Delta T) (°C)</th>
<th>Relative MW distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin 1</td>
<td>146</td>
<td>no full melt</td>
<td>&gt;100</td>
<td>Very wide</td>
</tr>
<tr>
<td>Fraction 1A</td>
<td>147</td>
<td>189</td>
<td>42</td>
<td>Med-narrow</td>
</tr>
<tr>
<td>Fraction 1B</td>
<td>57</td>
<td>80</td>
<td>24</td>
<td>Narrow</td>
</tr>
<tr>
<td>Fraction 1C</td>
<td>122</td>
<td>153</td>
<td>31</td>
<td>Med-narrow</td>
</tr>
<tr>
<td>Fraction 1D</td>
<td>199</td>
<td>225</td>
<td>26</td>
<td>Narrow</td>
</tr>
<tr>
<td>Lignin 2</td>
<td>129</td>
<td>est. &gt; 230</td>
<td>&gt;100</td>
<td>Very wide</td>
</tr>
<tr>
<td>Fraction 2A</td>
<td>194</td>
<td>220</td>
<td>26</td>
<td>Narrow</td>
</tr>
<tr>
<td>Fraction 2B</td>
<td>178</td>
<td>211</td>
<td>33</td>
<td>Med-narrow</td>
</tr>
<tr>
<td>Fraction 2C</td>
<td>81</td>
<td>99</td>
<td>18</td>
<td>Very narrow</td>
</tr>
<tr>
<td>Fraction 2D</td>
<td>157</td>
<td>194</td>
<td>37</td>
<td>Med-narrow</td>
</tr>
</tbody>
</table>

**Figure 4 – Examples of lignins obtained via the successive solvent extraction of two kraft lignins.**

**REFERENCES**

Fiber-based Probes and Sensors
New surface functional nanofibers were developed, incorporated into microfluidic channels and the durability of those fibers within the channels proven. Gold electrodes were patterned adjacent to the microfluidic channels to control for the positioning of the nanofibers across the channels. Nanofibers used in this study were designed to be hydrophilic with either partial positive ($\delta^+$) or partial negative ($\delta^-$) charge at the fiber surface under flow conditions in the microfluidic channel. The phenomenon of a formation of charged surfaces at the interface between a solid and an electrolyte is well-known. These charges arise either from surface ionization (group dissociation) or ion adsorption. Our main interest in this study was to develop hydrophilic fibers with charged surfaces suitable for bio-applications. Highly hydrolyzed PVA polymers (> 99%) were blended with functional polymers targeted to provide a polarizable surface. PVA is especially useful for the materials in the bio-analysis system because it can be processed from hot water eliminating risk that the fabricated PVA nanofiber webs contain any toxic solvents which might interfere with analytes in solution. The resulting electrospun nanofibers are stabilized by strong intermolecular hydrogen bonding and do not swell significantly or dissolve in the room temperature aqueous solutions used for bioanalysis. Two types of functional polymers, Hexadimethrine bromide (Polybrene, PB) and Poly(methyl vinyl ether-alt-maleic anhydride) (Poly(MVE/MA), PMA), which have positive and negative functional groups, were blended with PVA in the electrospinning dope to provide additional functionality (Fig. 1). The amine groups or carboxyl groups in the functional polymers can be protonated or deprotonated in the pH of the solutions. The protonation or deprotonation of the functional polymers usually results in positive or negative charges on the fiber surface, incorporating the functional polymers. The charged surfaces on the electrospun fibers were induced when they met with the aqueous solutions due to the dissociation (ionization) of the functional groups on the surface or the adsorption (protonation) of ions from the solutions. XPS and FTIR were employed to detect and characterize the incorporation of PB and PMA in the electrospun fibers.

Nanofiber alignment within the microfluidic channels was easily controlled during the spinning process and was not disrupted by the assembly of the full microfluidic device (Fig. 2). Nanofiber stability in the microfluidic channels before and after high rates of fluid flow was evaluated by regular light microscopy. The effluent was collected from the microfluidic channels and analyzed using FTIR and H-NMR to confirm nanofiber durability. The current of the ionic blend nanofibers was measured by a thermally stimulated current (TSC) experiment. The fabrication of the microfluidic channel incorporated with the charged nanofibers is aimed at the concentration or purification of target substance from a solution. Incorporation of nanofibers into microfluidic channels can add significant surface area and functionality for separation of a target analyte from a mixed fluid.
The nanofibers in this study were fabricated to create patterns on the PMMA chip with gold electrodes and integrated into polymer-based microfluidic channels to create functionalized microfluidic systems. Functional polymers with charged chemical groups and a surfactant were successfully incorporated into PVA nanofibers and incorporation of the additives and migration of the surfactant to the fiber surface was confirmed by XPS and FTIR testing. The alignment of nanofibers between two electrodes was achieved by grounding the electrodes and charging the spinneret of the electrospinning device. Fibers were successfully aligned at lengths up to 15 mm. Thus, it is possible to influence the layout of the nanofibers within and across microfluidic channels via electrode placement, size and design. This will be further exploited in future research by creating nanofiber tufts within microfluidic channels, using them as guiding lines along a channel. A gap between two electrodes of 5 mm was chosen to prepare aligned electrospun nanofibers for further assembly into microfluidic devices with nanofiber aligned perpendicular to the fluid flow direction within microfluidic channels. An evaluation of the hydrophilic nanofibers showed that the nanofibers maintained morphology during flow of DI water at high rates through the microfluidic channel. Further studies have been carried out using these microfluidic nanofiber systems for sample concentration assays and zeta potential measurements in situ.

Acknowledgment

The authors are grateful for the financial support from NSF CBET-0852900 and the National Textile Center. Partial funding for this research was also provided by the Cornell Agricultural Experiment Station through federal funding project 356: "Novel Nanofiber Biosensor for Food Safety".

References


Micro- and Nanofiber Bundles as a Platform for Sensitive Detection of Biomacromolecules

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OBJECTIVE
Demonstrate the analytical figures of merit of shaped polymer fiber and nanofibers bundles as a microfluidic platform for biosensing.

INTRODUCTION AND APPROACH
We have developed a polymer fiber-based microfluidic platform that can be used for the handling and analysis of minute volumes of fluids with high sensitivity and specificity. These include small bundles of polyvinylidene fluoride (PVDF) nanofibers and micron-sized polypropylene (PP) shaped fibers with outstanding fluidic properties (Figure 1). Fiber bundles are prepared by pulling multiple fibers through a transparent 0.8mm inner diameter fluoropolymer capillary. The fibers are washed with methanol and water to remove surface contaminants and the surfaces of the fiber bundles are modified by adsorption of capture and/or sensing molecules. Following surface modification, the bundles are cut into 0.5cm lengths and attached to a disposable pipette tip (Figure 2).

RESULTS AND DISCUSSION
Polymer fiber bundles of micron- or nanometer-sized polymer fibers provide a platform for development of a compact flexible device which can integrate fluid sampling and sensing for quantitative analysis. In the first example, shaped polypropylene fiber bundles have been used for analysis of mRNA. Electrospun polyvinylidene fluoride (PVDF) nanofiber bundles have also been used with similar results. Since nearly all mRNA has a poly-A tail, affinity capture of mRNA can be facilitated by attaching a 20-25 base poly-dT to the bundle surface. Up to 2μg of neutravidin was adsorbed on each bundle followed by incubation with biotinylated poly-dT to functionalize the surface for mRNA capture. A total of 3μg (50μl) purified total RNA from J774A.1 macrophages treated with lipopolysaccharide and interferon-γ to dramatically increase expression of tumor necrosis factor alpha (TNFα) was then passed through the fiber bundle by centrifugation followed by washing in phosphate buffered saline (PBS). Next a fluorescent-labeled single-stranded DNA oligonucleotide (ssDNA) probe specific for TNFα was passed through the bundle and again washed with PBS. Fluorescence from the bundle was measured using a fluorescence microscope.

FIGURE 1. (A) SEM image of shaped fiber bundle cross section. (B) SEM image of nanofiber bundle cross section.

FIGURE 2. A shaped polymer fiber bundle attached to pipette tip.

Several classes of fiber bundles were prepared. We report on surface modifications of polymer fiber bundles with poly-dT and molecular beacons for measuring levels of gene expression. Detection limits in the femtomole to attomole range have been observed. Antigens and antibodies have also been adsorbed to the fiber bundle surface and immunoassays performed that show significant improvements in sensitivity and limit of detection versus conventional immunoassays using identical antigens and antibodies. Fiber bundles are easily produced and use very small reagent volumes making the bundles very inexpensive. These fiber-based devices are potentially useful for point-of-use diagnostics in the laboratory or the clinic and represent an alternative paradigm from existing microfluidic devices.

FIGURE 3. Relative fluorescence observed by a fiber bundle assay targeting TNFα mRNA (blue). Relative fluorescence from control bundles that were treated identically except no mRNA was added (red). Error bars are standard deviation from 3 individual bundles for each condition.
Figure 3 shows detection of TNFα mRNA versus a control that received no mRNA. We have also shown that we can effectively multiplex this assay using multiple fluorophores conjugated to different ssDNA probes (e.g. TNFα (green) and β-actin (red) (data not shown) as controls for gene expression or as a miniature gene expression array. The level of TNFα mRNA detected was approximately 300 femtomoles based on titration complementary oligonucleotides. The calculated limit of detection is approximately 500 attomoles by this method. Hence, using a neutravidin coated fiber surface, a 25-base biotinylated poly-dT oligonucleotide capture motif and fluorescent ssDNA probes, we have a rapid and sensitive assay for gene expression. Similar results have been observed using biotinylated molecular beacons attached to the fiber surface.

We have also performed a sensitive sandwich immunoassay to detect human chorionic gonadotropin (hCG) using by adsorbing the capture antibody to the shaped fiber bundle surface. The surface was washed with PBS, then treated with 0.3 μg hCG. This treatment was again followed by a wash, then incubated with the fluorescein-labeled detection antibody. The fluorescence from the bundles was measured using a fluorescence microscope and representative data are shown in Figure 4.

CONCLUSIONS
The polymer fiber bundles are a promising platform for sensitive sensing for a variety of biomolecular analytes in a simple format.

ACKNOWLEDGMENT
This research was funded in part through a grant by the National Science Foundation (EFRI 0937985).
Fabrication and Characterization of Electrospun Semiconductor Nanoparticle-Polyelectrolyte Ultrafine Fiber Composites

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STATEMENT OF PURPOSE/OBJECTIVE
Fluorescent composite fibrous assemblies of nanoparticle-polyelectrolyte fibers are useful multifunctional materials, utilized in filtration, sensing and tissue engineering applications, with the added benefits of improved mechanical, electrical or structural characteristics over the individual components. Composite fibrous mats were prepared by electrospinning aqueous solutions of 6 wt% poly(acrylic acid) (PAA) loaded with 5, 10, 15 and 20%v/v, carboxyl functionalized CdS/ZnS nanoparticles.

INTRODUCTION
Multifunctional fluorescent composite fibrous assemblies of semiconductor nanoparticles (SNPs) – polyelectrolyte fibers promise improved performance over their thin film analogues in applications such as filtration, sensors, security, light harvesting and tissue engineering applications. Specifically, the increased surface area, realized by fiber diameters of less than 200 nm, has been demonstrated to enhance performance in gas sensing [1].

APPROACH
In order to determine the optimal SNP loading, a series of 6 wt% PAA solutions with increasing SNP loadings (0.05, 0.10, 0.15, 0.20, 0.40 % v/v Qdot 525) were electrospun and characterized.

2.1 Materials
Powdered poly (acrylic acid) (PAA) polymer (Mw≈250,000 g/mol) was used as provided by Sigma Aldrich. Water soluble Qdot® 525 ITK™ carboxyl terminated CdSe/ZnS SNPs (λem = 525) were purchased from Invitrogen and used as received. Water used in preparing samples was twice deionized to a resistivity of 18.2 MΩ/cm.

2.2 Polymer – SNP solution preparation
Solutions containing the Qdot 525 SNPs were prepared by adding 5, 10, 15 or 20 μLs of 8μM Qdot 525s solution to 10 mLs of deionized water. Each suspension was sonicated for 3 min and then 2 mLs of the suspension was kept in reserve for spectroscopy. To the remaining 8 mL of solution, PAA was added for a total polymer content of 6 wt%. The PAA-Qdot 525 solutions were mixed for 24 h to completely solvate the polymer.

2.3 Polymer – SNP solution characterization
Polymer – SNP solution conductivities were measured with OakTon Con 510 bench top meter and acidity was measured with Mettler Toledo Delta 320 pH meter. Absorption and photoluminescence (PL) spectra were taken with Ocean Optics USB UV-VIS spectrometer with a DH 2000 Deuterium Tungsten Halogen light source (absorption spectra) and UV long wavelength lamp for PL spectroscopy.

2.4 Electrospinning apparatus
The electrospinning station consisted of a Gamma High Voltage Research power supply (0-60 KV), Harvard Apparatus 11 plus metered pump, copper screen grounded electrode, and 10 mL BD syringes with 21 gauge needles. Fibrous mats of composite and pristine fibers were collected on aluminum foil or waxed paper.

RESULTS AND DISCUSSION
Table I outlines the electrospinning parameters for PAA [2] and PAA/Qdot composites. In each instance, electrospun fibrous mats were formed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voltage (kV)</th>
<th>Target Distance (cm)</th>
<th>Pump Rate (mL/hr)</th>
<th>Temp °C</th>
<th>Relative Humidity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA</td>
<td>11</td>
<td>12</td>
<td>0.5</td>
<td>22.7</td>
<td>39</td>
</tr>
<tr>
<td>PAA 5μL Qdot 525</td>
<td>8</td>
<td>12</td>
<td>0.9</td>
<td>21.1</td>
<td>22</td>
</tr>
<tr>
<td>PAA 10μL Qdot 525</td>
<td>8</td>
<td>12</td>
<td>0.9</td>
<td>21.1</td>
<td>22</td>
</tr>
<tr>
<td>PAA 15μL Qdot 525</td>
<td>9</td>
<td>12</td>
<td>0.9</td>
<td>21.1</td>
<td>22</td>
</tr>
<tr>
<td>PAA 20μL Qdot 525</td>
<td>9</td>
<td>12</td>
<td>0.9</td>
<td>21.1</td>
<td>22</td>
</tr>
<tr>
<td>PAA 40μL Qdot 525</td>
<td>11</td>
<td>12</td>
<td>0.9</td>
<td>23.0</td>
<td>39</td>
</tr>
</tbody>
</table>

Figure 1 illustrates the relationship between fiber diameter and SNP loading. In general, increasing the SNP loading increases the fiber diameter, but not significantly. The fibers with the higher SNP loading had more uniform diameters and produced more consistent mats.
Fiber diameters are a function of both the solution properties and process parameters. In this case, the change in the relative humidity affected the solvent evaporation rate. The lower concentration of moisture in the air encourages solvent evaporation in the nascent fiber. This solidifies the fiber sooner, limiting the minimum fiber diameter and suppressing the effects of the solution surface tension resulting in larger fibers with fewer defects. Additionally, there is a 75% increase in fiber diameter for a 25% increase in SNP loading. This increase may be due to electrostatic repulsion between the charged carboxyl groups on the PAA chain and the SNPs.

Although the composite fibers are larger, the quality of the mats and the fiber yield are sufficient as a foundation for the future intended sensor platform.

**CONCLUSIONS**

The resulting composite fibrous mats exhibited uniform fiber morphologies with increasing fiber diameters with increasing SNP loading. Fluorescence micrographs reveal luminescent fibers with evenly distributed fluorophores in the higher loaded samples. Moreover, laser excited fibers manifest SNP intermittency correlated with small clusters and single SNPs suggesting excellent dispersion in the PAA matrix. PL spectroscopy of the fiber mats display a SNP emission peak ($\lambda_{em} = 560$ nm) that is red shifted when compared to the emission peak of the SNP-PAA solution ($\lambda_{em} = 525$ nm) due to SNP-SNP energy transfer as the fluorophores are effectively frozen position in the solid PAA fiber matrix.

**FUTURE WORK**

The creation of a viable aqueous sensor platform will require crosslinking the PAA fibers to prevent their dissolution which is under investigation.

**ACKNOWLEDGMENTS**

This research was funded in part through an NSF grant CMMI 0804543.

**REFERENCES**


Development of a Rapid Fiber-based Immunoassay

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OBJECTIVE
The goal of this study is to incorporate a common immunochromatography test into nanofiber yarns. Availability of such yarns would allow rapid fiber-based tests for a variety of conditions embedded into everyday household items leading in the long term to cheaper and faster over-the-counter diagnosis.

INTRODUCTION
Fiber-based test could be incorporated into daily-use products such as facial tissue or clothes to rapidly detect presence of various infections or disease markers. This would allow earlier treatment and reduced recovery time. This would be especially helpful in third world countries where there is a shortage of funds and medical care.

APPROACH
Currently, many diagnostic tests are based on an immunochromatography technique. For instance, pregnancy tests utilize gold nanoparticle labeling of human chorionic gonadotropin (hCG) and migration of the gold nanoparticle-labeled hCG along an immunochromatographic strip [1]. Our study focuses on the incorporation of immunochromatography technology into nanofiber yarns. In the future, such yarns can be embedded into everyday use items and used for self diagnosis of various conditions. The goal of this pilot study was demonstration of a proof-of-concept for such fiber-based devices.

Antibody Immobilization on poly(acrylonitrile)-cellulose acetate (PAN-CA) Yarn
Goat anti-rabbit IgG was labeled with Alexa Fluor 594, and was then immobilized on the surface of the PAN-CA fibers via covalent cross-linking using UV-sensitive Sulfo-NHS-LC-Diazirine cross-linker. A mask was placed over the yarn so that cross-linking of the antibody to the PAN-CA fibers would be localized in a desired portion of the yarn.

Gold-Antibody Conjugate Preparation
Au-Rabbit anti-bovine antibody (RAB) conjugates were prepared by physical adsorption. An immunoprecipitation assay was conducted to test the reactivity of the gold nanoparticle-labeled RAB IgG towards the goat anti-rabbit IgG. The test was performed by adding a large excess of goat anti-rabbit IgG (200 μl). The samples were incubated for 30 minutes with shaking at 37°C in an incubator.

Immunochromatography Assay
The goat anti-rabbit IgG conjugated PAN-CA yarn was immersed in the Au-RaB conjugate solution. The Au-RaB soaked PAN-CA yarn was then washed to ensure all the unreacted Au-RaB conjugates were removed from the goat anti-rabbit IgG immobilized PAN-CA yarn.

RESULTS AND DISCUSSION
The immunoprecipitation assay confirmed the reactivity of the rabbit anti-bovine IgG towards the goat anti-rabbit IgG. Immobilization and localization of the goat anti-rabbit IgG on the PAN-CA yarn was confirmed via fluorescent microscopy, as shown in figure 1.

Accumulation of the Au-RaB conjugates was apparent after immersion of the PAN-CA nanofiber yarn. After washing the yarn with Millipore water, it is apparent that Au-RaB conjugates were only retained in the region of the PAN-CA yarn with immobilized goat anti-rabbit IgG, shown below in figure 2.

FIGURE 1. Fluorescence image of the PAN-CA fiber after washing with blocking solution. A) The area of goat anti-rabbit IgG immobilization labeled with Alexa Fluor 594. B) The control end of the PAN-CA fiber with no immobilized goat anti-rabbit IgG.

Accumulation of the Au-RaB conjugates was apparent after immersion of the PAN-CA nanofiber yarn. After washing the yarn with Millipore water, it is apparent that Au-RaB conjugates were only retained in the region of the PAN-CA yarn with immobilized goat anti-rabbit IgG, shown below in figure 2.
FIGURE 2. PAN-CA fibers after immersion in gold nanoparticle labeled rabbit anti-bovine IgG (top) and PAN-CA fibers after washing in Millipore water for 1 day (bottom). A) The retention of the Au-RaB conjugates in the region of immobilized goat anti-rabbit IgG.

After initial immersion in the Au-RaB conjugate solution, preferential accumulation in the region of goat anti-rabbit IgG immobilization. This gives some indication of initial reactivity. Accumulation of Au-RaB conjugates elsewhere on the fiber (Fig. 2, top image) shows that the quantity of Au-RaB conjugates was too high and exceeded the binding capacity of the goat anti-rabbit immobilized on the PAN-CA yarn.

CONCLUSIONS
The images of the fluorescently labeled goat anti-rabbit IgG on the PAN-CA yarn show that the yarn is a promising material for antibody immobilization for deployment in a fiber-based immunoassay. The results of the immunoassay prove that the PAN-CA/gold nanoparticle system is a viable option for a fiber-based immunoassay, providing a region of specific reactivity between the antibodies immobilized on the yarn with the gold nanoparticle-labeled antibodies.

FUTURE WORK
Future work will be focused on immobilization and isolation of a control sample to validate the immunoassay. Quantification of the binding efficiency of the goat anti-rabbit IgG to the PAN-CA fibers and optimization of the Au-RaB quantity required to equal the binding capacity of the antibody immobilized on the fiber are needed. Future work can also be done to produce a biosensor specific to certain conditions.

ACKNOWLEDGMENT
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Fiber-based Biosensors for mRNA Extraction from Cells

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STATEMENT OF PURPOSE/OBJECTIVE
The ultimate goal of this research is to design a fiber-based PCR device for analysis of protein expression in individual cells. The short-term goal of this study is to show the feasibility of using fibers for mRNA extraction and PCR analysis from cell lysates obtained from large number of cells.

INTRODUCTION
A variety of biosensors are currently used in environmental applications, medicine, agriculture, food analysis, and drug discovery. Fiber-based biosensors may have an advantage because of their small diameter, which enables one to perform precise tasks (such as piercing and probing an individual cell) and the possibility to achieve extremely high specific surface area, which leads to increased signal-to-noise ratio and the capability to detect extremely small amounts of analyte.

As a model system we used vascular smooth muscle cells (VSMC), which have two different phenotypes – synthetic and contractile. Cells with the synthetic phenotype are softer, do not have a defined shape and have a high proliferation rate. Contractile cells are stiff, have a spindle-like shape and do not proliferate. This model is clinically important because transition from the contractile to synthetic phenotype is associated with restenosis. The two phenotypes show different levels of actin expression. Contractile (healthy) cells have a higher level of $\alpha$-smooth muscle (SM) actin expression, while synthetic cells have a decreased level of $\alpha$-SM actin expression. The contractile phenotype also has higher expression levels of other structural proteins such as $\gamma$-actin, $\beta$-actin, and smooth muscle myosin heavy chain.

APPROACH
Fibers made of different materials were modified by streptavidin (overnight physical adsorption) and then coated by a biotin-oligo dT (25) complex. The fibers are incubated with cell lysates to allow reaction of the mRNA polyA tail with oligo dT. The fibers are then removed from the cell lysates and mRNA bound to the oligo dT on the surface of the fibers is extracted by heating to 65-70°C with free oligo dT primers. After this step, the fiber is removed from the reaction mixture and reverse transcription is carried out to transform mRNA to complimentary DNA. The cDNA is further used in the conventional PCR reaction to monitor gene expression.

PCR data analysis
PCR data was analyzed using the double delta CT method according to the literature \cite{1}. Briefly, difference in gene expression was calculated based on the difference of CT values for targeted and control genes. This method allows using variable amount of cells for experiments as we use the housekeeping gene, expressed similarly in both types of cells, as the control. Schematic of the procedures (shown as planned for analysis of gene expression in individual cells) is shown in Figure 1.

RESULTS AND DISCUSSION
Fibers modification
The following fiber materials have been tested: Nylon, Polyacrylonitrile (PAN), Cellulose acetate (CA) with addition of polymethylmethacrylate (PMMA) and polyethylene oxide (PEO), CA/PMMA, CA/PAN, PAN/PMMA. Fibers were prepared using the electro-spinning method. Experiments with fluorescently labeled streptavidin demonstrated that

Schematic of the proposed on-fiber PCR experiment.
streptavidin can be successfully immobilized on the surface of the fibers. This protein coating is not removed after vigorous washing (3 h in DI water).

**Cell culture model**

Starvation of vascular smooth muscle cells for PCR experiments was performed according to the previously reported protocol [2]. Briefly, the cells were starved in FBS free medium for 15 days to allow them to undergo the phenotypical change. Starved and fed cells were collected and lysates were prepared using an ultrasonic homogenizer. These lysates were used in future experiments.

**mRNA extraction from lysates**

We have established a protocol that allows us to extract mRNA from cell lysates using streptavidin-oligo dT coated fibers. We demonstrated that such fibers can be used to extract mRNA from vascular smooth muscle cell (VSMC) lysates. The gene expression ratio between β-actin mRNA (targeting gene) and L32 ribosomal protein mRNA (housekeeping gene) was monitored. Figure 2 shows the relative amount of β-actin and L32 mRNA expression in lysates from contractile and synthetic VSMC. There was no significant difference ($p<0.05$) between the β-actin expression ratios determined using conventional PCR (left) and fiber-based PCR (second left).

**Dilution experiment**

To show that fiber-based PCR can be performed with smaller number of cells, we performed dilution of cell lysates and treated oligo dT coated fibers by the amount of genetic material corresponding to $10^7$, $10^5$, $10^3$ and 10 cells, respectively. We found that although average CT values for these diluted samples have increased from 21 (10$^7$ cells) to 27 (10$^5$ cells), 36 (10$^3$ cells), and to 53 (10 cells), the ratios between β-actin expression by contractile and synthetic VSMCs remained the same as for the original cell lysates. These findings indicate that fiber-based PCR has the potential for analysis of gene expression in very limited number of cells, possibly in individual cells.

**CONCLUSIONS**

In conclusion, we have successfully designed fiber based biosensors for mRNA extraction from cells. These fibers can be used to perform PCR analysis from extremely small amounts of genetic material corresponding to approximately 10 cells. Cellulose acetate fibers with PMMA and PEO outperformed other types of materials, showing the most consistent data.

**FUTURE WORK**

Further research is needed to show that these fibers could be used to extract mRNA from individual cells. It is also necessary to design the device that would allow piercing individual cell to collect its genetic material with the fiber.

**ACKNOWLEDGMENT**

This work has been supported by the National Science Foundation, Grant No. EFRI 0937985. The authors wish to thank Dr. Kenneth Christensen from Clemson University for productive discussion and Olga Reukova for help with figures preparation.

**REFERENCES**

Self-assembly of Optically Responsive Nematic Liquid Crystal/Polymer Core-Shell Fibers

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We report here the formation and structural characterization of optically-responsive, and highly birefringent, electrospun nematic liquid crystal (LC) microfibers. The LC microfibers are electrospun from a solution of polyactic acid (PLA) and low molecular weight 4-pentyl-4'-cyanobiphenyl (5CB) in chloroform/acetone solvent. In the electrospinning process, the low molecular weight 5CB phase-separates and self-assembles to form a planarly aligned nematic core within a PLA shell. The solubility limit of 5CB in PLA and the degree of phase separation of LC in the 5CB/PLA core/sheath fibers is determined using the phase transition enthalpies associated with LC and polymer components. Structural analysis revealed that the LC core and dissolved LC in the fibers promote the formation of the \(\alpha\)-form of PLA crystals and increase the degree of crystallinity of the PLA shell in 5CB/PLA fibers from 6.6 to 52\%. Competition between 5CB droplet formation and PLA fiber formation is observed as a function of spinning solution composition and applied electrospinning voltage. Alignment of the 5CB within the PLA core is confirmed by polarizing optical microscopy.

LC materials and LC/polymer composites have been extensively utilized in a variety of flexible light modulating devices.\(^1\) Recently researchers have prototyped reflective cholesteric liquid crystal displays on fabric substrates by sequential coating of functional layers on a planarized surface of fabric.\(^2\) Other display technologies have also been incorporated into fibers, such as light emitting diode (LED) illuminated optical fibers\(^3\) and organic-light-emitting-diode (OLED) coated glass fibers.\(^8\) Nevertheless, most of the previously reported prototypes negatively impact the physical characteristics of textiles by, for instance, reducing flexibility and breathability.

Polymeric liquid crystal materials have been formed into fibers to utilize some of the unique properties, such as mesophase properties, self-ordering at the molecular level, birefringence, and exceptional mechanical properties. The electrospinning of liquid crystalline elastomers has also been studied for potential use as mechanical actuators because of the anisotropic physical characteristics associated with this class of materials.\(^5\) The electrospinning of liquid crystalline polysiloxane with a cholesterol side chain and a low molecular weight LC has been reported.\(^6\) No phase separation of polysiloxane and the low molecular weight LC was observed. In order to obtain fibers with a low molecular weight LC core and polymeric shell, coaxial electrospinning was used to prevent mixing between the polymer and the low molecular weight LC to ensure that the LC phase was in the core. In other approaches, the solutions of polymers mixed with additives has generally been implemented by a coaxial electrospinning to ensure the partitioning of the small molecules in the core,\(^7\) rather than on the surface,\(^8\) of the fibers. For example, Lagerwall et al. reported on the coaxial electrospinning of nematic LCs into a poly(vinylpyrrolidon) (PVP)/TiO\(_2\) sheath in order to introduce optical properties of LCs into fibers.\(^9\) In this method, LC material was pumped via a separate channel into the core of the fiber. Even though these previous studies show methods for creating birefringent fibers, they do not provide insight into optical, structural, and morphological characteristics of the core-shell LC microfibers, or the effect of a LC core on the properties of a fiber shell.

Figure 1: Polarized Optical Microscopy (POM) and SEM images of PLA/5CB fibers collected at 0.6 mL/h, 10 cm, (a)-(d) 14 kV, (b)-(c) 20 kV, and (c)-(f) 22 kV. Top row: A 10X objective was used and inset scale bars indicate 100 mm.

Here we successfully demonstrate the self-assembly of low molecular weight liquid crystals in the core of a microfiber during electrospinning. The information obtained from the structural analysis of the fully flexible and electrospun 5CB/PLA microfibers are correlated to the optical properties of fibers. In addition, the optical characterization of the ordered LC fibers provides additional information to show the light modulating
properties of the LC fiber arrays. Electrospinning of a homogeneous LC/polymer solution results in highly birefringent and optically responsive LC microfibers. We present the optimization of the optical properties and the morphology of LC fibers by varying the concentration of LC material and altering the electrospinning parameters. The POM observations and thermal analysis are used to confirm that 5CB is phase-separated and self-assembled in the core of the PLA at above 28 wt% 5CB. We also studied how the soft matter properties of 5CB affect the crystallinity of the PLA shell by using wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). 10

Figure 2: Dependence of the PLA crystalline melting temperature ($T_m$) on the weight % of 5CB in the 5CB/PLA nonwoven fabrics.

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Functionalization of Fiber Surfaces
Microwave-promoted Deposition of Functionalized Nanoscopic Silica Coatings for Protective Textile Applications

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Textiles composed of natural fibers such as wool, cotton, and silk are typically easy to functionalize, as methods of doing so have evolved over centuries. Unfortunately, the US military’s need for fire retardant and ballistic protective garments is driving a move to military garments comprised of harder-to-treat synthetic fibers such as meta- and para-aramids, poly(p-phenylene-2,6-benzobisoxazole) or PBO, ultra-high-molecular-weight (UHMW) polyolefins, such as Dyneema™, poly{diimidazo pyridinylene(dihydroxy) phenylene} or M-5™ fiber, etc.. Functionalizing and processing of these high-performance textile compositions is extremely challenging, as traditional treatment methods are not suitable.

An emerging textile and fiber treatment process that has shown significant promise in treating both synthetic and natural fiber compositions and that can be easily integrated into existing textile manufacturing lines is the use of microwave irradiation of functionalized siloxanes to treat various fiber compositions. In 2010 this treatment method was used to impart textile compositions of FR-rayon—aramid—nylon with water/oil repellency, anti-bacterial, sporicidal, and chemical warfare agent neutralizing qualities. So treated materials self-extinguished upon exposure to burning solvents, exhibited water contact angles of >150° with 8 µL droplets, and dodecane contact angles of >135° with 8 µL droplets, and resisted absorption and degradation when exposed to 1:3 solutions of nitric and hydrochloric acids (aqua regia), to 1:3 solutions of 30% aqueous peroxide and concentrated sulfuric acid (piranha solution), and 15% aqueous sodium hypochlorite. Additionally, these treated materials exhibited >250% increase in air permeability vs. untreated controls.
Surface-tethered (Bio)Macromolecular Nanostructures
Synthesis and Characterization

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ABSTRACT

We show that stimulus-responsive polymer brushes and surface-grafted biomacromolecules offer exciting possibilities for sensing and actuation applications because they provide a means to amplify changes in the solvent environment (such as changes in pH, temperature, ionic strength) by a change in their molecular conformation. Furthermore, we discuss surface-initiated, enzymatic polymerization (SIEP) of DNA to synthesize high molecular weight DNA nanostructures in situ, while incorporating a broad range of unnatural nucleotides in the polymerized DNA. These nanostructures are used in the development of a novel and versatile detection and amplification platform technology that is applicable to a broad range of on-chip sensors, heterogeneous immunoassays, protein and DNA microarrays.
Surface Functionalization of Fibers by Grafting to Method

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ABSTRACT
Modification of fiber’s boundary with ultrathin grafted polymer layers can provide a powerful synthetic route to designing the surfaces with necessary characteristics. Permanent covalent grafting of polymers to a fiber surface can be accomplished by “grafting from” or “grafting to” methods. The “grafting from” technique involves polymerization that is initiated at the substrate surface by anchored initiating groups. In contrast, the “grafting to” technique involves reaction of functionalized polymer molecules with complementary functional groups located on the surface, resulting in the formation of tethered chains. The major advantage of the “grafting to” method over other polymer attachment techniques is that the polymer can be thoroughly characterized prior to the grafting. Well-defined polymers with a narrow molecular weight distribution can be used for grafting, resulting in the synthesis of well-defined brushes. Additionally, the grafting method is less challenging from a chemical point of view, since it does not involve elaborate synthetic procedures. In this presentation a reasonably universal approach for modification of fibers with the grafted layers using the “grafting to” method is discussed. The polymer grafting technique developed can be readily applied to generate hydrophobic, hydrophilic, switchable, optically active, and sensing materials.
INTRODUCTION

The objective of this work is to present inkjet printing equipment specifically designed for printing narrow fabrics.

Literature review revealed that inkjet printing technology is generally capable of printing narrow fabrics. This conclusion is supported by Rouette [1] and Kipphan [2] who describe in detail that digital printing, including inkjet printing is commonly used in the textile market. Will [3] on the other hand describes the machinery equipment that is available for printing textile fabrics. However, specific equipment that meets distinct requirements of the narrow fabrics industry is not available so far, since according to Will, the inkjet market is driven by machinery equipment for the Large Format Printing (LFP) market section, which are fabrics usually wider than 800mm. The specific needs of the narrow fabrics industry can be listed as follows:

- **Width:**
  - Thinking about shoe laces, narrow fabrics can be just as wide as 1mm.
  - A maximum width is approximately 300mm
  - The highest number of narrow fabrics can be found between 15 – 70mm, since the highest number of narrow fabrics machines are working in this range [4].
  - This means multi-tape transport and handling to print several ribbons simultaneously, when working with an inkjet shuttle.

- **Thickness:**
  - Narrow fabrics can vary enormously in thickness.
  - Lightweight taffeta ribbons, such as gift ribbons, are extremely thin (~0.1mm).
  - Lanyard belts, or seat belts can reach thicknesses, above 1mm.
  - The thickness may be different over the width, since narrow fabrics often have a thicker edge, due to its knitted edge design, or that for example metal wires are included for fabric stability purposes (e.g. ribbons for the floristic industry).

- **Surface texture:**
  - Narrow fabrics also vary extremely in its surface texture (topography).
  - Satin ribbons can almost be flat as paper.
  - Belts e.g. barrier tapes are usually very rough.
  - Warp knitted fabrics can even exhibit open areas within the fabric.
  - Fast change over times and fast machine setting times are crucial, since there is a need in the narrow fabrics industry to handle orders enormously flexible, specifically to reduce machine down times.

A market research demonstrated that the basic technology of inkjet printing exists, as there are many international companies that manufacture and distribute machinery equipment in the LFP market sector (see TABLE I). Besides full machine suppliers, also print head suppliers are established, concluding that there is a global infrastructure available for inkjet equipment supply, marketing and service, which is advantageous, since it limits development risks.

<table>
<thead>
<tr>
<th>Supplier of Inkjet Printing Equipment</th>
<th>Supplier of Inkjet Print Heads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eurotech Printers</td>
<td>Fujifilm Dimatrix Inc.</td>
</tr>
<tr>
<td>AGFA-Gevaert Group; (Gandi Innovations Holdings LLC)</td>
<td>Konica Minolta IJ Technologies, Inc.</td>
</tr>
<tr>
<td>Hewlett Packard Company</td>
<td>J. Zimmer Maschinenbau GmbH</td>
</tr>
<tr>
<td>Mimaki Engineering Co., Ltd</td>
<td>Kyocera Corporation</td>
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<tr>
<td>Mutoh Industries Ltd.</td>
<td>Seiko Epson Corporation</td>
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<tr>
<td>Roland DGA Corporation</td>
<td>Xennia Technology Ltd.</td>
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<tr>
<td>Seiko I Infotech Inc.</td>
<td>XAAR plc.</td>
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<tr>
<td>Teckwin Technology</td>
<td>Hewlett Packard Company</td>
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<td>Igen International Inc.</td>
<td>Canon Inc.</td>
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<td>Xc N.V.</td>
<td>NEOLT S.p.A.</td>
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<td>JP&amp;I Co., Ltd.</td>
<td>Durst Phototechnik AG</td>
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<td>Stork Prints BV</td>
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</table>

MACHINERY CONCEPT

It was decided to design the machine with the following distinct units:

- Unwinding unit
- Fabric transportation unit
- Printing unit
- Fixation unit
- Rewinding unit
Main aspect is simultaneous fabric transportation for multiple ribbons, which was achieved by the integration of the printing unit and the fabric transportation unit. Although both units are spatially integrated, they are still independent units.

![Diagram of printing and transportation units](image)

Figure 1: Printing unit and fabric transportation unit are integrated, but yet separate

The fabric transportation itself is exclusively based on friction, which is achieved by a set of rubber rollers as demonstrated in Figure 2. Main objective in the design of this unit was to create high contact angles to achieve secure fabric transportation.

![Diagram of fabric transportation unit](image)

Figure 2: Detail of the fabric transportation unit

Next important unit and step in the process of printing is ink fixation. The overall design of the machine was done in a way that the printed side of the fabric is in no contact with any other machinery part until full ink fixation to avoid image disturbances.

Fixation itself is done using contact heat, generated by a hot surface in a half-shell design, which generates some kind of tension so that the fabric is pressed onto the hot surface. To avoid overheating, the unit has a hot and a cold side, which can be controlled in its angle to precisely control not only the temperature of the surface, but also the time, the fabric is exposed to this temperature.

![Diagram of ink fixation unit](image)

Figure 3: Unit for ink fixation, featuring a cold and hot surface for precise heat control

CONCLUSION AND OUTLOOK

The objective of this work could be achieved. Printing equipment that meets the specific needs of the narrow fabrics industry could be presented.

Since this work is part of a comprehensive project, future studies and publications will discuss applications and cover also the process engineering part of printing narrow fabrics using this equipment.

ACKNOWLEDGMENT

The authors like to extend their sincere thanks to Jakob Müller AG Frick, who is the sponsor of this work.

