Tuesday, October 9

Alumni Center

7:30  Registration and Continental Breakfast
8:10  Welcoming Remarks, Business and Announcements  You-Lo Hsieh, Conference Chair and President, Fiber Society

Morning Session

<table>
<thead>
<tr>
<th>You-Lo Hsieh, Day Chair</th>
<th>Ning Pan, Day Chair</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGR, Alumni Center</td>
<td>University Club, Club Room</td>
</tr>
</tbody>
</table>

**Session 1A. Electrospinning and Nanofibers**
**Heidi Schreuder-Gibson, Chair**

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:30</td>
<td>Correlation of Structure, Orientation and Morphology with Properties in Electrospun Polymer Nanofibers</td>
<td>John Rabolt, Keun-Hyung Lee, Steve Givens and Bruce Chase, University of Delaware</td>
</tr>
<tr>
<td>9:00</td>
<td>Analysis of Electrospinning Process Dynamics and Resulting Nanofiber Diameter Distributions</td>
<td>Michael Gevelber and Xuri Yan, Boston University</td>
</tr>
<tr>
<td>9:30</td>
<td>Physical Principles of Needle-less Electrospinning-Cleft Electrospinners</td>
<td>David Lukáš and Arindam Sarkar, Technical University of Liberec</td>
</tr>
<tr>
<td>10:00</td>
<td>Fabrication and Evaluation of Electrospun Nanofibrous Antimicrobial Nylon 6 Membranes</td>
<td>Kuiatan Tan and Kay Obendorf, Cornell University</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:30</td>
<td>Correlation of Structure, Orientation and Morphology with Properties in Electrospun Polymer Nanofibers</td>
<td>John Rabolt, Keun-Hyung Lee, Steve Givens and Bruce Chase, University of Delaware</td>
</tr>
<tr>
<td>9:00</td>
<td>Analysis of Electrospinning Process Dynamics and Resulting Nanofiber Diameter Distributions</td>
<td>Michael Gevelber and Xuri Yan, Boston University</td>
</tr>
<tr>
<td>9:30</td>
<td>Physical Principles of Needle-less Electrospinning-Cleft Electrospinners</td>
<td>David Lukáš and Arindam Sarkar, Technical University of Liberec</td>
</tr>
<tr>
<td>10:00</td>
<td>Fabrication and Evaluation of Electrospun Nanofibrous Antimicrobial Nylon 6 Membranes</td>
<td>Kuiatan Tan and Kay Obendorf, Cornell University</td>
</tr>
</tbody>
</table>

10:30 Break

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:45</td>
<td>Fabrication, Structure and Properties of PS / CNT Electrospun Fibers</td>
<td>Saeedeh Mazinanip1, Abdellah Ajjii2 and Charles Dubois1, École Polytechnique of Montreal, 1Industrial Materials Institute, 2Industrial Materials Institute</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Controlled Growth Factor Release from Poly (lactide-co-glycolide) Nanofibers</td>
</tr>
</tbody>
</table>

10:45  Fabrication, Structure and Properties of PS / CNT Electrospun Fibers  Saeedeh Mazinani1, Abdellah Ajjii2 and Charles Dubois1, 1École Polytechnique of Montreal, 2Industrial Materials Institute  Controlled Growth Factor Release from Poly (lactide-co-glycolide) Nanofibers  Steven Givens, Kristi Kiick, Bruce Chase and John Rabolt, University of Delaware
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Location</th>
<th>Chair</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:15</td>
<td>Silk Fibroin / Nylon 66 Blend Nanofibers by the Electrospinning Process</td>
<td>Development of Eye Patch Protector for Neonates Used in Phototherapy Treatment</td>
<td>Sachiko Sukigara, Masanori Akada and Masaya Kotaki, Kyoto Institute of Technology, Deng Yong-mei¹, Yick Kit-lun¹, Kwok Yi-lin¹ and Wong Siu-chun², ¹Hong Kong Polytechnic University, ²Hong Kong Queen Mary Hospital</td>
</tr>
<tr>
<td>11:45</td>
<td>SnO₂ and SnO₂ – MWNTs Nanofibers: Synthesis, Structural Characterization and Sensing Properties</td>
<td>Pressure Performance of the Compression Bandages in the Treatment of Venous Leg Ulcers</td>
<td>An Yang, Xiaoming Tao, Charles Surya and Lee Shun Cheng, Hong Kong Polytechnic University, Monica Sikka, S. Ghosh and A. Mukhopadhyay, Ambedkar National Institute of Technology</td>
</tr>
<tr>
<td>12:15– 1:40</td>
<td>Lunch — on your own</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Afternoon Session**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Location</th>
<th>Chair</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:40</td>
<td>Student Paper Competition: AGR, Alumni Center</td>
<td>Session 2B. Protective / Functional Applications I</td>
<td>Suresh Shenoy</td>
</tr>
<tr>
<td></td>
<td>Session 2A. Biobased-Fiber and Polymers</td>
<td>Session 2B. Protective / Functional Applications I</td>
<td>Suresh Shenoy</td>
</tr>
<tr>
<td></td>
<td>Lu Wang, Chair</td>
<td>Ron Postle, Chair</td>
<td></td>
</tr>
<tr>
<td>2:45</td>
<td>Models of Cellulose</td>
<td>Photocatalytic Functional Cotton Fabrics for Protective Clothing</td>
<td>Alfred French and Glenn Johnson, USDA Southern Regional Research Center, Kyung Hwa Hong and Gang Sun, University of California, Davis</td>
</tr>
<tr>
<td>3:15</td>
<td>Property and Higher Order Structure of Poly(l-lactic acid) / Poly (d-lactic acid) Blend Fibers</td>
<td>Quantification of Oily Contaminants in Flame Resistant Thermal Protective Textiles—A Radiotracer Analysis</td>
<td>Hideki Yamane¹, Daisuke Masaki¹, Yoko Fukui¹, Kiyotsuna Toyohara², Midori Ikegame² and Bunso Nagasaka³, ¹Kyoto Institute of Technology, ²Innovation Research Institute, ³University of Alberta</td>
</tr>
<tr>
<td>3:45</td>
<td>Break</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>4:00</td>
<td>Effective Removal of Poisonous Arsenic (As) from Drinking Water by Using Wasted Coffee Beans</td>
<td>Ultraviolet Protection of Clothing</td>
<td>Masatomo Minagawa¹, K. Horigane¹, K. Konno¹ and H. Akashi², ¹Yamagata University, ²Higashi Nippon International University, Ron Postle¹ and Michael Pailthorpe², ¹University of New South Wales, ²AgResearch Ltd.</td>
</tr>
<tr>
<td>Time</td>
<td>Event</td>
<td>Authors</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>4:30</td>
<td>Research on Dyeing and Antimicrobial Activities of Vegetable Dyes Extracted from W-CT Wool Fabric</td>
<td>Sha Xiangyu¹, Wang Lu¹,², Zhang Xinlong³, Jia Shunhua¹ and Zhou Qicheng¹, Donghua University, Ministry of Education, Heilan Group</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>A Dynamic Mannequin for Virtual Performance Testing of Functional Clothing</em></td>
<td>Colby Swan, Matthew Rasmussen, Rob Williams, Xiaolin Man and Salam Rahmatalla, University of Iowa</td>
<td></td>
</tr>
<tr>
<td>5:00–7:00</td>
<td>Poster Presentations and Table Top Exhibits — refreshments provided</td>
<td>University Club</td>
<td></td>
</tr>
</tbody>
</table>

**Wednesday, October 10**

*Alumni Center*

7:30 Registration and Continental Breakfast

**Morning Session**

*You-Lo Hsieh, Day Chair*  
AGR, Alumni Center

*Ning Pan, Day Chair*  
University Club, Club Room

| Session 3A. Fibers with Nanotubes and Nanoparticles  
*Takeshi Kikutani, Chair* | Session 3B. Innovative Uses and Enhancement I  
*Ian Hardin, Chair* |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8:30 Carbon Nanotube Reinforced Recombinant Spider Silk for Tissue Engineering Scaffolds</td>
<td>Modifying the Surface Properties of Specialty Polyolefin Elastomer-Based Elastic Nonwovens Through Additives</td>
</tr>
<tr>
<td>Milind Gandhi¹, Frank Ko² and Costas Karatzas³, Drexel University, University of British Columbia, Nexia Biotechnologies</td>
<td>Raja Dharmarajan, Smith Kacker, Vincent Gallez, A. D. Westwood and C. Y. Cheng, ExxonMobil Chemical Company</td>
</tr>
</tbody>
</table>

| 9:00 Preparation and Characterization of Polymer-Carbon Nanotube Fibers  
*Brett Ellerbrock, Konstantin Kornev, Phil Brown and Kate Stevens, Clemson University* | Towards a Photocatalytic Fiber for Degradation of Malodor  
*Felix Reifler, Axel Ritter, Giuseppe Fortunato, Andri Vital, Kranthi Akurati and Rudolf Hufenus, Empa* |
| Electrospinning of Nanoparticles-Filled Nanofibers  
*Heejae Yang¹, Wei-Heng Shih², Yoshihiro Yamashita³ and Frank Ko³, University of British Columbia, Drexel University, University of Shiga Prefecture* | Morphological Study of Fine-to-Nanosized Filaments from Polymeric Thin Films  
*Kyung-Ju Choi, AAF International* |
<table>
<thead>
<tr>
<th>Time</th>
<th>Session 4A. Fiber Formation: Process Technology I</th>
<th>Session 4B. Innovative Uses and Enhancement II: Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:00</td>
<td>The Development and Mechanical Properties of Carbon Nanotube Fibres</td>
<td>Understanding Coordination Polymerization and Its Value to Producing Stereoregular and Chiral Polymers</td>
</tr>
<tr>
<td></td>
<td>Ya-li Li, Marcelo Motta, Ian Kinloch, V. Premnath, Martin Pick, Alan Windle¹ and Michael Jaffe², ¹University of Cambridge, ²New Jersey Institute of Technology</td>
<td>Navzer D. Sachinvala</td>
</tr>
<tr>
<td>10:30</td>
<td>Break</td>
<td>Break</td>
</tr>
<tr>
<td>10:45</td>
<td>Melt Spinning of Poly(ethylene terephthalate) Using Water-Quenching Bath Placed at Extremely Short Air-Gap Length</td>
<td>Homogeneous Modification of Cellulose with Chloro-2-Hydroxypropyl Trimethylammonium Chloride</td>
</tr>
<tr>
<td></td>
<td>Tomoyuki Enya, Hiroshi Ito and Takeshi Kikutani, Tokyo Institute of Technology</td>
<td>Khaled El-Tahlawy and Renzo Shamey, North Carolina State University</td>
</tr>
<tr>
<td></td>
<td>Kensuke Nakahara¹ and Takeshi Kikutani², ¹Japan Chemical Innovation Institute, ²Tokyo Institute of Technology</td>
<td>Siqiang Zhu and Douglas Hirt, Clemson University</td>
</tr>
<tr>
<td>11:45</td>
<td>Fiber Extrusion of Highly Immiscible Polymer Blends</td>
<td>Green Chemistry for Fibers and Textiles</td>
</tr>
<tr>
<td></td>
<td>Pratapkumar Nagarajan, Kathryn Abbott, Sarang Deodhar and Donggang Yao, Georgia Institute of Technology</td>
<td>Ian R. Hardin, University of Georgia</td>
</tr>
<tr>
<td>12:15–1:30</td>
<td>Lunch — on your own</td>
<td></td>
</tr>
</tbody>
</table>