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Formation and Application of Functional Coatings on Synthetic Fibers

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ABSTRACT

We present two simple methods for modifying synthetic fibers made of polypropylene (PP) and poly(ethylene terephthalate) (PET). Specifically, we alter the inert PP fiber mats by physisorbing denatured proteins, and cross-linking the protein layers using glutaraldehyde. The amino- and hydroxyl-functionalities present in the protein coatings serve as attachment points for polymerization initiators. In addition, PET fibers are modified chemically by amidation with 3-aminopropyltriethoxysilane (APTES), followed by hydrolysis, which yields silanol groups that permit surface attachment of the initiator molecules. “Grafting from” polymerization from such modified PP and PET surfaces is employed following the atom transfer radical polymerization protocol to form functional and responsive polymer coatings. These include arrays of poly(2-hydroxyethyl methacrylate) (PHEMA) as well as chemically-modified PHEMA layers. Selected applications of these functional fibers will be outlined briefly, including, capture of metals or other contaminants from waters, prevention of protein adsorption, and attachment of metallic nanoparticles.
Stimuli-responsive Alginate Fibers

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INTRODUCTION
The well-established commercial application of alginate hydrogel fibers is as a functional component in wound dressing. The alginate-fiber-containing dressings offer important advantages over traditional cotton and viscose gauzes, such as biocompatibility, nontoxicity, and the ability to absorb fluids from exuding wounds and maintain a moist local environment which aids in wound healing. Furthermore, the introduction of silver ions into alginate hydrogel provided the fibers with antimicrobial properties. Alginate hydrogel fibers are usually chemically treated to partially exchange calcium ions bound to carboxyl groups of alginate with sodium ions, which makes the fibers highly water swellable due to the ionization of the carboxyl groups. Such fibers are said to possess superabsorbent properties in the sense that they can absorb large amounts of water (more than 10 times their own weight). This property extends the possible range of applications to absorbent pads and hygiene products (e.g., disposable diapers and sanitary napkins). Since alginate is biodegradable, it may serve as a good substitution for synthetic polymers (polyacrylate, polyacrylamide, and maleic anhydride copolymers) that are currently used in superabsorbent materials and that pose certain environmental problems associated with synthesis and disposal. An alginate hydrogel can be chemically cross-linked using the reaction with glutaraldehyde. In this case, calcium ions can be completely substituted with sodium ions for optimal absorbency.

OBJECTIVES
The overall objective of this research is to develop a novel method for the fabrication of porous hydrogel fibers with the diameter of tens to hundreds of micrometers, i.e., the typical size of textile fibers, which possess a highly developed hierarchical porous structure. First, unlike nonporous hydrogels, the capillary network enables unobstructed diffusion of large solutes into and out of the interior of the fibers. Here, by large solutes we mean molecules and colloids whose size is much smaller than the diameter of the capillary but exceeds the mesh size of the polymeric network. Their diffusion through the polymeric network will thus be hindered. Examples of such solutes include high-molecular-weight synthetic and natural macromolecules, macromolecular assemblies (e.g., proteins, polymeric micelles and capsules), and inorganic nanoparticles. Furthermore, a high surface area available for adsorption and immobilization of various functionalities can be used to design adsorbents for nanoparticulates and catalytic supports.

RESULTS AND DISCUSSION
We prepared a number of stable o/w microemulsions from mineral oil, surfactants and an aqueous solution of sodium alginate with different oil content and size of oil droplets.

We found that the presence of alginate did not alter the morphology of the microemulsions (in particular, the size of oil droplets). Dynamic Light Scattering (DLS) was used to characterize the average size and size distribution of oil droplets. The microemulsions had a relatively narrow size distribution (a standard deviation of ~30%). The average size of oil droplets depended on the oil content and surfactant concentrations; it was found to be in the range from 10 nm to 300 nm for the different microemulsions.

FIGURE 1. SEM micrographs of alginate fibers (in the dry state) prepared by wet spinning an o/w microemulsion with alginate in the aqueous phase into a coagulation bath containing Ca2+ ions as acquired after extraction of the oil phase.

Alginate fibers were fabricated by wet spinning an o/w emulsion (with an oil-to-water ratio of 1:10 and an average size of oil droplets of 254 nm) composed of mineral oil and a solution of sodium alginate. In our experiments, we injected a 2 wt% solution of sodium
alginate through a fine spinneret into a solution containing Ca²⁺ ions (coagulation bath) with the extrusion speed of 125 ml/hr. Alginate precipitated from the spinning solution due to ionotropic gelation and formed continuous smooth fibers with a diameter of a few hundred micrometers. The fibers were chemically cross-linked via hydroxyl groups using glutaraldehyde as a cross-linking agent, and calcium cross-links in the hydrogel were replaced with sodium counter-ions by ion exchange. The chemically cross-linked fibers demonstrated excellent stability when subjected to various buffers as well as highly acidic and basic solutions. They also showed about one order of magnitude stronger swelling in water (up to 20 times of their dry weight) compared to the calcium cross-linked fibers owing to additional osmotic pressure originating from ionized sodium carboxylate groups of alginate. The porous structure associated with oil droplets can be clearly identified in the SEM micrograph of the fiber acquired at high magnification (Figure 1).

Using the same methodology and following the procedure described in Ref. [1], we spun alginate fibers loaded with single walled carbon nanotubes (Nanoledge, Fr). The alginate fibers filled with carbon nanotubes were electroconductive. These fibers demonstrated swelling properties dependent on pH and ionic strength. We proposed that these fibers, that combine porous structure, electroconductive properties and pH-responsiveness, can be used to regulate mass transport of various solutes, mediate biocatalytic processes and electrochemical reactions.

ACKNOWLEDGMENT
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Protective Clothing and Wetting of Textiles
Dynamics of a Drop on Elastic Fibers

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The motion of limited amounts of liquid in fibrous media is important in various systems, including wicking in textile fabrics, drying of fibrous filters, wetting of the adhesive pads of insects... The simplest system that can be considered consists of a liquid drop placed on two parallel fibers, or “rails”. Minor et al. [1] reported experiments on drops on rails using various fibers and liquids. They observed that below a critical distance between the fibers the drop spontaneously wicked in the inter-fiber channel until complete depletion of the drop reservoir, forming a liquid column, while tending to draw the fibers together. A drop of finite volume of liquid sitting on a rail can then adopt two configurations, depending on the fiber spacing: an “unduloid” drop or a liquid column, which spreads between the filaments. For rigid fibers, Princen [2] determined the equilibrium shape of a liquid column formed between the rails, and showed that this column can only exist for fiber spacings smaller than a critical spacing $d_c$. More specifically, the drop-to-column transition can occur for $0.57 < d_c/r < \sqrt{2}$, where $r$ is the fiber radius. This transition was proposed as a novel way of manipulating small quantities of fluids by using a conduit formed by two parallel fibers and changing the interfiber spacing, in order to either pin the drop at the point of deposition or drive it to spread along the interfiber channel [3]. However, these studies focused on rigid fibers, while it is clear that the flexibility of the fibers is relevant to many applications, in particular to understand some of the behavior described by Minor et al. [1]. Previous studies investigated the deformation of flexible brushes dipped into a liquid, and revealed that capillary forces can stick the fibers together [4].

Here, we study the behavior of a finite volume drop on tracks formed by two flexible fibers, clamped at one end and free to deflect at the other (Fig. 1a). The elasticity of the fibers leads to spontaneous motion of the drop, even above the critical spacing $d_c$. As the drop is deposited onto the rails, capillary forces bend the fibers, drawing them together and deforming the initially parallel rails to a “conical” shape (Fig. 1b). The drop then spontaneously moves toward the free ends of the fibers. As the drop advances, the gap between the fibers is reduced. For long fibers, the gap reaches the critical spacing at which the drop spontaneously wicks between the fibers, forming a liquid column that effectively stick the fibers together (Fig. 1c). The length along which the drop spread is limited by the elasticity of the fibers, and depends on the material and liquid properties, and on the volume of the drop. Experimental results and mathematical models will be presented and compared.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{a: Schematic of the experimental set-up. b: The drop configuration. c: The liquid column configuration.}
\end{figure}

ACKNOWLEDGMENT
C.D. and H.A.S. gratefully acknowledge financial support from Unilever Research.

REFERENCES
Textiles for the Next Generation of Military Clothing

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The military is dependent on a wide variety of textile items in accomplishing its missions. Textile items include dress clothing, combat clothing, ballistic protective vests and helmets, chemical biological (CB) protective clothing, cold weather clothing, tents, sleeping bags, parachutes, and numerous other items. Many of these items are subjected to extreme conditions during their use. Since many of these items are life support items, they are designed and fabricated to very high standards of performance. Furthermore, the performance of these items is constantly being improved. At the same time, it is desired to reduce the weight of these items without sacrificing performance. Many of the developments in this area are based on advances in nanotechnology, biomimetic materials, and intelligent materials. The next generation of military textiles is benefiting from the integration of nanoparticles, nanofibers, and electronics into fabrics and is achieving a new level of performance. One area of interest involves improved repellency to liquid water and hazardous chemicals. Several approaches are being developed to address this particular aspect of protection.

CB protective clothing used by the military utilizes air-permeable or breathable textile systems consisting of an outer shell fabric and an inner fabric which contains an adsorbent, typically activated carbon. These layers work together to provide liquid and vapor protection. Liquid droplets are held at the surface of the outer shell fabric, while vapors are captured by the adsorbent carbon. The outer shell fabric is treated with an oil- and water-repellent fluoropolymer coating which prevents liquid droplets from soaking into the textile system and overwhelming the carbon layer. These coatings, typically perfluoroalkylated acrylates or polyurethanes, reduce the surface energy of the individual fibers to around 11 mJ/m². Because of this exceptionally low surface energy, the outer shell fabric is able to repel water, which has a surface energy of 72.8 mJ/m². It is also able to repel hazardous chemicals such as the chemical warfare blister agent sulfur mustard (surface energy = 43 mJ/m²) and the nerve agents tabun, sarin, and VX (surface energies = 25, 26, and 30 mJ/m², respectively).

The combined effects of textile structure and low surface energy can lead to fabrics which display very high apparent water contact angles. When the water contact angle exceeds 150°, the surface is considered to be superhydrophobic. Similarly, a surface having an oil contact angle greater than 150° is considered superoleophobic. One additional factor is the roll-off angle which should be less than 5 degrees. However, it is well known that roll-off angles are affected by the mass of the liquid droplet, the interfacial surface energy between liquid and solid, and the local geometry of the solid surface. It has been found that multi-scale structures, such as many fabrics, can reduce roll-off angles when treated with chemicals that impart low surface energy to the fabric surface.

Current processes for treating fabrics with fluorochemicals are either slow or require specialized equipment not widely available in the textile industry. It has been demonstrated that fluoroalkanes can be attached to reactive groups such as amines, hydroxyl groups, or carboxylic acid groups of polyamides or cellulosic fibers. This process is amenable to considerable improvement through the traditional wet (pad-dry-cure) process. The equipment for this process is widely available in the textile industry and could easily be used for the mass production of superhydrophobic, superoleophobic fabrics. These fabrics with advanced coatings will be self-cleaning in that dirt will not adhere to them. They will also provide increased chemical protection in that liquid droplets of hazardous chemicals will easily roll from the fabric surface.
This work aims at the development of novel smart textile materials for advanced, lightweight, self-cooling protective clothing by creating a laminated structure with a prescribed permeability gradient. This permeability gradient should allow moisture self-propulsion from the inside surface of the armor vest to the outside surface exposed to the atmosphere. This design of the body armor shell could make the soldier movement more comfortable eliminating the moisture excess from the uniform.

The most crucial part of the vest cooling arrangement is membrane assembly (system of two or more evenly stacked membranes). To this end, reliable and durable assembly has been prepared using PET membranes modified with hydrophobic polymer and metal wires as spacers (Figure 1). The single membrane itself has shown no significant resistance to water vapors and the assembly demonstrated smaller, but sufficient water permeability rate.

At the next stage of the studies the fabric with hydrophobicity/hydrophilicity gradient will be combined with the assembly in order to facilitate the liquid water transport from the region of active evaporation. It is expected to shift vapor-liquid water equilibrium and increase the evaporation rate and cooling efficiency significantly.

ACKNOWLEDGMENT
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Oleophobic Coating for Self-cleaning, Fluid-resistant Textiles

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STATEMENT OF PURPOSE
Luna Innovations Incorporated coated NyCo (50:50 Nylon: Cotton), MIL-DTL-44436 Class 6 fabric, with a novel, water based coating that imparts water and oil resistance demonstrated by contact angles of water and octane of 165° and 122° respectively. Army Combat Uniforms (ACU) were manufactured from the coated NyCo and tested during the Air Force Research Laboratories Technology Warrior Demonstration at Ft. Drum Army Installation, Ft. Drum, NY. The ACUs demonstrate water and soiling resistance and are an enabling technology towards chemical and biological warfare agent resistance therefore providing advanced equipment to US warfighters.

INTRODUCTION
Luna has demonstrated the use of a water based coating chemistry for textiles to produced extremely low surface energy nanostructured textiles for self-cleaning uniforms. The novel coated textile has significant advantages over conventional textiles. The inherent resistance of these materials to soiling with dirt, oils, or other chemicals will eliminate or minimize the amount of laundering required. This will significantly lower the logistics burden of the military force associated with laundering, particularly on the battlefield. These novel coated textiles can also provide enhanced chemical / biological warfare agent (CBWA) resistance while maintaining the breathability of uncoated fabric. Current CBWA clothing has problems with weight (e.g. activated carbon) or poor breathability (e.g. butyl rubber). Luna has developed a class of low surface energy fabric coatings with excellent water and oil resistance and durability. Besides these physical benefits, Luna’s coating process has a significant advantage over other fluid resistant technologies:
• Simple process – Luna’s coating uses conventional coating treatment process to be treated in any current textile mill
• Inexpensive – No additional equipment is necessary, and processing costs are comparable to current processes; the coating formulation is produced from readily available materials
• Scalable - Luna has successfully demonstrated the coating of 400 yards of 60” fabric; both the chemistry and process can be easily scaled
• Environmentally responsible – Luna’s coating is water based with no volatile organic compounds; the process is less energy intensive than other technologies (plasma deposition, microwave treatment, chemical vapor deposition, etc.

APPRAOCH
The fluid resistant coatings employ a hierarchical structure with nanostructured additives. Conventional, water-based textile coating resins are combined with the additives to generate a low surface energy coating with excellent durability. The very high fluid contact angles and low roll-off angles render the textile self-cleanable, resembling the self-cleaning effect of a lotus leaf.

Textile Coating
400 yards of fluid resistant NyCo was produced at Jaeger TTC (Rochester, NH) in cooperation with Shawmut Mills (West Bridgewater, MA).

Garment Manufacture
ACU were cut and sewn by Propper International (Weldon Spring, MO) and delivered to Luna Innovations. 25 garment sets were manufactured.

Technology Demonstration
Testing of ACUs for comfort, abrasion resistance and performance took place at the AFRL Technology Warrior Demonstration at Ft. Drum Army Installation, 18 June through 29 June 2011. The garments were donned by 12 soldiers who reported on their performance while participating in field testing objectives.

RESULTS AND DISCUSSION
NyCo treated with Luna’s fluid resistant coating was tested for repellency and strength (Table I). Contact angle and spray rating results demonstrated resistance superiority over untreated NyCo while abrasion resistance and water vapor permeability was maintained.
### TABLE I. Physical Properties of Treated and Untreated NyCo

<table>
<thead>
<tr>
<th></th>
<th>Treated NyCo</th>
<th>Untreated NyCo</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Tension</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water CA&lt;sup&gt;1&lt;/sup&gt;</td>
<td>165</td>
<td>Wets</td>
</tr>
<tr>
<td>Octane CA&lt;sup&gt;2&lt;/sup&gt;</td>
<td>122</td>
<td>Wets</td>
</tr>
<tr>
<td><strong>Spray rating (AATCC 22)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>Octane</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td><strong>Tensile Break Strength (lbs/in) (ASTM D5034)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Warp</td>
<td>81±2</td>
<td>111±6</td>
</tr>
<tr>
<td>Fill</td>
<td>52±14</td>
<td>54±1</td>
</tr>
<tr>
<td>Intermediate</td>
<td>72±5</td>
<td>87±2</td>
</tr>
<tr>
<td><strong>Stiffness (lbs/in²) (ASTM D5034)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Warp</td>
<td>345±26</td>
<td>423±15</td>
</tr>
<tr>
<td>Fill</td>
<td>230±34</td>
<td>284±22</td>
</tr>
<tr>
<td>Intermediate</td>
<td>141±21</td>
<td>162±8</td>
</tr>
<tr>
<td><strong>Abrasion Resistance (cycles to failure&lt;sup&gt;III&lt;/sup&gt;) (ASTM D3884)</strong></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>11 000</td>
<td>11 000</td>
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<tr>
<td><strong>Water Vapor Permeability (g/m², 24 hrs) (ASTM E96)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>14.5</td>
</tr>
</tbody>
</table>

<sup>[I] MIL-83429B Class 6</sup>  
<sup>[II] Water surface tension =72.8 mN/m; Octane surface tension=21.6 mN/m.</sup>  
<sup>[III] Cycles to failure (increment of 1,000) for visible holes to appear</sup>

**Demonstration** ACUs made from treated NyCo (Figure 1) were showcased at the AFRL Technology Demonstration and results regarding their performance and ability to meet program objectives are forthcoming.

**CONCLUSIONS**  
Self-cleaning uniforms have demonstrated repellency to water, oil and other soiling agents. The garments demonstrated maintained water vapor permeability, a critical comfort parameter and show excellent promise to be a keystone technology to protect soldiers.

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**ACKNOWLEDGMENT**  
This material is based upon work supported by the U.S. Army RDECOM Acquisition Center, Natick Contracting Division, Natick, MA under Contract No. W911QY-10-C-0071. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the U.S. Army RDECOM Acquisition Center, Natick Contracting Division, Natick, MA.
Observations on the Behaviour of Chemical Warfare Agents and Other Liquids on Super-repellent Textiles

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OBJECTIVE
The objective of this work was to demonstrate the potential for producing super-oleophobic, self-cleaning materials which would repel chemical warfare agents (CWAs).

INTRODUCTION
Air-permeable CB protective clothing usually consists of two separate components: an outer fabric layer made from woven yarns, and an underlayer containing an adsorbent material – typically activated carbon – to remove toxic vapours. The outer fabric layer is treated with an oil- and water-repellent fluoropolymer finish which prevents toxic liquids soaking into the textile layers and overwhelming the underlying adsorbent material. These treatments contain comb-like polymers (typically based on perfluoroalkylated acrylates or polyurethanes) which reduce the surface energy ($\gamma$) of the individual fibres to around 11 mJ·m⁻² [1] (note: $\gamma$ for polytetrafluoroethylene (PTFE) = 18 mJ·m⁻²).

The exceptionally low surface energy of these treatments means that the outer fabric layer is able to repel not just water, which has a relatively high $\gamma$ of 72.8 mJ·m⁻², but also liquid chemical warfare agents such as the blister agent sulphur mustard (HD) ($\gamma$ ≈ 43 mJ·m⁻²) and the nerve agents GD, GB and VX ($\gamma$ ≈ 25, 26 and 30 mJ·m⁻² respectively).

Superoleophobic, self-cleaning materials — that is those materials which display contact angles greater than 150° with organic liquids — are extremely rare. However, it has been demonstrated that so-called “re-entrant” surface structures in combination with a low surface energy treatment can display extreme resistance to wetting from low surface tension liquids, including alkanes [2]. For example, remarkably high advancing and receding contact angles of 163° and 145° respectively have been reported for octane ($\gamma$ = 21 mJ·m⁻²) on perfluoroalkylated micron-sized pillers. However, these and similar structures are not readily applicable to the development of robust, superoleophobic, self-cleaning textiles.

In a military context, the ability of liquid CW agents and other substances such as fuels, oils and lubricants to roll effortlessly off contaminated clothing would greatly improve protection and aid decontamination procedures. Furthermore, such an effect would potentially eliminate contact hazards altogether since the liquid agent would not adhere to the clothing in the first place.

RESULTS AND DISCUSSION
Previous work at Dstl showed that textiles constructed from “hairy” fibres displayed exceptionally high levels of liquid repellency, not just to water ($\gamma$=72 mJm⁻²), but also very low surface energy liquids such as hexane ($\gamma$=18 mJm⁻²) [4]. Similarly, previous research reported by Seeger et al [3] describes growing sub-micron diameter hairs (or filaments) onto textile fibres to produce superhydrophobic materials. The filaments, which consist of cross-linked poly(methyl silicone), are produced by exposing the textile to trichloromethylsilane vapour under controlled levels of humidity. Importantly for practical applications, these hierarchical textile structures are reported to display good durability to mechanical abrasion [5].

The plasma-modified material was found to be extremely hydrophobic, to the extent that no appropriate images could be recorded. For example, water droplets failed to detach themselves from syringe needles when brought into contact with the superhydrophobic textile, whereas attempts to drop small droplets of water onto the material resulted in the near-perfect spheres of water rapidly rolling off. Contact angle hysteresis for water was therefore very low.

The material was also highly repellent to isopropyl alcohol and heptane (often used as test liquids to probe repellency) although the contact angles (approximately 140° for both isopropyl alcohol and heptane) are less than 150°, indicating that this material is not formally superoleophobic according to definition. Nevertheless,
isopropyl alcohol detached with difficulty from the syringe needle when brought into contact with the material and a 20µl droplet displayed a roll off contact angle of approximately 30° when tilted by hand. Heptane droplets were somewhat easier to detach than isopropyl alcohol and displayed a roll off angle of approximately 60° for a 20µl droplet. The material was even shown to be repellent towards hexane which displayed an unstable contact angle of approximately 120°, although the droplets displayed surface wetting and did not readily roll off the fabric, even when tilted at 90°.

FIGURE 2 a) Isopropyl alcohol droplet on treated fabric, b) heptane droplet on treated fabric
Images of the fabric with droplets of isopropyl alcohol and heptane are shown in Figure 2 a and b respectively. It was observed that both the isopropyl alcohol and heptane droplets evaporate symmetrically, in agreement with the observed self-cleaning behaviour.

FIGURE 3 a) HD droplet on treated fabric, b) VX droplet on treated fabric
The material displayed very high levels of repellency towards HD and VX (Figure 3a and b respectively). Both liquids sat as bright, spherical droplets on the material and displayed a roll off angle of approximately 20° (for 20µl droplets).

FIGURE 4 a) GB droplet wetting into fabric, b) GD droplet wetting into fabric
In contrast to HD and VX, the lower surface energy liquid agents GB and GD displayed poor repellency. Both liquids slowly wet the material, GD wetting faster than GB (Figure 4). Results from different samples of GB and GD gave similar results.

CONCLUSION
Structural and chemical modification of a woven textile has produced experimental materials displaying self-cleaning to IPA and heptane, as well as the CW agents HD and VX. Despite these materials displaying very high oil- and water-repellency ratings to test liquids, they displayed limited or no repellency to GB and GD.

The complex wetting behaviour displayed by these materials is not readily understood; textile structure, the polar and dispersive components of the surface energies, the surface chemistry of certain dyestuffs and possibly the visco-elastic properties of the liquids may all play a role.

FURTHER WORK
It is strongly recommended that confirmation of a fabric’s repellency to chemical warfare agents be carried out using the actual agents themselves. In addition it is intended to investigate the chemical and physical properties of major CW agents including their polar / non-polar contributions to surface energy and visco-elastic properties. The wetting behaviour of liquids on textiles should also be studied in terms of metastability and intermolecular interactions.

REFERENCES

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Moisture Transport and Reaction Enhancements in Fabrics

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The role of water in protective fabrics is critical to comfort and material performance. Excessive perspiration in clothing causes discomfort, and bound water can adversely affect the ability of carbon to adsorb chemicals. Yet the presence of water can also improve the moisture vapor transport of protective polymer films, and is essential for the hydrolytic destruction of nerve agents. Reported here are the findings of wicking and drying experiments conducted on various hydrophilic and hydrophobic cover fabrics that demonstrate the influence of wetting on permeation through fabrics. The influence of water content on reactive polymers capable of degrading nerve agent simulant is also discussed, and the importance of a novel “delivery system” for water to the reactive components through the use of a wicking fabric is introduced.

Novel drying experiments were developed to measure drying time by means of vapor flux from spreading liquids in a modified permeation test cell (Figure 1).

Fabric surface temperature was also monitored during the wicking and drying process as another indicator of drying time, since the evaporation of the liquid causes a drop in surface temperature (Figure 2).

FIGURE 1. Test cell modified to accommodate an infrared thermocouple viewing fabric surface in the cell.

FIGURE 2. Simultaneous vapor flux and temperature drop measurements for a fully-wicking layer, and a reactive polymer laminate that includes a wicking fabric layer on the inner surface.

FIGURE 3. Water on inner and outer surfaces of fabrics for drying experiments. (a) Single layer fabric with hydrophilic treatment on inner surface, and hydrophobic on outer surface (b) Standard carbon inner liner and outer shell fabric.

FIGURE 4. Typical drying behavior of fabrics with various wicking treatments on the inner and outer surfaces of a single layer of fabric [1].
These measurements demonstrated that rate of liquid wicking was conveniently reflected in a measurable cooling effect on the fabric surface due to water evaporation. Results from vapor transport testing with wetting/non-wetting fabrics show that there are very large differences in drying time that can impact the rate at which the evaporating sweat from the body is transported through the fabric to the environment.

Outer shell fabrics have been modified with reactive compounds that are designed to hydrolytically decompose chemicals that are analogues for nerve agents. One such compound is the polymeric supernucleophilic pyridine catalyst called poly(butadiene-co-pyrrolidinopyridine) (polyBPP) [2,3], which has been coated onto the fabric and function to completely degrade the nerve agent surrogate diisopropyl fluorophosphate (DFP).

FIGURE 5. Poly(butadiene-co-pyrrolidinopyridine).

The water content and nature of the water wicking interaction on the degradation kinetics of DFP revealed that there must be a sufficient amount of water and complete contact between the DFP, water and catalyst for rapid and complete destruction of the surrogate. Delivery of the liquid water from the interior of the protective fabric to the exterior regions containing the reactive compounds is an important process that has been designed into a layered fabric system comprised of a wicking comfort layer next to the skin, bonded to a polymer membrane capable of degrading DFP, and covered with a protective outer shell fabric that can be modified with polyBPP. Previous work on water interactions with chemical protective polymer membranes has shown that water content of the polymer layer is importance for permeation of water and chemical agent simulants [4-6]. Of particular interest is the increase in efficiency that the wicking comfort layer might contribute to the hydrolytic degradation of DFP within the reactive membrane. This effect of water interactions with reactive compounds within layered fabric systems will be discussed.

REFERENCES


Acknowledgement

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INTRODUCTION
Recently, novel properties have been observed when superhydrophobic and superhydrophilic surfaces are combined. For example, the Stenocara beetle, an insect in the Namib Desert, has an incredible ability to capture fresh water from air for its survival in the dry desert environment [1]. Such a feature derives from its special wing that has a hydrophilic-patterned superhydrophobic surface. Materials having a similar surface feature also exhibited a similar water-harvesting function [2]. A spider silk has been reported to show a periodic alternation of hydrophobic and hydrophilic surfaces along the fiber-length direction [3], which can quickly collect water from air. It was also observed that water droplets moved in one direction along a superhydrophobic-to-superhydrophilic gradient surface [4]. However, all these works are based on two dimension surfaces. The work on water transfer through porous media induced by a gradient wettability change has received little attention until very recently [5].

In this study, we have developed a simple, but very effective and versatile, method to produce wettability gradient across the thickness of fabrics, and demonstrated that the fabrics have the ability to spontaneously transfer water unidirectionally through the fibrous architecture. A plain weave polyester fabric was mainly used as a sample material.

APPROACH
The coating solution was prepared by hydrolysis of titanium tetraisopropoxide with two silanes, tridecafluorooctyl triethoxysilane (FAS) and 3-trimethoxysilylpropane thiol-1 (TMSPT). The coating solution was applied to the fabric through a dip-coating process. To achieve the directional water transfer effect, one side of the coated fabric was exposed to a multi-wavelength ultra-violet (UV) beam.

RESULTS AND DISCUSSION
As illustrated in Figure 1, the coated fabric became superhydrophobic. Water drop on the coated fabric formed a spherical droplet that could stay on the fabric for a long time (Fig 1a). The water contact angle measurement revealed that the contact angle of the treated fabric was as high as 170 °. In comparison, water drop on the un-coated pristine polyester fabric only stayed for a few seconds before spreading into the fibrous matrix (Figure 1b), although the fabric itself was hydrophobic with a water contact angle of 117 °.

When the coated fabric was irradiated with UV light just from one side at 60 °C for 2 hours, the irradiated surface changed its wettability significantly. Figure 2 shows the process of dropping water on the treated fabric. On the UV irradiated fabric surface, water just spread rapidly along the fabric, but not moved to the opposite surface (Figure 2a). The contact angle measurement indicated that the directly irradiated surface changed the water contact angle from 170 ° to 39 °. Similar results were observed by repeatedly dropping water droplets onto the UV-irradiated side of the coated fabric.

When water was dropped onto the back side of the fabric, which was not directly irradiated by UV light, the water drop moved immediately across the fabric thickness and spread on the UV irradiated front side, although a large contact angle was maintained between the droplet and the fabric (Figure 2b). Repeatedly dropping water on the fabric led to the same result. These results clearly reveal that the UV treatment renders the fabric with a directional water-transfer effect. Because of this water transfer effect, directly measuring the water contact angle of the opposite fabric surface was difficult. Instead, an indirect method in which two layers of the same treated fabric were closely pressed together and irradiated by UV light under the same condition was used. In this case, the water contact angle for the front side of the second fabric layer should
be very close to that on the back side of the first one, which changed only from 170 ° to 156 ° (Figure 3) after the UV treatment. This result indicates that the UV treatment has very little influence on the back side of the irradiated fabric and the back surface still maintained its superhydrophobic feature.

Figure 3 also shows the breakthrough pressure of the fabrics, which can be used to understand water transport across the fabric. For the uncoated pristine polyester fabric, only 2 cmH2O of pressure was formed when water started to pass through the fabric, and there was no difference between the two fabric sides. For the coated fabric, the breakthrough pressure increased to 35 cmH2O, and side difference was not observed either. However, for the UV-treated fabric, the breakthrough pressure was side dependent. On the UV-irradiated surface, a breakthrough pressure of 25 cmH2O was measured, which is slightly lower than the coated fabric without any UV treatment. The breakthrough water pressure on the back side of the UV irradiated surface was only 4 cmH2O, which is similar to the pristine fabric. The different breakthrough pressures between the two fabric sides could be another indication of the directional water-transfer effect. The changes in wettability and breakthrough pressure due to the UV irradiation did not happen for the uncoated pristine polyester fabric.

FIGURE 3. Water contact angles and breakthrough pressures on the fabrics

The chemical functionalities of the treated surface were examined by X-ray photoelectron spectroscopy. It was found that -COOH and -SO3H groups were formed on the irradiated fabric surface, and the formation of the water absorptive groups was the main reason for the surface to become hydrophilic after the irradiation treatment. Because of the intensity dependence, the photo oxidation reaction on the fabric surface that received the strongest UV light had the highest reaction yield, rendering the surface with the largest decrease in the water contact angle, while the light intensity decayed along the fabric thickness, leading to gradually reduced photo oxidation reaction. As a result, a gradient change from hydrophilicity to hydrophobicity across the fabric was created.

The UV treatment time affected the wettability and breakthrough pressure. A longer UV irradiation period led to lower contact angles and reduced breakthrough pressure on both the fabric sides. The changes of the wettability also resulted in difference in water-transfer effects. When the UV treatment was longer than 2 hours, water was able to transfer from both fabric sides, despite the difference in the breakthrough pressure. When the treatment time was shorter, e.g. less than 30 minutes, the directional water transfer became very slow, taking about a few seconds to allow a droplet to transfer through.

Apart from the polyester fabric, other fabrics from wool and cotton, paper, carbon fiber nonwoven membrane and thin porous foam were also studied.

CONCLUSIONS
We have demonstrated that a wettability gradient from superhydrophobicity to hydrophilicity can enable the fabrics to have a directional water-transport function: water can easily transfer across the fabric from the superhydrophobic side to the hydrophilic one, but not in the opposite direction unless a sufficient external force is applied. The directional water-transfer fabrics also showed an apparent difference in the critical pressure allowing water to break through from the two fabric sides. The directional water transfer fabrics may find applications in various areas especially for those that involve fluid transport in both daily life and industry.

ACKNOWLEDGMENT
Funding support from the Australian Research Council through a discovery project, the Defence Science & Technology Organisation and Deakin University under the Central Research Grant Scheme is acknowledged.

REFERENCES
Generation of Short Hypersonic Water Jet for Testing of a Material’s Rain Erosion Resistivity

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Composite materials have become core materials for many applications in the aerospace industry. In many cases, one of the key issues defining the application of a material is its resistivity for rain erosion. Rain erosion has been a concern of the aviation and missile industries for many decades. Rain erosion resistance is an extremely important parameter of the materials interaction with the flight environment, since bodies moving at high speeds through a rain-field can experience severe damage caused by the impingement of raindrops on their surfaces.

Even though rain erosion has been investigated in the laboratories the past 60 years, due to continues increase of the speeds of interest and growing demand in mass experiments, there is a big interest in creating cheap laboratory methods for rain erosion modeling.

We present here a cheap method of generating short water jets (droplets) moving with speed of 1000-1500 m/s with perspective to increase it up to several km/s.

The current device represents deeply modified Split Hopkinson Pressure Bar using the acoustic wave time management.

On the Figure 2 the effect of the hit of short water jet moving with speed 1100 m/sec on the fiber composite cone.

Figure 2. Water impact on the glass-fiber based composite cone. Speed of droplet-jet 1100 m/s.

Physical background of creation fast moving water jets with the help of wave management is discussed.

On the Figure 1 the impact of the high-speed jet on the fiber-base sample is presented.

Figure 1. The High speed video captures of the jet hit the fiber –based composite sample with speed 700 m/s.
Biomimetics for Fiber Science
Artificial Proboscises

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STATEMENT OF OBJECTIVE
This talk reviews recent results on fabrication of artificial proboscises for probing and analyses of liquids available in a form of tiny droplets or trapped in single cells or pores.

INTRODUCTION
Almost 160,000 species of butterflies and moths have a coilable proboscis hypothesized to have evolved once. The food canal of the proboscis is formed from two semi-cylindrical halves, the maxillary galeae, that are linked together at their borders by cuticular linkage devices. Butterflies and moths not only imbibe floral nectar but also feed from rotten fruits and wet soil, suggesting that the suction pressure they produce is sufficiently high. The proboscis can be considered as a flexible microfluidic device with extraordinary ability to probe, deliver, and sense different fluids. The proboscis evolution, organization and functionality are poorly understood, though its design is attractive for making artificial probes for single cell analyses. In this talk we will discuss recent results on the mechanisms of fluid absorption by butterflies. Using these results, we will show a range of possible designs of nanofiber-based probes.

RESULTS AND DISCUSSION
Using X-ray phase contrast imaging we were able to observe the process of fluid imbibitions into the food canal of a butterfly: the discovered mechanism drastically differs from the conventional. The proposed mechanism heavily relies on different pore sizes found in the proboscis. The problem of spanning the scales also arises when we study the liquid penetration into bioinspired probes made of nanofibers. All these problems constitute a new challenge for flow analysis when one needs to bring nanofeatures in order to describe the flow at the microscale. Figure 1 illustrates the complexity of natural proboscis and explains the strategy of making artificial cousins.

We developed a technique to fabricate artificial proboscises from different polymers. PVDF/PEO fibers have been electrospun into ordered bands and subsequently twisted into yarns. By controlling the electrospinning time and revolution rate of the proposed twisting device, we formed the bio-mimetic proboscis probes with repeatable transport and mechanical properties. Varying the chemical composition of polymer blends and environmental conditions for electrospinning, porosities as high as 82% were achieved for single fibers.

Depending on the application, the probe can be made ferroelectric or magnetic. Further, we showed that owing to the ferroelectric and magnetic properties of the probes produced in this work, these probes can function as artificial proboscises and can be manipulated remotely to absorb droplets. Figure 1 shows an example of such action when a ferroelectric probe is deployed by an external electric field. As the tip of the nanofiber probe approaches the droplet, it absorbs it. The chemical composition of this drop can be further analyzed using different techniques. We will show an example of such an analysis based on fluorescence microscopy and PCR assay.

ACKNOWLEDGMENT
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Botanical Hygroscopic Shape Change Mechanisms for Composite Textile Systems

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Smart materials and structures use a variety of stimuli (temperature, electrical current, pH, etc) to trigger shape or property changes; environmental moisture is a less explored stimulus yet very important factor in the performance of textile structures. Moisture-induced shape change in textile structures is mainly regarded as a negative effect especially in clothing applications where it reduces air permeability of the structure and causes discomfort. Hygroscopic shape change mechanisms are vital to many plants for the dispersal of seeds and spores. These structures detect specific moisture levels in the environment that signal optimal conditions for seed or spore dispersal. The mechanisms are based on simple bilayer systems; this paper reviews a range of botanical hygroscopic mechanisms and creates models simulating this behavior that could be implemented in fibre or textile structures.

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SUMMARY

Fire ants (*Solenopsis invicta*) have the unique ability to survive floods by linking their bodies to build rafts. They are thus a natural example of a self-assembling and self-healing water-repellent material. We present recent efforts to measure the geometry and water-repellency of their network. We flash-freeze ant rafts using liquid nitrogen and visualize their spacing using micro CT scans. Based on 3-D images, we observe the characteristic size of the voids between ants is 0.8 mm because of their inter-weaving of appendages, which is half of our previous estimations based on the distances between ant bodies. This results in even larger submersion depths before water penetrates the weave than previously thought. We also present a review of our previously published mathematical model describing the dynamics of raft formation.

INTRODUCTION

Swarms, flocks and schools are studied for their complex group patterns and behaviors that emerge from the repeated simplistic movements of individuals. Simplifying the chaotic dynamics of groups into predictive mathematical relations has many applications, including models of human crowds and the design of modular robotics [1]. Swarms of ants also have attractive physical properties such as astounding levels of water-repellency that may also yield new insight into the design of porous water-repellent textiles.

A study by Anderson on insect self-assemblages outlines several different insect species that aggregate forming “functional group-level adaptive structures” such as bivouacs, bridges, droplets, festoons, flanges, ladders, ovens, pulling chains, rafts, tunnels, and walls [2]. Fire ants in particular are known to have a natural tendency to stick together in cohesive clumps when disturbed (Fig 1a). Their adhesion is accomplished through the use of adhesive pads and claws at the ends of their legs as shown in an extensive series of studies by Federle [3].

Currently there are very few studies on water repellency of these insect aggregations. One study on honeybee self-assemblages by Cully shows how aggregated honeybees will orient themselves so that their wings are arranged like tiles on a roof to shed water during rainy or humid conditions [4].

In a previous study on ant rafts, we find fire ants have special adaptations for flotation, despite the ants being denser than water. Specifically, the highly textured surfaces of their exoskeleton (Fig 1b-d) allows them to effectively trap air pockets and repel water [5] in a manner similar to that of a super-hydrophobic lotus plant. A study on the mechanisms of lotus leaf hydrophobicity suggests that such surfaces could be used for underwater retention of air bubbles or films [6]. Both of these mechanisms are examples of the Cassie-Baxter Law at work. The Cassie Baxter Law, provides an equivalent contact angle, $\theta^*$ for roughened surfaces characterized by solid islands surrounded by pockets of air: $\cos \theta^* = \phi \left( \cos \theta_{\text{exo}} + 1 \right) - 1$, where $\phi$ is the area fraction of ant hair/air contact with water and $\theta_{\text{exo}}$ is the contact angle of water with the ant exoskeleton [7].

Our current work investigates the internal structure of the ant raft with the aim of better understanding the raft’s water-repellent limits.

![Figure 1](image)

(a) floating raft of 1,000 ants. (b) linkage between several ants’ tarsi. (c) ant tarsus deflecting the water surface. (d) SEM image of the numerous hairs at the tarsal tip.

APPROACH

Since the network of clumped ants is opaque and in constant motion, simple observation of a live clump of ants reveals little about its packing properties. In order to visualize the internal connections, we used liquid nitrogen to freeze clusters of ants instantaneously thereby preserving their arrangement. To measure planar packing density we used this technique on a rafting group of ants, freezing the ants and the water. Next, all of the ants were removed from the raft except for the ones in direct contact with the water (Figure 2a), allowing us to visually measure a planar inter-ant distance.
Figure 2. (a) Networking among a single layer of frozen ants. (b) Inter-raft connections visualized by 3-D micro-CT scan.

Although this approach was useful for visualizing the layer of ants offering support for the rafting colony, to visualize the 3-D network within the clump, we used CT x-ray scanning to assemble cross-sectional images of the ant network to yield a 3-D visualization. Ants were rolled into a ball using a beaker and liquid nitrogen again was used to preserve their structure. Hairspray was further used to fix the ants during the hour-long scan. Examination of slices of the scan using Matlab allowed us to better estimate the connections of ants in 3-D.

RESULTS

Using Fig. 2a, we measured the average planar density to be 34 ants/cm² based on images from four different rafts. The average spacing between ants was calculated from distance calculations between the center of each ant’s gastor to that of its nearest neighbors. Average nearest neighbor distance was 2±0.4mm.

Figure 2b shows our 3-D visualization of the raft using a CT x-ray scan. Although the internal structure is obscured from view in this image, quantitative data about the structure was measured using other views. The voids in a representative section of the interior of the ball were less than 300 μm in characteristic size. Based on the small ant cluster scanned, the volume fraction was 16%. Since the density of ants is a little greater than water, the watertight ant structures prove to be extremely buoyant.

Inside the raft, we examined in detail three ants surrounded by their neighbors. We find the ants are strikingly well connected, having 2±0.4 links with each of 7±2 neighboring ants (N=3), forming a very strong network. Even though this seems like a geometrically impossible number of connections, keep in mind the ants’ legs can cross to fill in spaces and the ants have a high aspect ratio and are non-convex. The strength associated with the large number of connections represents a factor of safety in maintaining the structural integrity of the raft. We also observe the connections are mainly appendage-to-body, suggesting the tarsal pads are the primary means by which inter-ant adhesion is created.

Using our CT and SEM images, we determine three characteristic length scales that determine the wetting properties of rafts: the spacing, δ between ant bodies ~2.5mm, linked tarsi ~0.8mm, and individual hairs ~10μm (as shown in Fig 1). Applying Jurin’s Law of capillary rise, ΔP=2σ cosθ*/δ yields estimations of the pressures, ΔP and depths, z necessary for water to penetrate the raft for each δ [7].

<table>
<thead>
<tr>
<th></th>
<th>δ (mm)</th>
<th>ΔP (Pa)</th>
<th>z (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>body</td>
<td>2.5</td>
<td>19</td>
<td>0.19</td>
</tr>
<tr>
<td>tarsi</td>
<td>0.8</td>
<td>60</td>
<td>0.61</td>
</tr>
<tr>
<td>hairs</td>
<td>0.01</td>
<td>4,788</td>
<td>48</td>
</tr>
</tbody>
</table>

The predicted values for z are substantially smaller than those found experimentally where bubbles were released in the range of 3-20cm. For these values the ants would need to be much more densely packed.

DISCUSSION

Our methods were of insufficient resolution to distinguish legs from antennae, and thus we are likely over-counting the number of connections between ants. We were also unable to distinguish the heads of the ants from the gastors, which would potentially be useful in determining whether the network is isotropic.

The discrepancy between our theoretical and experimental submersion depths might be due to two factors that we did not consider in our study. First, we have observed ants actively constricting the raft by pulling on their neighbors when submerged. Since the CT scan was performed on an unsubmerged ant clump, we may have under-estimated the packing density. Second, we based our measurements on ants inside the clump; ants on the outside surface of the clump have fewer neighbors and thus potentially more legs with which to prevent water from penetrating the raft.

ACKNOWLEDGEMENTS

[2] This research was funded in part through a grant by NSF.

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ABSTRACT
To further our knowledge on structure function relationships in spider silk proteins, several chimeric spider silk proteins with basic repeat sequences mixing different ratios of one of the two different Flagelliform silk like elastic motifs ([GPGGX GPGGX]n with X=A/A or Y/S) and the dragline silk crystalline forming/strength motif ([GPSGPGS(A) 8) from Masp2] were engineered. All of these chimeric silk proteins were produced recombinantly in E. coli bacteria and used to generate fibers that were subjected to post spinning modifications using alcohols and water to improve their mechanical properties. For each synthetic fiber type and at each step of the processing, structural (NMR, XRD, Raman Spectroscopy, morphological (SEM) and mechanical data were collected. In all cases, we find that water treatment was overall beneficial and had a plasticization effect on the silk fibers.

INTRODUCTION
Dragline and flagelliform silks are unusually tough natural fibers because they combine high strength and extensibility [1-3]. These mechanical properties, unmatched by any man-made fibers, originate from the primary sequences of the silk proteins making up these fibers [3-4]. Understanding basic structure function relationships in silk proteins is necessary to be able to engineer high performance protein-based materials matching the mechanical properties of these silks. In this paper we investigate the behavior of designer chimeric recombinant silk proteins, their abilities to generate fibers, and the mechanical performances of these fibers before and after post fiber formation processing. Structural analyses reveal the nature of the molecular changes and fiber internal organization that can be directly related to the mechanical performances measured for these different fibers at each processing step.

METHODS
Chimeric silk proteins: The purified recombinant His-tagged chimeric silk proteins were used to generate fibers either from spontaneously self-assembled silk protein films in aqueous environments or by extrusion using organic solvents as described in [5].

Post spinning modifications: All synthetic fibers were subjected to multi step post-spin drawing while immersed in alcohols (isopropyl alcohol or methanol)/water mixes and/or water.

Structural analyses: NMR, XRD, Raman Spectroscopy were performed on the lyophilized proteins and generated synthetic fibers at each step of the processing.

Morphological analyses: SEM analyses of each fiber type at the different steps of the processing were also collected.

Mechanical analyses: All spun fibers were tested using a 10 g load cell (Transducer Techniques; Temecula, CA) mounted on a MTS Synergie 100 system (MTS Systems Corporation; Eden Prairie, MN). The mechanical data were recorded at ambient temperature and relative humidity (20-22°C/18-20%) using a strain rate of 5 mm/min and a frequency of 250 MHz. These data allowed for the successive calculation of the engineered stresses and strains. Stress/strain curves for each fiber were plotted.

RESULTS AND DISCUSSION
Protein spinnability: Fiber formation ability depends highly on both the primary structure of a given silk protein and the method of fiber formation used (aqueous versus organic).

Fiber morphologies: SEM data reveal morphology differences between synthetic silk fibers generated by the two different methods used (extrusion/organic vs formation from self-assembled protein films/aqueous).

Fiber processing: Post spin drawing techniques need to be adjusted depending on the fiber type i.e. the primary structure of the chimeric silk protein used to generate the fiber. Single-step post-spinning treatments with drawing after alcohol treatment (isopropanol or methanol), or double-step post-spinning treatments with initial drawing
after alcohol treatment and additional drawing after water treatment were investigated. Single-step fiber processing using methanol increased the brittleness of the fibers. Double-step fiber processing using isopropanol and water improved drastically all critical mechanical parameters (tensile strength, extensibility and toughness). Structural analyses revealed the presence of β-sheets in the water insoluble fibers.

CONCLUSIONS
Different post spin draw applied to the different protein fiber types had various results depending on the primary structure of the synthetic silk protein. All different processing sequences worked out for each particular protein fiber rendered the fiber water insoluble due to the formation of β-sheet structures in the polyalanine regions. For extruded fibers, the initial post spin stretches in isopropanol was usually beneficial to increase tensile strength depending on the protein fiber type. However, successive water treatment was crucial to increase their extensibility thus toughnesses. The best mechanical data for extruded fibers were obtained after processing using the double step IPA/water treatment. This type of processing generated fibers averaging toughness values less than 3 times than those recorded for native dragline silk.

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REFERENCES
Biopolymer-assembled Nanofibers

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Natural polymers such as polysaccharides, proteins and polyphenolics are among the most abundant renewable resources. They are integral parts of cells, contributing toward the structure and functions of living organisms. In their native structures or minimally processed forms, many have been used as food, feed, fibers and materials. When isolated, these biopolymers become valuable platforms for advanced materials, provided they can be processed.

Cellulose, the major polysaccharide in plants and the nature's most abundant polymer, is unique in that it has the highest structure regularity, both chemically and structurally. Cellulose is a homopolymer, unlike other biopolymers including other polysaccharides (chitin, starch, alginate, etc), proteins and polyphenolics. It's β-1,4-D(+)-glucopyranose building blocks in long chain length and extensively inter- and intra-molecular hydrogen bond structure contributes to the highly rigid and crystalline characteristics, irrespective of its sources and has the potential to become the major renewable sources for a great variety of chemical feedstock and materials, including engineered nano-materials.

Chitin contains the same β-1,4-D(+)-glucopyranose backbone as cellulose, except for the C-2 acetyl amine pendant groups, when deacetylated to varying degrees becomes chitosan, a heteropolymer. Proteins consist of amino acids of various types and proportions, thus are heterogeneous along the chain lengths as well. As all these biopolymers are non-thermoplastic, the major challenge is to render them either soluble into stable solutions or derivatized to thermoplastics for processing into products.

This paper presents the approaches we have developed and are working on to prepare nanofibers and nanofibrous structures from biopolymers including cellulose, chitin, chitosan, proteins and polyphenolics.

Chemical reactivity of the primary (C6) and secondary (C2, C3) hydroxyl groups in cellulose and the C3 and C6 hydroxyls and C2 acetal amine groups of chitin (see reaction and NMR) offer opportunities for chemical modification to impart significant improvement in solubility and thermal behavior, thus enhanced processibility, to afford efficient electrospinning from various aqueous and organic solutions. The chemical and structural potential of these biopolymers has been exploited by coupling chemistry and polymer physics principles in electrospinning to reduce fiber sizes to nanometer ranges, to create novel morphology, and to alter surface chemistry. Examples include hybrid and multi-component fibers of sheath-core, nanoporous structure and multiple stimuli-responsive hydrogel and enzyme bound fibers.

Fiber surface modifications with chemical reactions, ligand binding and electrostatic layer-by-layer (LBL) self-assembly (see diagram on right) can also provide effective means to create new surface chemistry without altering the surface topography of fibers. The surface bound molecules included polysaccharides and proteins, generating the first reported new nanofibrous materials completely based on nature polymers.
In addition, cellulose nanocrystals (CNCs) prepared from different biomass are ultra-high modulus and low thermal coefficient nanomaterials that can be incorporated into nanofibers to create new chemical functionality and nano-structured fibrous materials. Cellulose nanocrystals are 10-50 nm in diameters and 200-400 nm in lengths (TEM below) have been prepared by acid hydrolysis and freeze-drying. These cellulose nanocrystals have highly β crystalline structure with sharper (200) crystal lattice (2θ=22.6°) and (110) planes (2θ=14.7°) and much smaller mesopores (average diameter=91.99 ± 2.57 Å) than the micropores (214.64 ± 7.23 Å) in the original cellulose. The BET surface area of these cellulose nanocrystals is 13.362 m²/g, ~10 times of the original. The super high specific surface and hydroxyl functionality were utilized to significantly improve the strength of electrospun membranes (stress-strain behaviors of CNCs filled fibers below).

Recent and on-going work on incorporating enzymes and proteins derived from plants and animals as integral part of fibers will be presented as well. These new nanofibrous membranes have potential applications in areas such as catalysis, super-hydrophobic surfaces, dye-sensitized solar cells, separation, super-hydrophobic surfaces, sensors, drug-delivery and medical diagnosis, etc.

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Biochemical Characterization of Spidroin Self-assembly

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ABSTRACT

Spiders produce a variety of high performance structural fibers that are among the strongest and most flexible biomaterials in the world [1]. Native spider silks have mechanical properties that are unparalleled in the environment and comparable to the best synthetic fibers produced by modern technology. Because of the superior intrinsic properties of spider silks, there is considerable interest in the production of protein-based, spider silk-inspired polymers for a wide range of applications. However, the unique features of protein-based spider silks remain largely unexplored because domestication of spiders for large-scale protein production is hampered due to their territorial and cannibalistic nature.

Perhaps even more impressive than the mechanical qualities of silks is the spinning process in which the spider silk proteins (spidroins) are assembled from a highly soluble storage state into a well ordered and insoluble fiber. Indeed, the ordered arrangement of spidroins, which is endowed by the spinning process, is a key determinant of fiber strength [2]. Spider silks are spun from concentrated solutions of spidroin proteins. The appropriate timing of spidroin assembly into organized fibers must be highly regulated to avoid premature fiber formation. Chemical and physical signals presented to the silk proteins as they pass from the ampulle and through the tapered duct include changes in ionic environment and pH as well as the introduction of shear forces. However, the molecular mechanisms through which spidroins respond those signals by establishing specific protein-protein interactions remain poorly understood.

Spider dragline silk consists almost exclusively of two large proteins (major ampullate spidroins, MaSp1 and MaSp2) that contain short non-repetitive N- and C-terminal domains (NTD and CTD, respectively) flanking a large, highly repetitive central domain. We have shown that the N-terminal domain of spidroins from the major ampullate gland (MaSp-NTDs) for both Nephila and Latrodectus spiders associate noncovalently as homodimers [3]. The MaSp-NTDs are highly pH-responsive and undergo a structural transition in the physiological pH range of the spider duct. Tryptophan fluorescence and NMR spectroscopy of the MaSp-NTDs reveals a change in conformation when pH is decreased, and the pH at which the transition occurs is determined by the amount and type of salt present. Pull-down assays both indicate that the lower pH conformation is associated with a significantly increased MaSp-NTD homodimer stability. By transducing the duct pH signal into specific protein-protein interactions, this conserved spidroin domain likely contributes significantly to the silk-spinning process.

Site-directed mutagenesis has allowed the production of altered MaSp-NTDs that display marked differences in pH-responsiveness. These are currently being studied by NMR to identify any structural changes and by pull-down assays to evaluate the ability and strength of homodimerization.

REFERENCES

Polymer Synthesis and Recycling
Removal of Spandex from Polyamide/Spandex-blended Fabrics by Selective Depolymerization

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INTRODUCTION
The use of spandex fibers has been increasing steadily in recent years, currently at close to 400,000 tons per year. Since spandex is most often blended with other fibers to make textile products, the amount of post-consumer and post industrial waste of spandex blended fabrics is very large. In polyamide (PA) /spandex blended fabrics, PA forms the major part of the blended fabrics. As a valuable polymer, PA waste can be effectively recycled into virgin quality polymer via depolymerization, purification and repolymerization. However, without separating the polymers, the PA 6/spandex blended fabrics cannot readily be recycled into useful products. Therefore it is important that the spandex in the blended fabric waste be removed so that PA can be recycled.

APPROACH
Spandex is a polyurethane-polyurea-polyether block copolymer. All the polymer segments present in the PA/spandex blended fabric, i.e. polyurethane, polyurea, polyether, and polyamide, can be depolymerized by hydrolysis, but the processing conditions for each polymer may be different. In this study, we attempt to find some conditions such that any spandex segments may be depolymerized while polyamide is not significantly degraded.

Because of temperature and pressure required, we have constructed several high-pressure reactors for the experimental study. Figure 1 shows a schematic and a photograph of the device.

RESULTS AND DISCUSSION
The processing variables investigated include temperature (160-220°C), time (1-4 hours), catalysts (water only, KOH solution, weak acid solution), among others. Table 1 summarizes some of the observations after the tests.

Fiber and fabric samples after processing are also analyzed by optical microscopy and characterized by attenuated total reflectance (ATR) spectroscopy.

Figure 2 shows ATR spectra for spandex fibers after treatment in water at 180°C for 4 hours, and polyamide/spandex blended fabrics at 180°C for 1, 2 and 4 hours. For the spandex fibers only, both diphenyl ether and amide groups are reduced due to depolymerization.
PA fibers are not affected by treatment up to 180°C for 4 hours, but some degradation may have occurred when treated at 200°C for 4 hours (chart not shown). For the PA6/Spandex fabric treated in water at 180°C for 1-4 hours, the spandex content appears to be reduced as the treatment time increases.

Depolymerization residues are removed by washing with different chemical solutions, including hot water, dimethylformamide, acetone, and ethanol.

**CONCLUSIONS**
Removing spandex from polyamide/spandex blended fabrics allows PA 6 to be recycled using existing technologies. This study shows that spandex removal via selective depolymerization is a promising route for recycling polyamide/spandex blended fabrics.

**ACKNOWLEDGMENT**
The authors wish to thank Aquafil USA for their support of this research effort.

**TABLE I. Test conditions and observations**

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Temp.</th>
<th>Time</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>180°C</td>
<td>2h</td>
<td>No change in appearance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4h</td>
<td>No change in appearance</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>2h</td>
<td>Slightly melted, into solid pieces</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4h</td>
<td>Melted into solid: hard &amp; brittle</td>
</tr>
<tr>
<td>Spandex</td>
<td>180°C</td>
<td>2h</td>
<td>Fiber disappeared; pasty soft</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4h</td>
<td>Fiber disappeared; pasty soft</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>2h</td>
<td>Fiber disappeared; pasty soft</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4h</td>
<td>Fiber disappeared; waxy soft</td>
</tr>
<tr>
<td>Fabric</td>
<td>180°C</td>
<td>1h</td>
<td>No change in appearance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2h</td>
<td>Melted into solid: a few holes, hard</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4h</td>
<td>Melted into solid: a few holes, hard</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>1h</td>
<td>Fiber disappeared; Porous, hard</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2h</td>
<td>Fiber disappeared; Porous, hard</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4h</td>
<td>Fiber disappeared; Porous, hard</td>
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OBJECTIVE
The current version of synthetic turf sports fields (STF) utilizes rubber filler that fits between the grass-like tufts and provides cushioning, hence the term “infill”. Even though infill is beneficial to athletic performance and impact safety, a host of issues creates the need for new material that keeps the ideal qualities of rubber while negating its negative aspects. In this project, the most important factor is the low cost of rubber that is due to its reclamation from discarded automotive tires. Therefore different types of discarded material from more benign products were tested in comparison to rubber to find a viable replacement.

INTRODUCTION
For the past decade, STF experienced an explosion in athletic and landscape uses especially in American football at municipal, academic and professional levels. The original Astroturf® fields provided durable, safe surface for indoor and urban areas by design in the 1960’s [1]. However, AstroTurf® was a simple outdoor carpet with a rubber underlying matt, which players complained was harder and less playable than natural turf. Other versions tried new materials and designs in STF to be more appealing. However, the second generation used sand infill to increase turf endurance and ballast against water, but did not address the athlete’s safety complaints [2]. As a result, STF remained a niche product until the 1990’s when a radical design that simulated natural turf like Figure 1 was commercialized.

Figure 1: U.S. Patent 6,723,412 B2 [2]

The tufts were longer and fibrillated like natural grass; the spacing was increased between the rows to allow more infill; and the infill was replaced with granulated crumb rubber infill (GCRI) that mimicked loose soil. This third-generation (3G) of STF was designated as FieldTurfSM after an STF company, and it looked more like natural turf. Replacing the rubber underlay with cushioning infill most probably lead to the resurgence of STF, which had only 7 new generation fields by the end of the 1990’s grow to 3500 fields by 2008 in the U.S. alone.

However, when 3G STF became popular, concerns arose over exposure. GCRI came from tire rubber, which was not designed for prolonged human contact. GCRI allowed exposure to thermal extremes and potential chemical hazards. Plus the reclamation process was not completely efficient since steel belts and polymer cords were not useful. Therefore, the alternative had to be reclaimed from safer polymer-based products like carpeting and drink bottles while retaining if not improving the safety and economic benefits of GCRI.

APPROACH
GCRI became the experimental standard because it was the most popular infill despite availability of commercial products, probably due to higher costs. Material reclaimed from discarded products would negate this issue. The backing of used carpet was a good example because the face fibers were recycled while the pulverized backing went to landfills. Post-consumer carpet from broadloom (PCCB) backing yielded a small average particle size material containing ~20% of loose fibers, while post-consumer carpet from tiles (PCCT) made larger particles with very little loose fiber. While polymers such as nylon and polyester were already efficiently recycled into carpet fibers, green pigmented polyester (PET) bottle resin was not universally successful because the inherent color limited it to only six commercially-viable shades of dyed carpet. Green PET flake was thus tested as a potential infill stream after size modification. The common link between these three alternatives was that they were discarded after effective recycling of other polymer components, so finding another use makes them more economical.

For the interim, the most important factors were composition and safety of infill, which became the focus of the experiments. Composition included the chemicals in the matrix, the size distribution that could fit into the tufts, and the bulk density that determined the overall amount that fit inside the turf.

For a safety factor, the most pressing concern became head injuries due to hard impact. However, the recent surge of STF was not accompanied by published research. Instead, the STF industry developed ASTM Method F355 to measure shock-
absorbing qualities of sports surfaces, so it was adopted for this study. Instead of measuring the physics of impact as energy or load, this method directly measured acceleration over time to correlate impact and probability of injury, which were designated as Gmax and Head Injury Criterion (HIC). According to various sources, serious injuries occur at values above 200 Gmax and 1000 HIC. In practice, Gmax is most popular, and industrial contractors aim below 100 Gmax in 3G STF.

RESULTS AND DISCUSSION
Particle size, shape and formulation had important influences on the amount of infill that could fill the empty volume of synthetic turf, but quantifying those factors required a variety of approaches. Size and shape used indirect analysis such as screen meshes and bulk density cup. Chemical content was measured by thermogravimetric analysis and Fourier-transform infrared spectroscopy. The results of the best performing alternatives were compared in Table I to GCRI due to lack of standardized specifications [3].

Table I. Particle size, bulk density and loading in 3G STF

<table>
<thead>
<tr>
<th>Source</th>
<th>Average Particle (mm)</th>
<th>Standard Deviation</th>
<th>Bulk Density (gm/cc)</th>
<th>Infill load (lbs/sq.ft.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCRI</td>
<td>1.16</td>
<td>0.37</td>
<td>0.43</td>
<td>2.3</td>
</tr>
<tr>
<td>PCCB</td>
<td>0.53</td>
<td>0.51</td>
<td>0.25</td>
<td>1.2</td>
</tr>
<tr>
<td>PCCT</td>
<td>0.84</td>
<td>0.37</td>
<td>0.35</td>
<td>1.8</td>
</tr>
<tr>
<td>PET</td>
<td>1.53</td>
<td>0.41</td>
<td>0.49</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The sizes and ranges overlapped, but the bulk densities were significantly different enough to affect loading the turf with infill. In Table II, other substantial differences were the particle components.

Table II. Chemical Components

<table>
<thead>
<tr>
<th>Source</th>
<th>Volatiles (%)</th>
<th>Polymers (%)</th>
<th>Filler (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCRI</td>
<td>7-15</td>
<td>29-40</td>
<td>30-42</td>
</tr>
<tr>
<td>PCCB</td>
<td>0</td>
<td>10-28</td>
<td>65-92</td>
</tr>
<tr>
<td>PCCT</td>
<td>20</td>
<td>14</td>
<td>66</td>
</tr>
<tr>
<td>PET</td>
<td>0</td>
<td>86</td>
<td>14</td>
</tr>
</tbody>
</table>

Table II does not mention that GCRI and PCCB polymers were elastomeric, while PCCT and PET were thermoplastics. How the sum of the differences and/or similarities affects performance remains to be seen.

Head impact was selected as the most important performance property. Recent studies suggested that short-term exposure (Gmax) creates concussions and long-term exposure leads to amnesia, depression and suicide [4]. As shown in Table III, only the PCCT backing came closest to the standard GCRI impact values:

Table III. Impact Properties without and with STF

<table>
<thead>
<tr>
<th>Source</th>
<th>Gmax</th>
<th>HIC</th>
<th>Gmax</th>
<th>HIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCRI</td>
<td>177</td>
<td>585</td>
<td>112</td>
<td>319</td>
</tr>
<tr>
<td>PCCB</td>
<td>330</td>
<td>1311</td>
<td>190</td>
<td>608</td>
</tr>
<tr>
<td>PCCT</td>
<td>259</td>
<td>849</td>
<td>132</td>
<td>323</td>
</tr>
<tr>
<td>PET</td>
<td>241</td>
<td>921</td>
<td>169</td>
<td>536</td>
</tr>
</tbody>
</table>

CONCLUSIONS
As a flexible elastomer, GCRI was expected to have the lowest Gmax and HIC, with and without turf. Nonetheless, the thermoplastic PCCT came closest to GCRI, while latex rubber/calcium carbonate-based PCCB had the highest. Despite differences in size, density, composition and even impact without turf, the STF improved all the alternatives with PCCT reaping the most benefit.

FUTURE WORK
The components of STF such as the backing and tufts require individual studies to determine the mechanism(s) that contribute to impact absorption. Another issue is rebound of the infill versus time.

ACKNOWLEDGMENTS
This research was funded in part by Georgia Traditional Industries Program (TIP) - Polymer, Fiber and Fabric Products (PFFP) Sector. Material support came from Universal Textile Technologies, Inc.; General Sports Venue, LLC; Astroturf; Mohawk Industries, Inc.; InterfaceFLOR; and Biomechanica, LLC. The authors wish to thank the School of Materials Science and Engineering at Georgia Tech for help and efforts to complete this research.

REFERENCES
OBJECTIVE
The present work has as main objective, to verify how the properties of fibers derived from recycled material will influence the final quality of clothing product, through the analysis of important features for user comfort. The project also will talk about their production processes and also the possible combination with natural fibers such as cotton. For the study, it was used two types of wire, one with 80% polyester/20% recycled PET and other with 50% recycled PET/50% cotton. To test the significance of experimental values was used a comparison of two means with a confidence interval of 95%.

INTRODUCTION
With the growing concern about sustainable development, a lot has been researched, discussed and applied in various industries, always building upon the preservation of natural resources so that they are not exhausted in future generations. This reality implies the development of new technologies and production methods that support this position.

A big problem in society today is the disposal of packaging materials and high production of waste, so the production that uses recycled materials can be a sustainable alternative, since it avoids the extraction of virgin raw material, besides saving resources in production phase, such as reducing energy consumption, carbon dioxide (CO\textsuperscript{2}) and other emissions.

FIBER OF RECYCLED POLYESTER
The recycled polyester (PET) fiber is obtained through the recycling of packaging materials from synthetic polymers formed from the reaction of terephthalic acid and ethylene glycol and has the original colors white, green and beige. It can be mixed with cotton, linen and viscose in order to improve the lightness, softness and comfort of the fabric [1].

In Brazil, the percentage of recycled PET over the virgin material consumption is about 55,6%, and the textile industry is the one that gets more benefits of the recycling PET bottles. In 2009, 39% of the recycled volume was absorbed by the sector, where 45% of the textile applications were nonwovens, 35% were applications in ropes, bristles and monofilaments and 23% were used in clothing [2]. For the fashion market, the advantage of using recycled PET fiber goes beyond physical characteristics; the acceptance is higher due to the ecological appeal, forcing to re-think on the issue of garbage accumulation and environment degradation.

The recycling process can happen in two ways:

- Depolymerization: chemical recycling process where the molecular structure of the polyester is broken, removing all stains and impurities, and returning to the original raw material form.
- Mechanical: the process where the post-industrial waste and/or post consumer is melted and reshaped to its original form. This process is more efficient than the chemical method since requires less energy [3]. See Figure 1 and Table I for details.

![Figure 1](image_url)

**TABLE I. Process comparison**

<table>
<thead>
<tr>
<th>Process Comparison</th>
<th>Virgin Polyester</th>
<th>Recycled Polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Oil Well Head</td>
<td>Process Eliminated</td>
<td></td>
</tr>
<tr>
<td>Crude Oil Refinery</td>
<td>Process Eliminated</td>
<td></td>
</tr>
<tr>
<td>Naphta</td>
<td>Process Eliminated</td>
<td></td>
</tr>
</tbody>
</table>
Xylenes | Process Eliminated
---|---
Paraxylene | Process Eliminated
Terephthalic Acid & Mono Ethylene Glycol | Process Eliminated
Polymerization | Chip Production
Extrusion | Extrusion
Texturing | Texturing

**MATERIALS AND METHODS**

For the manufacture of the knitted fabrics were used the following yarns: Spun yarns Recycled PET/Cotton (50%-50%): 19,7x1tex and Filament yarns Recycled PET/Polyester (80%-20%): 167f88dtex.


**RESULTS AND DISCUSSIONS**

The difference in the tests of weight, wales/cm, and courses/cm is explained by the nominal title variation of the yarns used in the manufacture of the fabrics.

Comfort can be defined as the fiber capacity to retain body humidity [11]; by analyzing the values found the articles made with Recycled PET/Polyester are more comfortable.

It is understood by durability the guarantee of use conditions of the product for a period of time [11]. To test this property in the fabrics, tests of burst pressure, elasticity and elongation. Therefore, the articles made with Recycled PET/Polyester are stronger. And the fabrics made by Recycled PET/Polyester have fewer tendencies to pilling formation. See Table II for results.

**CONCLUSIONS**

It was concluded that in the field of clothing is very important to study the fiber properties establishing a relation between these and the functionality of clothing, consumers that are more concerned about the environment also aim for products of good quality, so the studied fibers have large potential to provide differentiation for the clothing market, with concrete results that offer a concept beyond marketing alone, it is capable to combine modern men worries in relation to the environmental problems with their needs in relation to clothing.

**REFERENCES**

Optical Fibers
INTRODUCTION
Many inorganic fibers are sensitive to subcritical crack growth activated by environment. Failure occurs although the applied stress is much smaller than the fracture stress. This mechanism has been extensively investigated on ceramics, glasses and glass fibers, at room temperature essentially. It has been recently evidenced on SiC-based fibers at high temperatures. The present paper proposes a very powerful approach to static fatigue. It is based on tests performed on multifilament tows under deformation-controlled condition (load relaxation technique). This technique, which has not been used before, because of practical difficulties for deformation control during long-term tests, permits the application of identical constant stresses on all the fibers during a single test. Thus it provides a statistically significant rupture time database containing quite as many data as there are fibers in the tows.

Bundles about 2000 E-glass filaments were used in the present paper. The samples were immersed in water during the static fatigue tests. Crack velocity - stress intensity factor diagrams for single filaments were derived from experimental stress - rupture time data. A closed form expression for statistical distributions of fibre lifetimes was established. It was found to compare fairly well with the experimental results, which assessed the approach, and validated new findings.

MODEL
The subcritical crack growth model is based on the simple power form of crack velocity versus stress intensity factor, which is usually employed to describe the slow propagation of cracks caused by environment under load in ceramics and glass materials:

\[ V = \frac{da}{dt} = V^* \left( \frac{K_i}{K_{IC}} \right)^n \]  

where \( V \) is crack velocity, \( a \) is crack length, \( t \) is time, \( K_i \) is the stress intensity factor, \( K_{IC} \) is the critical stress intensity factor, \( V^* \) and \( n \) are constants depending respectively on environment and material.

The lifetime of a single fiber under constant stress is given by equation (2):

\[ t = \frac{2K_{IC}^2}{V^* \sigma^2 \sigma_{IC}^2 (n-2) \left( \frac{\sigma_f}{\sigma} \right)^{n-2} - 1} \]  

The reference strength of each fiber \( \sigma_f \) can be calculated using the well-known Weibull equation of distribution of failure stresses measured in inert environment:

\[ P = 1 - \exp\left( -\frac{\sigma}{\sigma_0} \right)^m \]  

Then, the statistical distribution of single filaments rupture times is given by equation (4):

\[ P(t, \sigma, \nu) = 1 - \exp\left( -\frac{\nu}{\nu_0} \left( \frac{\sigma}{\sigma_0} \right)^m \left( 1 + \frac{t}{t^*} \frac{n-2}{2} \right)^{m-n}\right) \]  

where \( P(t, \sigma, \nu) \) is the failure probability at time \( t \), under stress \( \sigma \), for a fiber with volume \( \nu \). \( t^* \) is a stress dependent scale factor: \( t^* = \frac{K_{IC}^2}{V^* \sigma^2 \sigma_{IC}^2} \).

This equation is important for lifetime predictions and establishing Strength/Probability/Time diagrams.
RESULTS

Load relaxation follows a power law, with $n$ as force exponent. The slow crack growth constants were extracted from the load relaxation curve. The crack propagation diagrams $V(K_i/K_{IC})$ were found to consist of two distinct curves characterized by $(n \approx 30, V^* \approx 10^{-6} \text{ m/s})$ and $(n \approx 12, V^* \approx 10^{-9} \text{ m/s})$ (figure 1). This unusual diagram results from the presence of two families of fibers: a family of weak fibers with short life, and a family of strong fibers with long life. The family of weak fibers was present only under small deformations. The family of strong fibers was found to dominate under larger deformations ($\varepsilon > 0.8\%$, $\sigma > 600 \text{ MPa}$).

Figure 1: Slow crack growth diagrams for the couples of slow crack growth constants ($n$, $V^*$) derived from the static fatigue tests.

Figure 2 shows that predictions are in excellent agreement with experimental data, when both populations of fibers are taken into account. This definitely validates the model, as well as the hypothesis on the presence of two families of fibers in the bundles. Figure 2 also shows that predictions with $n = 12$ are satisfactory when the weak fibers have not been completely eliminated. Equation (4) can be used to establish the stress-probability-time diagrams.

Figure 2: Statistical distributions of lifetimes predicted using equation (4) and comparison with experimental results.

CONCLUSIONS

It was shown that the life of each fiber in a bundle is commensurate with the fiber reference strength (equation (2)). Then, it was shown that the rank of each failing fiber could be derived from relaxation of the load on bundle, so that the reference strength of each failing fiber is no longer an unknown. This is an important result that is worth pointing out. Stress-failure time relations were established, as well as the equation of rupture times distribution. This latter equation depends on stressed volume, time and applied stress. It can be used for lifetime predictions, as well as for establishing stress-probability-time diagrams.
Advances in Semiconductor Core Optical Fibers

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ABSTRACT— Progress in the synthesis and properties of crystalline semiconductor core optical fibers is reviewed. This new class of optical fibers may significantly advance the fields of nonlinear fiber optics and infrared power delivery.

INTRODUCTION
Though still a relatively young field, glass-clad crystalline semiconductor core optical fibers are generating considerable global interest. Summarized herein are initial efforts in crystalline unary (Si [1], Ge [2,3]) and binary (InSb [4]) semiconductor core optical fibers synthesized using a “molten core” method. In order to achieve this, a semiconductor rod is sleeved inside a tube of cladding glass, the draw temperature of which is greater than the melting temperature of the core. The molten semiconductor core is therefore contained within the constraints of the inner walls of the cladding glass tube. This approach provides for the direct fabrication of long lengths of semiconductor core fiber, using conventional fiber draw methods.

RESULTS AND DISCUSSION
Figure 1 provides electron micrographs of the cross-sections of the as-drawn and cleaved end-faces of the silicon (left) and germanium (right) optical fibers. The fibers possess good circularity and a well-defined interface between the crystalline semiconductor core and the glass cladding.

As crystallographic strain can be induced by thermal expansion mismatch between the core and the cladding materials, crystallographic orientation data has been obtained on glass clad Ge, Si and InSb optical fibers in order to determine the nature of the crystallinity of the material. In the simplest experiments, powder x-ray diffraction was used to identify whether the core was crystalline or amorphous, and determine the phase purity of the core material. Initial expectations were for the cores to be amorphous given the highly non-equilibrium conditions under which fibers are drawn. The x-ray diffraction patterns of the fibers developed to-date are shown in Figure 2. In all cases and under all draw conditions, the unary (Si [1], Ge [2,3]) and binary (InSb [4]) semiconductor core optical fibers were found to be highly crystalline and phase pure. Given that there are no extraneous peaks in the diffraction patterns any oxygen present as indicated by elemental analysis is likely present as an amorphous oxide precipitate or another amorphous non-equilibrium phase.

Figure 2. X-Ray diffraction patterns of Si, Ge and InSb fiber core.

Given the rapid rate of crystallization associated with the fiber draw process an especially interesting question is whether these crystal-core optical fibers contain significantly large regions of single crystalline material and, if so, what crystallographic orientations can be resolved. A convenient technique for tracking crystallite orientations as a function of position along the longitudinal direction of the fiber was developed and permits the direct measurement of crystal domain size and polycrystallinity in regions where more than one crystallographic orientation is present in close proximity (i.e., within the 0.5 mm beam diameter of the collimated x-rays) [3].

While each of the crystalline core semiconductor fibers studied thus far has proven to be polycrystalline with respect to the entire length of fiber (ranging from several meters to over 200 meters of single length continuous fiber) they do exhibit localized single crystalline regions with the total amount and maximum lengths of these regions varying for each semiconductor core material. For example approximately 85% of the Ge fiber studied exhibited this localized single crystallinity (i.e., only one crystallographic orientation was
observed in a given 0.5 mm increment), and a given orientation was observed to persist for lengths up to 15 mm before an entirely new crystallographic orientation was encountered. The Si fiber had localized single crystallinity at approximately 67% of the positions studied, but here the longest persisting domain was limited to about 5 mm. It is possible that these differences are related to the slightly higher oxygen content in the Si-core fiber (17 atom % or, equivalently, 10.4 weight %) versus the Ge-core fiber (6 atom % or, equivalently, 1.4 weight %) since amorphous oxide precipitates present in such concentrations could conceivably interrupt continuous growth of the semiconductor core by providing secondary nucleation sites.

APPLICATIONS

The unary semiconductors are characterized by high refractive index and large third order nonlinearity. The Raman gain coefficient in silicon and germanium are much higher than in silica or germanosilicate fiber cores. For example, the Raman gain coefficient for silicon is approximately 10^4 times greater than that of silica, which suggests that silicon core fibers might make excellent Raman amplifiers for the 3 – 5 μm mid-wave infra-red (MWIR) spectral region. This band includes chemical absorption lines associated with the chemical precursors of weapons of mass destruction (WMD), and has very low solar and thermal background radiation. Their mid-infrared transmission capabilities have also generated much interest in their use in the biomedical industry, where there is an unmet need for robust IR waveguides in a variety of dental and medical procedures.

Raman fiber amplifiers have also demonstrated the potential to combine multiple pump beams and amplify a single mode beam at the Stokes wavelength. In silicon, this Stokes shift is about 520 cm⁻¹, and about 300 cm⁻¹ in germanium. The prospect of a silicon or germanium fiber Raman amplifier offers a dramatic reduction in fiber length and a large increase in average output power. In germanium, the transmission window extends well past 10 μm, enabling beam combining with CO, CO₂ and LWIR quantum cascade lasers (QCL). It may even be feasible to use germanium fibers as THz waveguides given the low loss of this crystal in the THz region.