**Afternoon Session**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 5A. Fiber Formation: Process Technology II</th>
<th>Session 5B. Protective / Functional Applications II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:30</td>
<td>Variation of Drawability with Storing Time for Melt-Spun Poly(ethylene terephthalate) Fibers</td>
<td>Development of Textile Fibers with a Conducting Metal Core</td>
</tr>
<tr>
<td></td>
<td>Akira Hamano¹ and Takeshi Kikutani², ¹Japan Chemical Innovation Institute, ²Tokyo Institute of Technology</td>
<td>Stephen Fossey¹, Thomas Godfrey¹ and James Brang², ¹US Army Natick Soldier RD&amp;E Center, ²Hills Inc.</td>
</tr>
<tr>
<td></td>
<td>Bugao Xu, Chair</td>
<td>Dominique Adolphe, Chair</td>
</tr>
<tr>
<td>Time</td>
<td>Title</td>
<td>Authors</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2:00</td>
<td>Shelf Life Extension of Pan-Based Carbon Fiber</td>
<td>Tracy B. Colwell¹ and Hung Ly², ¹Lockheed Martin Space Systems, ²YLA Incorporated</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Piezoresistive Response of Conductive Composite Fibers</strong></td>
</tr>
<tr>
<td>3:00</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>3:15</td>
<td>Analysis of the Tensile Behavior of Low-Twist Staple Fiber Assemblies</td>
<td>Xin Shao, Yiping Qiu and Youjiang Wang, Georgia Institute of Technology</td>
</tr>
<tr>
<td>3:45</td>
<td>Measuring Cotton Fiber Length and Length Distribution Using Image Analysis</td>
<td>Weilin Xu¹², Bugao Xu², Wen Bin Li¹ and Weigang Cui¹, ¹Wuhan University, ²University of Texas, Austin</td>
</tr>
<tr>
<td>4:15</td>
<td>Contribution to the Study of the Elongation of the Cotton Fiber</td>
<td>H. Benzina¹², O. Harzallah¹, J. Y. Dréan¹, E. Hequet¹ and N. Abidi², ¹ENSISA, ²Texas Tech University</td>
</tr>
</tbody>
</table>

4:45  General Body Meeting, University Club: **Open to Fiber Society Members Only**

6:30  Reception and Banquet, AGR, Alumni Center
Banquet Speaker: Prof. Charles W. Bamforth, Anheuser-Busch Endowed Chair of Brewing Science — Beer: Soluble Fiber and Much More Besides
Awards Presentation
Thursday, October 11

Alumni Center

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
<th>Speaker(s)</th>
<th>Institution(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:30</td>
<td>Registration and Continental Breakfast</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>You-Lo Hsieh, Day Chair</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AGR, Alumni Center</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8:30</td>
<td>Session 7A. Formation / Fabrication / Characterization and Modeling</td>
<td>Michael Ellison, Chair</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Multiweave-Multiaxial Technical Fully Interlaced Woven Fabric and</td>
<td>Mário Lima¹, Raul Fangueiro¹, António Costa², Christian Rosiepen³, Válter</td>
<td>University of Minho, ³P &amp; Maia Lda, ³ITA, ⁴IAITI</td>
</tr>
<tr>
<td></td>
<td>Prototype Weaving Machine</td>
<td>Rocha³, ¹University of Minho, ³P &amp; Maia Lda, ³ITA, ⁴IAITI</td>
<td></td>
</tr>
<tr>
<td>9:00</td>
<td>Modeling Radioactive Heat Transfer in Multifilament Fiber Melt-Spinning</td>
<td>Young-Pyo Jeon and Christopher Cox,</td>
<td>Clemson University</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9:30</td>
<td>Yarns Tension Distribution and Rapture Mechanism in Narrow Strip of</td>
<td>Mehdi Dolatabadi and Radko Kovar,</td>
<td>Technical University of Liberec</td>
</tr>
<tr>
<td></td>
<td>Plain Weave Fabric Under Bias Stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:00</td>
<td>Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:30</td>
<td>Biosynthesis and Application of Colorants from Microorganisms for Use</td>
<td>Farzaneh Alihosseini and Gang Sun,</td>
<td>University of California, Davis</td>
</tr>
<tr>
<td></td>
<td>on Textile Materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:45</td>
<td>Novel pH-Sensitive Hydrogel Fibers Based on Hydrolyzed-Polyacrylonitrile and Soy Protein</td>
<td>Liwei Yu¹, Gang Sun² and Lixia Gu¹,</td>
<td>Donghua University, ²University of California, Davis</td>
</tr>
<tr>
<td>11:15</td>
<td>Conference Concludes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Poster Presentations

5:00 PM–7:00 PM, Tuesday, October 9
Gang Sun, Chair

Enzymatic Formation of Colorants
Gisela Buschle-Diller, Presenter

Gas Transmission Rate Through Microporous Membranes
Yasser Gowayed, Presenter

Melt-Induced Grafting of Polypropylene with N,N-Diallylmelamine with Potent Antimicrobial Activity
Mohammad Badrossamay, Presenter

Detoxification of Organophosphorus Pesticides by N-Halamine Protective Textile Materials
Gang Sun, Presenter

Fiber Formation of Poly(tetrafluoroethylene) from Its Emulsion
Hideki Yamane, Presenter

Contribution to the Development and the Industrialization of a Three-Dimensional Nonwoven System for Automotive Interior Applications
Nicole Njeugna, Presenter

Effect of Wool Components in Pile Fabrics on Water Vapor Sorption, Heat Release and Humidity Buffering
Phil Gibson, Presenter

Numerical Analysis of Energy Absorption Mechanism in Multiply Fabric Impacts
Ju Hyun Kim, Presenter

Influence of the Technique of Sizing with Pre-Wetting on the Mechanical Properties of a Sized Yarn
Omar Harzallah, Presenter

Friction and Wear of Conductive Polyester Filaments
Omar Harzallah, Presenter

Melting Temperature (Tm) for Single Crystals of Stereoregular Isotactic Poly(acrylonitrile) Prepared by Isothermal Solution Crystallization from Different Organic Solvents
Masatomo Minagawa, Presenter

Moulding Conditions for Seamless Bra Cup
Yong-mei Deng, Presenter

Interactions in Cellulose Solutions
Min Xiao, Presenter

Nanocomposite Fibers Electrospun from Biodegradable Polymers
Chunhui Xiang, Presenter
Chitosan Nanofibers by Electrospinning from Aqueous Solutions
Jian Du, Presenter

Layer-by-Layer Polysaccharidic Self-Assemblies on Cellulose Nanofibers
Bin Ding, Presenter

Polyacrylamide Hydrogel Nanofibers by Electrospinning
Ping Lu, Presenter

Controllable Biotinylated Poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA) Nanofibers to Bind Streptavidin-Horseradish Peroxidase (HRP) for Potential Biosensor Applications
Gang Sun, Presenter

Analysis of Electrospinning Process Dynamics and Resulting Nanofiber Diameter Distributions
Xuri Yan, Presenter

Development of Thermoplastic Polyurethane Vascular Prostheses Using Solvent-Electrospinning Methods
Chung Hee Park, Presenter
SESSION 1A

ELECTROSPINNING AND NANOFIBERS
Motivated by the observation (1,2) that electrospun fibers collected on a charged, gapped plate exhibit uniaxial orientation, a thorough study of the dynamic effects of an electric field on moderately concentrated polymer solutions as the solvent evaporates has been undertaken. In addition, in several instances, the electrospinning process leads to changes in the conformation and/or crystal structure (3) of a polymer which is different, and sometimes less stable, than observed for either the bulk material or conventionally spun fibers. This suggests that the interaction of the electric field, used in the electrospinning and/or nanofiber collection process, with the evaporating polymer solution is a critical factor in determining the final properties of the electrospun fibers. Examples of uniaxial orientation in poly(ethylene oxide) nanofibers collected on a gapped plate (2) and studies of polymorphic transitions in electrospun poly(1-butene) fibers (3) will be discussed to illustrate these points.

ANALYSIS OF ELECTROSPINNING PROCESS DYNAMICS AND RESULTING NANOFIBER DIAMETER DISTRIBUTIONS

M.A. Gevelber and Xuri Yan

Boston University, Manufacturing Engineering Department, 15 St. Mary’s st. Brookline, MA, 02446, USA
email: gevelber@bu.edu, xryan@bu.edu

In many emerging, high value electrospinning applications, the fiber diameter distribution affects the fiber’s performance and production economics (production rate and material utilization of expensive feedstock in some biomedical applications). However, the current state-of-the-art electrospinning process is run open-loop, which in many cases, results in broad distributions that vary over time. This paper addresses issues for developing a real-time electrospinning control system that can enable greater control over nanofiber diameter distributions. The fundamental process dynamics are identified, and the relationship between measurable process states and the resulting fiber-diameter distribution is examined.

A well instrumented and computer based actuator control system has been developed. The sensing schemes (Fig. 1) include: a) measurement of the dynamic Taylor cone volume for determination of the flow rate entering the jet, Qjet, b) length of the upper jet Luj, since it reflects the local force balance related to the onset of whipping, c) angle of the whipping region, θ, as well as the motion in the upper whipping region since it reflects a region where there is a major reduction in fiber diameter, and d) high precision fiber current measurement which gives the charge amount embedded in jet/fiber.