The transmission and phase of light propagating in a crystalline semiconductor core fiber can be modulated by absorption of pump light propagating in the cladding and having a photon energy greater than the semiconductor bandgap energy. Photo-carriers induced by pump light absorption in the fiber core change its refractive index, thereby producing optical phase modulation of the transmitted signal, and at a sufficient density, can absorb the signal, thereby producing amplitude modulation of the transmitted signal. In a related application, the induced photo-carriers can transform the fiber core from a non-conducting to a conducting state. The potential application for such a photoconducting fiber is as an antenna similar to a plasma antenna that has no radar cross section in the absence of optical pumping, but can be instantly reconfigured [5].

CONCLUSIONS

Although the field of semiconductor core optical fiber is still young, progress has been by made groups around the world in a fairly short amount of time. Briefly discussed here was a review of the present state-of-the-art in crystalline semiconductor core optical fibers with a focus on molten-core derived variants. Though the best fibers to date exhibit optical attenuations on the order of 2 dB/cm in the near-infrared and about 4 dB/m in the mid-infrared is seems possible that attenuations on the order of 50 dB/km are possible with continued effort [6]. Indeed, attenuation values below about 1 dB/m would enable considerable opportunities over a wide range of infrared and nonlinear optical applications.

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REFERENCES

A Phototherapy Device Prototype for Neonatal Jaundice Based on POF Fabric

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ABSTRACT
This work describes the fabrication of luminous POF fabric device prototype developed for neonatal jaundice. Equipment using blue LEDs and designed POF fabric was conducted, optically characterized. The optical parameters of phototherapy device, like wavelength, light intensity, refer to the commercial equipment. Compared with the conventional equipment, our phototherapy prototype presents large and uniform area of irradiation, simplicity and low values of weight, no heating production and low cost. Therefore, the new device is candidate to systematic applications in phototherapy treatments.

INTRODUCTION
Neonatal jaundice is one of the most common symptoms that require medical attention among newborns. About 60% of term babies and 80% of preterm babies develop jaundice in their first week of life. 10% of breastfed babies are still jaundiced at 1 month of age [1]. Although most of neonatal jaundices belong to physiological jaundice and reflect a normal transitional phenomenon, they need to be monitored and conducted prophylactic treatment to prevent substantial damage because unconjugated bilirubin is potentially toxic to the central nervous system [2, 3].

Phototherapy is the most commonly used treatment for neonatal jaundice, which consists in the irradiation of jaundiced newborn with a high intensity light, in the spectral range of 430-490 nm, in order to promote the photochemical transformation of the bilirubin molecules in the areas exposed to the light. Commonly used phototherapy units includes light boxes with special blue fluorescent lamps or light-emitting diode (LED) lights, which have been found to be effective in clinical studies [4, 5]. The eyes and perineal region must be covered throughout the therapy to prevent possible retinal damage from exposure to the light when the infant is put into the light box. Nurse should check frequently the eye patches to assure retinal protection. The infant’s temperature should also be checked regularly to avoid dehydration and hyperthermia. Filtered halogen lights, often incorporated into fiber-optic devices (for example, BiliBlanket® Plus, GE, USA), are also used. When fiberoptic device is used, the eyes and perineal region do not require special protection. The phenomena of dehydration and hyperthermia are fewer compared with the therapy used light box. However, no matter what device used, the infants must be separated with their mother and kept in phototherapy for a long periods. Moreover, the phototherapy is interrupted during feeding, which also reduces the treatment effect.

Our equipment prototype is flexible and soft blanket which can be wrapped around the infant’s torso so that it can avoid the shortage of conventional equipment.

APPROACH
Woven fabrics were produced from POF and cotton yarns for phototherapy devices. Surface patterns were made on the POF fabrics for side emitting of light. The CO2 laser is used for surface modification of POF fabrics. The POF fabrics were incorporated with LEDs, power source and other components to form the phototherapy device prototype. The device was constructed in a rectangular blanket and the light-emitting area about 25*13 cm. LEDs was used for the light sources, the optical characteristics of which includes emission wavelength centered at 460 nm with a narrow band-pass of 30 nm of width and a luminous intensity of 6500 mcd.

An optical meter (Optometer P9710, Gigahertz-Optik, Germany) was used to record the power density of the phototherapy device.

RESULTS AND DISCUSSION
POF fabrics were fabricated by conventional textile weaving process. The automatic sample loom in our laboratory was used to weave the POF fabrics. Figure 1 shows the photo of POF fabric. The real weft cover factor is 55.7% and the warp cover factor is 33%.

FIGURE 1. Photo of woven fabrics produced from cotton yarns and POF with 250 μm diameter.

The POF fabrics were incorporated with 460 nm LEDs, power source and other components to form the phototherapy device prototype. The device was
constructed in a rectangular blanket and the light-emitting area about 25*13 cm, which responding to the medium size of a neonatal patient. Figure 2 shows the phototherapy device prototype based on the POF fabric.

The power density of light-emitting device is modulated about 33 $\mu$W/cm$^2$ according to the recent clinical use. The stability of light emission was test. Figure 3 shows the variation of power density of light emission in 2 hours. The power density almost keeps constant. The temperature also measured in ambient temperature. The device temperature is also stable as 23 °C.

CONCLUSIONS
The new phototherapy device for neonatal jaundice was fabricated. The characterization of this device was conducted. The surface power density stays stable during longer time. This equipment presents many positive characteristics, such as flexible structure, large and uniform area of irradiation, simplicity and low cost. The blank-like design also can avoid the separation of mother and infant, facilitates the maintenance of breast-feeding.

FUTURE WORK
The phototherapy equipment will be optimized in design and utility. The long-time properties of equipment will be characterized. The security of our phototherapy equipment will be evaluated according to international standards. The further biological experiments will be conducted to explore the effectiveness of our equipment.

ACKNOWLEDGMENT
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REFERENCES
Low-loss, High-strength Fibers from Improved Chalcogenide Glasses

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Protection of military aircraft against threats requires internal fiber optic components with improved transparency, good mechanical strength and resistance to laser-induced damage over currently utilized materials. This talk summarizes recent results aimed at developing high-purity chalcogenide glass (ChG) material for producing low-loss, high-strength infrared transmitting fiber devices. A range of promising compositions have been identified in the system Ge-As-S-Se. Subsequently, a systematic evaluation of the impact of the glass purity on the fiber transparency, strength and laser-damage threshold in the 1-5 µm window has been carried out.

ChGs contain at least one of the chalcogen elements (group VI in the periodic table) such as sulfur, selenium or tellurium. In most cases, these are combined with one or more of the following elements: arsenic, antimony, germanium, gallium. The glasses are produced by the co-fusion of the adequate raw elements, in the appropriated amounts, under vacuum in quartz reaction tubes. The melt is rocked at Tm to ensure complete homogeneity and then is rapidly quenched in order to freeze the material in an amorphous bulk structure. The most frequently encountered impurities are hydrogen, oxygen, water, carbon and silicon. Their presence has been shown to be at the origin of scattering, parasitic crystallization (micro-crystals), dramatic crystallization (macro-crystals), refractive index inhomogeneity, and specific absorption bands which can interfere with light propagation through the material in the 1-5 µm infrared window.

Systematic purification protocols for elemental Ge, As, S and Se are developed. A series of sublimation steps is used to drive off the relatively volatile surface oxides of the as-received constituents. A second stage is directed towards removing C, H and particulate contamination through distillation purification. Finally, in order to reduce the strength of each of the impurity absorption bands, we use a reactive chemical getter in the batched glass to scavenge any residual O, C, or H contaminants remaining from prior steps, as well as a distillation purification process to eliminate particulates from the glass. The purification protocol is used to produce high-purity large-scale preforms that are subsequently thermally drawn into fibers tens of meters in length. Optical and mechanical characterization results for low- and high-purity bulk materials as well as fibers are presented.
Inorganic nanoparticles doped with optically active rare-earth ions and coated with organic ligands were synthesized in order to create fluorescent polymethyl methacrylate (PMMA) and Polystryene nanocomposites. Aromatic aromatic ligands such as acetylsalicylic acid, ASA and 2-picolinic acid, PA were utilized in order to functionalize the surface of Tb3+:LaF3 nanocrystals. The selected aromatic ligand systems were characterized using infrared spectroscopy, thermal analysis, rheological measurements, and optical spectroscopy. Nanocomposite light emitting fibers and films were made via melt extrusion and bicomponent melt extrusion techniques were used to confine the nanoparticles within a sheath core structure.
Posters
ABSTRACT
This work is part of a project that deals with the optimization of the quantity and the nature of conductive fibers in antistatic felts used for filtering and sieving powders. Our research concerns the electrical properties at the mesoscopic scale. It aims at determining the conduction mechanisms and the distribution of the electric potential at the scale of the distance between the conductive fibers. In this paper, current-voltage (I-V) measurement results are presented and discussed. X-ray microtomography is used to obtain the geometry of the conductive fibers inside the felts before and after these I-V tests. The studied textile material is based on polyester fibers and stainless steel conductive fibers.

INTRODUCTION
Antistatic felts are often subjected to electrostatic charges liberated by contacts occurring by frictional forces while filtering or sieving powders. The accumulation of these charges can cause sparks and lead to an explosion in the presence of flammable substances or combustible dusts. Moreover, this risk increases with the reduction of the powder particle size [1]. To avoid this danger, it is important that these felts should be able to drain the accumulated charges to a grounded point. A classical way to handle this consists in incorporating conductive fibers into the filter media. However, one major bottleneck in optimizing the antistatic felt performances is the poor understanding of its conduction mechanisms when draining out the accumulated electric charges.

In this paper, the electrical properties of antistatic felts are considered at the mesoscopic scale, the objective being the investigation and elucidation of the conduction mechanisms. Particular emphasis is given to the current-voltage (I-V) measurement results. X-ray microtomography, a non-destructive imaging technique, is used to determine the geometry of the conductive fibers inside the felt samples before and after these I-V tests. These experimental methods are applied to felts based on polyester fibers and stainless steel conductive fibers.

SPECIMENS
The polyester felts used in this research were provided by the company SIOEN Felt & Filtration, Liège, Belgium. Stainless steel conductive fibers are incorporated in these felts. The rectangular samples have a typical area of few square centimeters with a thickness of 2 mm. Given this geometry, an electrical conductive silver paint is used to ensure the electrical contact between wires and both felt sample extremities. Due to the anisotropy of the properties of this textile material, its electrical properties are highly sensitive to fiber orientation; therefore all the experiments were carried out in both machine direction (MD) and cross directions (CD). Furthermore, all the specimens are tested in a controlled environment in terms of relative humidity and temperature.

EXPERIMENTAL METHODS
The circuit shown in Fig. 1 is used to obtain the I-V curve associated with a felt sample. The voltage between the electrodes of the latter is denoted $U_x$ and is swept between 0 and 1000 V. Note that a resistor of $1\,\text{M}\Omega$ is added to protect the high-voltage generator.

![Figure 1. Felt sample test circuit to record the I-V curves.](image)

The X-ray microtomographic tests are performed by using the Skyscan-1172 device (Skyscan, Kontich, Belgium), available at the Laboratory of Chemical Engineering. This microtomograph gives 2D cross section images of the felt samples with a high resolution. The specimens were fastened to an adapted sample holder minimizing the mechanical vibrations. A standard image thresholding technique [2] was then used to convert the felt images to binary images. If a pixel in the image is above a given global threshold then it is converted to white (polyester fibers or air) otherwise it is converted to black (stainless conductive fibers). From each binary image, a set of parameters associated to the conductive fibers were extracted, namely: their total number; the smallest distance between them; the coordinates of the global centroid and the variance of the relative distance to this centroid. The objective was to assess whether the location of the conductive fibers changes after a I-V test or not. This result can support or disprove a conduction mechanism based on an electromechanical activation.
RESULTS AND DISCUSSION

The method has been applied to a polyester felt sample with the stainless steel fibers in the (CD) direction. Its geometry and associated system axis are shown in Fig.2.

The specimen was conditioned environmentally at relative humidity of 35% and at temperature of 25°C during all the experimental tests.

Two successive microtomographic investigations were first carried out without any intermediate I-V test in between, but the sample was removed and placed in the sample holder between the first two tests. The objective was to analyze an eventual impact of the operator manipulation on the location of the conductive fibers. An I-V test up to 1000 V was then recorded before the third microtomographic test. The microtomograph gives the cross-section images parallel to the X,Y-plane with a pixel size of 7 µm.

As depicted in Fig. 3, the I-V curve of the felt sample exhibits a non-linear and hysteretic behavior. Note that a log-log system axis is used. First, it can be seen that the current increases with the voltage flowing almost the Ohm’s law. After a voltage threshold (here 825 V), the current rises suddenly and becomes 100 times higher than its previous value (from 10^{-7} A to 10^{-5} A). The associated power is in the range of 80-100 µW. The I-V curve becomes finally linear with a very small resistance (R≈100 kΩ) compared to the initial one (R≈4.5 GΩ).

Fig. 4 shows the evolution of the total number of stainless steel conductive fibers for each of the three microtomographic tests, the I-V curve being recorded after the second one. The results are given for a distance of z = 9.5 mm. The comparison of the curves (1) and (2) shows that the operator manipulation does not perturb the location of the conductive fibers significantly. However, applying an I-V test to the felt sample yields deviations of the value of the total crossing points of these fibers in a given plane perpendicular to axis z (here z = 9.5 mm).

These results suggest that the stainless steel conductive fibers may move inside the polyester felt when subjected to a continuous voltage. Moreover, the sudden transition noticed in the I-V curve could indicate a contact between these conductive fibers.

CONCLUSIONS AND FUTURE WORK

In this paper, the conduction mechanisms of an antistatic felt at the mesoscopic scale are considered. Current-voltage measurements results are presented and discussed. X-ray microtomography is used to obtain the geometry of the conductive fibers inside the felts before and after these I-V tests. The results suggest that the stainless steel conductive fibers may move inside the polyester felt when subjected to a continuous voltage. Moreover, the sudden transition noticed in the I-V curve could indicate a contact between these conductive fibers.

Details on the proposed method and the experimental setup, more results and discussion on the conduction mechanisms in the antistatic felts at mesoscopic will be included in the extended paper.

ACKNOWLEDGMENT

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REFERENCES

Properties and Preparation of Resistant Polyurethane-coated Fabrics to Ageing by Sol-Gel Thin Films

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STATEMENT OF PURPOSE
In this work hybrid thin films on polyurethane coated fabrics were prepared by sol-gel process with addition of TiO$_2$ and ZnO particles to reduce insufficient resistance to ageing in way of low colour fastness as one of the most common complaints about domestically produced seats of yachts and speedboats.

Sol-gel derived hybrid films were deposited by dip-coating from 3-glycidoxypropiltrimethoxysilane (GLYMO). By varying the concentration of precursor and auxiliaries, mass concentration of TiO$_2$ and ZnO particles, drawing speed as well as the methods and process of fabrics treating, optimal processing conditions were established. Samples were exposed for 300 hours to Xenon arc source. The retention of the textile character as an important requirement of a new textile material was successfully met. Hybrid films were further characterized by scanning electron microscopy and colour fastness by Datacolor.

INTRODUCTION
Today many applications of polyurethane-coated fabrics involve exposure to ageing effects. Insufficient resistance of polyurethane coated fabrics for seat covers on yachts, speedboats, etc. to ageing (water, UV radiation, moisture, etc.) is one of the most common complaints of producers. Manufacturers are trying to prevent ageing effects by use of additives, but some of them do not achieve long-lasting and significant results. Colour fastness and mechanical properties are very important for customers. The main complaints are about change in colour and loss of strength resulting in little holes and similar defects. Polyurethane is inherently susceptible to degradation (photo-oxidation, hydrolysis and microbial), and its prevention depends on the use of surface modification. The sol-gel process offers great opportunities in terms of creation of new surface properties of textiles. In our opinion this is a great solution for preventing of ageing effects on polyurethane coated fabrics especially for good colour fastness. Nanosols containing particles as ZnO and TiO$_2$ are reported to absorb radiation strongly and gave colorless finishing [1-3]. In the field of textile engineering number of published papers on sol-gel process has increased in the last fifteen years and some of them have modification which included durable UV-absorption.

Purpose of the research was to prepare and characterize hybrid thin films on polyurethane-coated fabrics and achieve good colour fastness to artificial light as tested by Xenon arc fading lamp test.

EXPERIMENTAL
Preparation of sols and textile materials
Chemicals of highest purity purchased from Aldrich were used. Based on our previous investigation two treatments on the basis of GLYMO were especially effective: the hydrolysis with the pure water and with the aqueous solution of hydrochloric acid as an acidic catalyst.

GLYMO was hydrolyzed at 20 °C with pure water with GLYMO:water ratio 1.3 and with hydrochloric acid with GLYMO:water ratio 1:1.5. Three mass concentrations of TiO$_2$ and ZnO particles were used as is shown in Table I.

Table I. Process conditions and variations of the mass concentrations of TiO$_2$ and ZnO particles

<table>
<thead>
<tr>
<th>Particle</th>
<th>Mass concentration</th>
<th>Precursor</th>
<th>Alkoxide-water ratio</th>
<th>Temperature and time</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>10 g/dm$^3$</td>
<td>GLYMO</td>
<td>1:3</td>
<td>20 °C, 1 h</td>
</tr>
<tr>
<td></td>
<td>20 g/dm$^3$</td>
<td>GLYMO</td>
<td>1:1.5 (acid catalysts)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 g/dm$^3$</td>
<td>GLYMO</td>
<td>1:1.5 (acid catalysts)</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>10 g/dm$^3$</td>
<td>GLYMO</td>
<td>1:3</td>
<td>20 °C, 1 h</td>
</tr>
<tr>
<td></td>
<td>20 g/dm$^3$</td>
<td>GLYMO</td>
<td>1:1.5 (acid catalysts)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 g/dm$^3$</td>
<td>GLYMO</td>
<td>1:1.5 (acid catalysts)</td>
<td></td>
</tr>
</tbody>
</table>

The samples 5 x 5 cm in size were dip-coated on a custom-made apparatus with a defined drawing speed of 0.5 mm/s, 1 mm/s, 1.5 mm/s and 2 mm/s in order to obtain a thin coating. Coated samples were left to gel at room temperature for 24 h, and then dried at 100 °C for 1 hour.

Coated textile materials produced by Čateks d.d. (Croatia) for marine program were used. Before the implementation of physical and chemical modification of samples, some basic characteristics of the textile were defined according to the standards, as listed in Table II.

Table II. Characterization of samples used for dip-coating

<table>
<thead>
<tr>
<th>Test characteristic</th>
<th>Standard</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Coating</td>
<td>PUR</td>
</tr>
<tr>
<td>Core material</td>
<td>41/2010</td>
<td>PUR</td>
</tr>
<tr>
<td>Mass per unit [g/m$^2$]</td>
<td>HRN EN ISO 2286-2</td>
<td>181.5 175.9</td>
</tr>
<tr>
<td>Purpose</td>
<td>Marine program</td>
<td></td>
</tr>
</tbody>
</table>
Instrumental methods
Surface structure, morphological characteristics of coated textiles were investigated by scanning electron microscope (SEM) TESCAN, VEGA TSS136LS with the operating voltage of 30 kV and secondary electron detector.

Colour fastness
Colour fastness of hybrid polyurethane-coated fabrics was determined in accordance with HRN EN ISO 105-B02: 2003, Textiles – Tests for colour fastness - Colour fastness to artificial light: Xenon arc fading lamp test. Wool references range from 1 (very low colour fastness) to 8 (very high fastness).

RESULTS AND DISCUSSION

Colour fastness
The samples were exposed to Xenon arc fading lamp test for 300 hours which correspond to the change of color standard 7 degree 4 gray scales for nearly all samples. The treated samples showed good fastness, even after washing (grades 6 and 7).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Treatment (precursor (alkoxide:water ratio)/mass concentration particles/drawing speed)</th>
<th>Change in colour</th>
<th>Numerical rating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ZaO</td>
<td>TiO2</td>
</tr>
<tr>
<td>0</td>
<td>Untreated (producer additive)</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>1</td>
<td>GLYMO: water ratio 1:1.5 (HCl) as acidic catalysts</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>10 g/dm³</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>1 mm/s</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>1.5 mm/s</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>2 mm/s</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>1 mm/s washed</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>1 mm/s washed</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>GLYMO: water ratio 1:3</td>
<td>1 mm/s washed</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>50 g/dm³</td>
<td>1 mm/s washed</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>GLYMO: water ratio 1:3</td>
<td>0.5 mm/s washed</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>10 g/dm³</td>
<td>1 mm/s washed</td>
<td>6</td>
</tr>
<tr>
<td>12</td>
<td>1.5 mm/s</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>13</td>
<td>2 mm/s</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>14</td>
<td>1 mm/s</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>15</td>
<td>1 mm/s washed</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>16</td>
<td>10 g/dm³</td>
<td>1 mm/s washed</td>
<td>6</td>
</tr>
<tr>
<td>17</td>
<td>20 g/dm³</td>
<td>1 mm/s washed</td>
<td>6</td>
</tr>
<tr>
<td>18</td>
<td>50 g/dm³</td>
<td>1 mm/s washed</td>
<td>6</td>
</tr>
</tbody>
</table>

Surface structure and morphological characteristics
Images of the surface of coatings by SEM (Table IV) show the modification of polyurethane coatings. Polyurethane surface with particles of ZnO is not covered only by hybrid thin films, the surface pores are also completely filled forming a composite organic-inorganic coating. Polyurethane surface with particles of TiO₂ show homogenous coating and more complete coverage of polyurethane.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mass concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLYMO: water ratio 1:1.5 (HCl) as acidic catalysts</td>
<td></td>
</tr>
<tr>
<td>10 g/dm³</td>
<td>ZaO  TiO₂</td>
</tr>
<tr>
<td>50 g/dm³ washed</td>
<td></td>
</tr>
<tr>
<td>10 g/dm³</td>
<td></td>
</tr>
<tr>
<td>50 g/dm³ washed</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSION
Treatments based on GLYMO and TiO₂ and ZnO particles are suitable for modification of investigated textiles. Hybrid thin films gave good colour fastness after 300 h of exposure in Xenon chamber. Treatments based with TiO₂ particles gave smoother coatings with greater interactions with polyurethane chains.

ACKNOWLEDGMENT
Authors would like to thank the Ministry of Science, Education and Sport of the Republic of Croatia for the financial support of this study which is a part of research project „Multifunctional Human Protective Textile Materials“ (117-1171419-1393).

REFERENCES
A Study on Physical Property of Cement Composite Reinforced with Silane-treated Basalt Chopped Fiber

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OBJECTIVE
The aim of study is to investigate the effect of fiber content and fiber length on the tensile and flexural properties of basalt chopped fiber reinforced cement composite. Physical properties of fiber reinforced cement composite are also investigated by the modification of interface between basalt fiber and cement using silane coupling agent.

INTRODUCTION
Cement is the most widely used materials because of its abundance and easy processing. However, its ultimate tensile strain is very small and its tensile, flexural and impact strength are very low, making a cement material brittle and easy to crack. Adding strong fibers into cement is an effective measure to improve the above shortcomings. Many organic and inorganic fibers have been utilized in this purpose. Alkali-resistant (AR) glass fiber, Stainless fiber, Kevlar, Polypropylene and Carbon fiber etc. are commonly used for the reinforcement of cement. However, durability of fiber for long period of time and cost of the fibers are the main obstacles for spreading out of fiber reinforced cement. Among many fibers, glass fiber is so widespread because of its good mechanical properties and the fact that continuous fiber can be produced. Better properties can be obtained from carbon fiber which has high thermal resistance and physical strength. However, these two conventional reinforcing fibers have unavoidable disadvantages. A disadvantage of using glass fiber is skin irritation by the fibers leaving out of the matrix which may have contact with the human skin. The disadvantage of carbon fiber is its high cost of processing. Recently, new type of fiber based on natural resource called Basalt rock has been actively developed. Since basalt fiber is relatively cheap and has extremely good mechanical, thermal properties and chemical resistance, the use of basalt fiber in reinforcing cement is highly promising. The aim of the present study is to investigate the effect of surface modification of Basalt fiber using silane coupling agents which have different functional group on the physical properties of cement composite.

EXPERIMENTAL
1. Materials
Type 1 ordinary Portland cement purchased from S company (Korea) was used. Basalt fiber roving supplied from Secotech(Korea) was chopped and used in 3 mm length. In order to modify the surface of Basalt fiber, 3-(trimethoxysilyl)propylmethacrylate, Chlorotriethoxysilane, 3-Aminopropyl triethoxysilane, Trimethoxypropylsilane were purchased from Aldrich, and used as-is without further purification.

2. Silane treatment of Basalt fiber
Hydrolyzed silane solutions in methanol were prepared for each silane coupling agents of 0.1, 0.3, 0.5, 1.0 wt% concentrations. Basalt chopped fiber was treated with this silane solution for 30 min, and dried at 110oC for 30 min.

3. Specimen preparation
The cement : water ratio of mortar was 3 : 1 in weight. During mixing of fiber cement mixtures, 0.1% methyl cellulose as an emulsifier and 0.5% AE water-reducing agent (by weight of cement) were added to ensure the uniform dispersion of fibers in cement matrices. The specimens with sizes of 2 cm x 1 cm x 10 cm were cast and stored at room temperature for 1 day. Then, all specimens were further cured in water for 28 days. Tensile properties and Flexural strength were investigated by UTM (LLOYD) at a crosshead speed of 5 mm/min (according to ASTM-D-638). Before all mechanical testing, the specimens were conditioned according to ASTM-D-618. Each group includes six specimens. A maximum and a minimum datum are deleted from the six data, and the remaining four data are used to calculate the average of the group. The fracture surfaces of impact specimens were observed by a scanning JEOL scanning electron microscope (SEM), The scanned surfaces were coated with a gold layer to avoid charging under the electron beam.

RESULTS AND DISCUSSION
It was found that halogenated silane coupling agent such as Chlorotriethoxysilane showed the most effective treatment, resulting in strong fiber-cement interface (Figure 1). Also physical properties of basalt chopped fiber reinforced cement composite are closely related to the fiber dispersion in the cement matrix. The tensile and flexural strength of cement composites are increased by addition of basalt chopped fiber, the shorter the fiber length is, the higher the tensile strength shows. Although the tensile and flexural strength of cement composites are decreased by addition of silane treated basalt chopped fiber, tensile and flexural elongation of cement composites are dramatically increased by addition of silane treated basalt chopped fiber.
FIGURE 1. Pull-out strength of Chlorotriethoxysilane treated basalt fiber pulled out from cement matrix.

REFERENCES
OBJECTIVE
The purpose of this study is to evaluate the differences in the mechanical properties of natural and manmade fibers under compressive and tensile loads on a microscopic scale.

INTRODUCTION
The significance of the mechanical properties of a material depends on the types of stresses it will be undergoing in its typical working environment. Because they are anisotropic, fibers stressed in tension and those in compression often display very different properties [1]. Many fibrous materials work under tensile loads where the longitudinal Young’s Modulus of the material is of particular interest like in the case of ropes, fishing nets, or masts. The Young’s Modulus of the fibers can, in most cases, be easily obtained using the standard Instron tensile testing machine. However, in some situations, certain fibrous materials work under compression. For example, in the use of Kevlar for bulletproofing, the properties of the fiber under compression and the compression modulus are significant. There are very few methods to determine the compression modulus, and it is usually assumed to be in the order of the tensile modulus. In this work, we study the difference between the compression and tensile properties of natural and artificial materials.

EXPERIMENTAL
The compression modulus of Kevlar, PET, Nylon, glass fiber, and N. Clavipes spider silk were obtained using the Kawabata Compression tester for single fibers (KatoTech, Japan). The reversibility of the deformation from the compression testing was analyzed using microscopy and by evaluating the sample birefringence before and after testing. The tensile testing of the samples was conducted on the Instron 5582 tensile testing machine.

Kawabata Single Fiber Compression Tester
The fiber diameters ranged from five to seventy micrometers, and because of the smaller diameters, the common compression procedures were not applicable. To measure the compression modulus of the samples, we have employed instrumentation presented by Kawabata [1]. The single fiber compression tester had a .2mm by .2mm square tipped probe to press down on the fiber that was laid across a flat surface as displayed in Figure 1. An example of the force versus deformation curve obtained is shown in Figure 2.

RESULTS
Table I shows the preliminary experimental results for the compression moduli of the chosen fibers calculated using “Eq. (1)” as well as the tensile moduli of the samples.
obtained from literature. From the experimental data, it can be seen that the transverse modulus for the fibers is significantly less than the tensile modulus values showing a high degree of anisotropy.

TABLE I. Transverse Modulus of Fiber

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter (microns)</th>
<th>$E_T$ (GPa)</th>
<th>Tensile Modulus from Literature (GPa)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar</td>
<td>12.3</td>
<td>1.5</td>
<td>63.4</td>
<td>[1]</td>
</tr>
<tr>
<td>PET</td>
<td>26.5</td>
<td>1.16</td>
<td>1.8</td>
<td>[4]</td>
</tr>
<tr>
<td>Glass Fiber</td>
<td>8</td>
<td>.8</td>
<td>77.4</td>
<td>[1]</td>
</tr>
<tr>
<td>Spider Silk</td>
<td>5.8</td>
<td>1.046</td>
<td>12.71</td>
<td>[3]</td>
</tr>
<tr>
<td>Nylon</td>
<td>68</td>
<td>.2913</td>
<td>2.71</td>
<td>[3]</td>
</tr>
</tbody>
</table>

In the poster, we will further discuss the extent of the compressive and tensile deformations and the results of the ANSYS modeling.

ACKNOWLEDGMENT

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REFERENCES

Air flow across porous and permeable materials can interact with the fabric structure. For parachutes, fabric permeability plays an important role in both steady descent (affecting rate of descent and stability) and in the inflation phase, affecting inflation time and opening shock. It is during the inflation phase that fabric permeability is least understood. Static measurements of permeability are made under steady state flow conditions, whereas during inflation, dynamic permeability, as it occurs in situ, is of interest. An additional complicating factor is the high fabric stresses and associated deformations occurring during inflation; applied loads have been shown to significantly affect permeability (100 – 500 %) under limited static test conditions [1].

The porosity of parachute fabrics is an important parameter which affects the performance of the parachute canopy by influencing the inflation process of the canopy as well as the overall descent rate and stability of the parachute system. The concept of porosity is a term in parachute technology that is slightly different than conventional engineering use. Porosity is used to characterize the air flow characteristics of a parachute cloth. For the cloth itself, “porosity,” is defined as the airflow rate through the cloth at 0.5 inches of water pressure, as measured in a standard test method [2]. Parachutes commonly have slotted openings in the structure. This is also called “porosity,” and is characterized as the ratio of all open areas to the total canopy area [3]. The effect of variable fabric permeability on the performance of parachute systems has usually been studied based on the assumption that the fabric maintains a fixed permeability (e.g. the fabric permeability is an inherent parameter of the fabric and remains invariant).

High air flow and dynamic pressure can deform and stretch the fabric layer, or even cause failure [4]. Figure 1 shows an example of a standard nylon parachute fabric during air flow testing at two pressure levels, and the associated fabric deformation due to high air flow through spaces between woven yarns. Testing under higher flow rates and pressure loads provides information on steady state properties of parachute fabrics that may particularly influence canopy behavior during the inflation phase. For example, it may be desirable to increase fabric permeability during the canopy opening shock phase to decrease structural loads. Instrumented flow rate testing at high pressures, coupled with photographic examination of fiber/yarn behavior provides new insights into fabric behavior under these conditions.

Fabrics that absorb water vapor from the atmosphere undergo fiber swelling, which tends to close off the pores in the fabric and increase the resistance to air flow through the material. Many studies of structural factors influencing the air permeability of fabrics assume that gas or liquid flow takes place in the interstices between yarns. This approach works well for fabrics that have an open construction, where there are large open areas between yarns. For these open fabrics, the diameter and spacing of the yarns are the important structural factors, since almost all flow takes place through the interyarn pores. In more tightly woven fabrics, there is no interyarn space, and fluid flow takes place within the structure of the yarn itself. In this case, the diameter and physical arrangement of the fibers within the yarn are the most important factors influencing the fluid flow resistance across the textile layer (Figure 2).
FIGURE 2. Fabric construction affects magnitude of permeability changes due to variable fiber dimensions associated with water vapor absorption or desorption.

Of special interest is the peculiar tendency of nylon fabrics to show decreased flow resistance (increased permeability) at high humidity, which is counter to the behavior of other fabrics (Figure 3). This behavior is attributed to the tendency of nylon fibers to swell axially rather than radially as most other textile fibers do, thereby causing fabric pores to open up rather than close down.

Previous measurements on fifteen nylon fabrics [5] revealed that this is a consistent property of nylon fabrics and is common to many types of fabric weaves and thicknesses. Parachute fabrics (usually constructed of woven nylon fabric) were not specifically addressed in this previous study. New measurements address the magnitude of the permeability changes associated with water absorption for standard nylon parachute fabrics, in the context of flow rates and pressures associated with parachute opening and descent.

Since parachute fabric in use is under an applied load, the strained configuration of the fabric is most appropriate to use when measuring flow through the fabric. The coupling between the pressure distribution over the surface of the parachute canopy and the change in pore dimensions due to the applied load is anticipated to be of equal (or greater magnitude) than the dimensional changes associated with humidity-dependent fiber and yarn swelling. A particular focus of this study is highly elastomeric fabrics (as opposed to standard nylon parachute fabrics) and the measurement of fabric permeability under conditions of defined stress and/or strain, and how these measurements compare to those made under standard non-strained conditions.

REFERENCES


Effects of Heat Treatment on the Morphology and Mechanical Property of Electrospun PSU Nanofibrous Membrane

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INTRODUCTION
Polysulfone (PSU), with many excellent properties, such as chemical inertness, compressive strength, thermal stability, and mechanical strength, is one of the most popular synthetic polymer materials used for fabrication of membranes [1-2]. So far, PSU membrane has widely been applied to micro-/ultra-filtration, gas separation, pervaporation, membrane oxygenators, bioartificial organs, and so on [3]. With the increasingly mature of electrospinning technique, PSU fiber membranes have already been successfully obtained with fiber diameters ranging from scores of nanometers to several micrometers, light weight, excellent permeability, large specific surface area, high porosity [4-6]. This paper systematically studied the effect of heat treatment on the morphology and mechanical property of the electrospun PSU fiber membranes.

EXPERIMENTAL
Sample preparation
Polysulfone (PSU, Mn=80000) particles were dissolved in the mixture solvents of 99% DMF and 99.5% acetone (w/w=9:1) at room temperature, yielding 20% concentration. Electrospun fibrous nonwovens were fabricated at 20 cm, 12 kV, 4 mL/h.

Heat treatment and measurement
The as-spun fiber mats was placed in a oven at 180~195°C. The longitudinal images of fibers were observed by Hitach S-4700 SEM, and fiber diameters were calculated with HJ2000 software. The mechanical property of the membrane was tested by Instron 3365 with crosshead speed 10 mm/min, gauge length 10 mm, and sample size 40 mm × 2 mm, every sample was measured 10 times.

RESULTS AND DISCUSSION
Effect of heat treatment on morphology structure
Fig.1 shows the fiber diameter increased slightly after relaxation heat treatment, and with temperature from 180°C to 195°C, the straight fiber tended to be curved. For tension heat treatment (Fig.2), when the temperature reached 180°C, fiber diameter began to decline obviously, however, with the temperature continuing increasing, the descending tendency became gently, and there was no change existing in the surface morphology.

Table I lists the changes in the size of PSU membrane at different temperatures as the PSU membrane was treated with relaxation heating for 3 h. The increasing temperature led to the gradual decrease in the membrane size and increase in the membrane thickness, and also resulted in the densification of the membrane structure. While there existed almost no changes in the size of PSU membrane for the heat treatment loaded with tension.

TABLE I. Changes in the macroscopic size of PSU membrane with relaxation heating

<table>
<thead>
<tr>
<th>Sample</th>
<th>180°C</th>
<th>185°C</th>
<th>190°C</th>
<th>195°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length×width (cm)</td>
<td>4×4</td>
<td>3.6×3.6</td>
<td>2.7×2.7</td>
<td>2.5×2.5</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.070</td>
<td>0.080</td>
<td>0.140</td>
<td>0.250</td>
</tr>
</tbody>
</table>

Fig. 3 shows the SEM pictures of the PSU membrane heat-tension-treated at 190°C for 1h, 3h, and 5h. The pictures demonstrated that the fiber diameter declined obviously after heat treatment for 1~3h, while the heating time reached 5h, there was almost no change in the fiber diameter any more.
Effect of heat treatment on the mechanical properties

The statistics in Table II is the mechanical property of PSU membrane heat-tension-treated at different temperatures. The results indicated that, with the increase of the temperature, the mechanical property was improved gradually, and when the temperature was 190°C, the initial modules, breaking stress, and breaking strain all reached the maximum value, but then declined as the temperature continued increasing to 195°C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Initial modules (Mpa)</th>
<th>Breaking stress (Mpa)</th>
<th>Breaking strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>35.78±1.82</td>
<td>0.67±0.04</td>
<td>25.33±3.63</td>
</tr>
<tr>
<td>180°C</td>
<td>51.31±5.72</td>
<td>1.18±0.04</td>
<td>30.48±3.23</td>
</tr>
<tr>
<td>185°C</td>
<td>77.13±9.63</td>
<td>3.79±0.26</td>
<td>52.09±7.17</td>
</tr>
<tr>
<td>190°C</td>
<td>84.01±17.18</td>
<td>4.96±0.21</td>
<td>104.06±17.53</td>
</tr>
<tr>
<td>195°C</td>
<td>49.64±15.71</td>
<td>4.48±0.22</td>
<td>80.91±8.98</td>
</tr>
</tbody>
</table>

CONCLUSION

(1) When the as-electrospun PSU membrane was treated with relaxation heating, the fibers tended to curve and shrink, the membrane size reduced, and the membrane thickness increased. Loaded with tension, the heat treatment resulted in the increase of compactness and the smoother surface for the PSU membrane, but did not affect the membrane size.

(2) When heat-treated with tension, the diameter of PSU fibers reduced and the mechanical property was improved with the increase of either temperature or time. The best mechanical property of electrospun PSU membrane was achieved at 190°C, 3h.

ACKNOWLEDGMENT

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REFERENCES

The Influence of Spinning Parameters on PVDF Nanofiber Crystallinity and Crystalline Phase Formation

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By controlling the solution concentration and temperature, Poly (vinylidene fluoride) (PVDF) fibers with maximized beta crystal form will be prepared by an electro spinning process. PVDF in the beta crystal form has piezoelectric properties. Piezoelectric PVDF nanofibers can be used for power generation or detection circuits in fiber based devices. In order to maximize beta crystal structure, PVDF concentration in solution and temperature will be investigated. The increase in PVDF concentration will cause the increase in the polymer viscosity and eventual gelation. The molecular interactions associated with gelation will be used in combination with the electrospinning process to influence the crystallinity and crystalline polymorph of the electrospun fibers. Preliminary solution rheology experiments will be used to determine the concentration and temperature conditions where gelation occurs. Morphology of the electrospun fibers will be characterized using SEM, XRD and Differential Scanning Calorimeter (DSC).

PVDF polymer chains consist of a carbon backbone with every other carbon atom bonded to pairs of hydrogen atoms or pairs of fluorine atoms. In the structure of PVDF shown in Figure 1, hydrogen atoms are electropositive and fluorine atoms are electronegative. The alpha, anti-parallel conformation, and beta, transverse conformation, are the most common crystalline phases of PVDF chain. Alpha phase is found commonly and it is non-polar molecule that creates no net dipole and hence no piezoelectric effect. The beta phase, which does exhibit the piezoelectric effect, is less common. When PVDF chains are crystallized in the piezoelectric beta phase, all hydrogen atoms are move to one side and fluorine to opposite side. When mechanical stress is applied to the beta phase, hydrogen and fluorine atoms shift relative to each other and generate an electric dipole and field. In order to have power generation property, fibers must have beta phase PVDF crystals.