Stable operating conditions were determined (Fig 2) for two, 400K molecular weight PEO concentrations of 6% and 8%. For high voltages, a narrow tapered Taylor cone was observed (image 3 at point 3 in Fig. 2), while for low voltages, a larger volume was observed (image 2 for point 2 in Fig. 2). Finding the stable operating condition for some material solutions can be small (eg. 6% PEO, low flow rate).

Fig. 3 shows the dynamic variations of these variables for condition 1 while Fig. 4 shows the resulting fiber diameter distribution. These experiments reveal that large variations of measured variables are correlated to the resulting large variations in fiber diameter, suggesting that implementing real-time control can provide an enhanced...
ability to control diameter distributions. While for all of the conditions evaluated, there are variations in all variables, these variations remain bounded, and the process is operating in a bounded stable state, since while there are variations, they do not grow without bound. Note, condition 1, which has large variations, is considered only marginally stable, in that it produced continuous fibers, but the large variations in state (current, cone volume, etc) resulted in large variations in fiber diameter.

Fig. 5 and Fig. 6 shows the Fourier power spectral decomposition of charge density, upper jet length, and measurement of the whipping region in terms of interference with a laser beam that crosses the whipping region for one operating point. All three reveal that there are dominant low frequency modes of variation (on the order of 6 Hz and less), but that the laser measurement system is picking up important higher frequency modes that are expected to have a significant impact on variations.

To examine the need for control, five, 30 minute runs of the same condition were conducted in order to mimic the process variations that occur when the electrospinning system is cycled on and off. Several interesting variations are observed: a) there are large transient excursions (spikes that are over twice the volume level), but they are slow enough (10 sec) to be controlled, b) the final steady-state condition varies from run to run even though the same input conditions are achieved (a 17% variation in steady-state current), and c) there is a long initial transient period (25% of the run time changing the states by 25%). Similarly, Fig. 7 shows the drift that was observed over 11 days, requiring a 14% change in inputs to maintain the same process window. These results indicate the desirability of a closed loop system in order to minimize run-to-run variation.

To aid in designing a real time control algorithm, we have conducted system characterization experiments. A step change in the power supply voltage is made to observe the dynamic response characteristics in terms of the steady state gain (indicating how large the output value changes for a change in input) as well as how fast the process responds when a potential control input is changed. Fig. 8 shows the current has a large overshoot, while change density (I/Qjet) has characteristic right-half-plane dynamics, and both have dynamics on the order of 2 seconds. These dynamic characteristics pose issues that need to be considered in designing the control algorithm.

Lastly, a low order model is presented to provide insight into the relation of process dynamics to the operating condition.
Electrospinning is a novel method to spin very tiny fibers. The contribution is focused on physical aspects of highly productive and so industrially applicable needleless variant of the technology. Electrospinning has been traditionally studied and realized on so-called needle electrospinners, where polymeric jets, from which nano-fibers are born, are created from a static hypodermic needle. The physical description of this phenomenon is based on nonequilibrium between capillary and electric forces. On the other hand needleless electrospinning, where polymeric jets are self-organized on a free liquid surface, is a result of polymeric solution surface dynamics. The main role in the dynamics plays a development of unstable surface waves, which amplitudes are ruled by the value of external electrostatic field strength. Theoretical consideration shows some substantial differences between needle and needleless electrospinning. Let us mentioned the dependence of critical field strength on polymeric solution surface tension, self-organization of jets in the needleless case and the fact that a jetting density in the instance of needleless electrospinning is govern be the field strength value.

The contribution contains both: the introduction to physical principles of needleless electrospinning and to experiments. Experiments were carried out with the free polymer solution surface realized in narrow slots between two parallel metallic plates. These devices are called here cleft electrospinners.

Keywords: Needleless Electrospinning, nano-fibers, cleft electrospinner
FABRICATION AND EVALUATION OF ELECTROSPUN NANOFIBROUS ANTIMICROBIAL NYLON 6 MEMBRANES

Kuitian Tan† and S. Kay Obendorf‡

Fiber Science, Cornell University, Ithaca, NY 14853-4401, USA.
email: kt89@cornell.edu; sko3@cornell.edu

With the growing public health awareness of the pathogenic effects, malodors and stain formations caused by microorganisms, there is an increasing need for antimicrobial synthetic materials in many application areas, especially as protective clothing for medical and chemical workers, first receivers, sportswear, underwear and other health related products, which will act against a wide range of gram-positive and gram-negative bacteria by inhibiting their growth (Cookson 2005; McDonald 2006). Many antimicrobial agents, such as antibiotics, silver ions, quaternary ammonium, N-halamines, and other biocidal agents, have been applied to textiles and membrane materials by various chemical and physicochemical finishing techniques to protect the substrates from chemical and biological activities. Among which, N-halamines have been extensively studied as an antimicrobial agents (Worley, Wheatley et al. 1992; Sun and Sun 2003; Chen and Sun 2006; Tan and Obendorf 2007).

To extend the application of N-halamine chemistry, in this study, a series of structurally different N-halamines, chlorinated 5,5-dimethylhydantoin (CDMH), chlorinated 2,2,5,5-tetramethylimidazolidin-4-one (CTMIO) and chlorinated 3-dodecyl-5,5-dimethylhydantoin (CDDMH), were introduced into the electrospinning dope of nylon 6 as antimicrobial additives for nanofibrous membranes. One of the major advantages of using N-halamines is that they are hydrophilic organic compounds which can be dispersed evenly to form a homogeneous spinning solution. Therefore, aggregation, which is one of the major drawbacks in mixing inorganic particles into polymeric matrices, and the resultant reduction of the bonding strength and decrease in the mechanical performance due to poorly exfoliated particles, can be avoided (Pukanszky 2005; Liu, Huang et al. 2006). Effects of N-halamine addition on the properties of electrospun nanofibrous membranes were investigated to better understand the structure-property relationship for making value added antimicrobial materials. Effects of N-halamine addition on the properties of electrospun nanofibrous membranes were investigated. Nuclear Magnetic Resonance (NMR) and attenuated total reflectance mode Fourier Transform Infrared Spectroscopy (ATR-FTIR) were used to identify the synthesized N-halamine structures. Differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD) revealed that the fraction of $\gamma$ form crystals ($T_m \approx 212 \, ^\circ C$) increased with the increase in the N-halamine content. Energy Dispersive X-ray mapping patterns confirmed the uniform distribution of N-halamines on the membrane surface. A total reduction of both *Escherichia coli* (gram-negative bacteria) and *Staphylococcus aureus* (gram-positive bacteria) was observed after a short contact period (Fig. 1 and Fig. 2). The migration or diffusion of N-halamines from the nanofiber surface and the fiber matrix raise the concern of potential antimicrobial activity reduction and skin irritation in use. Therefore, absorbance at 250 nm, which was attributed to the hydantoin ring absorption, was monitored over a 24 h period to study the leaching kinetics of N-halamines from the electrospun nylon 6 membranes (Fig. 3). There were very weak UV absorptions for both CDMH and CTMIO containing nylon 6 membranes indicating slight leaching, while there was no observable leaching for CDDMH containing nylon 6 membranes during the experimental period using methanol which is a good solvent for N-halamines. Since N-halamines have limited solubility in water as compared to methanol, potential leaching in water is expected to be negligible.

References


Figure 1. Antimicrobial efficacy of nanofibrous nylon 6 membranes with different N-halamine additives against (a) *S. aureus*, (b) *E. coli*. Active chlorine contents were 1125 ±50 ppm for the samples.

Figure 2. Antimicrobial efficacy of electrospun nylon 6 membrane with CTMIO additives at two different level of active chlorine content (Low: 743 ppm, High: 1125 ppm) against (a) *S. aureus*, (b) *E. coli*.

Figure 3. Leaching kinetics of electrospun 25% (wt %) nylon 6 membranes containing 5%: (a) CDMH, (b) CTMIO, (c) CDDMH.
FABRICATION, STRUCTURE AND PROPERTIES OF PS/CNT ELECTROSPUN FIBERS

Saeedeh Mazinani ¹, Abdellah Ajji ², Charles Dubois ³

1) CREPEC, Department of Chemical Engineering, Ecole Polytechnique of Montreal, P.O. Box 6079, Station Centre-Ville, Montreal, Quebec, Canada H3C 3A7. E-mail: saeedeh.mazinani@polymtl.ca

2) Industrial Materials Institute, National Research Council Canada, 75, de Mortagne, Boucherville, Quebec, Canada JB4 6Y4. E-mail: Abdellah.Ajji@imi.cnrc-nrc.gc.ca

3) CREPEC, Department of Chemical Engineering, Ecole Polytechnique of Montreal, P.O. Box 6079, Station Centre-Ville, Montreal, Quebec, Canada H3C 3A7. E-mail: charles.dubois@polymtl.ca

Introduction
Exclusive properties of various types of carbon nanotubes (CNTs) such as their mechanical, electrical and optical properties have made them reasonable candidates to be employed for fabrication of novel composite materials. The exceptional electrical conductivity of CNTs generated a lot of interest in the recent few years and various CNT composite materials have been studied to exploit this property. Electrospinning is establishing itself as the best recognized way of manufacturing nanofibers. This process is applicable for variety of materials such as ceramics and polymers of different molecular weights, structures, compositions and morphologies (Burger et al., 2006), (Seeram Ramakrishna, 2005). Electrospinning of CNTs based composite polymeric nanofibers has been employed with polymers such as PAN, PEO, and PMMA (Ge et al., 2004), (Lim et al., 2006), (Sundaray et al., 2006). Recently, it was applied to the system PS/MWCNT as a template for the self-assembly multi-layer technique (Pan et al.). In this work, we limit our attention to a simple system of PS/CNT employing different types of CNTs. Our aim is to assess the effects of the composition (polymer and CNT concentration, and CNT type) and of the electrospinning process conditions on the properties of the resulting nanofibers. The PS/CNT system is particularly suited for studying the process conditions controlling the electrospinning operation since CNTs are easily dispersed in the polymer solution. In addition to being easy to dissolve, the PS can also be readily removed by solvent from the resulting composites, if one wants to use this material as a temporary template.