The piezoelectric effect for PVDF is also temperature sensitive. Above the Curie temperature, piezoelectric material loses its spontaneous polarization and its characteristics because in semi-crystalline polymers, the amorphous phase supports the crystal orientation and polarization only below the Curie temperature. Curie temperature for PVDF is 340 Kelvin when the room temperature is 300 Kelvin, so nothing will be affected by the temperature. While it is less expensive than other ceramic piezoelectric materials, it has wider applications than brittle ceramic piezoelectric.

PVDF can also be processed into fibers. Fibers can be stressed mechanically in either the longitudinal or transverse mode but the transverse direction is more convenient for power generation because it allows placement of electrodes along the length of the fiber. PVDF has high a piezoelectric coefficient which allows it to endure large strain and it also has bio compatibility and low acoustic and mechanical impedance. Fibers which generate electric charge can be produced using PVDF and can be incorporated into sails, garments, flags, wind socks, upholstery, draperies or tents to generate power from textile objects during their normal use.

The electrical response of piezoelectric materials is a function of stress and the strain and piezoelectric effect can be explained by tensors (Figure 2). A net dipole moment exists along the direction of polarization when polarization is separation of the positive and negative charges. The piezoelectric effect is the combination of electrical behavior, \( D=\varepsilon E \), and Hooke’s Law, \( S=\varepsilon T \), where \( D \) defined as volumetric charge density, \( \varepsilon \) as the permittivity, \( E \) as electric field strength, \( S \) as the strain, \( s \) as the compliance and \( T \) as the stress. The piezoelectric coefficient relates the applied electric field to the strain in the same direction. While other materials expand, PVDF compresses under the same applied electric field. Figure 3 shows that voltage and current have opposite signs under tensile and compressive stresses. This is because a compressive stress in direction 3 or tensile strength in direction 1 or 2 results in polarization and positive piezoelectric coefficient.
PVDF is the semi-crystalline polymer which demonstrates strong and stable piezoelectric properties and the price is economical and can be applied where ceramics cannot be. While alpha phase is the most common in PVDF, in order to have power generating property, it must have beta phase crystals. Thus, the project will be focused to produce the fiber with power generating property while maximizing beta phase by controlling electrospinning condition.

Electrospinning is a simple method for drawing polymer fibers with diameters at nano or micron scale using high voltage supply. Electrospun fibers are semicrystalline and have characteristics of high porosity, small diameter, excellent pore interconnectivity and high surface to volume ratio. Also, electrospun fibers can be uniaxially aligned over long length in centimeter scale. Gelation of polymer is driven by the interaction between solvent molecules and polymer chains and the gelation of PVDF can be affected by various solvents. Combination of DMAc or DMF and acetone will lead to the formation of beta phase. Gelation can happen when PVDF is fully dissolved in solution or during the electrospinning and latter is preferable for practical application. Moreover, gelation can be affected by PVDF concentration, electrospinning feeding rate, applied voltage during the electrospinning, temperature of the solution at the electrospinning and the distance between the needle tip and the grounded substrate.

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Coiled Fibers of Poly (amide-co-imide) and Poly (trimellitic anhydride chloride-co-4, 4’-methylene dianiline) by Using Mechano-Electrospinning

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OBJECTIVE
Non linear coil shaped uniform fibers were synthesized with the blend solution of Poly (amide-co-imide) PAI (torlon)/Poly (trimellitic anhydride chloride-co-4, 4’-methyene dianiline) (PTACM) in solvent mixing ratio of DMSO and THF (6:4) by using mechano-electrospinning. The linear shape and decrease in size of fiber was observed as the concentration of blend solution decreases from 30-27 %. However, if concentration reduced to 26 % then regular coil shaped uniform fibers were produced. We also found that except for solution prepared in 6:4 (DMSO/THF) and concentration less than 26 % did not facilitate continuous electrospinning. The properties of these blends were investigated using a rotational rheometer and SEM, in an attempt to understand the relationships between their rheological and morphological properties. It was concluded that concentration of solution played an important role to the diameter of fiber and significant impact on the shape of fiber.

INTRODUCTION
PAI thermoplastics have been the material of choice for the fabrication of large load bearing composites due to their high strength, superior stiffness, excellent thermal resistance and high performance. PAI has been extensively used in filtration media, wire enamels and for reinforcement by virtue of its superior chemical resistance and physical properties at higher temperature. Electrospinning is an enabling technique which can produce nanoscale fibers from more than 100 different polymers [1]. Due to bending instability of the jet, the electrospun fibers are often collected as cross-sectional shapes, branches, beads, buckling coils and nonwoven mats in the form of randomly oriented structures [2-4], which are acceptable only for some applications such as filters, wound dressings and tissue scaffolds. Meanwhile, obtaining continuous aligned fibers and high-volume production is very important for many areas such as fiber reinforcement and device manufacturing. Several techniques have been developed to align electrospun fibers and some breakthroughs have been obtained. The results are promising, but these methods need to be further improved for practical applications. In the technique of using a rotating drum as the collector only partial fiber alignments have been achieved. Few recently developed techniques can produce well-aligned fibers, but only of limited length and area [5]. In this study we obtained highly continuous and aligned fibers. We also found that except for solution prepared in 6:4 (DMSO/THF) and concentration less than 26 % did not facilitate continuous electrospinning. The linear shape and decrease in size of fibers were observed as the solid content of blend solution decreases from 30-26 %.

TABLE I. Sample composition used to make blended fibers in the solution of DMSO/THF/6:4 ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Blending ratio</th>
<th>Total Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAI/PTACM05-26</td>
<td>50</td>
<td>26 %</td>
</tr>
<tr>
<td>PAI/PTACM05-27</td>
<td>50</td>
<td>27 %</td>
</tr>
<tr>
<td>PAI/PTACM05-28</td>
<td>50</td>
<td>28 %</td>
</tr>
<tr>
<td>PAI/PTACM05-29</td>
<td>50</td>
<td>29 %</td>
</tr>
<tr>
<td>PAI/PTACM05-30</td>
<td>50</td>
<td>30 %</td>
</tr>
</tbody>
</table>

APPROACH
Continuous fibers were prepared using 26-30 % concentration of PAI and PTACM (50:50) resins in the blending solution of 6:4 (DMSO: THF) under water coagulation bath as shown in Scheme 1 (A) and (B).

SCHEME 1. Effect of concentration on the morphology of electrospun PAI/PTACM fibers (A) 27%-30% aligned fibers (B) 26 % coiled fibers.

After various PAI/PTACM blended solutions had been prepared in solution of mixed solvent system of 6:4 (DMSO: THF), they were ejected from the syringe needle at throughput rate of 100-150 ml/min in response to the tensile forces generated by the applied electric field of 8-
15 kV. Under these conditions, the preformed fiber became unstable and then it came in contact with the surface of water. The obtained fiber was highly aligned in the water bath under mechanical tension applied by the high speed winding roller. The electrospun fibers were collected together on an Alumina cylindrical drum collector at the speed of 1000-1500 rpm from this water bath. Finally vacuum dried at 190 °C for 1 hr to completely remove the solvents in vacuum chamber.

RESULT AND DISCUSSION
In this study various blended solutions were prepared with different concentration of PAI/PTACM as shown in Table I in order to investigate the effects of concentration on the physical properties and size of fibers. As shown in Scheme 1(A) highly continuous fibers were produced having concentration from 27-30 % and in Scheme 1(B) coiled fibers were formed having concentration of 26 % as showed in inset picture the path of electrospinning jet contained bending instability resulting coil like features of small loops. Figure 1(A) showed the SEM images of 27-30 % PAI/PTACM solutions with a (6:4 DMSO/THF) ratio produces continuous aligned fibers. However with decrease in concentration from 30-27 % fiber diameter also decreases from 10-3 μm respectively.

![FIGURE 1. SEM micrographs of electrospun PAI/PTACM highly aligned fibers as a function of the concentration (A) 27 %, 28 %, 29 %, 30 % at 20 μm scale (B) 26 % at 200 μm scale and 20 μm scale.](image)

We observed at 26 % concentration coil shaped highly aligned fibers were obtained. It does not facilitate electrospinning if percentage was lesser than 26 %. However regular coil shaped fibers of 26 % PAI-AL272 blend were collected only if we simultaneously decrease the collecting speed of drum. The bending perturbations increase rapidly as the solid content in the blend solution decreases as shown in inset of Scheme 1(B), and then rapidly turned into a coil shape, under the influence of the charge carried with the jet. After the electrical bending caused the path to coil, the trajectory of each short segment of the coil became almost perpendicular to its own axis [4]. The growing perturbed path of the charged jet was quickly bent into a three-dimensional coil, and was continuously floated on the water surface. Basically, the typical path of the jet was a straight segment followed by a coil of increasing diameter. As the concentration of blend starts decreasing a new electrical bending instability formed a smaller coil on a turn of the larger coil and several turns were formed. The turns of the smaller coil transformed into an even smaller coil, and finally by solidification of the coil under water coagulation bath. Water also provides a medium and the residence time for fiber to get aligned, as the polymer blend is immiscible with the aqueous phase. Hence the alignment of the fiber occurs in one dimension as shown Figure 1. That was how we collected these highly aligned coated fibers floated onto the water surface due to decrease in concentration and collecting speed of collector.

CONCLUSION
The optimal conditions to get the continuous fibers were investigated by controlling solvent composition, and concentration. It was observed that continuous fibers could be electrospun only by using mixed solvent system and with water coagulation bath. The continuity of the fibers was highly dependent on the formation of stable drop at the end of capillary tip. The onset of electrical bending instability produces the coiled fibers which were influenced by the concentration of polymer blend. In our case, we observed that 26 % concentration of the polymer blend and mixed solvent ratio of 6:4 yielded continuous coiled fibers and concentration was the most significant factor impacting the diameter and shape of fiber.

FUTURE WORK
Coiling is scientifically interesting e.g., DNA, proteins, etc. derived from nature, and a connection is being made at the nanoscale between carbon based inorganic and organic forms. We envision that such a highly aligned and coil shaped electrospun PAI/PTACM fibers will be an innovative approach and can be used for fiber reinforcement and new device manufacture such as nanoscale electrical inductors and mechanical springs.

REFERENCES
Highly Aligned Electrospun Nanofiber Yarns

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²Faculty of Textile Engineering, Technical University of Liberec, Czech Republic
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INTRODUCTION
Nanofibers have gained great attention in recent years as promising materials for building different constructs and nanodevices [1-3]. Electrospinning is a simple and inexpensive method to produce micro- or nano-fibers from molten polymers or polymer solutions in external electrostatic field. More than one hundred polymers have already been electrospun in the form of nanofiber mats/layers. Nanofibers can be made porous or hollow and can be bundled and twisted into yarns [4]. Because of their flexibility and porosity, these nanofiber yarns show great potential as materials for probing and mapping tissue fluids from a hidden internal part of the organism. We describe the probes made from different polymer blends: Polyvinylidene Fluoride (PVDF) and Polyethylene Oxide (PEO) blends, Polyacrylonitrile (PAN) and Polymethyl methacrylate (PMMA) blends, and Cellulose acetate (CA) and Polymethyl methacrylate (PMMA) blends. We developed a semi-automatic device to collect nanofibers from these polymer blends and twist them into yarns. 15-20 cm long yarns were successfully produced by using the rotating electrode with subsequent nanofiber collection and twisting on a home developed special twisting machine. These produced yarns are quite uniform; for example, PVDF/PEO yarns of ~200 microns diameter have only about 5 microns standard deviation. We studied the mechanical and wetting properties of electrospun nanofiber yarns and show that these properties are repeatable if all parameters of the twisting device are maintained under control. The auto-collection and twisting device shows a promising method for scaling it to the industrial level.

APPROACH
Materials
Polyvinylidene fluoride (PVDF) was purchased from Goodfellow Corporation. Polyacrylonitrile (PAN, Mₐ=150 kDa), Polymethyl methacrylate, (PMMA, Mₐ=120 kDa and ~996 kDa), Polyethylene oxide (PEO, Mₐ=1,000 kDa), and Cellulose acetate (CA, Mₐ=~37 kDa) were obtained from Sigma-Aldrich. Dimethylacetamide (DMAc) was obtained from Alfa Aesar. All chemicals were used as received without further purification.

Polymer blends preparation
2 g PVDF and 0.2 g PEO were dissolved in 10 g DMAc at 75°C. 1 g CA and 0.4 g PMMA (~996 kDa) were dissolved in 10 g DMAc at 75°C.

Yarn manufacturing
The prepared polymer solution was placed in a 10-mL syringe. For PVDF/PEO blends, a flexible syringe heater (Watlow, EHG SL10) was attached to the syringe to maintain the temperature at 55°C. PAN/PMMA and CA/PMMA blends were electrospun at room temperature. A rotating mandrel with four alumina bars separated from each other by 20 cm was used as a fiber collector. A high-voltage power supply (Glassman High Voltage, Inc.) was connected to the syringe through a stainless-steel needle (Gauge 20, EXEL). The flow rate was controlled at 0.2 ml/hr for all materials. A positive voltage varying between 8-10 KV was applied to the needle until Taylor cone produced. The device for fiber collection consists of two circular wire brushes with the diameter of ¾ inches each, mounted co-axially and attached to two miniature DC motors. The same device was used to form yarns by spinning the brushes in the opposite directions. The number of revolutions and the rate of twisting is controlled with totalizer counters (Crouzet 2108) and optical reflection sensors (OPTEC Technology OPB704WZ) operating in the infrared range of light thus avoiding any interference with other devices. Ambient temperature and relative humidity were maintained at 24°-25.5°C, and 55–65 RH%.

RESULTS AND DISCUSSION
Different materials were electrospun and collected by the designed twisting device. Table 1 shows the longest length of polymers which were prepared.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Length of yarn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA/PEO</td>
<td>10-15 cm</td>
</tr>
<tr>
<td>CA/PMMA</td>
<td>10-15 cm</td>
</tr>
<tr>
<td>PAN/PMMA</td>
<td>15-20 cm</td>
</tr>
<tr>
<td>PAN/CA</td>
<td>15-20 cm</td>
</tr>
<tr>
<td>PMMA</td>
<td>5-10 cm</td>
</tr>
<tr>
<td>PEO</td>
<td>2-5 cm</td>
</tr>
<tr>
<td>PVA (Polyvinyl alcohol)</td>
<td>5-10 cm</td>
</tr>
</tbody>
</table>

The yarn diameter was examined by the optical microscope (Olympus BX-51) at 10 points along each yarn (Figure 1A). The thicker the fiber band to start with,
the easier it is to produce yarns with reproducible diameters. The thinnest reproducible yarns in this work were 20 µm in diameter. The micrographs of scanning electron microscope (Figure 1B) suggest that the produced fibers are highly aligned after the collection and twisting.

![Image](image1.png)

Figure 1. (A) The measurements of PVDF/PEO yarns by the optical microscope (Olympus BX-51). (B) The SEM images of aligned PVDF/PEO fibers.

**Tensile strength**

The tensile strength was examined by the Instron (model 5582). The yarns were placed in the U-shape frames (distance: 1 cm) and mounted on the jaws of the clamps without stretching the yarns. The tensile stress of PVDF/PEO yarns (Figure 2) shows that the yarns can be stretched up to ~300% before they are broken. That is, these yarns show potential to manipulate by external force and to be used as probes.

![Image](image2.png)

Figure 2. The tensile stress vs. strain of PVDF/PEO yarns.

**Wetting properties**

The non-volatile droplets, hexadecane (HEX) and tributyl phosphate (TBP), were used for the evaluation of wicking properties of the yarns. Figure 3 shows a sequence of pictures of a hexadecane droplet during its absorption by the yarn. In order to confirm that the droplet does not evaporate during absorption experiments, but does be absorbed by the yarn, a reference hexadecane droplet was placed on a copper wire (Figure 3). The change of the droplet volume \( V(t) \) as a function of time was filmed and analyzed. The absorption kinetics for both tested liquids followed the square-root of time law, which is known as the Lucas-Washburn law [5-6] written in Eq (1)

\[
\frac{V_0 - V}{A} = c \sqrt{t}
\]

Where the \( V_0 \) is the initial drop volume, \( V \) is the drop volume at time \( t \), \( A \) is the yarn cross-section, \( c \) is the wicking constant.

![Image](image3.png)

Figure 3. A series of pictures illustrating the absorption kinetics of hexadecane droplet into the PVDF/PEO yarn. The 80 µm copper wire (left-hand) with a hexadecane droplet was used as the reference. Red arrows mean the droplet was absorbed in two directions.

The wicking constants (0.0033±0.0003 m/sec\(^{1/2}\)) in four PVDF/PEO yarns were almost same suggesting that the yarn properties are very repeatable from one sample to another.

**CONCLUSIONS**

A technique was developed to fabricate aligned electrospun nanofiber yarns. Different materials have been successfully electrospun into ordered bands and subsequently twisted into yarns. By controlling the electrospinning time and revolution rate of the proposed twisting device, we formed these yarns with repeatable transport and mechanical properties.

**ACKNOWLEDGMENT**

This work has been supported by National Science Foundation, Grant No. EFRI 0937985.

**REFERENCES**


INTRODUCTION
There are only a few medical devices that give the possibility of probing and analyzing biofluids from single cells when the amount of liquid is measured in picoliters. The main problem in the real-time cell analysis is that all existing procedures of cell piercing lead to irreversible damage of the cell membranes. In order to track the cell response to a given stimulus, the cell piercing protocol should be significantly changed. A single cell suspended or spread over a surface has the diameter varying from 10 to 70 micrometers. Therefore, for the cell operation, one requires new materials with the tip radius measured in nanometers.

Modern microfluidic devices are made of non-flexible glass/polymer/plastic-based hollow tubes [1, 2] or plates with imprinted mazes of channels. In order to take full advantage of these devices, it is desirable to equip them with a flexible probe that can be manipulated and positioned with a great accuracy in the cell proximity.

In this work, we show recent developments in design of fiber-based probes. The probe is designed with a core made of a tungsten wire that has a nano-sharp tip at the end. The skin is made of biocompatible porous nanofibers. These nanofibers are produced by electrospinning. The tungsten wire is needed to pierce the cell membrane and the fibers are needed for wicking up the biofluid from the cell. This poster discusses a technique that we developed for the preparation of the tungsten nanoneedles with the tip size measured in the range 30-300 nm. Successful experiments on cell piercing are also presented.

APPROACH
Electropolishing [3, 4] technique with a three-electrode system was used to develop tungsten needles with nano-sharp tips at the end. Platinum wire was served as a working electrode (cathode). Ag/AgCl electrode was used as a reference electrode. Tungsten wire was served as a counter electrode (anode). All electrodes were connected to a power supply and immersed into 2M KOH electrolyte. By choosing different depths of immersion, applied electric voltage and current, one can control radius of curvature, length and shape of the needle.

Once the tungsten needle with a nano-sharp tip was produced, it was wrapped with porous nanofibers around it, yet leaving the very end of the tip open. Polycrylonitrile (PAN), cellulose acetate (CA) and polymethylmethacrylate (PMMA) nanofibers were used for coating. These nanofibers were produced by electrospinning [5].

For further applications to cell piercing, the obtained probe was attached to a manipulator (Figure 1).

A set up for cell piercing is shown in Figure 2. It consists of a manipulator and an Olympus BX 51 optical microscope with an attached video camera (Diagnostic Instruments).

Smooth vascular cells and probe were observed in the optical microscope and the probe manipulation was achieved with a high accuracy. To prove that the cells were successfully pierced, we applied live-dead-cell kit [6, 7].

Kit Components:
- Component A, Calcein AM, two vials, 50 μL each, 4 mM in anhydrous DMSO.

FIGURE 1. Nanomanipulator with the needle and dish with the cells on a stage.

FIGURE 2. Set up for single cell piercing with tungsten tip.
RESULTS AND DISCUSSION
Using electropolishing, sharp nanotips were produced with different shapes. The tip radius was less than 30 nm. By controlling the current, the etched region varied between 0.3 and 2.5 mm. What is more important, these needles were long and had uniform smooth shape. In Figure 3 shows a scanning electron microscope (SEM) picture of the tungsten needle.

![SEM images of tungsten tip](image)

Applying electrospinning technique, PAN/PMMA and CA nanofibers were spun on the needle until uniform coating was achieved. However, the very end of the tip was left open, so that cell piercing can be performed.

With the newly developed set up for cell piercing, we performed experiments on biofluid probing from single cells. In order to understand the efficiency of the piercing procedure, a live-dead-cell kit was used. Pictures of cells were taken before and after piercing to analyze how the fluorescent response of the cell was changed after the piercing was performed. The live-dead assay is based on the reaction of a fluorescent reactive dye with cellular amines. When the dye was added to a Petri dish with cells, the polyanionic dye calcine is well retained within live cells. This produced an intense uniform green fluorescence in the cells (ex/em ~495 nm/~515 nm). Yet, after cell piercing was performed, the EthD-III entered cells with damaged membranes and bonded to nucleic acids producing a bright red fluorescence in dead cells (ex/em ~530 nm/~635 nm). Thus, using such a technique shows that cells can be successfully pierced with minimal damage to its membrane.

CONCLUSIONS
By implementing newly developed electropolishing regime, we were able to produce sharp tips with the tip radius less than 30 nm. Using these tips, we proved the concept: smooth vascular cells were successfully pierced with these tips. Also, by applying the live-dead cell staining method, we showed that the biofluid can be withdrawn through the produced hole in the cell.

ACKNOWLEDGMENT
This work has been supported by National Science Foundation, Grant No. EFRI 0937985. The authors wish to thank Dr. Alexey Vertegel, Viktor Maximov, Taras Andrukh and Marius Chyasnichyus of Clemson University for their help and efforts completing this research.

REFERENCES
INTRODUCTION
Living/controlled free radical polymerization was an alternative technique to prepare polymers with predictable molecular weight, narrow polydispersity and well-defined architecture. Atom transfer radical polymerization (ATRP) is the most powerful, versatile, simple and inexpensive method in controlled free radical polymerization [1].

Recently, an improved ATRP technique, activators regenerated by electron transfer ATRP (ARGET ATRP) has been developed. This method allows an ATRP process to be conducted with a very active transition metal catalyst in a tiny amount in the presence of a sufficiently large excess of reducing agent such as ascorbic acid, tin(II) 2-ethylhexanoate, glucose, etc. [2]. Additionally, the catalyst and excess reducing agent could effectively scavenge and remove dissolved oxygen from the polymerization system[3].

In the present work, silk was grafted with N,N-Dimethylaminoethyl Methacrylate (DMAEMA) through ARGET ATRP in water aqueous. During the copolymerization, CuBr$_2$ was used as catalyst, N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) was used as ligand, vitamin C (Vc) was used as reducing agent. The structure and properties of the grafted silk was investigated in this study.

APPROACH
The procedures of synthesis of the macroinitiator and surface-initiated ARGET ATRP, and characterization apparatus were provided in our previous article [4]. The weight gain was calculated as:

$$\text{weight gain} (%) = \frac{w_2 - w_1}{w_1} \times 100$$

where $w_1$ and $w_2$ denote the weight of S-Br(silk macroinitiator) and S-g-DMAEMA, respectively.

RESULTS AND DISCUSSION
The optimal grafting technic Through single factor experiments, the effects of monomer concentration, the proportion of CuBr$_2$ and PMDETA, grafting temperature and time on the silk grafting were discussed, and the optimal grafting technic was obtained: 0.306mmol/L of DMAEMA monomer, 0.16 mmol of CuBr$_2$, n (PMDETA) : n (CuBr$_2$) = 2:1, 0.15mmol/L of Vc, grafted under pH 8, at 80 °C for 2h.

FT-IR spectra FT-IR analysis (Figure 1) was used to demonstrate the presence of polymer grafted onto the silk surface. There was no weight gain for the S-Br macroinitiator (0% sample). The spectra of the silk all showed the characteristic absorption peak of amide linkage at about 1650 cm$^{-1}$ and 1530 cm$^{-1}$. However, A carbonyl peak at 1726 cm$^{-1}$ was a positive indicator for the poly (2-(dimethylamino) ethyl methacrylate) (PDMAEMA). The carbonyl peaks were clearly seen on the S-g-DMAEMA samples but not on S-Br macroinitiator. The FTIR results suggested that DMAEMA monomer was grafted on silk fabric.

Surface characteristics Figure 2 shows the surface of the S-g-DMAEMA fiber with different weight gain values. At low weight gain, the silk surface was similar to that of the untreated sample, while at higher gain a thin polymeric film partly covered the fibers. As the weight gain further increased, the film became thicker attributed to the homopolymerization. However, the homopolymer was supposed to establish strong interactions with silk, by means of physical forces or chemical bonds, because it is resistant to methanol treatments. And the homopolymer was not too much. Because in ATRP grafting system, there was no initiator in the grafting solution, theoretically the monomer could only react with the macroinitiator.

Thermal properties Figure 3 shows the DSC curves of silk with different weight gain values. The control sample
displayed an intense endothermic peak at 325 °C, attributed to the thermal decomposition of silk with oriented β-sheet structure. New endothermic peaks appeared at about 243 °C in the curve of S-g-HEMA with 21.9% of weight gain, which was attributed to specific thermal transitions of poly(DMAEMA) chain (melting). The decomposition peak of silk in the grafted samples showed a tendency to move upwards with the increase of weight gain. Hence the effect of grafting DMAEMA onto silk was to make silk more thermally stable though the change was small.

FIGURE 2. SEM photos of silk with different weight gain (a) 0%; (b) 14.7%; (c) 21.9%.

FIGURE 3. DSC curves of silk

**Crystalline Structure** In order to identify the crystalline structure of the S-g-DMAEMA before and after grafting, X-ray diffraction was analyzed as shown in Figure 4. The silk with different weight gain all exhibited a major X-ray diffraction peak at 20.5 degrees, corresponding to the crystalline spacing of 4.39 Å, which is characteristic of silk with highly ordered β-structure. The position and intensity of the major X-ray diffraction peak did not change regardless of the introduction of DMAEMA. The results indicated that the crystalline structure with oriented β-crystals was not directly modified by the graft-copolymerization reaction by ARGET ATRP method. It was also reasonable to assume that the DMAEMA monomer was grafted into the amorphous region and not in the crystalline region.

**Anti-bacterial** Table I shows the anti-bacterial properties of quaternized S-g-DMAEMA. It could be seen that the quaternized silk had good anti-bacterial properties to both Staphylococcus aureus and Escherichia coli. The inhibition rate increased with the weight gain increasing, and nearly have no change with the increase of washing times.

![Graph](image)

**FIGURE 4. X-ray diffraction intensity cures of silk**

<table>
<thead>
<tr>
<th>Washing times</th>
<th>Quaternized S-g-DMAEMA with 14.7% of weight gain</th>
<th>Quaternized S-g-DMAEMA with 21.9% of weight gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Staphylococcus aureus</td>
<td>Escherichia coli</td>
<td>Staphylococcus aureus</td>
</tr>
<tr>
<td>0</td>
<td>90.74</td>
<td>84.27</td>
</tr>
<tr>
<td>20</td>
<td>90.46</td>
<td>83.18</td>
</tr>
<tr>
<td>50</td>
<td>90.35</td>
<td>82.86</td>
</tr>
</tbody>
</table>

The percentage rate data in the table were inhibition rates.

**CONCLUSIONS**

In conclusion, we have successfully developed a method for producing silk fibroin grafted DMAEMA using ARGET ATRP method. FT-IR characterization of the grafted silk showed that DMAEMA had been grafted on the silk surface. The quaternized S-g-DMAEMA had good anti-bacterial property.

**ACKNOWLEDGEMENT**

This research was funded in part through a grant by National Natural Science Foundation of China (Grant No. 50673071) and the Natural Science Foundation of Jiangsu Province (No. BK2010254) and A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

**REFERENCES**

INTRODUCTION

Porous materials are of large interest to many fields of engineering, and the behaviors of liquids on these porous materials are often unknown. There are several theories that aim to explain interactions of liquids with porous materials. These theories assume that liquid penetrates the material and flows through it following Darcy’s law. [1] However, this flow scenario becomes questionable when the pore size decreases to nanometers and the materials permeability drops down significantly. It is natural to assume that the drop would spread over the material, since it would be a non-porous. Thus, Tanner’s law should describe the expected spreading kinetics. [2]

\[ R \sim (\sigma \Omega^2 / \eta)^{1/10} \] (1)

Where \( R \) is the radius of the drop base, \( \Omega \) is volumetric flow rate, \( \eta \) is liquid viscosity, \( \sigma \) is surface tension, and \( t \) is time. Hence, the drop radius should scale as \( t^{1/10} \). In order to check this hypothesis, we used nanoporous aluminum membranes (Whatman Anodisc 25). Because of the special processing conditions, each side of the membrane had different size of pore openings. Therefore, each membrane was tested twice, once on the bottom side and once on the top.

APPROACH

Three liquids, Tri-butyl phosphate (TBP), Diethyl Phthalate (DEP), and Hexadecane, were selected because of their low vapor pressures, which are around 5000 times smaller than water’s. All membranes were placed in a Petri dish, and held off the bottom of the dish by Scotch double-sided sticky tape. The tape also held them in place. The droplets were deposited on the membranes from a small 25 µm wire. All the experiments were run in approximately two minutes. The droplet spreading during that time was recorded with a high-speed camera placed on the Olympus MVX10 microscope. Their diameters and volumes were calculated from the collected pictures.

RESULTS AND DISCUSSION

The first set of experiments presented two types of kinetic laws for the drop spreading. One being a square root of time kinetics found for the 20 nm bottom side membrane pore openings. The second being Tanner’s law of kinetics, which droplets on all other pore size membranes showed and is shown in Figure 2. Figure 1 shows the membrane that has the best representation of square root of time kinetics. The red and blue lines match up with the blue and green dots respectively on the 20nm bottom side membrane.

The second set of experiments were geared towards determining the differences in kinetics based on different liquids. Figure 1 shows spreading kinetics of a Hexadecane droplet. The hexadecane results roughly match up with TBP because they have around the same liquid properties, in terms of surface tension, viscosity, and vapor pressure. On the other hand, DEP followed along closely with Tanner’s law because it is much more viscous then TBP and hexadecane.
CONCLUSION
In conclusion, the membranes with 20nm pore openings demonstrate an unexpected dynamics of droplet spreading. All other membranes tested presented Tanner’s law of drop/substrate interaction. TBP and Hexadecane presented similar square root of time kinetics, while DEP presented Tanner’s kinetics.

ACKNOWLEDGMENT
This work has been supported National Science Foundation, Grant No. EFRI 0937985 and partially by U.S. Air Force contract FA8650-09-D-5900.

REFERENCES
Development of Surface Differential Scanning Calorimeter for Evaluation of Evaporative Cooling Efficiency

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INTRODUCTION

Materials for protective clothing have high fiber density that significantly decreases their permeability. A reduction of the material’s permeability results in a dramatic decrease of the natural efficiency of evaporative cooling of the human body and, in many cases, it leads to thermal stresses [1, 2].

Our group has been working on the design of a new nanostructured materials that would enable the evaporative cooling and prevent the body temperature from rising. We designed and fabricated a Surface Differential Scanning Calorimeter (SDSC) which is able to assess the efficiency of the materials under development. SDSC measures temperature ($\Delta T$) or power ($\Delta P$) differences between two heating systems: one heater works as a reference simulating the body surface with standard protective clothing on it; the other one contains a material in question. This way, the measured difference assesses the evaporative cooling efficiency of the structure in question. SDSC consists of a computer, data acquisition system (Keithley 2700), two power suppliers (TDK-Lambda ZUP) to heat thin flexible Kapton heaters and RTD (Resistance Temperature Detector) sensors placed at the center of the heaters. Computer runs a LabView program implementing proportional integral (PI) control algorithm and data logging. SDSC can be run in two modes: a constant power mode and a constant temperature mode. In the constant power mode, the equivalent power is supplied to the systems, while temperatures of the heater plate are monitored. A temperature difference between the heater system with and without test fabric is used as a characteristic of the evaporative efficiency of the fabric. In the constant temperature mode, the systems are maintained at a constant temperature while the power supplied to each system is monitored. The difference between the power levels required to maintain the heater systems at the same temperature is used as another characteristic of the efficiency of the evaporative cooling. We show preliminary results demonstrating the measurement capability of the fabricated system.

APPROACH

Design and Fabrication of SDSC. The design of the system is based on the standard test method for thermal and evaporative resistance of clothing materials using a sweating hot plate (ASTM- F1868). As shown in Figure 1, SDSC has two heating systems. In order to prevent the heat loss from one side of the heating films (Figure 1(a)), the heating systems are placed onto the styrofoam insulation (Figure 1(d)). Therefore, the heat flows only in the upward direction. The heaters (Figure 1(a)) in both systems are covered entirely by cotton fabrics (Figure 1(b)). Cotton fabrics are dipped into water (Figure 1(c)) to keep them wet thus simulating a body surface. The first system, which is a control system, is isolated from ambient environment by covering the fabric surface with a plastic film to obtain the temperature and power values for non-evaporating condition. The second system, which is a test system, is used to test the evaporative heat transfer of the fabric construct.

The SDSC equipment is placed inside a controlled temperature/humidity chamber (Blue-M, Model: VP-100AT-1). The temperature and relative humidity (R.H.) fluctuations are in the range of $\pm 0.5^\circ\text{C}$ and $\pm 2\%$, respectively.

Testing of SDSC reliability. In order to ensure that both heating systems are identical, we conducted a systematic study. Cotton fabrics from both heating systems were removed and the SDSC system was left with only bare heater plates. LabView program was run in the power control mode varying the power in
the range of 0.07W-1.9W. In addition, we conducted experiments in the temperature control mode varying the temperature in the range of 25°C-44°C.

Testing of Evaporative Efficiency. We conducted three sets of experiments (1-comparison, 2-2mm air gap, 3-5mm air gap) in order to measure the evaporative efficiency at three different relative humidity values. Evaporation was suppressed in 1st heater system by covering wet fabric surface with plastic film and silicon foam. 1st heater system was kept the same for each test. 2nd heater system was arranged with glass separator (2mm, 5mm) (Figure 2(a)) then covered with insulting silicon foam (Figure 2(b)). 1st and 2nd heater systems were the same at comparison setup. Humidity chamber was controlled the environmental temperature and humidity. Temperature was kept at 35.0±0.5 °C and R.H. was changed from lower to higher value for each setup.

![Figure 2](image)

FIGURE 2. 2nd Heater System (a): Glass separator, (b): Insulation silicon foam.

After the environment in the chamber was equilibrated, the temperature control mode was executed at 40°C for both systems and difference between the power values (ΔP) was recorded. Then power control mode was executed and the averaged power value of the 1st system was put as a power set point. The difference between the temperature values was determined.

RESULTS AND DISCUSSION
Testing of SDSC shows that both heater systems are identical. Power released to the heaters can be controlled to better than ±0.01W of the set point and temperature of the heater plates can be controlled to better than ±0.1°C of the set point.

Table 1 shows ΔP and ΔT versus relative humidity from three sets of test. Comparing the results, we observe that there is 0.1°C difference between two systems and it is not changing with the chamber R.H. This difference is very small compared to the ΔT values of the other sets. 5mm air gap set up shows up to 7.3°C ΔT at lowest R.H. (38%) and decreases to 3.2°C ΔT at 83% R.H. 2mm air gap set up shows up to 1.6°C ΔT at lowest R.H. (40%) and decreases to 0.8°C ΔT at 86% R.H.

<table>
<thead>
<tr>
<th>2nd Heater System</th>
<th>ΔP (Watt)</th>
<th>ΔT (°C)</th>
<th>R.H. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparison of Systems</td>
<td>0.01</td>
<td>0.1</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.1</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.1</td>
<td>78</td>
</tr>
<tr>
<td>2mm air gap</td>
<td>0.08</td>
<td>1.6</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>1.2</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>0.8</td>
<td>86</td>
</tr>
<tr>
<td>5mm air gap</td>
<td>0.78</td>
<td>7.3</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>0.63</td>
<td>5.4</td>
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</tr>
<tr>
<td></td>
<td>0.39</td>
<td>3.2</td>
<td>83</td>
</tr>
</tbody>
</table>

CONCLUSION
We successfully fabricated and tested the SDSC equipment. The equipment was capable to assess the evaporative cooling efficiency with high precision and reliability.

ACKNOWLEDGMENT
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REFERENCES
Imbibition of Liquids into Capillaries

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INTRODUCTION
Typically, the absorption of liquids by napkins and fibrous probes is measured in tens of milliseconds. In many cases, the amount of liquid (drop or pool of liquid) and wetting properties of the materials are the most important parameters controlling the absorption kinetics. To design and define the engineering parameters of fiber-based probes we studied the absorption kinetics of liquids into model fibrous materials. The main effort was concentrated on the understanding of the effect of pore size on kinetics of liquid rise into capillaries. We tested the applicability of the available theories against the experimental results for the liquid uptake by a single capillary with hundred to thousands microns in diameter.

APPROACH
We studied the kinetics of absorption of liquids by single glass capillaries (Wale Apparatus). Tributyl Phosphate (TBP), hexadecane (VWR) were used as the model liquids. The absorption process was filmed using high-speed MotionPro X3 camera (Princeton Instruments). To control the liquid/capillary contact, we used 2-D linear micromanipulator (VT-21, Micos USA). The images were quantitatively analyzed in MatLab.

RESULTS
An example of our image analysis of the meniscus movement is shown in Fig. 1 where we plot the meniscus position versus time. As seen from the graph, for the tubes with the inner diameters of hundreds micrometers, the liquid fills the capillary in tens of milliseconds! We used the following Bosanquet equation to describe the liquid flow through a capillary of radius R vertically immersed into the pool of a wetting liquid:

\[
\frac{d}{dt}\left(\rho R^2 \frac{dh}{dt}\right) + 8\pi \mu h \frac{dh}{dt} + \rho g \pi R^2 h - 2\pi R \sigma \cos \theta = 0
\]

where, \(h\) - is the front position, \(t\) - is the time, \(\rho\) - is the density, \(\sigma\) - is the surface tension and \(\mu\) - is the dynamic viscosity of the liquid, \(\theta\) - is the contact angle, \(g\) - is the acceleration of gravity. This equation states, that the liquid column rises in a capillary due to the surface tension force \(2\pi R \sigma \cos \theta\), which action is opposed by the gravitational force \(\rho g \pi R^2 h\), viscous (friction) force \(8\pi \mu h \frac{dh}{dt}\) and the force of inertia \(\frac{d}{dt}\left(\rho R^2 \frac{dh}{dt}\right)\) acting on the propagating column.

In the poster, we present the analysis of front propagation as well as its theoretical description using the Bosanquet equation. We showed that the Bosanquet equation cannot describe the process of liquid absorption by small capillaries. After introducing one more force, the force caused by meniscus friction, we were able to completely describe the kinetics of meniscus advance. Analyzing the experimental data we concluded that the absorption process can be divided into two stages characterized by their characteristic height and characteristic velocity.

ACKNOWLEDGMENT
We acknowledge support from the National Science Foundation through the Grant No. EFRI 0937985.