Materials and Experiments
For preparing the initial solution for the electrospinning process, we used an extrusion grade polystyrene (PS), purchased from BASF Co., Di-Methyl Formamide (DMF) (PS solvent and CNT dispersion media) purchased from Aldrich Co. and different types of carbon nanotubes (CNTs) powder obtained from Helix Co. Neither coupling agents nor surface treatments were used to disperse the CNTs in the PS solution. The dispersion process was however assisted by a sonication method and for each CNT concentration evaluated, the mechanical mixing time was adjusted to achieve a satisfactorily dispersion of the CNT in DMF. The effect of the CNTs on the rheology of the suspension was studied using viscometry method. The final morphology of the nanofibers as well as CNTs presence and orientation were primarily assessed by a Scanning Electron Microscopy (SEM) technique using a JEOL, JSM-6100 and also field emission SEM (FESEM) Hitachi S-4700, X-ray diffraction measurements were conducted on D8, Discover (Bruker) equipment.

Results and Discussions
In this work, we studied different polymer concentrations along with various amounts and types of CNTs such as SWCNT (Single-wall Carbon Nanotube) and DWCNT (Double-wall Carbon Nanotube) and MWCNT (Multi-wall Carbon Nanotube). Nevertheless, we mainly focus on MWCNT as the main nanoparticle of study. We prepared several CNT suspensions in DMF solutions of PS and CNT, with different values of PS and CNT concentrations. The time of dispersion by sonication method depends on the amount and type of CNT added to the system. In solutions with higher amounts of CNTs, a longer period of time is necessary to achieve a stable mixture of PS/CNT solution.

At first, we performed viscometry measurements to study the change in the mixture viscosity by addition of CNTs. The other important parameter in electrospinning is conductivity and was expected to increase. The results obtained depict that adding CNT (1%) to PS solutions at different concentrations of polymers (5%, 10% and also 20%) causes into a decrease of flowing time in viscometry tests and in conclusion of viscosity. Therefore, the change in these two major electrospinning factors is expected to greatly influence the final fiber structure, morphologies and sizes. Electrospinning of pure PS solution and PS/CNT mixture was performed in stable condition of operation at different values of polymer concentrations. Even though, the grayish color of the electrospun PS/CNT samples obtained prove the CNT existence, we employed XRD to detect the MWCNT peak in 2θ = 26° which is exclusively related to MWCNT (Jason et al., 2004), since amorphous PS does not show any characteristic peak in this region.
Increasing the amount of PS and CNT could interestingly change the stable condition of operation. For instance, the jet zone length and surface area of splashed jet considerably decreases in the case of PS concentration increment. To investigate the final nanofibers sizes and morphologies, we employed SEM tests whose results for two polymer concentrations (10% and 20% PS) with various MWCNT amount are shown below.

![Electrospinning at the same processing condition. Flow Rate: 0.8 mL/hr; Distance: 15 cm; V=23 kV. a) 20% PS/DMF; b) 20% PS ; 1 wt% MWCNT/DMF](image)

The results obtained show the important effect of CNT addition on final fibers sizes and morphologies. The changes in morphology show that there is a transition from bead morphology to fiber by increasing CNT concentration. Therefore, not only PS concentration and molecular weight is vital as reported before for determining the fiber morphology (Shenoy et al., 2005), but also the characteristics of the particles inside could be an influential factor in bead/fiber transition morphology. The results prove that by adding CNTs, followed by changes in the amount of solution viscosity and conductivity changes the force balance in the system. As a result, the elastic, electrical and surface tension forces of the system change comparing to pure PS solution. Therefore, the characteristics of the system, such as bead/fiber morphological transition zone greatly changes.

**References**


SILK FIBROIN/NYLON 66 BLEND NANOFIBERS BY THE ELECTROSPINNING PROCESS

Sachiko Sukigara*, Masanori Akada*, Masaya Kotaki*

*Kyoto Institute of Technology, Advanced Fibro-Science, Graduate School of Science and Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan. Email: sukigara@kit.jp

1. Introduction
Silk fibers have been of great interest in the textile field for its attractive visual and tactile properties. Apart from textiles, silk has many applications such as scaffolds for tissue regeneration, membranes and cosmetic because of their outstanding biocompatible and biodegradable properties.

Electrospinning is a unique method capable of producing nanoscale fibers and nanocomposites. Utilization of this technique, regenerated silk nanofibers has been produced (Sukigara et al. 2003) to create the new property which natural silk fiber does not have. The tactile property generated from silk nanofiber assemblies are unique, probably because the combination of silk fibroin nature and the geometrical structure of fine silk fibroin fibers.

However the regenerated electrospun nanofiber is dominated by a random coil structure (silk I) thus partly water-soluble and the strength of nanofiber assemblies were not strong enough compared to the natural silk fiber nonwovens. For the improvement of the property, the common method is blending a synthetic polymer with silk without disturbing the unique tactile property. In blending other polymers with silk fibroin film, phase separation is one of the problems. Yi Liu et al. investigate a series of blend films of silk fibroin with nylon 66 and showed nearly miscible in all ratios except 50wt% silk. In this paper, the silk fibroin/nylon 66 blend nanofiber web was made by the electrospinning process and investigate the effect of blend ratio on the structure and surface properties of electrospun nanofibers and their assemblies.

2. Experimental
2.1 Preparation of Spinning Dope
The degummed silk fibers were dissolved in mixtures of aqueous calcium chloride and ethanol (H2O - CaCl2 - EtOH= 5:4:1 weight ratio) for 30 minutes and dialyzed against de-ionized water for 3 days. The regenerated silk fibroin sponge (SF) was obtained by lyophilization. This silk fibroin sponge and Nylon66 (Aldrich 32131-17-2) was dissolved in formic acid (Nacalai tesque, 98-100%) at the SF/Nylon blend ratio of 100:0, 90:10, 80:20, 70:30, 50:50, 30:70, 20:80, 0:100 in weight. The total concentration of SF/Nylon against formic acid was 10wt% constant in all spinning dope.

2.2 Electrospinning
The electrospinning setup Nanon (MECC Co.) was used with 27 gauge needles at the flow rate of 0.1 ml/hour. The applied voltage was 17 - 24kV at 15 cm distance between the collection plate and the needle. In the case of SF100% spinning dope, continuous pure silk nanofibers were not electrospun because of the low viscosity. Coaxial electrospinning (Sun et al. 2003) was carried out to fabricate the core( nylon )-shell(silk) structured nanofibers.

2.3 Characrerization
The diameter and morphology of the electrospun fibers were examined by scanning electron microscope SEM (Hitachi SSEMEDX-III) and AFM (Nano Scope IIIa, Digital instrument). FT-IR (Shimadzu IR Prestige21) and DSC (Perkin elmer, DSC7) was used to investigate the conformation of silk, nylon and blend webs. As one of the surface characteristic related to the tactile property, the surface friction of the electrospun web was measured by KES-SE tester (Kato tech. Co) using the contactor consists of 10 piano wires under the weight of 0.14N with a sliding speed of 1 mm/sec.

3. Results and Discussions
Figure 1 shows the DSC curves of silk fibroin, Nylon, Silk fibroin/Nylon 66 blend electrospun webs. The grass transition temperature $T_g$ for fibroin is around 80°C and shifted to 58°C of Nylon 66 with varying blend ratio. It is also noted that the crystallization peak was observed around 210°C for fibroin but disappeared to the increase in
the nylon blend ratio. Those finding confirmed that both silk and nylon were contained in the electrospun webs. Figure 2 shows the relationship between the fiber diameter and the silk blend ratio of electrospun web. Increasing the silk blend ratio decreases the fiber diameter. A methanol treatment in which web was immersed in methanol followed by drying was carried out to investigate the structure change of blend fibers. According to the AFM observations of silk fibroin/nylon66 fibers, the decrease of fiber diameter was observed at the blend ratio of SF80%/nylon20% samples treated methanol. According to the FTIR spectra of samples, only silk fibroin was crystallized by the methanol treatment. If silk fibroin was more exists outside a fiber, the crystallization of silk fibroin was reflected in the decrease of fiber diameter and also surface smoothness. It is considered that silk/nylon hybrid fibers may be constructed.

Coefficient of friction which can be an approximate measure of fabric smoothness was obtained for all the electrospun webs. The coefficient of friction (MIU) for the fiber assemblies is influenced by the fiber property, fiber orientation and also diameter. The obvious effect of fiber diameter on MIU was not found in this study. Values of MIU for pure nylon web is larger than those of silk rich webs such as the silk content becomes more than 80%. The MIU obtained by sample fabricated by the coaxial electrospinning indicated the same levels of those samples containing 80%SF. In the case electrospun web of 50% SF, values of MIU is similar to that of Nylon 100%.

4. Conclusions
Silk fibroin and nylon66 was dissolved in formic acid and the nanofibers were fabricated at the different blend ratios. Adding 10wt% nylon to silk fibroin in formic acid, the processability to fabricate nanofibers was improved. According to the DSC and FT-IR characterizations, both silk fibroin and nylon were confirmed in the electrospun blend web. Methanol treated blend nanofibers showed the crystallization of silk fibroin in a fiber by the AFM observation. It is considered that silk/nylon hybrid fibers may be constructed at the high blend ratio of SF.

References
Due to their large surface-to-volume ratio and small grain size, nano-structured semi-conducting materials have been predicted and demonstrated to be excellent candidates for ultrasensitive and highly miniaturized sensors. The fundamental sensing mechanism of these devices relies upon the change in electrical conductivity due to the interaction between the semi-conducting materials and the gas molecules to be detected, and is significantly influenced by the surface region grains. One-dimensional (1-D) and quasi-1-D semi-conducting metal oxide nanostructures, such as nanowires and nanobelts, have the smallest dimension for effective electron transport and therefore can be used as sensitive and efficient sensors that translate the gas recognition into an electrical signal (Kolmakov et al., 2005). SnO₂ has a large bandgap and high achievable carrier concentration that make it suitable for a wide range of applications such as gas sensors (Comini et al., 2005), transparent electrodes (Minami, 2005), and optoelectronic devices (Andersson et al., 1998). Electrospinning is a relatively simple and cost effective technique to produce nanofibers from a wide variety of polymer solutions. Li et al. prepared Sb-doped SnO₂ nanofibers by electrospinning a solution containing poly(vinyl pyrrolidone) (binder), tin and antimony (III) alkoxides, acetic acid and organic solvents (Li et al., 2003). Pinto et al. synthesized electrospun SnO₂ microfibers using a precursor solution containing dimethyldecanoate tin, PEO/water and chloroform (Wang et al., 2004).