REFERENCES
STATEMENT OF PURPOSE
In this study, high surface area, microporous, nanofibrous cellulose membranes will be functionalized with catalytic molecular polyoxometalates (POMs) in order to examine their self-decontamination performance. The POMs will be grafted to traditional microporous nanofibrous electrospun cellulose membranes as well as super high surface area channeled cellulose nanofibers. It is hypothesized that by using the channeled cellulose nanofibers, the surface area of traditional microporous nanofibrous cellulose membranes will be increased providing more active sites to which the POMs will bind. This increase in POM active sites will enhance the catalytic degradation performance of methyl parathion, an organophosphate simulant of the chemical warfare agent (CWA) VX. It is also hypothesized that the adsorption and penetration of parent compounds and decomposition products in the cellulose membrane will be load dependent. The overall objective of this work is to incorporate high loads of self-decontaminating compounds in semi-permeable, breathable, textile substrates and characterize their self-decontaminating performance in order to reduce the penetration of CWAs and maintain thermal comfort in personal protective apparel for defense personnel.

INTRODUCTION
Polyoxometalates are heteropolyanions, otherwise known as polymeric oxoanions, formed by the condensation of more than two different oxoanions. These negatively charged nanoclusters of oxide and transition metal ions in their highest oxidation state have the general formula of $\text{XM}_{12}\text{O}_{40}$. $X$ can be $\text{Si}^{4+}$ or $\text{P}^{5+}$ etc, and $M$ can be tungsten, molybdenum, vanadium and other metals. The oxoanions Mo, W, V, Nb, and Ta are present as acidic elements in aqueous solutions and polymerize to form polyanions at low pH. In their free acid form polyoxometalates are referred to as heteropoly or isopoly acids. POM free acids and their salts act as strong acids and have been widely used as acid catalysts and oxidation catalysts that yield better oxidation performance than hydrogen peroxide, ozone, and molecular oxygen when environmental profiles and efficiency of oxidation are taken into account [1]. Vanadates, niobates, tantalates, molybdates, tungstates, and mixed metal heteropolyanions make up the different classes of polyoxometalates. Mixed metal polyanions can include molybdovanadates, tungstovanadates, niobotungstates, and molybotungstates [2]. The majority of polyanions with tetrahedrally-coordinates heteroatoms have structures based on what is known as the Keggin anion (Pope, 1983).

H$_3$PV$_2$Mo$_{10}$O$_{40}$ is a heteropolylybdovanadate free acid and is classified as an $\alpha$-Keggin structure. Figure 1 illustrates what is known as an $\alpha$-Keggin type polyoxometalate [3]. Figure 2 illustrates the rapid, reversible redox changes that classify these nanoparticles as catalytic and self-regenerating. When the oxidation reaction occurs, the POM is reduced. Oxygen or any oxidant in the system can then re-oxidize the POM to its original state [4].

![Figure 1: Structure of an $\alpha$-Keggin type polyoxometalate](image1)

![Figure 2: Catalytic cycle of polyoxometalate nanoparticles](image2)

POMs have been incorporated into fibers and fabrics such as polyacrylic, nylon, cotton, carbon-based fabrics such as electrospun Estane$^\text{®}$ microfibers, and polyurethane sponges in order to examine their catalytic self-decontamination of volatile organics, air toxins, and chemical warfare agents. POMs grafted to cotton and other cellulosic substrates have been examined for breathable protective performance apparel [5], [6], [7]. POMs have also been incorporated into electrospun, microporous, nanofibrous cellulose membranes in order to increase the number of active POM binding sites on fibers. This increase in surface area has enabled increased catalytic decontamination performance due to the large fiber surface area [5], [6].

POMs such as H$_3$PV$_2$Mo$_{10}$O$_{40}$ have been prepared by Dr. Craig Hill of Emory University and can be incorporated into micro- or nano- electrospun fibers and film coatings for fabrics [8]. 10-Molybdo-2-vanadophosphoric acid has been incorporated into cellulose substrates to degrade volatile organics and chemical warfare agents such as CEES and VX [5], [6], [9].
The current approach to achieving enhanced methyl parathion degradation with POMs in channeled cellulose nanofibers entails the fabrication of the high surface area cellulose membrane, its characterization, POM synthesis, the grafting of POMs to the cellulose membrane, and the characterization of the POM functionalized membranes.

**APPROACH**

**Fabrication & Characterization of High Surface Area Cellulose Membranes**

Electrospun cellulose acetate nanofibers will be converted to channeled cellulose nanofiber membranes via alkaline hydrolysis in a process known as deacetylation, which involves treating a cellulose acetate fibrous membrane with sodium hydroxide and ethanol for an hour. The membrane is then washed, neutralized, and dried under vacuum. FTIR analysis is performed in order to confirm the removal of the acetyl group and the complete conversion of the cellulose acetate to cellulose fibers [10], [11].

The pore size, pore size distribution, adsorption, penetration, fiber size, fiber morphology, and surface area of these membranes is measured using a porometer, a scanning electron microscope (SEM), and a gas adsorption technique known as BET. The measurement of additional mechanical and thermal properties also helps to characterize the strength and composition of the membranes [11].

These electrospun regenerated cellulose nanofiber membranes can be loaded with the self-decontaminating POM H₅PV₂Mo₁₀O₄₀ via a grafting process. In this process a reactive oxygen species (ROS) is created by reacting the hydroxyl groups on the surface of the cellulose with a diisocyanate, which thus provides a grafting site for H₅PV₂Mo₁₀O₄₀. The reaction is performed under a nitrogen purge in the presence of a tin (II) catalyst, a toluene solvent, and a swelling agent [12]. The membranes are then submerged in a hexane solvent containing methyl parathion for designated time intervals. The catalytic degradation, adsorption, and penetration of the methyl parathion is determined via high-performance liquid chromatography (HPLC) and weight analysis.

**Polyoxometalate Synthesis:**

10-Molybdo-2-vanadophosphoric acid (H₅PV₂Mo₁₀O₄₀) is synthesized via a known process involving the reaction of sodium metavanadate (NaVO₃) with disodium phosphate (Na₂HP0₄) and the resulting compound’s reaction with concentrated sulfuric acid and sodium molybdate (Na₂MoO₄) in methanol. The acid is purified to obtain the correct stoichiometry. After extraction the resulting compound is a reddish orange crystal [13].

**RESULTS & DISCUSSION**

Experiments are currently underway, and results will be forthcoming. Expected outcomes include the use of the microporous cellulose nanofiber membrane will lead to an increase in the fiber surface area. The increased surface area will produce more active sites to which H₅PV₂Mo₁₀O₄₀ will bind. More active sites for molecular POM binding will increase the catalytic degradation of methyl parathion. It is also predicted that the adsorption and penetration of parent compounds and decomposition products in the membrane will be load dependent.

**CONCLUSIONS**

(To be Determined)

**ACKNOWLEDGMENT**

This research is funded by the Department of Fiber Science and Apparel Design at Cornell University. Great thanks are extended to Dr. S. Kay Obendorf, Laurie Lange, and Dong Jin Woo of Cornell University for their help and efforts in the development of this project.

**REFERENCES**


Mechanism of Surface Roughness Development in Melt Spinning of Blend Fibers for Artificial Hair

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STATEMENT OF OBJECTIVE
We found that the fibers with highly developed surface roughness can be formed in the melt spinning of polyamide 6/poly(ethylene terephthalate) blend fibers under certain spinning conditions. To elucidate the necessary conditions for the development of roughness on the fiber surface, melt spinning of polymer blends of various combinations of polymers was carried out under a wide-range of spinning conditions. The mechanism of roughness development was analyzed further through wide angle X-ray diffraction, differential scanning calorimetry and observation of axis and cross sections of blend fibers with a scanning electron microscope and an optical microscope, meanwhile the spinning conditions for the development of rough surface have been expounded with more details.

INTRODUCTION
Surface roughness is one of the most important characteristics in the production of fibers for artificial hair. Conventional technologies for the formation of surface roughness include three methods: (i) enhancement of the formation of spherulites in the melt spinning of polyamide fibers, (ii) extraction of soluble component after formation of blend fibers, and (iii) mechanical scraping of fiber surface by sand-blasting. On the other hand, we found that the fibers with highly developed rough surface can be formed in the melt spinning of polyamide 6 (PA6)/poly(ethylene terephthalate) (PET) blend fibers when the extrusion temperature was lower than the melting temperature of PET. According to these clues, melt spinning of blend fibers of various combinations of polymers were carried out in this study with the aim of elucidating the rule for the development of surface roughness. Crystallizability and melting temperature of each component, and extrusion temperature for blend fibers of various combinations of polymers were the factors of interest, meanwhile the mechanism for the formation of roughness was investigated by analyses of thermal properties and the observation of the axis and cross sections of blend fibers.

EXPERIMENTAL
The materials we applied in this research were polyamide 6 (PA6) (NOVAMID 1020, DSM Japan Engineering Plastics), poly(ethylene terephthalate) (PET) (PETMAX RE530A, TOYOBO Co., Ltd.), amorphous co-polyester (co-PCT) (AN004, Eastman Co., Ltd.), amorphous co-polyamide (co-PA) (NOVAMID X21, DSM Japan Engineering Plastics), poly(butylene terephthalate) (PBT) (PBT 500LP, Polymers Co., Ltd.), PBT copolymer (co-PBT) (PBT 600FP, Polymers Co., Ltd.) and polypropylene (PP) (Y2000GP, Idemitsu Kosan Co., Ltd.). Dry-blended polymer pellets were melted and extruded through a twin screw extruder, metering pump and a spinning nozzle. In all cases, the highest temperature in the twin screw extruder was set to be higher than the melting temperatures of both components, whereas the low spinning temperatures were achieved only by changing the temperature in the vicinity of the spinning nozzle. Composition of major/minor components was fixed at 80/20 wt%. Melt spinning was carried out at a take-up velocity of 270 m/min. Crystalline structure and thermal properties of as-spun blend fibers were analyzed by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) measurements, respectively. Surface morphology, axis section and cross sections of blend fibers were analyzed by a scanning electron microscope (SEM) with the Energy Dispersive X-ray Detector-analysis (EDXD) and an optical microscope (LM).

RESULTS AND DISCUSSION
Melt spinning of blend fibers of various combinations of polymers were carried out. Characteristics of polymers used as major and minor components, and the results of the possibility of the appearance of surface roughness for a series of blend fibers are summarized in Table I.

<table>
<thead>
<tr>
<th>Major component</th>
<th>Melting temperature Tm (°C)</th>
<th>Minor component</th>
<th>Melting temperature Tm (°C)</th>
<th>Possibility of appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>220</td>
<td>PET</td>
<td>257</td>
<td>O</td>
</tr>
<tr>
<td>co-PA</td>
<td>△</td>
<td>PET</td>
<td>257</td>
<td>O</td>
</tr>
<tr>
<td>PA6</td>
<td>220</td>
<td>co-PCT</td>
<td>△</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>165</td>
<td>PBT</td>
<td>223</td>
<td>O</td>
</tr>
<tr>
<td>PP</td>
<td>165</td>
<td>co-PBT</td>
<td>170</td>
<td>X</td>
</tr>
</tbody>
</table>

△: Amorphous polymer, O: Rough surface, X: Smooth surface
When there was a development of surface roughness, it was enhanced by decreasing the extrusion temperature. This table suggested that the necessary conditions for the development of surface roughness are (1) the minor component needs to be crystallizable, (2) the major component needs to have melting temperature (or glass transition temperature in case of amorphous polymer) lower than the melting temperature of minor component, and (3) the extrusion temperature needs to be lower than the melting temperature of the minor component.

The detailed structural analyses of the co-PA/PET fibers prepared with the extrusion temperatures of 235, 245 and 255 °C were carried out by WAXD and DSC measurements. Use of amorphous polymer as the major component enabled us to analyze the crystalline state of the minor component with higher precision. Results of WAXD measurement of the co-PA/PET blend fibers are shown in Figure 1.

A shoulder at around the diffraction angle of 26°, which can be assigned to the (100) reflection of PET triclinic crystals [1], was observed only for the fibers prepared at the extrusion temperatures of 235 and 245 °C. According to previous research, well-developed crystalline structure of PET could be formed only at high take-up velocities in the melt spinning single-component PET fibers. On the other hand, the result in Figure 1 clearly indicated that the crystallization of PET occurred in the melt spinning of co-PA/PET blend when the surface roughness was developed because of low extrusion temperatures. The crystalline state of PET component of those co-PA/PET blend fibers was also analyzed by the DSC measurement. The DSC results with photographs of surface morphology of blend fibers are shown in Figure 2. It was found that the fibers prepared with the three different extrusion temperatures showed melting peak of PET in that the fiber with smooth surface showed slightly lower melting temperature. When samples were started to be cooled without holding time after heating up to 300 °C in the DSC measurement, clear exothermic peak appeared only for the samples with rough surface, indicating that the PET component in the fibers with rough surface keeps high crystallizability even after its melting.

REFERENCES

The Challenges of Material Selection for Compliant Robotic Surfaces

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ellisom@clemson.edu

INTRODUCTION
There is current interest in the field of robotics in the research and development of intelligent-interactive actuated systems capable of adapting in response to changes in their environment. Advancement towards the goal of enabling adaptive robotic behavior has been increased by results from recent efforts in the disciplines of electrical and computer engineering. The design of these systems additionally includes the aim to minimize constraints on dynamic performance. Essentially unrestricted range of motion is being developed, enabling the actuated system to have precise control over any and all movement during adaptive reconfiguration. Robotic systems having these ideal qualities are of increasing interest for use in applications involving direct human-machine interaction. Systems actuated in response to human interaction with their external interface are conceived to support, assist, and improve the quality of life of individuals co-occupying space in that robot’s environment. Such human-interaction actuated systems vary greatly in scale and even more so in their application possibilities. Projected uses of these systems support the living experiences of persons ranging from the sick and the elderly to the adolescent and adventurous.

As intelligent robotic systems become increasingly ubiquitous in daily life, the material selection for sheathing and substrates of those systems correspondingly become more critical. Actualization of the developing systems will be dependent on material selection as the source from which necessary system properties are derived. For example, in healthcare settings sheathings need to be hygienic for maintenance requirements of sterile surfaces, while in educational settings sheathings need to be durable and resistant to damage from prolonged exposure to the rough handling of children.

Clemson University’s Institute for Intelligent Materials, Systems and Environments (iMSE)[1] includes teams working on the design and development of human-assisting systems. A cross-departmental group of architects and electronic and computer engineers has applied the existing technology of pneumatic muscle actuators[2] (figure 1) to their production of interactive robotics.[3]

Inspired by the fluid-like movement of biological systems in nature, they have created a novel combination design of muscles and skin (the substrate and sheathing) which they can program and control. Air pressure pumps are used as the controllers of pneumatic muscles and are electronically programmed according to desired end results. Muscles are attached directly to a continuous compliant substrate to form a unified system that moves in response to programmable actuation.

Working physical prototypes of this robotic and computational system have driven the group’s implementation of it as the fundamental technology on which to build all further continuous compliant robotic surface design. With pneumatic muscle technology being fairly well developed, the next element to consider in optimizing the system design is material selection.

APPROACH
Optimization of the use of this muscle technology is dependent on the material selection, and the design of the substrate and sheathing “skin” used in the assembly of the interactive, adaptive and dynamic continuum surface. The response of different materials to the actuated muscle movement will correlate directly with the properties of the skin in which those muscles are embedded. Observable motion results from the force applied on the substrate material by the muscles consequent to controlled regimes of applied air pressure that result in a 3-dimensional surface displacement. This displacement is, however, clearly dependent on the intrinsic mechanical properties of the materials comprising the substrate and sheathing on which the muscles apply force. Specifically, the ultimate displacement associated with an applied force will be impeded by less compliance in, and the time to achieve this limit will be affected by the viscous nature of, the skin.

Experiments are currently being performed to obtain data on the dynamic response of a constant continuous material with various arrangements of attached pneumatic actuators. The present material being used is a simple cellular foam sheet. The data from these tests provide the graphical relation between pneumatic actuator arrangements and resulting compliant surface configuration.

The aim of performing this testing is to support predictive modeling of the robotic continuum surface response to the muscle action for the present substrate. We will extend this procedure to include alternate substrate material systems, testing under constant substrate sample size, muscle placement and pressure application regimes. Data compiled from these efforts will provide comparable
dynamic performance results that directly correlate to the combined muscle and continuous material system. The current experimental procedure can thus be used throughout our continued research to validate theoretical material system designs. The development of optimal substrate and sheathing material(s) can be experimentally driven with such testing.

The results of dynamic behavior tests on sample substrates can be used by the team to compile a portfolio of material properties, muscle types, and resulting final configurations for design use.

Tensile loading tests can provide data on many of the critical material property requirements necessary for the target application. Inasmuch as the extent of deformation does not approach the ultimate elongation limit of the skin system, tensile testing to failure is not needed, nor is fatigue failure testing. Of critical importance to our research is the small deformation viscoelastic behavior. The results from these tests will aid in decision making for material system design of the robotic systems surface.

RESULTS AND DISCUSSION
The testing procedure mentioned previously was performed on two alternate substrate materials (figure 2). Testing of these sample continuum surfaces occurred under identical conditions, with the single exception of their substrate material. The lighter colored material on the left of the image pairs was common commercial foam while the darker substrate on the right of the pairs was a polymeric material regularly used as yoga mats.

Simple visual observation makes evident the influence of material properties on the actuated continuum surface response. These images reveal essential parameters for material selection including the limiting effect substrate density has on system performance which is clearly evident in the reduced response of the yoga mat material.

CONCLUSIONS
The relatively low resolution visual data presented here shows the validity of our proposed testing of different material systems, in that there is a marked difference in the response of these two material systems. The source of this behavior is a direct consequence of the intrinsic properties of the material selections for the continuum surface substrate. Material testing will be a fundamental contribution to deriving application specific parameters that will dictate the optimal material system design and selection which will in turn optimize performance quality of the interactive robotic continuum surface.

FUTURE WORK
Additional substrate candidates will be evaluated by muscle-actuated displacement data acquisition, and material property testing. The results from material testing will provide property information intrinsic to the skin and substrate to further optimize the design of the material system composition. The projected result of our research efforts will be the production of detailed guidelines for the engineering of optimal system substrates, which will enable optimization of the actuated continuum surface performance. The initial exploratory efforts made in developing these actuated robotic continuum surfaces, as reported here, will enable the future enhancement of the human-robot interaction experience. The thoughtful selection of the materials critical in intelligent, adaptive systems dedicated to educational, leisure, work and health applications, has the promise to advance the quality of human life.[3][4][5][6]

ACKNOWLEDGMENT
The research was supported in part by an NSF/IIS/SHB award (proposal 1116075).

REFERENCES
[1] The Clemson University Institute for Intelligent Materials, Systems and Environments [iMSE], www.CU-IMSE.org
Melt Spinning of Soy Flour-based Fibers

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OBJECTIVE
This study is directed towards developing a melt-process for converting soy flour-based biomaterials into non-food, value-added products such as fibers, nonwovens, and films. In this paper, we discuss the blending of soy flour with polyethylene (PE), fiber processing via melt route, and assessment of fiber properties.

INTRODUCTION
Soy protein is available in different grades: soy protein isolate (SPI) contains 90% protein, soy protein concentrate (SPC) contains 70% protein, and soy flour (defatted) contains about 50% protein. Defatted soy flour was used as the filler in polyethylene matrix to produce PE-soy fibers; soy flour is considerably inexpensive at 50 cents/lb [1]. Soy flour by itself is brittle with poor thermoformability to enable it to be drawn into practical fibers [2]. However, blending it with traditional melt spinnable polyolefins, like PE, may enable tailoring of new nonfood applications of soy flour while maintaining mechanical properties and allowing processability via traditional manufacturing routes. Such fibers would possess some level of biodegradability as they originate from renewable resources [3]. Additionally, such fibers provide the advantage of reducing dependence on oil-based resins, whose market has been greatly affected by the recent volatility in crude oil prices. Polyethylene resin now sells for about 95 cents/lb when it was only 50 cents/lb a decade ago [4]. Therefore, a significant market has come open in recent years for using soy flour as a particulate reinforcement or filler in polyethylene for producing fibers, nonwovens, and films.

EXPERIMENTAL
Soy flour was obtained from ADM Specialty Food Ingredients. The flour was compounded in a DSM mixture with a suitable grade of polyethylene (PE). It was observed that dispersion of soy flour in the PE matrix was poor and often caused cooking and burning of the soy flour resulting in poor quality fibers in addition to limited processability in terms of drawing the melt into fibers. Hence compatibilizers were introduced which enhance dispersion and processability [2].

RESULTS AND DISCUSSION
The viscosity of PE-soy was measured using an ARES rheometer with a cone and plate geometry at low shear rates of $0.1\text{s}^{-1}$ to $10\text{ s}^{-1}$ at $150^\circ\text{C}$. From these measurements, the power law parameters were calculated following the constitutive power low model, equation 1.

$$\eta = \text{m} \cdot \gamma^{n-1}$$ (1)

Viscosity and power law parameters are shown in Table I. It was observed that PE-soy blend had lower viscosity compared to pure PE and essentially low shear thinning behavior as its power-law constant was 0.63 as compared with 0.24 for pure PE. This is likely attributed to the presence of the compatibilizer that allows easy slide of PE-soy layers. The blends were successfully melt-spun into continuous lengths of fibers, as displayed in Fig. 1.

The microstructure of PE-soy fibers, shown in Fig. 2, was studied using S4800 scanning electron microscope. Images of the cross-section of the fiber indicate a well consolidated morphology with no clear distinction of phases. Inspection of the lateral surface also reveals generally uniform features of the fibers though some elements of fibrils are also observed.

Spun fibers were tested for their tensile properties according to ASTM D2256 on ATS tensile testing machine. Tensile modulus, tensile strength and failure strain of the blend fibers are listed in Table II. The base PE fibers had tensile modulus of 457MPa and strength of 52MPa while the soy-PE fibers had a tensile modulus of 823MPa and tensile strength of 49MPa.

CONCLUSIONS
Studies demonstrated that blends of PE-soy can be successfully spun into fibers via continuous, melt spinning route. The soy-PE fiber tensile properties are comparable to those of the pure PE. The use of soy flour, the cheapest of all the soy protein alternatives, provides for economically viable and greener olefinic fibers without sacrificing the mechanical integrity.

ACKNOWLEDGMENT
This research was funded through the United Soybean Board USB Grant # 9480 and utilized equipment acquired through The Engineering Research Centers Program of National Science Foundation Award Number EEC 9731680. Thanks also go out to Dr. Russ Egbert, ADM Company.
REFERENCES

FIGURE 1. Spool of PE-soy fibers with an average diameter of 30±3µm

FIGURE 2. SEM micrographs showing the crosssection and lateral surface of PE-soy fibers

TABLE I. Viscosity as function shear rate, and the power law parameters of PE-soy blend and pure soy.

<table>
<thead>
<tr>
<th>strain rate (s⁻¹)</th>
<th>Base PE</th>
<th>PE-soy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>1334</td>
<td></td>
</tr>
<tr>
<td>0.18</td>
<td>1000</td>
<td>852</td>
</tr>
<tr>
<td>0.5</td>
<td>921</td>
<td>609</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power law constant</th>
<th>Consistency index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24</td>
<td>272</td>
</tr>
<tr>
<td>0.63</td>
<td>470</td>
</tr>
</tbody>
</table>

Table II. Tensile properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base PE</td>
<td>457± 220</td>
<td>52 ± 8</td>
<td>728±216</td>
</tr>
<tr>
<td>PE-soy</td>
<td>823±341</td>
<td>49±4</td>
<td>344±120</td>
</tr>
</tbody>
</table>
The Effects of Silver Antimicrobials on the Physical and Thermopysiological Properties of Burn Pressure Garments

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STATEMENT OF PURPOSE

It is aimed to progress the healing characteristics and to increase the effectiveness and functions of the pressure garments to burn scar treatments by providing infection risks.

INTRODUCTION

The biocidal properties of silver compounds have been known for thousands of years and have been increasingly used nowadays to impart antimicrobial properties to textile materials for hospital use. The purpose of their uses is to prevent and control the formation of hypertrophic scars by applying counter pressure to the affected area. Pressure garments normally contain elastic yarns and the exerted pressures are determined by clinical trials for to produce custom-made garments\cite{2,3,4,5,6}. Hygiene is required for the use of these garments in order to increase the effectiveness and functions \cite{12}. The textile structure and the fiber content have to be considered into account to obtain the best antimicrobial performance.

APPROACH

In this study, a highly elastane nylon/spandex warp knitted fabric, used for burn pressure garments, was treated with a silver-based antimicrobial by pad-dry-cure method. The physical and thermopysiological properties were tested in order to evaluate the thermophysiological comfort properties of the burn garments. Cause they should be worn for up two years in order to achieve recovery. Pressure garments should provide hygiene during a long period of use. So they should be comfortable to the patient. The results were found not statistically significantly different after treatment.

RESULTS and DISCUSSION

Silver Efficacy

Silver was observed for the treated samples (Fig.1). XPS analysis were conducted at NCSU AIF Department.
Textile Protection and Comfort Center (TPACC) in the College of Textiles at NC State University, for the characterization of heat and moisture transport properties that contribute to thermal comfort.

**TABLE 1. Stiffness and drapeability properties of the treated fabric**

<table>
<thead>
<tr>
<th></th>
<th>MD (Machine Direction)</th>
<th>CD (Cross Direction)</th>
<th>Mean (Face &amp; Back)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stiffness</td>
<td>17mm</td>
<td>16mm</td>
<td></td>
</tr>
<tr>
<td>(Average Bending Length (c),mm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drapeability</td>
<td></td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>(Drape Coefficient)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2. Thickness, weight and water absorption (wicking) properties of the fabric**

<table>
<thead>
<tr>
<th></th>
<th>Thickness (mm)</th>
<th>Mass per Unit Area (g/m²)</th>
<th>Absorption Capacity (g.g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.57</td>
<td>163.86</td>
<td>1.19</td>
</tr>
</tbody>
</table>

**Total Thermal Resistance (R达标), [(Δ°C)(m²)/W], Apparent Total Evaporative Resistance (Rref), [(ΔkPa)(m²)/W], Intrinsıc Thermal Resistance (R内), [(Δ°C)(m²)/W], Apparent Intrinsıc Evaporative Resistance (Rref), [(ΔkPa)(m²)/W], Iₜ, [clo], indicates the thermal resistance measured in units of clo which indicates the insulating ability of the test material, the Iₜ value, or permeability index, indicates the effect of skin moisture on heat loss as in the case of a sweating skin condition, Total Heat Loss (Qt or THL), [W/m²], a measure of the total amount of heat that can be transferred from the sweating test plate to the ambient environment.**

**CONCLUSIONS**

Elastane percentage of the fabric sample was a 80% Nylon 6.6 / 20% Spandex in warp knitted structure. Silver was detected on the fabrics by XPS analysis. Physical properties and thermophysiological properties were tested after antimicrobial treatments by a silver antimicrobial chemical. It was observed that bursting strength, drapeability, air permeability properties were decreased while stiffness were increased after antimicrobial treatments. According to thermophysiological test results, the treated samples provide microclimate to the skin by preventing wet feeling to the patient. This ability also prevents odor and provides comfortable wearing to the patient which eliminates infection risks by increasing rehabilitation rates and decreasing costs. Silver antimicrobial was used because it has an ability to increase the wound healing by preventing infection on the burn and hypertrophic scars during rehabilitation period.

**FUTURE STUDY**

Silver, Triclosan and its additives, QAC and QAC dendrimers are planned to be applied to different elastane percentage fabrics used for the rehabilitation of burn scar treatments.

**REFERENCES**

[5] AATCC Test Method 61 – 2007 “Colorfastness to Laundering; to Evaluate the Washing Durability of the Treated Fabrics”.
Imparting Multifunctional Properties to PES/Cotton Woven Fabrics by Fluorocarbon and Silver-based Finishing Agents

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INTRODUCTION
Recently consumer demand for functional textile materials and products has been increasing. Water repellency and antibacterial activity are important applications in textile processing. To obtain the water repellency of fabrics, various compounds such as fluorocarbon and silicon resins have been used. Several types of organic or inorganic antimicrobial agents can be used in the textile industry. But silver compounds are widely preferred for the applications in general textiles because they have no toxic and carcinogenic activities [1]. On the other hand the combination of water repellency and antibacterial activity provide multifunctionality to the textile fabrics and can give possibility to design safer products especially for medical textiles. Because of that the water repellent finishing improves the antibacterial activity of the product [2].

In this work antibacterial finishing agent synthesized in our previous works [3] was applied to the PES/cotton blended woven fabrics with or without water repellent agent. Antibacterial activity and water repellent properties of all treated fabrics were compared.

MATERIALS AND METHOD
Antibacterial finishes were prepared by calcium phosphate based silver doped nano powders. 20 g of antibacterial powder was added to 80 ml distilled water and was ground by attritor mill. Poly ethylene glycol (PEG 1,000) was added to the solution to prevent agglomeration. 25 ml of antibacterial solution was added into mixture of 10 ml isocyanate based cross linking agent and 65 ml aqueous emulsion of an acrylic copolymer under mechanical stirring.

Fluorocarbon based finishing chemical (Orgaguard FC 2100) was kindly provided from Organik Kimya Company/Turkey.

Antibacterial and water repellent chemicals were applied to 65/35% PES/cotton fabric samples (plain weave, 120 g/m²).

In the first part of the work, fabric samples were treated with antibacterial (A1) and water repellent (A2) finishes. Antibacterial solution and water repellent solution having concentrations 25 g/l and 30 g/l respectively were prepared and applied to the samples separately. In the second part, antibacterial (25 g) and water repellent (30 g) solutions were added to the 1000 ml distilled water and applied to one group of fabrics (A3). In the third part, after the antibacterial finishing, fabric samples were treated by water repellent finish (A4). pH value of all solutions were adjusted to 5.5 by acetic acid. Finishing was performed using a laboratory vertical padder (ATAC F350) for impregnation and a laboratory stenter (Rapid mini dryer QC A1708) for drying and curing. Sample codes and application conditions are given in Table I.

TABLE I. Application conditions of treatments.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Finish</th>
<th>Pick-up (%)</th>
<th>Dry</th>
<th>Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Antibacterial</td>
<td>75</td>
<td>160 °C, 2 min</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>Water repellent</td>
<td>80</td>
<td>120 °C, 1 min, 160 °C, 1:30 min</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>Antibacterial + water repellent</td>
<td>75</td>
<td>120 °C, 1 min, 160 °C, 1:30 min</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>First step: antibacterial</td>
<td>75</td>
<td>160 °C, 2 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second step: water repellent</td>
<td>80</td>
<td>120 °C, 1 min, 160 °C, 1:30 min</td>
<td></td>
</tr>
</tbody>
</table>

All fabric samples were washed 20 times and after each ten washing cycles water repellency of the samples were tested by contact angle measurement (Krüss DSA 100). Laundering processes were carried out according to BS EN ISO 26330 standard (5A program). A wascator laundering machine was used with 4 g/l of detergent. Reference fabrics and all treated fabrics were tested against Escherichia coli (ATCC 25922) according to the ASTM E 2149 method in Anadolu University Center for Applied Environmental Research. Air permeability of the treated fabric
samples were measured by Textest AG FX 3300 according to ISO 9237 standard.

RESULTS AND DISCUSSION
Contact angle of water droplet on the fabric samples were measured by the goniometer sessile drop method. Images of treated and untreated samples and contact angle measurements were given in Figure 1 and Table II respectively.

![Figures](image)


<table>
<thead>
<tr>
<th>Sample code</th>
<th>Contact angle (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 WC***</td>
</tr>
<tr>
<td>A2 (WR*)</td>
<td>121.3</td>
</tr>
<tr>
<td>A3 (AB**+WR)</td>
<td>124.3</td>
</tr>
<tr>
<td>A4 (AB1-WR2)</td>
<td>133.9</td>
</tr>
</tbody>
</table>

* WR: water repellent, **AB: antibacterial, ***WC: washing cycle

Antibacterial and air permeability test results of the treated fabric samples are shown in Table III and IV.

**TABLE II. Contact angle measurements of the samples.**

**TABLE III. Antibacterial test results of the samples.**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>R (log)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 WC</td>
</tr>
<tr>
<td>A1 (AB)</td>
<td>2.82</td>
</tr>
<tr>
<td>A3 (AB+WR)</td>
<td>2.20</td>
</tr>
<tr>
<td>A4 (AB1-WR2)</td>
<td>2.56</td>
</tr>
</tbody>
</table>

**TABLE IV. Air permeability test results of the samples**

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air permeability (L/m²/s)</td>
<td>326.00</td>
<td>329.00</td>
<td>302.93</td>
<td>300.62</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>17.39</td>
<td>14.25</td>
<td>19.34</td>
<td>13.71</td>
</tr>
<tr>
<td>Conf. Int. (95%)</td>
<td>Min</td>
<td>317.20</td>
<td>321.79</td>
<td>293.16</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>334.80</td>
<td>336.21</td>
<td>308.07</td>
</tr>
</tbody>
</table>

CONCLUSION
In this work silver doped calcium phosphate based antibacterial solution developed in our previous works was applied to the PES/cotton blended woven fabrics with or without water repellent finishes. Water repellent and antibacterial performances of all samples were compared. Contact angle measurement results showed that water repellent properties and washing fastness of the fabric samples to which water repellent finishes were applied following antibacterial (A4) are better than other samples. It means that antibacterial application before water repellent finish increases the water repellency of the fabrics without significant decrease on the air permeability of the fabric samples.

Strong antibacterial activity was obtained by all applications. All treated fabric samples preserved their antibacterial activities even after 20 laundry cycles.

ACKNOWLEDGMENT
This work was funded by the Anadolu University under Project No. 083315.

REFERENCES
Effects of Plasma Etching on Self-decontaminating Properties of Magnesium Oxide Nanoparticles in Polypropylene Fibers

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Email: lel72@cornell.edu

OBJECTIVES
The tested hypothesis was that increased surface exposure of magnesium oxide (MgO) in the polymer composition will enhance the degradation of methyl parathion due to the surface destructive adsorption mechanism of degradation of the MgO. The overall objectives of this research can be separated into three different sections. The first objective was to determine an optimum time and MgO loading for best possible degradation of methyl parathion. The second objective was to make and etch fibers to test the hypothesis above. The third objective was to determine if the etched fibers were more effective at degrading the methyl parathion when compared to the non-etched fibers, and to fibers not containing MgO.

INTRODUCTION
Pesticides pose a danger for agricultural workers through dermal absorption. Currently, some Personal Protection Equipment (PPE) involves impermeable barriers, which can be very uncomfortable for the user. The impermeable barriers prevent the penetration of toxic chemicals, but they also block the passage of water vapor and air from flowing through the material. In this study, fibers were developed with the ability to degrade methyl parathion. These modified fibers could potentially be incorporated into conventional fabric structures. In this way, agricultural workers could have both protection from harmful chemicals, and increased comfort.

APPROACH
First, MgO nanoparticles were tested with a 62.5 mg/L methyl parathion hexane solution with varying reaction times (1, 10, 100, 1000 min) and varying amounts of MgO loadings (50, 100, 200, 400 mg). The resulting amounts of methyl parathion and its main degradation product, 4-nitrophenol, were determined quantitatively with HPLC-MS analysis (Figure 1). Then, fibers with self-decontaminating functionality were developed by incorporating MgO nanoparticles into a polypropylene (PP) melt extruded fiber (25/75 wt% MgO/PP). This was followed by performing oxygen plasma etching on these fibers for 12 min at a low power to expose a maximum surface area of MgO. This resulted in four different fiber types: unetched polypropylene (PP), etched polypropylene (PP-E), unetched polypropylene containing MgO (MgO/PP), and etched polypropylene containing MgO (MgO/PP-E). Finally, the four different fibers (calculated to have 50 mg MgO near the surface, or equivalent volumes of PP) were all tested with the same 62.5 mg/L methyl parathion/hexane solution for one of two reaction times (1 or 1000 min). The concentration of methyl parathion for each sample was again determined by HPLC-MS analysis.

RESULTS AND DISCUSSION
Looking only at the methyl parathion concentration (Figure 2a), it is observable that as the amount of MgO in the samples increased, the amount of methyl parathion in the solution decreased. This result shows that by increasing the MgO loading from 50 mg to 100 mg, it is possible to get the same amount of methyl parathion degradation (e.g. about 70% loss) in a much faster time (e.g. 1000 min with 50 mg MgO versus 1, 10, and 100 min with 100 mg MgO). This occurs again when the MgO loading is increased from 100 mg to 200 mg MgO (e.g. 100% degradation of methyl parathion in 1000 min with 100 mg MgO versus 1 min with 200 mg MgO). This occurred because the increased concentration of MgO led to more surface active sites. This supports the idea that with lower loadings of MgO, there are fewer active sites that become occupied quickly. This
means that either site competition is occurring, or it takes a longer time for the methyl parathion to migrate to the empty active sites. The calculated total 4-nitrophenol concentration data (Figure 2b) inversely corresponds with the methyl parathion data. When all the methyl parathion is degraded, 4-nitrophenol was the only degradation product that remained on the surface.

![Figure 2](image)

**FIGURE 2.** MgO nanoparticles and methyl parathion reaction with varying reaction times and MgO loadings characterized by (a) decreasing methyl parathion concentration and (b) corresponding 4-nitrophenol concentration increase.

Due to the difficulty of controlling fiber diameter because of variability in the fiber spinning method, it is not possible to observe any differences caused by etching using SEM. However, it was possible to observe differences based on MgO content. Fibers containing MgO were significantly larger, with a mean fiber diameter of 90 µm, and greater variability, with a standard deviation of 29 µm. Conversely, the fibers without MgO had a mean fiber diameter of 59 µm, and a standard deviation of 7 µm. TGA showed that the MgO/PP fibers had 20.2 wt% MgO, the MgO/PP-E fibers contained 18.4 wt% MgO, and both PP-E and PP fibers had 0 wt% MgO. It was also necessary to determine how much mass was lost due to etching, so that an equivalent amount of etched fibers could be weighed out for each etched fiber treatment jar compared to an unetched fiber treatment. It was noted that more weight was lost from the MgO fibers (2.76% mass lost) compared to the PP fibers (0.48% mass lost), which in conjunction with the differences seen from the TGA data, indicates that MgO is being lost by performing the etching process.

All four fiber types (PP, PP-E, MgO/PP, MgO/PP-E) showed very little degradation of methyl parathion after the one minute reaction time. After 1000 minutes, MgO/PP-E showed the most degradation, followed by MgO/PP, PP, and then PP-E had the least degradation of methyl parathion. The MgO containing fibers were the only ones that actually showed significantly more degradation in the 1000 minute reaction times over the 1 minute reaction times (Table I). It was determined that the etching procedure was successful in exposing more magnesium oxide surface area, resulting in fibers that can more effectively degrade organophosphates and other pesticides.

**TABLE I.** Methyl parathion concentration after degradation with fiber samples based on reaction time and a starting concentration (t=0) of 62.5 mg/L. Reported values are average mg/L with standard deviation in parentheses.

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>After 1 min of Reaction Time</th>
<th>After 1000 min of Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>59.8 (0.10)</td>
<td>60.3 (0.26)</td>
</tr>
<tr>
<td>PP-E</td>
<td>60.2 (0.16)</td>
<td>62.2 (0.40)</td>
</tr>
<tr>
<td>MgO/PP</td>
<td>59.4 (0.10)</td>
<td>53.3 (0.14)</td>
</tr>
<tr>
<td>MgO/PP-E</td>
<td>59.8 (0.12)</td>
<td>48.7 (0.68)</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

It was confirmed that MgO stoichiometrically degrades methyl parathion by way of destructive adsorption. The etching process exposed more surface area of the MgO on the surface of the MgO/PP fibers, which were more effective in degrading methyl parathion. This means that the developed etched fibers were able to degrade methyl parathion better than unetched fibers.