In this paper, we report electrospinning of SnO₂ nanofibers from a precursor solution. Pure Tin oxide (SnO₂) and Multi wall carbon nanotubes doped (SnO₂-MWNTs) nanofibers prepared by the electrospinning method are used for the characterization and investigation of their sensing properties. Figure 1.1a is a low-magnification TEM image of pure SnO₂ nanofibers and the corresponding ringlike selected-area electron diffraction (SAED) pattern indicates that the nanofibers are polycrystalline. High resolution TEM micrograph (Figure 1.1b) reveals that samples calcinated at 500°C consist of random orientated nano-crystallites of SnO₂ with approximate 15nm in diameter. The in-plane bright field TEM image of SnO₂-MWNTs composite nanofibers and its corresponding dark field one are indicated in Figure 1.1c and Figure 1.1d, respectively. In these figures it can be seen that one nanotube is found to orient along the fiber axis, while another exhibit some degree of tortuosity. Figure 1.1e is a HRTEM image of the MWNT wall showing the 0.34nm separations between adjacent graphene sheets. This spacing coincides with the plane spacing of multi-wall carbon nanotubes. Figure 1.2a shows XRD pattern of pristine MWNTs and the diffraction angles at 2θ=26.23°, 44.38° can be assigned to the (002), (100) diffraction planes, respectively. The XRD patterns of the pure SnO₂ and SnO₂-MWNTs composite samples calcinated at 500°C, presented in Figure 1.2b and 1.2c, shows that all the diffractive peaks of SnO₂-MWNTs composite nanofibers are associated with rutile SnO₂ (JCPDS 41-1445). It is very difficult to elicit the characteristic peaks of the MWNTs (002), mainly because of the overlap of the broad rutile SnO₂ (110) peak and that of MWNTs. For the pure SnO₂ nanofibers calcinated at 500°C, shown in Figure 1.3, the fundamental Raman active mode A₁g, which usually appear in polycrystalline SnO₂ materials, is observed at 617 cm⁻¹. Figure 1.3a illustrates the
Figure 1.1 a,b) TEM images of SnO$_2$ nanofibers calcinated at 500°C. c,d) Bright field TEM images of SnO$_2$–MWNTs nanofibers calcinated at 500°C. e) Dark field TEM images of SnO$_2$–MWNTs nanofibers calcinated at 500°C. f) HRTEM image of a small section of MWNTs.

Figure 1.2 XRD patterns from (a) the MWNTs, (b) SnO$_2$ nanofibers and (c) SnO$_2$–MWNTs nanofibers.

Figure 1.3 Raman spectra of (a) SnO$_2$–MWNTs and (b) SnO$_2$ nanofibers calcinated at 500°C.

Raman spectrum of SnO$_2$–MWNTs composite nanofibers, indicating that the D and G modes of doped MWNTs at about 1362 cm$^{-1}$ and 1578 cm$^{-1}$, respectively. The room temperature of dc electrical conductivity of SnO$_2$–MWNTs fiber mats exhibits an improvement of about a hundred orders of magnitude from the pure SnO$_2$ fiber mats. Based on these fiber mats, two different types of sensing devices are developed. The measurement results show that these fiber based devices are promising in the fabrication of gas sensors for Nitric oxide (NO) and ammonia (NH$_3$).

References


SESSION 2A

BIOBASED-FIBER AND POLYMERS
Cellulose, a major component of plant cell walls, is found and often utilized in fibrous form. Cotton, rayon, lyocell (Tencel) and linen fabrics are all composed of cellulose, as is paper and many other products. The structure of cellulose has been the quintessential problem in polymer science. Landmark experiments include its identification as a unique material in 1838, initial X-ray diffraction studies in 1913, understanding of its polymeric nature in the 1920's, and discovery of different crystalline forms with X-ray and electron diffraction, as well as infrared and NMR spectroscopy, through the 1990's. Within the past decade, X-ray and neutron diffraction studies were applied to extremely crystalline samples to decipher the details of hydrogen bonding in several of the polymorphs. NMR and Atomic Force Microscopy also continue to provide details of the structures of cellulosic materials from a wide variety of sources. Despite this vast array of experimental technology, computer-based molecular models of cellulose continue to be of interest, both on their own and as important components of the experimental methods. This interest arises because almost none of the cellulose materials of commerce are as crystalline as the samples used for the recent diffraction studies. The usual crystallites often have roughly as many chains on the surfaces as in the interior, and those surface chains will, in general, be different than those within the crystallites. Non-crystalline regions are also observed. Experiment is much less definitive for the surfaces and non-crystalline regions, but those are the places where most of the interactions with other molecules occur.

Cellulose and other carbohydrates are difficult to model well because of their primary and secondary hydroxyl groups and their stereoelectronic effects. Consider the two anomic forms of single monosaccharide, with their rotatable groups in a few of the many orientations, for 15 different structures. The total potential energy may vary by about five kcal/mol. Several components of that energy, attributed to angle bending, torsion angle change, intramolecular van der Waals forces and dipole moments, will each have ranges of three to five kcal/mol. To successfully calculate the probabilities of the various arrangements, the force field must be very well balanced. Methods of calculating the energy continue to be controversial and, in some cases, limited by the available resources. Fortunately, computer speeds continue to increase, and clusters or “farms” of computers have become relatively inexpensive so the situation continues to improve. A substantial portion of our work has been dedicated to taking advantage of better computers to improve models of cellulose.

Our computer models have included extremely simple extrapolations of the observed crystal structures of very accurately determined small molecules that are closely related to cellulose (French & Johnson 2004). These models employ no energy calculations. Instead, the resulting structures are proposed based on the assumption that if the geometries of the individual glucose residues and their linkages can exist in the environment of the crystal, they are also possible in other environments. This work is heavily dependent on having a variety of small molecule crystal structures.

We have also employed sophisticated energy calculations. With the turn of the millennium, it has become practical to apply electronic structure theory (or quantum mechanics, QM) calculations to molecules such as cellobiose, the shortest cellulose chain French & Johnson 2006). Much remains to be done, as the simplest application is to the gas phase where isolated molecules are studied. The field is undergoing rapid development, especially with new Density Functional Theory methods becoming
available. They replace methods that have become obsolete in the light of newfound abilities to handle larger molecules.

Empirical force field methods, also known as molecular mechanics (MM), still are the mainstay of cellulose modeling. Both QM and MM can be used in various types of energy minimization studies, with answers from MM coming four or five orders of magnitude more quickly than credible QM results. QM and MM methods have also been combined in hybrid energy calculations. We have applied several popular types of MM methods, as well as QM::MM hybrid (French et al. 2000) and QM studies to cellobiose. For the results on isolated molecules to be truly predictive, we must break some established rules.

MM methods can also be used for much larger models, such as crystallites. These can be studied with both energy minimization and with molecular dynamics. Again, the results depend on the method used.

The lecture will summarize our work with these different scales of models. Besides showing the needed strategies for successful reproduction of experiment with the various methods, we will focus on a long-standing controversy in cellulose structure: whether the structures with two-fold screw axis symmetry are at a minimum in their potential energy.

References


PROPERTY AND HIGHER-ORDER STRUCTURE OF POLY(L-LACTIC ACID)/POLY(D-LACTIC ACID) BLEND FIBERS

1) Hideki Yamane, 2) Daisuke Masaki, 2) Yoko Fukui, 3) Kiyotsuna Toyohara, 3) Midori Ikegame and 3) Bunso Nagasaka

1) The Center for Fiber & Textile Science, Kyoto Institute of Technology, Kyoto 606-8585 Japan.
   (Email: hyamane@kit.ac.jp)
2) Graduate School of Science and Technology, Kyoto Institute of Technology, Kyoto 606-858, Japan.

1. Introduction

Poly(L-lactic acid) (PLLA) is one of the bio-based polymers obtained from natural resources and expected to be used as fibers, films and other products. However it does not have enough thermal stability for some applications such as textile fibers. Although most synthetic fibers, such as nylon 66, nylon 6, and PET have a melting point higher than 200°C, PLLA has a melting point around 180°C. One of the fundamental ways to increase the melting temperature of poly(lactic acid) is to produce so-called “stereocomplex type crystal” formed in the equimolar blend of PLLA and poly(D-lactic acid) PDLA. This stereocomplex crystal has a melting temperature about 50°C higher than that of PLLA.

In this study, we investigated the effect of the blending condition of PLLA and PDLA on the efficiency of the stereocomplex formation in the blend. Further the mechanical property and the higher-order structure were examined for the blend fibers melt spun from the PLLA/PDLA blend prepared.

2. Experimental

Poly(L-lactic acid) (PLLA: Mw = 1.97 x 10^5, OP ~ 100%) and poly(D-lactic acid) (PDLA : Mw = 1.77 x 10^5, OP ~ 100%) were used. These were vacuum dried for 2 hrs at 80°C and for 12 hrs at 130°C before use. Equal amounts of PLLA and PDLA were mixed in a laboratory size mixer and a single screw extruder at various temperatures between 180 and 250°C. Melt spinning of the blend was carried out at 250°C in the same extruder equipped with a mono-hole die. As spun fiber was then drawn and annealed under tension at various temperatures. Mechanical and thermal properties were examined by tensile test and DSC measurements, respectively. Higher-order structure was investigated with WAXD and SAXD.

3. Results and Discussion

When PLLA and PDLA were mixed at a temperature higher than 220°C, the blend melt was extruded. DSC curves of the quenched blend melts showed a crystallization peak around 100°C, and two melting peaks around 180 and 230°C as shown in Fig.1. These two endothermic peaks are considered to be due to the melting of PLLA or PDLA homo-crystal and that of the stereocomplex crystal. On the other hand, when they were mixed at a temperature between 180 and 210°C, the solid blend came out from the mixer and this solid blend only showed a melting peak of stereocomplex crystal at 230°C. The mechanism of the stereocomplex formation in this process may be as follows: When PLLA and PDLA were blended at a temperature between 180 and 210°C, these PLAs melted and stereocomplex formed efficiently at the interface between PLLA and PDLA melts. However the blend shows two melting peaks after being re-melted and quenched. This result indicate that the stereocomplex crystal once formed in the blend easily separates into PLLA and PDLA pure phases when the blend was melted in a static state. However when the blends were melt kneaded again in an extruder, they only showed a melting of stereocomplex.