**REFERENCES**


A Novel Silver Sulfadiazine-loaded Electrospun Nanofiber Wound Dressing

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STATEMENT OF PURPOSE
In his study biodegradable and biocompatible polymers (PCL-Poly(Ɛ-caprolactone) and PEO-poly(ethylene oxide)) were electrospun as nanofibers. As a model of wound dressing, electrospun PCL/PEO/PCL layered nanofiber webs was studied and silver sulfadiazine was added to PEO solution as a drug. The fiber morphology and diameter were determined by scanning electron microscopy.

INTRODUCTION
Wound dressings are medical technical textile products which protect the wound from bacterias and infections, also help healing process of wound. Nowadays, finding a new generation of biopolymers and the development of new production techniques as an alternative to traditional wound dressing, functional wound dressing materials can be produced. Silver sulfadiazine is used for drug release. Silver sulfadiazine is a topical sulfonamide/silver antibacterial used as a topical burn cream on burns, including chemical burns. It prevents the growth of a wide array of bacteria, as well as yeast, on the damaged skin. Silver sulfadiazine is typically delivered in a 1% cream or aqueous suspension. Well-known proprietary brand names are Sliverex, Silvadene, Silvazine and Flamazine [1].

The electrospinning method is one of the simplest methods among all the preparation of fibrous mats as extracellular matrix (ECM) and scaffolds produced from electrospun nanofibers that mimic the structure and biological functions of naturally occurring ECM. Thus nanofibers provide a better environment for cell adhesion and proliferation [2, 3].

APPROACH
Electrospinning method contains a high voltage supplier, a solution charger unit, a collector and a solution feeder unit. Firstly high voltage is applied to the polymer solution and a voltage difference is formed between the nozzle tip and collector. The voltage difference causes the deformation of droplet into a Taylor cone shape [4]. When the electrostatic force overcomes the surface tension of polymer solution, jet or jets of solution are ejected from the nozzle. And then continuous nanofibers are collected on to the collector. Advantage of electrospun nanofibers is used in order to improve the healing of second degree burns. Poly(Ɛ-caprolactone (PCL) and poly(ethylene oxide) (PEO) biodegradable and biocompatible polymers were electrospun. As a model wound dressing, electrospun PCL/(PEO + silver sulfadiazine)/PCL layered nanofiber webs was studied. (See figure 1)

Figure 1: Layer by layer model of wound dressing

PCL was prepared at a concentration of 9% (w/w) in an 80:20 mixture of methylene
chloride (MC):dimethyl formamide (DMF) (v:v). 3.5% (w:w) concentration of PEO and 1% (w:w) concentration of silver sulfadiazine

RESULTS AND DISCUSSION
Different nanofiber layers are seen clearly from SEM images. (Fig. 1) In these layers drug can be encapsulated. Also using SEM images average fiber diameter was calculated as 330-380 nm. When PCL nanofibers are smooth and uniform, PEO nanofibers are fine but include beads. These bead formations effects nanofiber morphology.

%1 silver sulfadiazine loaded nanoweb was examined using SEM, average fiber diameter recorded as 200-250 nm. In figure 2 SEM images show silver sulfadiazine particles. This demonstrates, silver sulfadiazine was loaded into nanofibers successfully and nanofibers can be used as drug delivery vehicles. In the web there are no beads and fiber morphology is better than without silver sulfadiazine nanofibers.

Figure 2 : SEM images Nanofiber wound dressing with silver sulfadiazine

CONCLUSION
Silver sulfadiazine particles are loaded into nanofibers to be released into the wound. Also finer fibers are obtained and less bead formation is observed when silver sulfadiazine is added in PEO solution.

FUTURE WORK
As a next step, this work will focus on in vivo studies established on rats. Painkillers, anti-inflammatory drugs, growth factors can be added other than silver sulfadiazine if necessary. Controlled drug release tests must be done over an extended period to avoid frequent changes of wound dressing.

Keywords: wound dressing, electrospun nanofibers, silver sulfadiazine

REFERENCES
Enzymes have increasingly gained importance as biocatalysts in textile wet processing. They are bulky protein compounds with only a small portion of their structure being their highly specific “active site” where the catalytic reaction occurs. Enzymes are large high-molecular weight protein structures with highly specific active sites within the molecule that perform the catalytic reaction. Enzymes are widely used for preparation and finishing of cotton fabrics, degumming of silk, anti felting of wool, and also finishing of polyester, although there are many more processes like dyeing and printing of various substrates using enzymes, yet to be commercialized.

The application of enzymes on fabric both by exhaust and padding process, leaves large amounts of enzymes deactivated in the exhaust bath. In other words we achieve good processing with enzymes but the exhaustion of the enzymes on to the fabrics is 20-25% If we could reuse the enzymes from the exhausted bath there will be very less in the effluent and the efficiency of the process also increases. The present project aims at using maximum amount of enzymes present in the treatment bath, by replacing enzymes with simpler compounds that mimic the behavior of these biocatalysts which could significantly increase the reaction rate, facilitate the enzymatic process and decrease costs. The key point in this project is whether enzymes could be replaced with simpler compounds that mimic the behavior of these biocatalysts.

This work focuses on reactions of Oxidoreductases in connection with oxidative bleaching of cellulosic materials. Thus by using different types of enzymes like Glucose oxidase, Laccase. Glucose oxidase belong to oxidoreductases enzymes which is capable for producing H$_2$O$_2$. GO enzyme consist Flavin adenine dinucleotide (FAD) as a cofactor which is replaced by Vitamin B$_2$ Riboflavin, which leads to an increase in the amount of H$_2$O$_2$. By applying biomimetic compounds for the active sites of these enzymes we also try to gain a more profound knowledge of the fundamental mechanisms of the catalytic reaction of these enzymatic systems. Honey and glucose oxidase in combination leads to efficient bleaching as a result one can bleach and simultaneously impart antimicrobial finish on fabric. This antimicrobial property imparts resistant to microbial attack even after 40 washes. Thus biomimicking the enzyme in combination with natural polymers have led to a different line of research and simultaneous bleaching and finishing is also achieved on cotton fabrics.

**Keywords**: Enzyme, Wet Processing, Biomimicking, Glucose oxidase(GO), Riboflavin.
REFERENCES


Microwave Heating Study of Carbon Nanofiber Nanocomposites

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INTRODUCTION
Electrical and thermal conductivity of materials are typically correlated, while some applications, for example thermoelectric, require these parameters to be controlled independently. Such independent control of thermal and electromagnetic properties can be achieved by using nanocomposite materials. High aspect ratio, high conductivity carbon nanofibers (CNF) allow significantly improving microwave response of the nanocomposite using low fraction of nanofibers mixed with the matrix materials. Microwave absorption by carbon nanoparticles based composite materials finds numerous applications including cancer treatment1, electromagnetic interference shielding and radar absorption materials2. Interaction of carbon nanoparticles with microwaves is a subject of active ongoing research, and the mechanism of the microwave absorption by carbon nanoparticles is still poorly understood3.

APPROACH
In this study, nanocomposite materials were produced by mixing a small amount of conductive carbon nanofibers (CNF) with Paraplast®, which has low thermal and practically zero electrical conductivity. When the fraction of nanofibers in the paraffin matrix is very low (below 1%), the thermal properties of nanocomposites are essentially the same as those of pure Paraplast®, while electromagnetic properties are significantly different. Three types of paraffine-based composites were fabricated, using two types of commercially available nanofibers (graphite nanofibers, Aldrich, and PR-24-XT-LHT nanofibers, Pyrograf) and a 50/50 nanofiber (Aldrich)/cobalt nanoparticle mixture (10-12 nm, STREM Chemicals) (Fig.1). The nanocomposite samples were heated in a microwave oven and the heating rates were measured. The results demonstrate that the heating rate of nanocomposites increases with the increase in CNF concentration. Qualitative explanation of the observed dependence is given in the theoretical section.

CONCLUSIONS AND FURTHER WORK
The paraffin-based nanocomposites heating rate during the microwave irradiation was measured. The heating rate increases significantly with increasing nanoparticle concentration. The dependence is close to linear, which agrees qualitatively with the theoretical predictions. Further analytical and numerical modeling is required to better understand the observed trends.

ACKNOWLEDGMENT
This research was funded by Air Force Research Laboratory.

REFERENCES

FIGURE 1. Scanning electron micrographs of Sigma-Aldrich (left) and Pyrograph (right) carbon nanofibers.
Upper Body Sweat Rate, Skin Temperature, and Clothing Microclimate Distribution During Winter Cycling with Air Flow

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sjyoo@khu.ac.kr

STATEMENT OF PURPOSE/OBJECTIVE
The aim of this study is to investigate physiological responses during the winter cycling using body mapping technique for developing an upper cycling wear.

INTRODUCTION
In today’s energy and climate era, clothing and textiles field also pay attention to sustainability. Cycling is a way to promote ‘low carbon, green growth’ as well as healthy lifestyle. The development of high performance cycling wear can contribute to the environment because an offer of comfortable environment in terms of clothing can drive an increase of cycling population and promote of health. In particular, an air flow in winter cycling can affect physiological responses.

This study was conducted to investigate the sweat rate, skin temperatures, clothing microclimate and subjective sensations of the upper body during cycling using body mapping technique and to examine effects of the air flow on physiological responses.

METHOD
Participants and experimental clothing
Ten healthy male volunteers with the following characteristics were recruited (mean±SD): age 22.5±1.8yr, height 178.9±3.4cm, body weight 70.4±5.4kg and BSA 1.88±0.1m². After being informed, each participant provided written consent to the procedures, which were approved by the Commission for IRB of Kyung Hee University (KHU IRB 2010-014). The subjects wore long-sleeved shirts (205g), long pants (422g) and panties (73g) and participated in a randomised order, on four different days.

Experimental conditions and test protocols
All tests were conducted in a climatic chamber (12±0.5°C and 50±5%RH) under two different conditions: with air flow (2m/s) (WAF) and without air flow (0m/s) (CON). Air flow is produced by a 76cm diameter pan. Trials were conducted each day at the same hour in order to exclude the effects of circadian rhythms. Subjects arrived at the laboratory and rested for 30 minutes after setting up the equipment and changing clothes. During trials, subjects sat still on a cycling (Ergometer X1, Kettler, Germany) while exposed to each condition for 90 minutes (2 set of exercise (40min) and rest (5min)).Participants commenced cycling at 50W (55rev/min, 5min) and then the work rate was increased 75W.

Measurements
Local sweat rate (PA 42025, Sartorius Corp., Germany) were measured with body mapping technique and the right side of upper body was subdivided into 18 body parts (A1 ~ A9, P1 ~ P9) (Figure 1) (Havenith et al., 2008). Whole body weight loss (CH3G-150IG-H, Sartorius Corp., Germany) was measured. Skin temperatures (six spots: chest, abdomen, scapula, back waist, upper arm and lower arm) and clothing microclimate (four spots: chest, abdomen, back, upper arm) were measured with data recorder (MSR12 Signal Data Recorder, MSR Electronics GmbH, Switzerland). These measures were taken every one minute. Subjective sensations were determined by ratings of thermal sensation (11-point scale, -5=very cold, +5=very hot) and wet sensation wet sensation (11-point scale, +5=very wet, -5=very dry) (Winakor, 1982) and thermal comfort (7-points scale, 1=comfortable, 7=uncomfortable) on five body parts: shoulder, chest, back, upper arm and lower arm, and recorded every 10 minutes during cycling and every 5minutes during resting.

RESULTS AND DISCUSSION
Sweat rate
Overall, local sweat rates were higher in posterior (P1~P9) than those in anterior (A1~A9), and particularly, those of P2, P3 and P4 in body parts were high. All of upper body parts had high sweat rate in CON conditions and effects of air flow were big particularly in P2 and P4 (p<.01, Table 1). Whole body weight loss was higher in WAF than that in CON, at 163g/m² and 228g/m², respectively.
<table>
<thead>
<tr>
<th></th>
<th>Body mapping of sweat rate in upper body (unit: mg/cm²)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A1</strong></td>
<td>7.7±3.7, 15.6±5.5</td>
<td><strong>P1</strong></td>
</tr>
<tr>
<td><strong>A2</strong></td>
<td>15.4±7.7, 28.9±13.7</td>
<td><strong>P2</strong></td>
</tr>
<tr>
<td><strong>A3</strong></td>
<td>10.0±4.3, 17.7±6.6</td>
<td><strong>P3</strong></td>
</tr>
<tr>
<td><strong>A4</strong></td>
<td>16.1±7.2, 30.0±14.0</td>
<td><strong>P4</strong></td>
</tr>
<tr>
<td><strong>A5</strong></td>
<td>9.8±4.1, 15.6±7.9</td>
<td><strong>P5</strong></td>
</tr>
<tr>
<td><strong>A6</strong></td>
<td>7.7±2.8, 14.3±7.2</td>
<td><strong>P6</strong></td>
</tr>
<tr>
<td><strong>A7</strong></td>
<td>8.4±3.9, 14.5±6.7</td>
<td><strong>P7</strong></td>
</tr>
<tr>
<td><strong>A8</strong></td>
<td>5.7±2.1, 11.0±3.3</td>
<td><strong>P8</strong></td>
</tr>
<tr>
<td><strong>A9</strong></td>
<td>6.2±3.6, 12.1±4.2</td>
<td><strong>P9</strong></td>
</tr>
</tbody>
</table>

**Skin temperatures**

Both in WAF and CON, skin temperature was the highest in the back waist and this parameter decreased in the following order: chest, abdomen, scapular, upper arm and lower arm (p<.01). Effects of air flow in skin temperatures were high in lower arm and scapula (Table II).

<table>
<thead>
<tr>
<th></th>
<th>Skin temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WAF</strong></td>
<td><strong>CON</strong></td>
</tr>
<tr>
<td>Chest</td>
<td>30.99±1.34</td>
</tr>
<tr>
<td>Abdomen</td>
<td>30.36±1.82</td>
</tr>
<tr>
<td>Scapula</td>
<td>30.09±1.53</td>
</tr>
<tr>
<td>Back waist</td>
<td>32.47±1.26</td>
</tr>
<tr>
<td>Upper arm</td>
<td>29.43±1.52</td>
</tr>
<tr>
<td>Lower arm</td>
<td>25.51±2.43</td>
</tr>
</tbody>
</table>

*The Δt means a difference between with air flow(WAF) and without air flow(CON).*

**Clothing microclimates**

Both in WAF and CON, temperature inside clothing was the highest in the scapula and this parameter decreased in the following order: upper arm, chest and abdomen (p<.01). Humidity inside clothing was the highest in the chest and this parameter decreased in the following order: back, abdomen and upper arm(p<.01, Table III).

<table>
<thead>
<tr>
<th></th>
<th>Clothing microclimates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WAF</strong></td>
<td><strong>CON</strong></td>
</tr>
<tr>
<td>Temp. inside clothing (°C)</td>
<td>Chest 25.13±2.3</td>
</tr>
<tr>
<td>Abdomen</td>
<td>19.90±3.6</td>
</tr>
<tr>
<td>Scapula</td>
<td>26.99±1.8</td>
</tr>
<tr>
<td>Upper arm</td>
<td>25.66±2.3</td>
</tr>
<tr>
<td>Humidity Inside clothing (%RH)</td>
<td>Chest 45±14</td>
</tr>
<tr>
<td>Abdomen</td>
<td>39±9</td>
</tr>
<tr>
<td>Scapula</td>
<td>39±15</td>
</tr>
<tr>
<td>Upper arm</td>
<td>32±10</td>
</tr>
</tbody>
</table>

*The Δt means a difference between with air flow(WAF) and without air flow(CON).*

Mean temperature inside clothing was 2.5±0.5°C higher in WAF than that in CON at 23.94±0.81°C, 26.44±0.42°C in CON, respectively, and mean humidity inside clothing was 11±5%RH higher in WAF than that in CON at 40±8%RH, 51±12%RH, respectively. According to the time course, microclimate temperature decreased whiles microclimate humidity increased.

**Subjective sensations**

Thermal sensation, wet sensation and thermal comfort were the highest in the back part and these parameters decreased in the following order: chest < shoulder < upper arm < lower arm (Figure 2). Also, all subjective sensations were less hot, less wet and less uncomfortable in condition with air flow than those in CON condition.

**CONCLUSION**

The upper cycling wear is required the differentiation with detailed body parts for alleviating thermal burden during cycling. Particularly, the centers of upper body in both the anterior and posterior sides need to be considered in an aspect of the sweat management.

**ACKNOWLEDGMENT**

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No.2010-0006475).

**REFERENCES**


“Green” Composites Using Soy Protein Resin and Novel Low-cost Carbon Source-based Bacterial Cellulose

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STATEMENT OF PURPOSE
A novel low cost carbon source, sugar containing soy flour extract (SFE), was obtained from defatted soy flour (SF) to culture bacterial cellulose (BC). The enriched protein remaining in SF was used as resin to form BC reinforced ‘green’ composite. The goal of this research was to fabricate soy protein based membrane-like green composite with excellent tensile and thermal properties and inexpensively grown BC.

INTRODUCTION
BC nanofibers produced by Acetobacter xylinum, are fully biodegradable and have same chemical structure as the plant-based cellulose. However, BC fibers display many unique characteristics including high purity, high degree of polymerization, high crystallinity, high tensile strength, high modulus and strong biological adaptability [1-4]. Many pure sugars such as glucose, sucrose, fructose, etc. and sugar alcohols such as mannitol, xylitol, sorbitol, etc., have been used as carbon source for BC culture [5]. However, these sugars and sugar alcohols are expensive and, hence, are not ideal for large scale, inexpensive BC production.

Defatted soy flour (SF), an inexpensive material (about $0.20/lb), is obtained as a by-product after extracting oil from the soybeans. It is commercially available and consists mainly of protein (52-54%) and sugars (30-32%). The sugars in SF include fructose, glucose, sucrose, raffinose and stachyose [6]. Fructose, glucose and sucrose have been used routinely as carbon sources for BC production [7]. To obtain higher protein content from SF, the sugars are removed in the form of SFE, a by-product. SFE is a mixture of five sugars and, if used as obtained, can be an inexpensive carbon source for producing BC. The present research discusses the use of SFE as a carbon source to produce BC.

After removing SFE from SF, the residual purified protein (PSF) has higher protein content of 65-70%. PSF based resin has been shown to have better tensile properties than those of SF based resin [8]. This is because plasticizing sugars have been removed. PSF resin also has higher interfacial bonding with ramie fibers compared to SF resin [8]. As a result, composite using PSF resin have much better mechanical properties than those using SF resin.

APPROACH
SFE was extracted from SF by dissolving water-soluble sugars in water. BC cellulose was cultured using Acetobacter xylinum, ATCC 23769 in SFE containing culture medium at 30°C incubator for 10 days. Thin membrane-like BC-PSF resin composites were fabricated using BC and PSF resin obtained after separately producing the two. Tensile and thermal properties of the composite were characterized. BC, SF and PSF resin sheets and BC-SF resin composites were prepared and characterized and properties compared. Weight contents of BC in all composites were maintained to approximately 50%.

RESULTS AND DISCUSSIONS
FIGURE 1 shows SEM images of freeze dried BC and freeze dried BC-PSF resin composite. The composite was not hot pressed and hence shows pores. In FIGURE 1 (a), the BC network and porous structure can be observed clearly at the surface of the membrane. FIGURE 1 (b) shows the structure of BC-PSF resin composite. PSF resin penetrated into the BC network structure and filled in most of pores of BC which were filled when the composite was hot pressed.

Table I lists the tensile properties (Young’s modulus, tensile strength and tensile strain) of BC, SF and PSF resin sheets as well as BC-SF and BC-PSF resin composites. The results indicate that PSF resin and BC-PSF resin composite have higher Young’s modulus and tensile strength than those of SF resin and BC-SF composite, respectively. The data indicate significantly higher PSF resin properties (modulus and tensile
strength) due to high protein content in the PSF resin (67%) compared to SF resin (53%). In addition, the SF resin contains low molecular weight sugars which plasticize the resin. This is evident in higher fracture strain and lower Young’s modulus obtained for SF compared to PSF resin. The higher properties of the PSF resin get reflected in the BC-PSF composite properties as well. The data in Table I confirm higher modulus and strength for PSF resin based composites compared to SF based composites.

**TABLE I.** Tensile properties of BC, soy protein resin and BC-soy protein resin composites

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>2493</td>
<td>78.9</td>
<td>5.7</td>
</tr>
<tr>
<td>SF resin</td>
<td>62.3</td>
<td>7.5</td>
<td>110.7</td>
</tr>
<tr>
<td>PSF resin</td>
<td>104.3</td>
<td>7.5</td>
<td>23.4</td>
</tr>
<tr>
<td>BC-SF resin composite (50 wt% BC)</td>
<td>1178</td>
<td>43.3</td>
<td>3.4</td>
</tr>
<tr>
<td>BC-PSF resin composite (50 wt% BC)</td>
<td>1231</td>
<td>47.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

*: Values in the parentheses are % coefficient of variation values.

Figure 2 shows typical TGA thermograms obtained for the BC-SF composite and BC-PSF composite. These TGA curves confirm that the BC-PSF resin composite has better thermal stability than that of BC-SF resin composite. The degradation temperature, T_d, for BC-SF composite was found to be around 205ºC compared the 220ºC obtained for BC-PSF composite. This was, again, due to the higher protein content in the PSF resin than that in SF resin after removing sugars. The sugars start to degrade much earlier than the degradation temperatures of proteins and cellulose.

**ACKNOWLEDGMENT**

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Mechanical Properties of Polymer Nanofibers Revealed by Interaction with Streams of Air

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INTRODUCTION
Measurements of mechanical properties of electrospun nanofibers [1-2] are needed for process control and for design of structures that are durable, conformal and hierarchical. An air-stream-assisted, simple and low-cost method to perform rapid mechanical measurements on fibers that can be produced by electrospinning was developed. This method complements difficult mechanical measurements of polymer nanofibers and low strength microfibers made on miniature mechanical testing devices.

Electrospun nanofibers [3] were captured directly between two steel rods that functioned as the "grips" of the tensile testing apparatus. Tension was applied to the selected nanofiber by displacing one of the grips at controlled rates or in steps. The stress was revealed by the deflection of a nanofiber, caused by the drag force from a broad stream of air, which flowed perpendicular to the fiber at a known velocity. The deflected position and shape of the nanofiber was observed with a light arrangement optimized to produce bright glints that were photographed with a camcorder (see FIGURE 1). Image analysis of the catenary shapes of the nanofibers was combined with scanning electron microscopy measurements of the diameter of the ends of the tested fibers to evaluate the mechanical properties.

APPROACH

ELECTROSPINNING ONTO GRIPS

AIR-STREAM-ASSISTED MECHANICAL TESTING

ILLUMINATION

exerted on the testing fiber at the tethered ends were in equilibrium in each measured image of the fiber. The stress was defined as the tension force in the sample divided by the cross-sectional area at any instant.

When the fiber radius approaches the mean free path of the gas molecules (68 nm at STP), corrections of drag force for the non-continuum effects are required [4].

RESULTS AND DISCUSSION

![Figure 4](image1.png)

**FIGURE 4.** The “true” stress-strain curves of six electrospun polymers. Each of the stress-strain curves starts at (0, 0), but the responses of the electrospun polymers to the stresses below the initial levels produced by the air drags were below the measurement resolution in this experiment.

![Figure 5](image2.png)

**FIGURE 5.** The mechanical hysteresis curves of ultrathin electrospun (left) PEO, Tecophilic® and (right) Nylon 6 fibers.

Measurements of properties, including tensile strength, tensile modulus and elongation-to-break, of thin electrospun fibers were obtained on six chemically different polymers: nylon 6, poly(ethylene oxide), polyvinylpyrrolidone, poly(2-ethyl-2-oxazoline), Tecoflex® and Tecophilic® polyurethanes, as shown in FIGURE 4. To the best of our knowledge, this is the first report of tensile data on single polyvinylpyrrolidone and poly(2-ethyl-2-oxazoline) nanofibers. These soft nanofibers with low strain to break rarely survive the sample loading procedures where single fiber manipulation is involved. Mechanical hysteresis curves were attained that show the recoverable and non-recoverable tensile deformation of PEO, nylon and Tecophilic® polyurethane fibers (see FIGURE 5).

CONCLUSIONS

Simple and rapid characterizations of mechanical properties of ultrathin electrospun polymer fibers were achieved by interaction with streams of air. Mechanical measurements, particularly of nanofibers and low strength microfibers, can be done rapidly enough to make “real time” electrospinning process adjustments.

Scanning electron microscopy is the method of choice for accurate measurement of the diameter of the broken fiber ends that remained on the grips. Optical imaging, scattering, or absorption, laser light diffraction, synchrotron x-ray imaging, neutron scattering, and other single fiber experiments may be useful where such methods are available. SEM measurement of diameter does not cause radiation damage to the part of the fiber actually tested. This method can be used to study mechanical changes caused by UV, X-ray, or electron radiation. The instrument can also be equipped with a sensitive load cell to measure the force in the fiber.

Uniaxial deformation of single nanofibers is the principal example in this paper, but the methods can be extended in straightforward ways to yarns, or to sheets where biaxial deformation, or combinations of biaxial and uniaxial deformation are of interest.

ACKNOWLEDGMENT

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REFERENCES

OBJECTIVE
The purpose of this paper is to differentiate between the elasto-wetting and elasto-capillary effects observed in the fibrous materials placed in contact with the wetting liquids. The magnitude of elasto-capillary effect is estimated in the experiments on partially saturated freely-suspended samples.

INTRODUCTION
Elasto-wetting effect. The interfacial tension is an important cause of deformations observed in pliant materials such as thin films, carbon nanotubes, and mesoporous materials [1-2]. The elasto-wetting effect is caused by the change of the interfacial tension of the material. The example is shown in Figure 1. Two paper strips (7.5cm × 0.8cm × 0.01cm) were fixed horizontally and a cotton ball with hexadecane was applied to the lower face of the left strip. As seen from Figure 1 the pre-wetted stripe spontaneously bent toward the dry face.

![Figure 1](image1.png)

For dry stripes, the stress balance reads: \( 2 \gamma_{sg} = \sigma h \), where \( \gamma_{sg} \) is the surface tension of the solid/gas interface; \( \sigma \) is a spontaneous stress in the strip, which tends to stretch the internal parts of the strip to counterbalance the compression tensions at the interface; and \( h \) is the strip thickness. After wetting one surface of the strip, two new surfaces are created; the tension then changes to \( 2 \gamma_{sg} \to \gamma_{sg} + \gamma_{sl} + \gamma \), where \( \gamma_{sl} \) is the surface tension of the solid/liquid interface and \( \gamma_{sg} > \gamma_{sl} + \gamma \). Thus, in the wet strip, the internal stress becomes uncompensated \( \sigma h = 2 \gamma_{sg} > \gamma_{sg} + \gamma_{sl} + \gamma \), and forces the strip to bend. The asymmetry is explained by the disbalance of the local stresses at different surfaces: here, the stresses are stronger at the dry side of the stripe.

Elasto-capillary effect.
In the elasto-capillary effect, the menisci trapped in the pores of a fibrous material, exert a capillary pressure on the fibers, resulting in the fiber bending and displacement [3]. In Figure 2 we show a drop of Galwick spreading over a channel formed between two freely suspended tungsten wires.

![Figure 2](image2.png)

FIGURE 2. Droplet of Galwick absorbed by the fiber rails composed of two tungsten wires. Observe the contraction of interfiber gap when the drop transforms into a liquid bridge with concave menisci. The thickness of interfiber space at the first moment is 128 µm which then changes to 67 µm after drop spreading.

The visible deformation of the stretched wires suggests that the capillary pressure \( P_c \) created by the menisci, forces the fibers to snap off the gap between them. Considering the wire rails as two beams subjected to the distributed load one can estimate the magnitude of the stresses, causing the rails to bend. In contrast, in densely packed fibrous materials the motion of individual fibers is restricted due to their interactions with matrix. Thus, some other method to estimate stresses, induced by the presence of the liquid menisci in structure is needed.

In this paper we study the capillary induced stresses in the matrix of the freely-suspended pliant material with high surface-to-volume ratio, caused by liquid wicking.

ELASTO-CAPILLARY EFFECT IN PARTIALLY WET SAMPLES
In fibrous materials, the applied stresses are distributed over both the matrix and saturating fluid. Therefore, when one part of the material is wet and another is dry, the stresses acting upon the fibers in both wet and dry parts of the specimen differ [4-5]. Consider a rectangular nonwoven material such as a strip of paper or a piece of fabric clamped from one edge and subjected to a tensile force \( F \) from the other. We assume that the force is distributed uniformly over the edge.

In-plane stresses. In the dry sample, we can write the force balance as \( F_\perp = \sigma^- A_\perp \), in which \( \sigma^- \) is the normal stress acting over the edge cross-section. Assuming that the atmospheric pressure is set to zero, we can say that this stress is supported only by the fibers. We can also introduce an average stress exerted on each fiber, \( T^- \). The force balance can be rewritten as

\[
F_\perp = \sigma^- A_\perp = T^- (1 - \varepsilon) A_\perp
\]

(1)
In the mechanics of porous materials, $\varepsilon_{\perp}$ is considered identical to the sample porosity, i.e. the ratio of pore volume to the sample volume. In the wet samples subject to the same load, the average normal stress is supported by the liquid and fibers [6]. Again, the force balance is written for the wet sample as:

$$F_{\perp}^* = \sigma_{\perp}^* A_{\perp} = T_{\perp}^* (1 - \varepsilon_{\perp}) A_{\perp} - P_l \varepsilon_{\perp} A_{\perp}$$

where $\sigma_{\perp}^*$ is the average stress acting on the wet sample, $T_{\perp}^*$ is the tensile stress experienced by each fiber, and $P_l$ is the pressure in the liquid, sometimes called the pore pressure. The compressive pressure is considered positive. The pressure term, eq. (2), permits an elucidation of the elasto-capillary effect. The stresses caused by spontaneous wicking of a wetting liquid into a sample illustrate the differences between the stress state in both dry and wet materials. Assume that the sample is subject to tensile force $F$ and the liquid invades the sample from the loaded side. When the liquid wicks into the material, it forms a wetting front separating dry and wet parts. One can immediately infer that the same force $F$ is supported by the stresses $\sigma_{\perp}$ and $T_{\perp}$.

$$T_{\perp}^* = F / (1 - \varepsilon_{\perp}) A_{\perp}$$

Concave menisci formed by wetting liquids produce a negative pressure in the liquid, $P_l < 0$. We thus conclude that tension $T_{\perp}^*$ on the wet fibers is always smaller than tension $T_{\perp}$ on the dry fibers. The stronger the suction of the liquid in the dry fibers, the greater the difference between $T_{\perp}^*$ and $T_{\perp}$. Similar arguments are applicable to the analysis of trans-planar stresses. Therefore to find the stresses acting on the matrix of the wet and dry sample one needs to know the tensile stress in the materials cross-section and the pressure in the liquid inside the material.

**APPRAOCH**

The elasto-capillary effect is estimated in the experiments with freely hanging samples, sucking the liquid from one end (Figure 3a). In our previous work [7] we showed the ability to predict the shape of the sample profile at a given saturation level. The solution of the quasi-static problem allowed us to extract the values tensile forces $F_{\perp}^*$ acting along the sample in both wet and dry parts. The shape of the sample was approximated by the combination of two catenaries (Figure 3b). We apply the Darcy’s law [8-9] in the form (4), in order to find the negative pressure $P_l$ along the liquid column and predict the reduction of stress on the wet fibers (3).

$$\varepsilon_{\perp} \frac{ds^*}{dt} = -\frac{k}{\eta} \frac{\partial}{\partial s} \left( P_l + \rho g y' (s,t) \right) \bigg|_{s=s^*}$$

where $s^*$ is the liquid front position along the sample, $\varepsilon_{\perp}$ is the sample porosity, $k$ is the sample permeability, $\eta$ is the liquid viscosity and $\rho$ is its density, $H$ is the height of the suspension points, $P_l$ is a capillary pressure of the sample.

The experimental results on the wicking kinetics are in a good agreement with theoretical predictions (4). The evolution of stresses is analyzed in details.

**REFERENCES**


Anti-soiling Finish of Polyester Fabrics

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ABSTRACT
Natural fibers and synthetic fibers both attract dirt and get soiled but synthetic fibers attract soil to a greater extent than natural fibers; and they do not release soil easily during washing. In the above context a soil release treatment becomes very essential to maintain the cleanliness of the synthetic fibres. Soil release finish in general refers to chemical finishes that permit relatively easy removal of soils with ordinary laundering. These finishes are necessary because hydrophobic fibers have very low water absorbency. It accomplishes the result of making the fiber more absorbent (hydrophilic), thus permitting better wet ability for improved soil removal.
Chemical soil release finishes come with some inherent problems, like they adversely affect the fastness properties of the dyes. Some of the dyestuff also tend to migrate to the wash liquor due to the application of soil release finish. As such in our present work an alternate method for improving the soil release properties of polyester was attempted by giving an alkaline treatment to the polyester fabric.
The conditions for alkaline hydrolysis were optimized in terms of NaOH concentration, temperature and time by means of Box-Benken modeling with three factors at three levels. The optimized conditions were then replicated onto the polyester fabric. The soil release testing was then done by using a test soil and applying it on the fabric. They were then washed and the results were then evaluated visually as compared to the untreated and a commercially treated sample.

RESULTS AND DISCUSSION
These three samples commercial soil release finished sample. Untreated sample and alkali finished sample are undergone a crystalline analysis in scanning electron microscope (SEM).
The SEM photographs of the alkali treated polyester looks finer and more even as compared to the untreated samples. The SEM photographs of the polyester treated with commercial sample indicates some commercial sample foreign particles which may due to the treatment of soil release chemical which has been applied by pad-dry cure method.

FIG 5: ALKALI FINISHED SAMPLE
3.4 SOIL RELEASE TEST
All the above samples were then soiled with a similar soiling agent and were then washed in a soap solution of 2% concentration with MLR 1:50 in beaker dyeing machine. The results as seen visually indicate better soil release in the alkali treated sample.

3.5 MOISTURE REGAIN
The better performance of the alkali treated sample as compared to the untreated sample can be attributed to the fact that there is a increase in moisture regain of the alkali treated sample as compared to that of untreated sample.

Table VII: Table for moisture regain values of alkali treated and untreated samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Moisture regain values</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>Alkali treated</td>
<td>0.39</td>
<td>0.41</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.84</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The increased moisture regain helps in better adsorption of detergent and absorption of water leading to soil – fibre interface by washing liquid. as we are aware that particulate soil is released from fibre by a two step process First a thin layer wash liquid penetrates between particle and fibre interface enables surfactants to adsorb on to the particle surface. The particle then becomes collated and is transported away from the fibre and in to the wash liquid by mechanical action.

CONCLUSION
Hence alkali treatment can be used as a soil release treatment with improved absorption, adsorption and excellent moisture regain properties. The fabric produced from it can be used as a good alternative to commercial soil-release agents. It enables the fabric in good absorbency and soil releasing. Thus the application of alkali is endless.

REFERENCES
Intelligent Footwear System for Continuous Dynamic Foot Monitoring in Daily Activities Based on Fabric Pressure Sensors

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ABSTRACT
Foot conditions are useful measures in footwear evaluation, athletic training, clinical gait analysis and pathology foot diagnosis. However, many of the present systems for foot monitoring are clumsy thus cannot be used for uncontrolled dynamic activities such as long-term outdoor use. This paper presents the development of an intelligent footwear system, which is able to measure and record, during daily activities, spatial and temporal plantar pressure distributions, in-shoe temperature and humidity, center of pressure (COP), and 3-axis accelerations. It demonstrated satisfactory accuracy, repeatability and wearing comfort, and has been used for 24-hour continuous monitoring of foot conditions of human subjects in uncontrolled daily activities.

INTRODUCTION
Two main types of foot condition measurement systems are available on the market or in the research laboratories: platform systems and in-shoe systems. Both use electrical wires to connect in-shoe sensors and data acquisition system around the waist, which causes inconvenience and discomfort during strenuous exercises. The poor fatigue resistance hence short use-life of those thin-film sensors does not support a long term continuous usage. There has been no report on long-period outdoor trials as the previous studies were conducted in labs and clinics. With the purpose of collecting valid long-period foot condition data in all kinds of activities, this paper presents an intelligent footwear system integrated based on fabric pressure sensors.

METHODOLOGY
A family of soft pressure sensors has been recently developed by using electrically conductive textile fabric sensing elements [1] and is now commercially available [2]. As shown in Figure 1, the pressure sensor was fabricated by adhering a conductive fabric strain sensing element with conductive yarns and a top and bottom conversion layer, prepared by moulding of elastomers of varied Young’s modulus. The fabric strain sensing element has a strain gauge factor of approximately 10 or above and excellent fatigue resistance (>100,000 cycles) for strain up to 40%. The pressure sensor measures pressure from 10kPa to 1MPa, suitable for a wide variety of human-environment interfaces, such as loosely fit garment, pants for sitting, gloves, beds, sleeping garments and walking/running shoes. The accuracy is 5% and zero drift in seven days is less than 5%.

The fabric pressure sensors as well as temperature and humidity sensors were embedded in the insole of the presented intelligent footwear system. Sensor positions were determined by high plantar pressure areas measured from F-Scan® system and functional areas recommended by the professional orthopedists, shown in Figure 2.

The intelligent footwear system is then presented based on the sensors and body area networking platform, as shown in Figure 3. Two sensor nodes with acceleration sensors (HAAM-313B) are attached at the outer side of each shoe, and connected with the insoles, where eight soft textile pressure sensors and a temperature and humidity sensor (SHT11) are embedded. Plantar pressure, temperature, humidity and 3-axis accelerations of each shoe are wirelessly transmitted to a smart phone using Bluetooth and then to a remote monitoring computer by WiFi technology.
EXPERIMENTAL RESULTS AND DISCUSSIONS

Ten subjects in total, including six male subjects (age = 29.3 ± 1.9 years (mean ± SD), weight = 64.2 ± 6.7 kg, height = 175.7 ± 2.9 cm, foot size (Euro size) = 42.0 ± 0.8) and four female subjects (age = 27.3 ± 1.7 years, weight = 52.5 ± 6.3 kg, height = 163.3 ± 3.9 cm, foot size = 36.9 ± 0.8) participated in wear trials for evaluation of the intelligent footwear system. The accuracy of plantar pressure data was evaluated by a comparison with Novelemed®-at system. Repeatability validation protocol [3] was employed in the tests that were performed in a 40 m long corridor to allow the subjects to walk with their normal speed at a consistent gait rhythm. A questionnaire study on wearing comfort [4] was conducted to the 10 subjects in the wear trials. Evaluation results are summarized in Table I, which indicate the system obtains an acceptable accuracy, good repeatability and general wearing comfort.

<table>
<thead>
<tr>
<th>Evaluation Item</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy</td>
<td>Average 7.7% (std 2.7%) difference with Novelemed® system.</td>
</tr>
<tr>
<td>Repeatability</td>
<td>Average 6.4% (std 2.6%) variation in two sessions of trials with an interval of 7 days.</td>
</tr>
<tr>
<td>Wearing Comfort</td>
<td>Average rating to “Comfortable shoes” reaches 3.9 (Rating: 1 Strongly Disagree, 2 Disagree, 3 Nurture, 4 Agree, 5 Strongly Agree.)</td>
</tr>
</tbody>
</table>

A case of daily continuous foot monitoring (Male, 28 year old, 72 kg weight, 176 cm height, 42 euro size foot, BMI = 23.2 kg/m²) with 24-hour monitoring data including plantar pressure, in-shoe temperature and humidity, COP coordinates, and foot 3-axis accelerations is reported.