The blend prepared at 190°C was melt spun at 250°C and the fiber obtained was drawn and annealed. The fiber drawn at 80°C up to 4 times showed a broad WAXD reflection of the homo-crystal and no reflection from stereocomplex were observed. The fiber annealed at a temperature between 140 and 180°C under tension showed only WAXD pattern of highly oriented stereocomplex crystal. The strength and the modulus of the fiber increased and the elongation at break decreased with annealing temperature.
Effective Removal of Poisonous As in Drinking Water
by Using Wasted Coffee Beans

Masatomo Minagawa, Keigo Horigane, and Keitarou Konno
Graduate School of Science & Engineering, Yamagata University,
Yonezawa-campus, 992-8510, Japan
Tel&Fax:+81-238-26-3042; E-mail:minagawa@yz.yamagata-u.ac.jp

Hideaki Akashi
Department of Environment and Social Welfare, Higashi Nippon
International University, Iwaki, 970-8567, Japan

ABSTRACT: In Africa and east-Asia, there live numerous people suffering from poisonous As contained in drinking water. Many attempts have been taken to solve this problem from an industrial point of view by using nano-technology, etc. Some of these are bringing about good results. However, these methods require a large amount of money and their applications to these areas have been limited. In our Laboratory, a very simple experimental method was found. When As-pollutioned water was passed into thick layer of wasted coffee beans in a glassy column, As was effectively absorbed. More than 80-90% of As was removed by this method. In contrast, such an effect was not observed in black tea and green tea. The optimum conditions were extracted. Since wasted coffee beans can be prepared easily in these countries, many non-rich people suffering from this serious problem can be saved by their own hands. The experimental process leading to the optimum conditions are discussed in detail. We consider that the most important point is alteration of our philosophy from (give and take) to (give and give) from a global point of view for the solution of the complicated and serious problems in these countries in the 21st century.
RESEARCH ON DYEING AND ANTIMICROBIAL ACTIVITIES OF VEGETABLE DYES EXTRACTED FROM W-CT ON WOOL FABRIC

Sha Xiangyu1, Wang Lu1, 2,*, Zhang Xinlong3, Jia Shunhua1, Zhou Qicheng1

1 College of Textiles, Donghua University, Shanghai, 201620, P. R. China
2 The Key Lab of Textile Science & Technology, Ministry of Education, Shanghai, 201620, P R China
3 Heilan Group, Jiangsu province, 214426, P. R. China
* wanglu@dhu.edu.cn

1. Introduction

The value of vegetable dyes has been reconfirmed recently in China, owing to its environmental friend property and rich resource. There are a few reports about research on applying vegetable dyes to the fabric for the antimicrobial action (Lin et al 2005, Rajni & Astha. 2005). This paper reports the dyes and properties of antimicrobial activities of vegetable dyes extracted from W-CT on wool fabric in quantitative analysis.

2. Materials and Methods

Vegetable plant W-CT was selected. Its coloring matter was prepared by water and ethanol extractions and dyed on the mercerized knitted wool fabric in the direct dyeing and alum mordant dyeing.

Main equipment are UV-Visible spectrophotometer, colour eye instrument and color fastness instruments with respect to wash, perspiration, rub fastness suggested by Chinese national standard.

Staphylococcus aureus. and Gram positive organism Escherichia coli. (ATCC No.6538. and No.8739.) have been selected. Minimum inhibitory concentration (MIC) has been used in the testing organisms. The antimicrobial activity of W-CT on wool sample was evaluated by Chinese standard FZ/T01021-92.

3. Result and Discussion

3.1 Thermal stability of W-CT

The spectral absorption curve of W-CT dye liquor extracted in different temperature of water showed that absorbance at the maximum absorption peak is gradually large with the increment of the water temperature (Fig 1). As the configurations of each pectral absorption curve is quite similar, it can be deduced that the thermal stability of the coloring matter from W-CT is quite good, and W-CT can be extracted in boiling water in order to enhance the extraction efficiency.

3.2 Antimicrobial activity of W-CT in solution

It is evident from Table 1 that the W-CT solution has strong antimicrobial activity either water or ethanol extraction. But for Escherichia coli, its MIC using water extraction is smaller than that using ethanol extraction, so it is indicated that the W-CT dye solution extracted with water have stronger antimicrobial activity. MIC of the dye solution using water extraction for Escherichia coli is 1.953mg/ml, and for Staphylococcus aureus is less than 1.953mg/ml. While MIC of the dye solution using ethanol extraction for Escherichia coli is 31.25mg/ml, and for Staphylococcus aureus is less than 1.953mg/ml. In our next experiment, we utilize water as solution to extract W-CT.
## 3.3 Dyeing of wool samples

The wool fabric samples have been dyed under the optimum conditions through the orthogonal experiments of W-CT direct dyeing and premordanting dyeing (Sha 2007). Fig. 2 indicated that the rate of dye-uptake of pre-mordanting dyeing is higher than that of direct dyeing. It can be concluded that mordants can strengthen to increase the dyes’ ability to stick to the fiber. The wool samples dyed by W-CT have good wash fastness and perspiration fastness on grey scale ranging above 3 which meet the national standard. But the wet rub fastness is not satisfied only 2 and 2-3 on grey scale ranging (Table 2).

### Table 2 Colour fastness of W-CT on wool fabric

<table>
<thead>
<tr>
<th>Dyeing method</th>
<th>Wash fastness</th>
<th>Rub fastness</th>
<th>Perspiration fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C.S.</td>
<td>C.C.</td>
<td>C.W.</td>
</tr>
<tr>
<td>Direct dyeing</td>
<td>4</td>
<td>4-5</td>
<td>4</td>
</tr>
<tr>
<td>Premordanting dyeing</td>
<td>3-4</td>
<td>3-4</td>
<td>4-5</td>
</tr>
</tbody>
</table>

### 3.4 Antimicrobial activity of W-CT on wool samples

Antimicrobial activity of wool samples dyed with W-CT in the optimum dyeing condition was shown in Table 3. For Staphylococcus aureus and Escherichia coli, the samples dyed by direct and by pre-mordanting dyeing have showed remarkable antimicrobial activity, the reductions of bacterial reach 100% and more than 96% respectively.

<table>
<thead>
<tr>
<th>Dyeing method</th>
<th>Percent reduction of bacterial (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Staphylococcus aureus</td>
</tr>
<tr>
<td>Direct dyeing</td>
<td>100</td>
</tr>
<tr>
<td>Pre-mordanting dyeing</td>
<td>100</td>
</tr>
</tbody>
</table>

## 4. CONCLUSIONS

The coloring matter from W-CT has good thermal stability and its solution has strong antimicrobial activity either water extraction or ethanol extraction. But for Escherichia coli, the W-CT dye solution extracted with water have stronger antimicrobial activity owing that its MIC is smaller than using ethanol extraction. The wool samples dyed by W-CT have not only good dyeing fastness in general but also good antimicrobial properties.

**References**


SESSION 1B

FIBERS IN HEALTH AND MEDICINE
NEW DIELECTRIC ELASTOMERS FOR FIBER ACTUATORS

Tushar Ghosh
College of Textiles, North Carolina State University, Raleigh, NC 27695

Fiber actuators are capable of dimensional change under applied electrical field. Dielectric elastomer based prototype fiber actuators have been fabricated using commercially available dielectric elastomer tubes and by applying appropriate compliant electrodes to inner cavity and outer walls of these tubes. The force and displacement generated by such actuators have been studied under different isometric conditions and as a function of applied electric field. The actuation characteristics such as, axial strains, radial strains, and actuation blocking forces produced in the prototype upon actuation were studied. Actuation strain and blocking force are strongly influenced by the applied prestrain and have a parabolic relationship to applied electric field. High actuation strains (>50%) are currently afforded by dielectric elastomers at relatively high electric fields (>50 V/\mu m). A new class of electroactive polymers, suitable for fiber formation, have been developed by incorporating low-volatility, aliphatic-rich solvent into a nanostructured triblock copolymer yielding physically crosslinked micellar networks that exhibit excellent displacement under an external electric field. Ultrahigh areal actuation strains (>200%) at significantly reduced electric fields (<40 V/\mu m) has been achieved.
INTRODUCTION

Blood vessel diseases such as atherosclerosis are one of the major causes of human death in modern society and Western society [1]. Coronary artery and peripheral vascular diseases are the largest causes of mortality, necessitating surgical interventions including small-diameter bypass grafting with autologous veins or arteries [2,3]. However, appropriate autologous vessels (usually internal mammary artery or saphenous vein) for bypass conduits are not available in many patients. Compliance mismatch between veins and arteries also contributes to myointimal hyperplasia, particularly at anastomotic sites [4], and thrombosis is a common problem. This portrait depicted underlines the need for patent compatible tissue engineered small-diameter (0-6 mm diameter) vascular grafts. Tissue-engineered vascular grafts require a compliant polymer scaffold to which endothelial cells (EC) can adhere, form an anti-thrombogenic luminal surface [5], exhibit vasoactive properties [6] and improve patency [6–10].

Biodegradable synthetic polymers as scaffolds for arteries (small and large diameter) pose some risks due to the degradation products. Naturally derived biocompatible polymers may also be harmful namely due to transfections from other species. Conventional synthetic polymers such as PET have good tracking of success but their lack of bioactivity and biomechanical features (e.g., compliance) still remain significant issues. Electrospinning to produce fiber structures, although promising, is still far from the level of development necessary to produce full-size vascular grafts and it is not obvious that nanofibers are necessarily needed. In this study, we therefore investigated nonwoven PET fibers structures obtained from the melt blowing process as vascular scaffolds. The nonwoven nature of these structure will allow for mechanical compliance adjustment, in contrast to woven structures such as woven PET grafts (Dacron). The variables include fiber diameter distribution and structure porosity. A typical structure is shown in Fig. 1. Endothelial and smooth muscle cells were seeded in the structures with and without gelatin coatings and their growth and attachment observed.