![FIGURE 4. Plantar pressure of left foot in a day: (a) forefoot, (b) midfoot and heel.](image)

Figure 4 shows the subject’s plantar pressure of left foot in a day. Some interesting observations of the plantar pressure are found in the data. Most peak pressures of left heel, left forefoot, right heel, and right forefoot occur, around 250kPa, 600kPa, 275kPa and 300kPa respectively. The unusual plantar pressure data are indicators of anatomical abnormalities of the wearer or structural problems of shoes. The wearer’s feet were checked and a callus was found at the second metatarsal head of left foot.

![FIGURE 5. Statistical Result: (a) Presence proportion of different pressures in a day. (b) Presence proportion of COP in a day.](image)

Figure 5 shows statistical results of the daily monitoring data. For the subject, the high plantar pressure (>300kPa) takes up 3.2% time of a day in left foot, seen in Figure 5(a), which has already caused a plantar callus. High plantar pressure takes up a small partition in his right foot, which is checked as healthy. Figure 5(b) shows the proportion of different COP statuses in a day. The no-COP status is linked with sitting down. That implies the subject spent 52.9% of a day’s time in sitting. This subject in the monitoring spent nearly 6 hours in sitting, which has already contributed to his increasing body weight.

CONCLUSION

An intelligent footwear system integrated with fabric pressure sensors is presented. In the wear trials by ten normal subjects, data of temporal and spatial distributions of plantar pressure, temperature, humidity and acceleration were collected, which represents, to the authors’ knowledge, the first reported continuous dynamic foot monitoring data of daily activities in the open literature. The technology and these data will be further used in a study of long-term monitoring of patients with diabetic foot syndrome.

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REFERENCES

The Effect of Annealing and Doping on Crystallinity and Conductivity in Polyaniline for Processable Films and Fiber

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OBJECTIVE
The goal of this research is to investigate the relationship between the electrical conductivity and the degree of crystallinity of polyaniline (PANI) that has been annealed at different temperatures. The morphology characterization was carried out using wide-angle X-ray diffraction method to understand the effects of annealing treatment on PANI crystalline structure. Conductivity measurements were made employing both two-point and four-point methodologies.

INTRODUCTION
Polyaniline (PANI) has been extensively researched for the past 30 years since its discovery as a conductive polymer. It shows great potential as a semiconductor for various applications in fields such as bio-sensing, as well as electrochemical and material science. Its simple synthesis method, environmental stability, and unique doping and de-doping mechanism give it an advantage over other conductive polymers [1]. The conductivity of PANI depends on various factors such as morphology, crystallinity, and dopants. Previous studies have shown a change in morphology of the emeraldine base, the deprotonated form of PANI, that has been annealed at higher temperature [2]. As the annealing temperature increases, the crystallinity of the sample decreases and becomes completely amorphous at about 200°C. Research conducted by Kobayashi et al reported that the conductivity of PANI increases as the annealing temperature increases [3]. It is suggested that by annealing the efficiency of charge transfer between polymer chains improves. Our group is currently conducting research to confirm the reciprocal relationship between conductivity and degree of crystallinity of PANI.

APPROACH
The synthesized PANI powder was annealed at different temperatures over the range of 25°C to 130°C in a vacuum oven under nitrogen gas at -30 inches of Hg for 12 hours. Wide-angle X-ray diffraction patterns were measured using CoKα beam (1.709 Å, 45kV, 40mA) in 2θ angle from 5° to 40° with a scan rate of 15°/min at room temperature. The X-ray measurements were taken before and after doping the annealed samples to determine the effect of doping on the morphology of PANI. The annealed samples were doped in 1.0M methane sulfonic acid (MSA) by stirring the annealed PANI powder in the solution for 1 hour and collected over vacuum filtration without washing with deionized water. All doped and annealed samples were purged under nitrogen gas and then dried under vacuum at room temperature for at least 12 hours. The dried powder was then pressed into pellets and the conductivities were measured using Keithley two-point and four-point probes. The pellets were 12.0 mm in diameter and 8.0 mm in thickness, and were pressed at room temperature.

PRELIMINARY RESULTS AND DISCUSSION
The X-ray diffraction patterns show a decrease in degree of crystallinity of the annealed and doped samples at 75°C and 125°C as shown in Figure 1. The sharp peak at around 2θ = 22° and 26° signifies a region of crystallinity, while the overall broader feature of the graph is associated with the amorphous region in the polymer chain. This characteristic of diffused sharp and broad peaks is evidence that ordered and disordered region coexist. The doped PANI annealed at 125°C shows a decrease in the sharpness of the peaks, as well as shifts in peak positions.

One possible explanation to this change is thermal treatment and doping of PANI alters the morphology of the polymer. In Figure 2, the X-ray diffraction patterns of unannealed PANI at 25°C confirms the effect of doping...
on the morphology. It is observed that by doping PANI the crystallinity in the polymer structure decreases.

![FIGURE 2. X-ray diffraction pattern of unannealed sample (upper) and annealed doped sample (lower). Both dried at room temperature of 25°C.](image)

Four PANI samples were prepared pressed into pellets: undoped-unannealed at 25°C, doped-unannealed at 25°C, doped-annealed at 75°C, and doped-annealed at 125°C. The conductivity of these pellets was evaluated. An increasing trend in conductivity was seen as the annealing temperature increased. Additional data currently is being obtained using four-point techniques. To date the information obtained is inconclusive. The overall data points out an inverse relationship between crystallinity and conductivity. This seems counter-intuitive since it should be expected that as the crystallinity increases the conductivity should also increase due to closer packing of the chains. Instead, it could be hypothesized that thermal treatment on PANI allows more of the dopant MSA to interface with the polymer chains.

**CONCLUSION**

Polyaniline powder was annealed at different temperatures and doped with 1.0M methane sulfonic acid. The effect of annealing on morphology was evaluated using wide-angle X-ray diffraction to determine the degree of crystallinity of PANI powder. The X-ray patterns show a decrease in crystallinity of doped samples as the annealing temperature increases. Likewise, the effect of annealing on electrical conductivity was evaluated by measuring the conductivity using the two-point probe technique with a DC input of 20V. A trend of increasing in conductivity was observed as the annealing temperature increased. In the near future we hope to be able to predict this increase in a more quantified manner.

**FUTURE WORK**

This study is currently under progress. Preliminary results, however, show that a strong correlation between the conductivity and the degree of crystallinity of PANI powder exist. The next approach is to determine the best combination of annealing temperature and concentration of dopant which will yield the highest conductivity. The degree of crystallinity can be calculated using the X’Pert High Score Plus software for X-ray diffraction, however this calculation will not be accurate because it is optimized for measurements for inorganic crystals. Therefore, a better calculation method for the crystallinity of PANI would be a necessity in order to obtain more accurate crystallinity data. In order for PANI to be processable for various fiber and film applications, it has to be cast into film. Our next approach is to the study whether PANI films that have been dissolved in differing solvents can be developed with improved conductivity by annealing the film. This will also include films formed on the surface of fibers.

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A History of Electrospinning 1600–1995

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The science behind the technology of electrospinning has a history that stretches back to the earliest days of scientific investigation. Current interest in the process is due to the ease with which nano-scale fibres can be produced in the laboratory. The history of the prior art in the process should be of great interest to the research and development community as it provides a rich vein of ingenious mechanisms to solve the problems of the manufacturer, and access to the theoretical considerations of several generations of scientists.

The first record of the electrostatic attraction of a liquid observed in the time of Queen Elizabeth 1 of England by William Gilbert [1]. This is the first record of the deformation of a drop of liquid into what would become known as the Taylor cone.

John Francis Cooley filed the first electrospinning patent [2] in which he proposed three types of indirectly charged spinning heads – a conventional head, a coaxial head, an air assisted model, and a spinneret featuring a rotating emitter. He also proposed the recovery of solvent and the use of a dielectric liquid instead of a gas as the medium.

Dipl. Ing Ludwig Rudolph Anton Formhals was born in Mainz on 24 Aug 1877. He worked for the Verein fur Chemische Industrie AG. His contribution to electrospinning is marked by at least 18 patents.

In 1938 N.D Rozenblum and I.V Petryanov-Sokolov at the Aerosol Laboratory of the L. Ya Karpov Institute in the USSR, generated electrospun fibres, which they developed into filter materials that became known as “Petryanov filters”. By 1939, this work had led to the establishment of a factory in Tver’ for the manufacture of electrospun smoke filter elements for gas masks. The material, dubbed BF (Battlefield Filter) was spun from cellulose acetate in a solvent mixture of dichloroethane and ethanol. By the 1960s output of spun filtration material was claimed as 20 million m² per annum [3] Between 1964 and 1969 Sir Geoffrey Ingram Taylor produced the beginnings of a theoretical underpinning of electrospinning. Taylor’s work contributed to electrospinning by mathematically modelling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone.

In the early 1990s several research groups (notably that of Reneker who popularised the name electrospinning for the process) demonstrated that many organic polymers could be electrospun into nanofibres. Since then, the number of publications about electrospinning has been increasing exponentially every year.

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REFERENCES


Blue Light Curable Ink Chemistry for Textile Digital Printing

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Yong Kim, Samuel Ugbolue (UMass Dartmouth), Richard Himmelwright (Cold Spring Technology, Inc., Three Rivers, MA); Graduate Students: Rohit Kankaliya and Francesco Piscani

We are designing and developing a feasible chemical system for blue light curable inkjet ink formulations using specifically selected chemicals including suitable monomers, oligomers, initiators, and auxiliaries. The technology thus developed will help reduce textile printing steps by eliminating heating (steaming), washing, and drying process required for the dye-based inkjet printing and screen printing. The success of the project can also help eliminate or at least minimize environmental impacts of pre- / after-treatments required in some types of digital textile printing. Overall the blue light curing technology can make the textile digital printing
Active Nano-coatings for Textiles

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Konstantin Kornev (Clemson University; Sergiy Minko (Clarkson University)

The primary goals of the project are (1) the design of novel nano-coatings for “active smart textiles” through the development of “universal” anti-adhesive coatings based on responsive mixed polymer brush-like layers, and (2) the development of “easily removable – easily renewable” self cleaning smart coatings based on responsive nanoparticles. The planned work is directly based on the foundations developed in our previous research devoted to the generation of stimuli-sensitive hybrid polymer nanolayers on the surface of fiber and textile materials (NTC M01-CL031) and ultrahydrophobic textile materials (NTC C04-CL062).

Properties of fibrous materials can be tailored via surface modification which is widely explored in the textile/fiber industry. However, modern achievements in nano-science and nanotechnology allow introducing new ways to accomplish the surface modification of fibers and textiles. For instance, recently, various approaches to ultrahydrophobic self-cleaning surfaces were developed for the surface modification of textile materials.3-9 Ultrahydrophobic surfaces demonstrate very high water contact angles (150°-180°) and a low wetting hysteresis. Water-borne solutions do not wet ultrahydrophobic surfaces. Water drops roll off and clean these surfaces. However, the situation is different for solutions of surfactants or oil-based solutions (for instance chemical and biological weapon). These solutions wet and contaminate ultrahydrophobic surfaces.
Novel Polymerizable Bifunctional Flame Retardants

Leader: Dr. Ahmed El-Shafei (NC State University, Ahmed_El-Shafei@ncsu.edu)  
Dr. Peter Hauser (NC State University)

This project aims to synthesize novel halogen-free flame retardant monomers. These monomers will employ a phosphorus/nitrogen synergistic system and will incorporate vinyl groups that are polymerizable under atmospheric pressure plasma. Different phosphorus/nitrogen contents and monomer configurations will be explored. The monomers will be applied to various substrates using an atmospheric pressure plasma-induced graft polymerization process to generate a grafted nanolayer of the flame retardant chemical. Several variables, including the exposure time of the treated fabric to the plasma discharge, the concentration of the monomer in the treatment bath and the presence of a photoinitiator and cross-linking agent, are to be examined. The treated substrates will be analyzed to determine the optimum combination of chemistry and plasma processing parameters that are needed to achieve durable flame retardance. Ultimately, our desires are to apply these processing parameters to treat fabrics on our full-width industrial-scale atmospheric pressure plasma machine and to develop a sustainable and low-cost method for achieving durable flame retardant substrates.
Polymer Flow in Confined Elastic Boundaries: Stronger Continuous Nanofibers

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We are developing fundamental experimental and theoretical knowledge in the area of polymer flow in confined elastic boundaries that will enable the controlled production of strong continuous nanofibers using conventional bicomponent extrusion techniques. We are developing new analytical techniques based on Acoustic Force Atomic Microscopy. These techniques are capable of assessing mechanical properties of bicomponent fibers with nanoscale precision. In particular, the objectives of this project include: (1) to characterize and to elucidate the nature of complex polymer flow phenomena present in bicomponent extrusion when individual polymer domains become of the order of tens of nanometers—some of these phenomena include domain encapsulation, coalescence of domains, domain dimensional instabilities, differential crystallization kinetics and induced superdrawing. (2) to relate these fundamental experimental and theoretical findings to observed macroscopic behavior; (3) to establish quantitative relationships between the bench scale experiments and the mathematical predictions and issues of industrial relevance in fiber processing operations such as the production and further processing of continuous nanofibers; and (4) to work closely with fiber and textile manufacturers to translate this knowledge into testing and operating methodologies relevant to the textile and its allied industries.
We developed innovative electromechanical devices to form fiber webs with controlled fiber orientation distribution (FOD) using electrostatic forces. This equipment is capable of forming fiber webs with desired multi-directions with in-plane fibers and fibers in the z-direction. The mechanical properties of currently produced composites from SMC can be greatly improved and engineered with predetermined performance and consistency if fiber orientation and volume fraction are positively controlled. Our main goal in this project is to achieve such improvements through undertaking a fundamental research program with the following objectives: 1) Create pre-forms made of fiber webs with short fibers of high aspect ratio and controlled 3-D FOD for fiber reinforced composite structures using the equipment developed in project F03-MD01. The equipment can form 3D short fiber pre-forms of sheet and disc shapes. 2) Characterize the 3-D fiber orientation distribution of these pre-forms. 3) Consolidate the pre-forms to form composite structures and evaluate their mechanical performance in terms of fiber orientation and fiber characteristics (type and aspect ratio, etc.). 4) Develop models to predict the composite structure’s mechanical properties in terms of fiber orientation, aspect ratio, volume fraction, and resin properties. Verify the models experimentally.
Fiber-based Bioreactor Media for Air Pollution Control

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Armand F. Lewis (UMassD), Chen-Lu Yang (UMassD)

Our present research involves evaluating flocked surfaces for the technology of bioconverting SynGas (essentially a mixture of CO and H2 gases) into ethanol biofuel. A laboratory-scale apparatus is under construction for testing various fiber-based (flocked) bioconversion media materials. Ultimately this work will also provide direction on how to engineer fiber-based bioconversion media with predetermined geometry and hence predetermined bioconversion capacity and properties. Our overall focus is to determine the fundamental materials and geometric parameters that will optimize the bioconversion efficiency of flock fiber-coated polymer sheets and textile fabric surfaces.
The goal of this research is to develop low cost, high-performance nanofiber/textile wound dressings. We are developing and characterizing processes for deposition of nanofiber webs onto existing textile-based wound dressings as a means to generate inexpensive wound care materials with significantly enhanced wound healing capabilities. Atmospheric pressure Helium/ Oxygen plasma has been used to enhance the adhesion and durability of the nanofiber coating and to sterilize the composite dressings.

The ability of atmospheric plasma treatment to enhance adhesion and durability of the coating and to sterilize the composite bandage was investigated by characterization of four sample sets: 1. No plasma treatment, 2. Pre-treat substrate with plasma, 3. Post-treat electrospun coating with plasma and 4. Pre- and post-treatment.
Fluids in Fabrics: Validation of the Integrated Upward-Horizontal-Downward Wicking Test for Providing Intensive Properties of Textile Fabrics

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Traditional wicking tests provide information that is specific to the test fluid, apparatus and conditions. As a result, this information cannot be used to make predictions about wicking rates beyond the respective test parameters. In contrast, a new upward horizontal-downward (UHD) wicking test has been presented that provides intensive properties of fabrics in the form of permeability ($k$) and effective capillary radius ($R_c$) as functions of saturation ($S$). The UHD test was developed using water as the test fluid. If the $k$-$S$-$R_c$ relationships are truly intrinsic to a given fabric, then they should not depend on the test fluid. Here, we conducted the UHD test on a knit fabric using three different test fluids characterized by different surface tensions, densities and viscosities: dodecane, tetradecane and hexadecane. All fluids fall on the same $k$-versus-$S$ and $k$-versus-$R_c$ curves, proving that these curves are intrinsic characteristics of the fabric. We then used the $k$-$S$-$R_c$ properties to successfully predict the in-plane horizontal and downward wicking rates of two different fluids, octanol and water, in the fabric. These results validate the UHD wicking test as a method for providing intensive properties of textile fabrics which can then be used for predicting wicking rates.
Melt Spinning of Cellulose-based Fibers

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Natural cellulose fibers such as cotton are in high demand due to their comfort characteristics and other beneficial properties. Interest in reassembling cellulose molecules into fibers with desired geometry (e.g., silk-like filaments) has led to the development of rayons and cellulose ester fibers by solution spinning. The process is complex, expensive and harmful to the environment. Effort to discover less harmful solvents for cellulose fibers in recent years has yielded some results but the limitations of solution spinning still exist. Melt processing is clean and inexpensive but it can only process certain thermoplastic polymers (e.g., polyester, nylon, polyolefin, etc). In this project, we are blending cellulose nano-whiskers with nylon and other polymers in a process similar to conventional melt spinning to produce novel cellulose-based composite fibers. Through selection of the cellulose nano-whiskers, surfactants/coupling agents, whisker volume fraction, thermoplastic polymer as matrix and processing conditions, the resulting fibers can be engineered to have excellent hand, superior strength and other characteristics.
This project underlines how researchers working in the areas of polymer, fiber and textile sciences are contributing to the development of a novel and innovative medical therapy called regenerative medicine. This approach to repairing injured and diseased tissues and organs relies on the body’s inherent natural capacity to repair injured tissues by cellular regeneration of viable tissues and organs. This involves culturing cells on a porous resorbable tissue engineering scaffold. The overall goal of this project has been to establish a specification for the commercial manufacture of textile tissue engineering scaffolds that will reduce their fabrication costs and ultimately bring significant savings to providing healthcare in this country.

In response to the severe shortage of viable organs for transplantation, we have proposed to harness the latest fiber spinning, textile knitting and surface bio-activation technologies to fabricate 3 dimensional (3D) porous bio-resorbable tissue engineering (TE) scaffolds that will be biocompatible and support the adhesion and proliferation of cells for use in a wide range of TE and regenerative medicine applications.
Fiber-based Biohazard Sensor Assemblies

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This project focuses on creating point of use biohazard detection systems, combining technologies for transport, purification, concentration, capture and detection of analytes. Sensor assemblies are created by including molecular sensors into electrospun non-woven fabrics and fabric structure and properties are optimized to maximize transport of analytes from liquids or moistened solid surfaces to sensing sites. Both structure and chemistry of fibers within the electrospun non-woven fabrics are investigated.

Stimuli-responsive fibers were created by incorporating pH-sensitive nanoparticles into electrospun cellulose acetate (CA) and poly(lactic acid) (PLA) fibers. The fluorescent silica nanoparticles, Cornell dots (C dots), have both a fluorescent core (518 nm emission), and a fluorescent pH-sensitive shell (572 nm emission). Using confocal microscopy, the signaling effectiveness of these fibers was studied by varying several parameters: fiber diameter, substrate, and surface hydrophilicity.
A key component in liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and other flat panel displays is the transparent conductor. At this point the standard system is Indium tin oxide (ITO) sputtered onto glass under vacuum. In some circumstances, ITO on plastic film does not have sufficient conductivity for low performance applications. In addition, OLEDs require a good oxygen barrier and LCDs require rigidity that prevents the application of plastic film substrates. Inexpensive printed electronics will often require displays and electroluminescent devices can offer a simple printable, flexible solution.

The primary objective of the project is to develop a flexible and transparent textile based conductor by printing or electrostatically depositing combinations of carbon nanotube (CNT), ITO and PEDOT into porous and transparent non-woven textiles that can be used for flexible electroluminescence devices. The specific objectives of the proposed research are: Investigation of the transparency-conductivity tradeoff for flexible PEDOT and/or CNT conductors on textiles; investigation of critical bend radius vs. optical transparency of the electrodes; examine the performance of these electrodes in textile-based electroluminescent devices.
Nanoscale Surface Embrittlement of Fibers

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Nano-indentation studies using atomic force microscopy (AFM) were conducted to investigate the effects of both hydrolysis and enzymatic degradation on mechanical properties of polyglactin 910 monofilament sutures and they were discussed with respect to surface and chemical analysis using scanning electron microscopy (SEM) and Fourier Transform Infra Red spectroscopy (FTIR) respectively. For hydrolysis degradation, the sutures were incubated in phosphate buffered saline (PBS) solution at three different pH conditions, 5, 7.4, and 10. For enzymatic degradation, esterase enzyme at 37 °C under an oscillation of 80 rpm was employed at pH condition of 7.4. The above investigation was performed for samples exposed to one to four weeks in increments of one week to hydrolysis degradation. However, only one to three weeks study was performed on test samples subjected to enzymatic degradation.

The hydrolysis degradation studies of polyglactin 910 monofilament sutures at pH 5 and 7.4 showed that after four weeks, most of their mechanical properties were deteriorated. The polyglactin 910 monofilament sutures were not able to retain their integrity after four weeks hydrolysis degradation at pH 10 and also enzymatic degradation at pH 7.4. The effects of degradation on Young’s modulus values across fiber cross section were studied by performing progressive nano-indentation from the center to the surface of the cross section of the sutures. Results indicated that overall the Young’s modulus values decreased as the number of degradation weeks increased. For a given degradation condition, Young’s modulus values remains constant across the cross section, indicating bulk degradation is primary method of degradation as reported in the literature. Macro scale tensile tests were conducted to correlate the results of nano-indentation to tensile strength and percentage elongation at break. Additionally, the scanning electron microscopy (SEM) studies were performed to investigate the surface roughness condition of degraded sutures and using Fourier Transform Infra Red spectroscopy (FTIR) was performed to verify the formation of new chemical bonds during degradation and connect these findings with nano-indentation and macro tensile testing results for comprehensive understanding of degradation phenomenon.
Electrospun Composite Nanofibers for Lithium-Ion Batteries

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Peter S. Fedkiw, Saad A. Khan, Behnam Pourdeyhimi (NC State)

Our goal is to fabricate one-dimensional nanostructured materials with high electrochemical performance for use in lithium-ion batteries via the electrospinning technique, which provides a unique approach to prepare versatile nanofibers from a rich variety of materials including polymers, composites, and ceramics. The work focuses on cathode nanofibers that have short-diffusion distance and high-lithium diffusion coefficient due to their one-dimensional structure. Such nanofibers have excellent charge/discharge rate capability and can produce cells with high capacity and extended cycle performance. In this project period, to optimize the use of composite nanofiber cathodes in lithium-ion batteries, we have prepared four different cathode materials. Polyacrylonitrile (PAN) was used as the precursor for the carbon. Functionalized CNTs and graphene flakes were used to increase the conductivity of the composite nanofibers.
Muscle-like Extruded Fiber Actuators

Tushar K. Ghosh, Leader (tghosh@ncsu.edu), M.K. Ramasubramanian

Fiber actuators are capable of changing their dimensions (length, diameter etc) as well as generate a force when activated using appropriate electric field. Our objective is to fabricate fiber actuators from electroactive polymers, specifically dielectric elastomers. Through appropriate experimental design and theoretical analysis we plan to understand the critical parameters in the design of the fiber actuator. For the analysis we are using finite element modeling (using ABAQUS) of the deformation of the actuator under electrostatic stress.

The majority of the devices developed by man to convert chemical or electrical energy into mechanical work involves thermo mechanical or electromagnetic principles. Such physical principles are different from the way biological machines generate force and accomplish work. Biological muscle is a magnificent actuator with the capacity to perform many functions like running, flying, swimming; muscle operate as motors, brakes, springs and struts. Considering the physical capabilities of biological muscle, considerable efforts to develop human made actuator technologies that can mimic muscle performance [1]. Muscles provide intermittent displacements and adaptable stiffness to absorb shocks and prevent damage. They convert energetic fuel to mechanical energy with high efficiency. Some of the artificial actuator technologies proposed in the literature are capable of matching or surpassing some of the performance characteristics of skeleton muscles. A class of electrostrictive polymers with low elastic moduli known as dielectric elastomers offers overall performance similar to biological muscles. Dielectric elastomers (DE) comes under the category of Electroactive Polymer (EAP) which can induce high strains compared to Electroactive ceramics (EAC) and are superior to Shape memory alloys (SMA) in high response speed and lower density.
Functional Fibers via Biomimetics and Inorganic-Organic Hybrids

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Members: Michael S. Ellison, Clemson University; Heidi Schreuder-Gibson, US Army Natick

This project expands the biologically inspired concepts from the organic biopolymer arena to the inorganics and organic-inorganic hybrids. As nature has shown in many organic-inorganic hybrid systems, the goal of this project is to integrate the concepts of biomimetics with organic-inorganic hybridized organization to discover ways to generate new fibers with novel structures and properties. This research builds on the successful achievement of a previous project on incorporating and converting protein compounds into fibrous structures. Specifically, several enzymes that break down fatty acids and sugars of varying structural properties have been effectively bound to nanofibrous templates via encapsulation, immobilization, covalent and ionic interaction mechanisms and in varying physical manners, i.e., internally, surface gels and bi- or multiple nanolayers. Structurally and functionally distinct classes of proteins and enzymes have been combined in various designed nanofiber structures.

Several mechanisms, including amphiphilic linkers, surface bristles and hydrogel fibers, on nanofibrous structures have been developed to fabricate effective bound systems for hydrolyzing enzymes in robust bio-catalysis. The main focus has been to protect the protein under extremely fabrication and use environments while creating advantageous properties. Protein-polymer hybrid structures have been devised to successfully entrap the very large and bulky β-galactosidase in non-ionic polyacrylamide (PAAm) hydrogel nanofibers as well as to efficiently bond enzymes via affinity dye ligands and engineer new fiber scaffolds with Spidroin 1-collagen proteins. A layer-by-layer (LBL) physical sorption process has been established to bind lipase enzyme on cellulose nanofiber surface. This simple approach uses strong secondary forces, such as electrostatic and ionic interactions, and is proven to be highly effective.
This work concerns fundamental investigations into the production and characterization of fibers containing functionalized nanoparticles. Currently nanoparticles are seen as the next major advance for textile materials. The inclusion of nanoparticles allows the industry a competitive advantage in that the products offered have a value added features, such as unique optical, electromagnetic, or sensing capabilities. Current approaches have yielded materials that do not meet the expectations that are associated with nanotechnology. We will accomplish this by investigating both the stability of specific ligands at high temperature, high shear environments (i.e. melt spinning) and determining the interfacial interaction of the particles within the polymer. Specifically, we will design surface ligands for metal and metal-oxide nanoparticles that allow for good suspensions in polymer matrices and can be easily introduced to existing melt spinning equipment.
Nanofibrous Materials as Sensors for Heavy Metals

Konstantin G. Kornev, Leader (kkornev@clemson.edu)
Igor Luzinov, Bogdan Zdyrko

The aim of this project is to develop a new sensory platform for detection of heavy metals. The design takes advantage of novel active fibrous materials responding to various stimuli by spontaneously folding-unfolding their structures. Within the reporting period, we constructed a prototype of a colorimetric sensor embeddable into nonwoven nanofibrous materials. The designed prototype after being dropped into polluted water deploys itself, adsorb the contaminants and suppose to change color. We used the technology developed within a previously completed NTC project, combining electrospun nanofibers to develop a self-deployable sensor based on nonwoven materials.

In this project, we explore the phenomenon of super-absorbency, in which the physicochemical energy of wetting and absorption is transferred into the mechanical energy of fiber bending. A super-absorbent layer is coated onto the fiber surfaces. The coating film is able to swell by ten times upon wetting. We designed a smart fibrous laminated scroll, which spontaneously opens up when placed in contact with water. In addition, in order to significantly increase the surface-to-volume ratio and hence to facilitate adsorption of heavy metals, the electrospun alginate nanofibers were incorporated into the matrix. At the next step, we intend to develop a technology to dye these alginate nanofibers with a heavy-metal-sensitive compound. Thus, combining two technologies, we propose to create new self-deployable colorimetric sensors for monitoring the composition of waste products in aqueous media.

In a previous report, we discussed the efforts devoted to the electrospinning of alginate nanofibers that would be stable in an aqueous environment.
This work is concerned with fundamental investigations into the production and characterization of polymers and fibers containing light emitting nanoparticles. This will be achieved by investigating the effects of the synthesis environment on nanoparticle behavior, in addition to their subsequent incorporation in a polymer matrix for melt extrusion into fibers.

This is coupled with the direct involvement of undergraduates in a scientific study in a creative inquiry component which aims to provide a firsthand research experience with the hope of inspiring the next generation of textile experts.
Bi-component fibers can be considered as state of the art materials in the field of Polymer Science and Engineering. After the commercialization of bi-component fibers by the DuPont Company in the 1960s, myriad sorts of polymers with distinct cross sections have been fabricated as bi-component fibers. According to the functionalities of the two components and the processing methods, these fibers can provide interesting applications, such as sensors, drug delivery process, electron or photon transport wire, and EMI shielding and these fibers can be considered as smart fibers or smart textiles. In addition, after the discovery of carbon nanotubes in 1991, various new nanocomposites have been produced with different polymers and single wall, double wall, or multi wall carbon nanotubes. Since carbon nanotubes can provide good mechanical reinforcement with high electrical and thermal conductivities, we can also significantly improve related fiber properties. Therefore, the goal of this project is to introduce the excellent advantages of nanocomposite to bi-component fibers.
Masculine Style(s): Shifting Identities and Textile/Apparel Industry Opportunities

Leader: Van Dyk Lewis, Cornell University (vdl4@cornell.edu)

We aim to examine how the menswear industry can become more strategic and flexible to adapt to a changing marketplace, beyond the stale framework that regards only femininity as fashionable. Our overriding objective is to examine the implications of a shifting male consumer culture for the textile and apparel industries, with special focus on the degree of synchronicity between consumer and industry perceptions.
In the polymer science field, UV technology is mainly applied to modify surfaces, initiate polymerization, as well as provide antibacterial effects. Photoinitiators are required to initiate the desirable reactions. More recently, dyes and colorants were found capable of serving as photoinitiators. In this research, three similar acid dyes: 2-anthraquinone sulfonate (2-AQS), 2, 6-anthraquinone sulfonate (2, 6-AQS), 2, 7-anthraquinone sulfonate (2, 7-AQS) have been used to initiate the polymerization of vinyl monomers under UVA irradiation. Their photochemistry and photo-physics have also been studied exclusively. In this poster, besides exploring the applicability of this method to protein polymers such as wool and silk, we report that under UVA irradiation, these compounds also demonstrate excellent antibacterial function when immobilized on the polymer.
Effective Thermal Conductivity of Fibrous Materials

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Youjiang Wang (Georgia Tech), Moran Wang (LANL)
Postdoc: Qun Chen (UC Davis)

We have developed a full set of numerical methods for predicting the effective thermal conductivity of natural fibrous materials accurately. It includes a random generation-growth method for generating micro morphology of natural fibrous materials based on existing statistical macroscopic geometrical characteristics, and a highly efficient lattice Boltzmann algorithm for solving the energy transport equations through the fibrous material with the multiphase conjugate heat transfer effect considered. Using the present method, the effective thermal conductivity of random fibrous materials is analyzed for different parameters. The simulation results indicate that the fiber orientation angle limit will cause the material effective thermal conductivity to be anisotropic and a smaller orientation angle leads to a stronger anisotropy. The effective thermal conductivity of fibrous material increases with the fiber length and approach a stable value when the fiber tends to be infinite long. The effective thermal conductivity increases with the porosity of material at a super-linear rate and differs for different fiber location distribution functions.
Development of Visual Fit Assessment Tool for Apparel Firms

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One of the greatest challenges facing apparel companies today is to provide quality fit to a broadly defined target market. Apparel sizing is a complex process that apparel companies are addressing with limited data, shrinking resources, and growing expectations on the part of the consumer. The goal of this study is to design, test, and implement a tool for apparel firms to collect and analyze visual data on the fit of their products. This new tool for the apparel industry would extend the effectiveness of traditional fit testing of garments on an in-house fit model and would facilitate testing across the full range of sizes of target market customers, using the 3D scanner and other image capture tools. The provision of well-fitting clothing for the population as a whole is a difficult task given the variations in body sizes, proportions, and postures of consumers, particularly in countries such as the U.S. where great ethnic diversity contributes to this variation.

The demands for well-fitting ready-to-wear clothing have increased in the last few decades, as consumers expect to find clothing that fits with no alterations. At the same time apparel companies competing with low cost imports have less time and fewer resources to assess their sizing. To provide good fit apparel companies identify a target market for their products that comprises a segment of the population based on age, income, lifestyle, shopping preferences and also to some extent body size and type. The company then chooses a fit model, a person whose body shape and proportions are consistent with their target market, for fittings of prototype garments in a single base size. A set of additional sizes are created using grade rules developed by the firm to create the full range of sizes for their sizing system. However, the full range of the sizes in the system is seldom tested. Most firms do not know how their sizing actually fits their target market, and data about fit is difficult to collect. Feedback from consumers on their problems with fit is limited. Retailers who interact directly with the customer are not trained in fit and the general shopping culture does not allow time for retailers to obtain fit data as customers are trying on clothing. The little information that is available is difficult to interpret and difficult to apply to sizing improvements. Technical designers, patternmakers and graders in the industry are highly skilled at fitting garments to the fit model and understanding the complexities of pattern grading and fit. These professionals could benefit from information about the fit of the garments throughout their size range on the various sizes and body shapes of customers in their target market. Apparel technicians have the knowledge to create innovative and effective sizing systems, but they need reliable and useful data to make decisions.

With the introduction of 3D body scanning, measurement data on body dimensions from the population are increasingly available, but interpolating from the body measurement data to the actual fit of the firm’s clothing throughout the size range is difficult. Body measurements are presented as mathematical data in a form that is unfamiliar to apparel practitioners. Though these data can certainly contribute to the development of effective sizing systems, a good understanding of statistical measures is necessary to understand and implement changes based on measurement data. Most apparel technicians do not have this knowledge. These data are also limited in their ability to fully characterize a variety of postures and body proportions of the target market. The rotating visual image from a 3D scan provides another type of data that can contribute to providing better fit. Both the numeric and visual data from scanning are useful for our research and also for a variety of industry initiatives to improve apparel fit using body scan data. The development of a tool to capture visual data on fit for the apparel industry using the 3D scanner and other image capture and analysis methods can contribute valuable information on sizing to apparel firms. Images can be captured and automatically organized in a format appropriate for viewing by apparel professionals who are familiar with the fit issues inherent in their sizing system, with their own styles, and with their own target market customers. This system would allow apparel companies to use the proven skills of their technical professionals on the application of scan data to apparel sizing decisions.
Integrated System to Design and Produce Engineered Knit Garments

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Nancy B. Powell, Lisa Parillo-Chapman (North Carolina State University)

Paradigm changing innovations in knitting technology, such as integral and seamless knitting, have intrinsically connected the creative designer and technical designer in the production of knitted garments. Knitted garments hold tremendous potential for providing innovative design solutions for aesthetic and performance challenges in applications such as medical, sports, fashion and military apparel. CAD systems utilized by designers can also drive the machinery used to produce fully fashioned and seamless garments. Shown below is a framework of identified technologies, materials, processes and linkages for creating and producing integral knit garments.
Designing and optimizing the supply chain has become a priority as well as a necessity for the survival of the US textile complex. However, the focus has been primarily on forward supply chain operations, and there has been very little consideration of utilizing recovered products or recycled raw materials and the reverse supply chain. As such, many of the current networks and/or products are currently not suitable for closed loop recycling. Closed loop recycling is becoming increasingly important due to consumers’ heightened environmental consciousness, governmental legislation, and raw material costs owing to fluctuations in oil prices. In 2007, the United States generated 254.1 million tons of municipal solid waste. Of this total disposal, 11.9 million tons were discarded textile wastes. Only 1.9 million tons, or 15.9%, were recovered for recycling, energy generation, or composting (U.S. EPA website). Because of the large amount of textiles consumed on a yearly basis, developing closed loop recycling systems has the potential to have a significant positive environmental impact, and, if efficient, a positive impact on revenues of textile companies as well.

Developing an efficient closed loop recycling system for textile materials involves both creating processes to transform the used material into a desirable output and then setting up and operating appropriate manufacturing and logistics distribution structures for the arising flows of recovered products. This project is investigating and focusing on the latter. The goal of this project is to determine how to design robust closed loop recycling systems for different sectors of the textile complex, addressing similarities and differences in methods of collection, distribution networks, and manufacturing management strategies. The outcome will be a set of new optimization models that can be used to design the closed loop system as well as forecast estimation models of returned products. From these models, companies will be able to determine the efficiencies and cost effectiveness of their proposed closed loop recycling systems.
This research will develop a “checklist manifesto” that maps the sustainability of new textile products before they are adopted for production. The concept of the “checklist manifesto” can be found in the airline industry and more recently being developed for medical surgeries as a way to prevent errors, failures, and potential catastrophes. As new products change from the Ideation stage through the research, design, development, approval, and product launch stages, many different corporate and customer requirements are infused. The textile complex does not have an organized plan to assess the “sustainability” of new textile products throughout the value-chain, nor through the new product development stages.

Sustainability is now recognized to have three pillars: Environmental, Social, and Economic, each with differing criteria that must be considered to assure Sustainability. Many of the texts and publications, while providing excellent insights into sustainability, have not developed the tools and practices needed to provide the textile industry with a way to approach sustainability. Developing the sustainability checklist manifesto seeks to build a system that integrates known sustainability measures into a “new product assessment” framework. This framework will reduce the incidences of non-sustainable products entering the textile complex.

The team plans to develop the Sustainability Checklist Manifesto, test, refine, and validate the manifesto, and make the system available to the industry. This approach will accomplish at least two major objectives: a) Provide a definitive approach to evaluate new products from a sustainability Go/NoGo perspective; b) Identify opportunities for the next generation of new textile products built on different platforms and adhering to new criteria as a way to sustain competitiveness.
Plants are largely composed of cellulose fibres in a matrix of some sort. The major variables are those which would be found in a textile (orientations of, and interactions between, the fibres) and a composite material (interactions of fibre and matrix, modifications of the matrix). Materials are unresponsive: examples are wood, which has inspired a material with very high specific toughness in impact, and a lily leaf, which has interesting fracture behaviour. Mechanisms can respond to their environment: examples chosen are based on bilayers, which can change shape in gradual or catastrophic modes in response to environmental cues. These examples are adaptive in some manner, illustrating the selective advantage they give to the relevant organisms and implying advantage for a biomimetic version. Commercial development will be illustrated.
Building Interactivity in Textiles and Related Fibers

Adrian Freed, Research Director
CNMAT, UC Berkeley, and Fine Arts, Concordia University, Montreal

After a quick review of recent rapid developments in intrinsic fiber and textile sensing and actuation, Dr. Freed will demonstrate pressure, stretch, position, acceleration, and multitouch sensors built with paper and textile structures. Their performance will be shown informally by integrating them into functional musical instruments. He will close with a vision of how a design theory and practice may be developed for these materials, illustrated with new, folded, and pleated piezoresistive structures that have just begun to be explored.
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