Cell Culture

HBEC and AoSMC were respectively trypsinized with 1ml of either GRP-2 (Cells systems) or GIBCO (0.25%) trypsin. The Fibrous scaffolds in the form of discs were placed on Falcon 24-well plates and pre-wetted overnight either with cell media or with 0.5% gelatin. 50 µl of culture media containing $10^5$ cells were applied to the meshes and let them sit for 20 min before filling the wells with additional 450 µl of media. Cells were allowed to grow on the meshes for 6 days at 37°C in humidified atmosphere of 5% CO₂/95%. To visualize and quantify the number of living cells on the nanofiber meshes, cells were washed twice with warm HBSS, incubated with 10µg/ml CFDA (Molecular Probes) at 37º for 45 minutes and then washed again with HBSS. Fluorescence of the cells grown both on the meshes and on the bottom of the well (after removing the meshes) was measured using a cytofluorimeter plate reader. The counts from fluorescence on the various structures for both HBEC and AoSMC are presented on Fig. 2 and 3 respectively. The effect of CGRP in the production of cAMP was assessed in HBEC growing on structure E. The cells were incubated (10 min) with increasing concentrations (0.5-1 μM) of CGRP in phosphate buffer saline containing 0.2% bovine serum albumin and 1mM 3-isobutyl-1-methyl-xanthine. Levels of Camp were determined with a commercial enzyme immunoassay kit (Biotrak, Amersham). The cells were dissolved in 0.1 NaOH and protein content measured by Lowry’s method. cAMP levels were expressed as a function of protein content in cell extracts. Good proliferation and growth were observed on some structures.

Scaffold Compliance

The compliance of the scaffolds was measured using our custom-made set-up. Pressure-diameter curves are shown in Fig. 4 for cycle 1, 3, 5, 10, 30 and 100. These curves show that the scaffold exhibits an approximately constant compliance (initial slope) and that it undergoes a slight permanent deformation (e.g., 0.05 mm/mm) upon pressure cycling, whenpassing from cycle 1 to 100. The average compliance obtained from Equation 2 for the 100 cycles is $1.0 \pm 0.05$ MPa. This compliance figure compares well with reported compliance for arteries of 1 to 5 MPa (cf., Materials and Methods), demonstrating that it is possible to reproduce the compliance of arteries with nonwoven fiber scaffolds. This modulus figure differs significantly from the reported Dacron modulus values of 2000 to 4000 MPa and expanded polytetrafluoroethylene (ePTFE) of 400 to 1800 MPa.
In conclusion, these PET fibrous scaffolds present promising characteristics for vascular graft fabrication such as: **Controlable porosity, fiber orientation and compliance, no toxicity, Good HBEC and AoSMC cell attachment and proliferation following fiber alignment, HBEC grown on polymers, retain AC machinery for vasodilation, Elastic modulus is comparable to that of native arteries (~ 1MPa) and better than those of Dacron or PTF and finally, Cheap production.**

REFERENCES

The change of mechanical properties of bio-absorbable fiber over degradation time is valuable information for many applications, for example, surgical suture and mesh. It guides us to design proper polymer and processing system to match the requirements of applications such as wound and tissue healing profiles. Traditionally, in-vivo methods with different animal models have been used. However, in-vitro methods are preferred for quality control during production of bio-absorbable fiber. Most used in-vitro method is based on hydrolytical degradation using buffer solution. The important testing parameters are pH and temperature of the buffer solution and degradation time.

In this work, a set of in-vitro degradation experiments were conducted using an experimental polydioxanone (PDS) fiber and buffer solutions with varies of testing parameters. The methodology of design of experiment (DOE) was used to design in-vitro tests, and to analyze the effect of those testing parameters on mechanical properties of PDS fiber and their interaction. A response surface method (RSM) was also used to further evaluate the relation among mechanical properties of PDS fiber, degradation time and testing parameters.

* Corresponding Author, Tel: (908)218-3513, Email: jzhou@ethus.jnj.com
Comparative study of novel alginate-chitosan (Alchite) fibers based on chitosans sourced from different manufacturers


University of Bolton, Centre for Materials Research and Innovation, Deane Road, Bolton, BL3 5AB, U.K.
Chembiotech Laboratories, University of Birmingham Research Park, Vincent Drive, Birmingham B15 2SQ, U.K.
Sumed International (UK) Limited, Unit 1, Wildmere Road, Industrial Estate, Banbury, Oxon, OX16 7TL, U.K.

Alginate and chitosan are well known polysaccharides with much talked about properties including biocompatibility, biodegradability and haemostatic abilities. Alginate fibers produced and manufactured under different brand names are established wound dressings. Chitosan, the deacetylated form of chitin is also known for its antimicrobial as well as wound healing ability. However, these products have been less popular as wound dressings due to their limited functionality. This paper will report on a newly patented technology where alginate and chitosan are combined/fused into a single fibre (Alchite) where both sets of properties can be utilized more effectively. The paper will in particular examines the effect of differently sourced/types of chitosan on the ultimate physicochemical properties of these unique fibers and would report on further analytical results as they become available.
Electrospun poly(lactide-co-glycolide) (PLGA) membranes were fabricated with bioactive heparin and heparin bound to four armed star polyethylene glycol (PEG-heparin). The electrospinning process permitted the fabrication of a three-dimensional, porous fibrous (175 nm in diameter) matrix suitable for growth factor sequestration and release. Tissue engineering scaffolds should mimic the native extracellular matrix in fibril size and functional surface features. Fibers were electrospun with heparin and PEG-heparin to improve binding and controlled release of vascular endothelial growth factor (VEGF). PEG-heparin electrospun PLGA fibers demonstrated a gradual release of VEGF over a more extended period than PLGA fibers spun with heparin alone.
DEVELOPMENT OF EYE-PATCH PROTECTOR FOR NEONATES USED IN PHOTOTHERAPY TREATMENT

Deng Yong-mei†, Yick Kit-lun†, Kwok Yi-lin†, Wong Siu-chun‡

†The Hong Kong Polytechnic University, Institute of Textiles and Clothing, Hung Hom Kowloon, Hong Kong, China. email: dengymfy@hotmail.com
‡ The Hong Kong Queen Mary Hospital, Department of Paediatrics, Hong Kong Island, Hong Kong, China email: mscwong@mail.com

Eye-patch protector is used in the neonatal units routinely to protect neonate’s eyes from retinal damage caused by phototherapy treatment of neonatal jaundice (Verman 2004). However, unsecured protection caused by ill-fitting and displacing are long stand problems of the existing eye-patch protectors used in local hospital in Hong Kong. The purpose of this study is to develop a new eye-patch protector to not only enhance its function of shielding eyes effectively and securely, but also improve their physiological comfort and reduces eye infection.

1. Anthropometric measurements of neonates

In this study, a measuring system based on the multi-camera convergent imaging geometry of close range photogrammetry is developed to meet the critical requirements and limitations of measuring neonates (Atkinson 1996). Obtained anthropometric data is foundation of development of sizing system, pattern and a standard neonate model. 41 full-term neonates (i.e. born after thirty-seven weeks of gestation) nursed in the Special Care Baby Unit of Queen Mary Hospital (QMH) in Hong Kong were selected. Amongst 16 anthropometric dimensions of neonates, head circumference is determined as key dimension for developing sizing system. Based on distribution of head circumference shown in Figure 1, two sizes that are able to cover neonates with 310-349mm and 350-389mm head circumference respectively are developed in new eye-patch protector to replace one size which only covers neonates with 300-350mm head circumference in existing eye-patch protector.

2. Fabrication of eye-patch protector

Study of effect of fabric structure characteristics and properties on light protection shows that color is one of the most effective factors to affect the light transmittance and black color is the most effective one (Figure 2). Three-layer composite is designed for front panel of eye-patch protector based on functional and psychological requirements and elastic fabric and loop are selected for fastening system of eye-patch protector based on secure and comfortable requirements. Fabrics for front panel and for fastening system are evaluated by weighting prioritization matrix ranking approach which is able to balance the multi-requirements in a fabric used for eye-patch protector (Kawabata 1980; Rajamaniclam, Park et al. 1998). The specifications of determined materials for eye-patch protector are shown in Table 1.

3. Design of new eye-patch protector

Based on design criteria including light blocking ability, wearing comfort, safety, easy to operation ability and disposability, an interaction matrix of design specification is developed (Orlando 1979) and prototype of new eye-patch protector is developed based on anthropometric data, fabrication of materials and design criteria. The pattern is presented in Figure 3 and wear trial condition of new eye-patch protector is shown in Figure 4.
Figure 1 Distribution of head circumference of full-term neonates nursed in QMH

Figure 2 Effects of fabric light transmittances influenced by different colors

Figure 3 Pattern design of new eye-patch protector

Figure 4 Wear trial

Table 1 Specification of materials of eye-patch protector

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Composite</th>
<th>Fastening system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inner-layer</td>
<td>Middle-layer</td>
</tr>
<tr>
<td>Content</td>
<td>50% cotton</td>
<td>96% cotton</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
<td>Black</td>
</tr>
<tr>
<td>Construction</td>
<td>Knitted</td>
<td>1/2 twill woven</td>
</tr>
<tr>
<td>Weight (g/m2)</td>
<td>120</td>
<td>180.6</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.53</td>
<td>0.39</td>
</tr>
<tr>
<td>Ends/wale</td>
<td>34.9</td>
<td>68.1</td>
</tr>
<tr>
<td>Picks/course</td>
<td>19.8</td>
<td>21.1</td>
</tr>
</tbody>
</table>

References
Pressure performance of the compression bandages in the treatment of venous leg ulcers

M. Sikka, S. Ghosh, A. Mukhopadhyay

Department of Textile technology, Ambedkar National Institute of Technology
Jalandhar, India
sikkamonica@yahoo.co.in

The chronic venous insufficiency all over the world is characterized by a combination of symptoms like varicose veins, deep vein thrombosis, edema, lymphoedema and finally ulcers on the legs. The recurrence rates of the ulcers are also high, with two third of the patients experiencing one or more recurrence. Graduated compression hosiery is accepted as an integral part for both as an active treatment for healing ulcers and having an essential role in the prevention of venous ulcer reoccurrence. The compression bandage form a major category among different bandage types that are used for the application of clinically effective levels of pressure, applied to modify or assist the physiological process of blood flow. These bandages need to give good holding capacity during use and also be suitable for repeated use. Furthermore these properties can be improved if the creep behavior, the frictional behavior and constructional parameters of the bandage material are optimized to give the required levels of pressure for a specific ailment.

A study has been conducted on the commercially available compression bandages and tailor made compression garments as regards their performance with time. Pressure mapping of these bandages is done using a fabricated pressure measuring device on a mannequin leg to see the relationship between pressure, creep and friction to predict the performance of the compression material. The results show that the creep behaviour has a significant effect on the pressure profile generated by the bandages and garments during application. The regression analysis shows that the friction inhibits the creep in a multilayer bandage system. In case of compression garments, the washing definitely improves the pressure generated but not to the extent of the pressure of a virgin garment. Compression bandage used for the similar application exhibit a lot of variability regarding the material used, constructional parameters of the yarn and fabric set. As regards holding capacity with time, the fabric of higher weight may not perform the best. Furthermore, in the existing bandage material, the bandage that is most suitable for repeated use may not be very suitable to offer good holding during use and vice-versa. In compression bandages the level of initial pressure on the pressure point at the mannequin leg for a particular level of stretching force is primarily influenced by the instantaneous extension and the diameter of the limb. The general relationship of pressure decay (at the pressure point of the mannequin leg) with material creep and friction shows that the decay parameter is largely governed by the creep and frictional force. Compression garments give a lower value of delayed extension and permanent set as compared to compression bandages. But high cost and unsuitability for use at night or during rest due to higher resting pressure suggests that a well rounded approach to complete therapy for the treatment of any ailment lies in the rotation between bandages and garments.
SESSION 2B

PROTECTIVE / FUNCTIONAL APPLICATIONS I
PHOTOCATALYTIC FUNCTIONAL COTTON FABRICS FOR PROTECTIVE CLOTHING

Kyung Hwa Hong and Gang Sun

Division of Textiles and Clothing, University of California, Davis, California 95616, USA.
Email: khong@ucdavis.edu and gysun@ucdavis.edu

1. Introduction
Benzophenone chromophoric group, known to undergo light-excitation to n, \( \pi^* \) triplet states are commonly used as photosensitizers in photochemistry. Triplet benzophenone radical structure can be readily quenched by oxygen, and can also abstract a hydrogen atom from any active hydrogen source to form a ketyl radical. Most likely, biological agents and toxic chemicals serve as the sources of active hydrogen, which could result in antimicrobial effect and decomposition of the chemicals. Therefore, the fabrics containing benzophenone chromophoric group would be easily excited to the radicals, which can then decompose not only bacteria but also toxic compounds when activated by UV light. In this study, self-decontamination fabrics containing benzophenone chromophoric groups were prepared by reacting cotton fabrics with 4-hydroxybenzophenone as a reagent, 1,2,3,4-butanetetra carboxylic acid (BTCA) as a cross-linker, and sodium hypophosphite as a catalyst via a pad-dry-cure method. The expectant scheme is as follows.

\[
\text{H}_2\text{C} = \text{C} - \text{O} + \text{H}_2\text{C} = \text{C} - \text{OH} + \text{HO}^{-} \rightarrow \text{H}_2\text{C} = \text{C} - \text{OH} + \text{HO}^{-} \rightarrow \text{H}_2\text{C} = \text{C} - \text{OH} + \text{HO}^{-} \rightarrow \text{H}_2\text{C} = \text{C} - \text{OH} + \text{HO}^{-}
\]

Scheme 1. Esterification of BTCA with cellulosic substrate and 4-hydroxybenzophenone.

2. Experiment
The cotton fabrics were immersed in a finishing solution containing designated concentrations of 4-hydroxybenzophenone, 0.1M of BTCA, and 0.1M of sodium hypophosphite hydrate. The fabrics were padded through a laboratory padder to have a wet pick-up rate around 100%. Then the treated fabrics were wet-fixed by putting them in plastic zipper bags and storing them in a convection oven for 30 min at 85°C. Then, the fabrics were cured at 160°C for 3 min, and then were washed with distilled water and air-dried in a conditioning room (25°C, 65% R.H.) for 24 h. The ultra-violet (UV) lamp (BLE-8 T365) was used for photoactivation of the treated cotton fabrics.

3. Results and discussions
FTIR-ATR spectra of pristine cotton fabric and the 4-hydroxybenzophenone/BTCA treated cotton fabrics were examined. The 4-hydroxybenzophenone/BTCA treated cotton fabrics only show relatively narrow and distinct peaks at 1560 and 1602 cm\(^{-1}\) assigned to aromatic C=C stretch. Also, the 4-hydroxybenzophenone/BTCA treated cotton fabrics reveal a peak at 1635 cm\(^{-1}\) assigned to carbonyl stretching, which seemed to be originated from the benzophenone chromophoric groups. Moreover, a peak at 850 cm\(^{-1}\) attributed to out-of-plane C-H vibration of para-substituted benzene ring and a peak at 1290 cm\(^{-1}\) attributed to ester C-O stretching were observed in the 4-hydroxybenzophenone/BTCA treated cotton fabrics. These findings could serve as a proof of the linkage between BTCA and 4-hydroxybenzophenone.
Tensile strengths of the BTCA only treated cotton fabrics and the 0.1M 4-hydroxybenzophenone/BTCA treated cotton fabrics were obviously lower than that of pristine cotton fabric. In general, BTCA treated cellulosic fabrics suffer a major loss of mechanical properties. However, there was no significant difference in the tensile strengths between the BTCA treated cotton fabrics and the 4-hydroxybenzophenone/BTCA treated cotton fabrics. Also it was observed that the average tensile strength of the 4-hydroxybenzophenone/BTCA treated cotton fabrics hardly changed after 10h UV illumination. Therefore, the benzophenone chromophoric radicals seemed to have limited effect the mechanical strength of the cotton fabrics.

Antibacterial effect of the 4-hydroxybenzophenone/BTCA treated cotton fabrics were examined against *S. aureus* and *E. coli* as shown in Table 1. When UV light irradiated the 4-hydroxybenzophenone/BTCA treated cotton fabrics during the contact with bacteria, the colony forming numbers of *S. aureus* and *E. coli* were significantly reduced, in a reduction rate of 99.99%.

**Table 1.** The colony numbers of *S. aureus* and *E. coli* after injecting the 0.1mL bacterial aqueous solution on the agar plates and incubating them at 37°C for 18h.

<table>
<thead>
<tr>
<th>Dilution ratio of <em>S. aureus</em> solution after contact time</th>
<th>Dilution ratio of <em>E. coli</em> solution after contact time</th>
</tr>
</thead>
<tbody>
<tr>
<td>× 10, × 10², × 10³, × 10⁴</td>
<td>× 10, × 10², × 10³, × 10⁴</td>
</tr>
<tr>
<td>Pristine cotton fabrics [UV treated]</td>
<td>∞, 57, 5, 0</td>
</tr>
<tr>
<td>Treated cotton fabrics [No UV treated]</td>
<td>∞, 12, 1, 0</td>
</tr>
<tr>
<td>Treated cotton fabrics [UV treated]</td>
<td>0, 0, 0, 0</td>
</tr>
</tbody>
</table>

4. Conclusions

Benzophenone chromophoric group incorporated cotton fabrics were successfully prepared by treating cotton fabrics in a finishing solution containing 4-hydroxybenzophenone, BTCA, and sodium hypophosphite via a pad-dry-cure method. Through the spectroscopic analysis of the 4-hydroxybenzophenone/BTCA treated cotton fabrics, formation of the cellulosic polymer-BTCA-benzophenone chromophoric group was verified. Also the antibacterial effect of the treated cotton fabrics was manifested only when it was irradiated by UV light, and this indicates that the benzophenone chromophoric group in the treated cotton fabrics was activated to form radicals under UV illumination.

5. Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-214-D00199) and the National Textile Center (NTC C06-AC01).
QUANTIFICATION OF OILY CONTAMINANTS IN FLAME RESISTANT THERMAL PROTECTIVE TEXTILES – A RADIOTRACER ANALYSIS

Chathuri V. R. Mettananda† and Elizabeth M. Crown‡

†Department of Human Ecology, University of Alberta, Edmonton, AB, T6G 2N1, Canada. email:chathuri@ualberta.ca
‡Department of Human Ecology, University of Alberta, Edmonton, AB, T6G 2N1, Canada. email:Betty.Crown@ualberta.ca

Introduction

Maintenance of protective properties of flame resistant (FR) textile materials is essential in providing optimum protection to workers who risk exposure to high heat flux environments. Accumulation of oily contaminants on FR textiles may negate their performance, depending on the material, degree of contamination, and distribution of contaminants. Therefore determining the quantity and distribution of oily contaminants present in FR fibres and investigation of mechanisms that degrade protective characteristics in the presence of contaminants are critical in developing both improved thermal protective materials and optimum maintenance procedures. This paper reports an experimental study wherein the quantity of oily contaminants present in FR fabrics before and after decontamination is determined.

Radiotracer Analysis

Radiotracer analysis was used as a means of quantification of oily contaminants. Radioisotopes have been used for many years in detergency studies. Due to high counting efficiency, liquid scintillation counting is the most commonly used method for the quantification of beta rays. This method involves placing the specimen in a suitable scintillation liquid comprised of a solvent and fluors. The energy of a beta particle emitted by the radiotracer during counting is absorbed by the aromatic solvent. It becomes excited and the energy is transferred to the fluor molecules with a series of molecular collisions. The fluor molecules become excited and emit a scintillant to return to the ground state. This scintillant is detected by the photo multiplier tubes and delivers pulses proportional to the energies of the absorbed beta particles. Quenching, or any process that interferes with the emission of scintillates during counting, is one of the main problems with liquid scintillation counting. Both chemical quenching and colour quenching can significantly reduce the counting efficiency of the scintillation process. Internal standardization, external standardization or the channels ratio method can be used to correct quenching and thereby to increase the counting efficiency. Internal standardization which is the most commonly used involves adding a known activity of a solution (internal standard) to the counted vials and recounting (Shebs 1987). Radiotracer analysis has been used by researchers to determine the amount of residual oil such as triolein (Obendorf & Klemash 1982; Webb & Obendorf 1988), oleic acid (Breen et al. 1984) and used motor oil (Chi & Obendorf 1999).

Experimental procedures

The experiment was a 3 X 2 X 2 X 2 full factorial design. The independent variables for the experiment include fabric type, detergent type, use of pre-treatments and the number of contamination/decontamination cycles. The dependent variables were the residual oily contaminants present in the fabric specimens and the decontamination percentage (percentage removal of oily contaminants) after one contamination-age-decontamination cycle.

Three FR fabrics (aramid, 65/35 aramid/FR viscose and 88/12 FR cotton/nylon), typical of what is worn by field workers in the oil and gas sector, were used for the study. All fabric samples were pre-washed following AATCC 135-1995 and conditioned in a standard atmosphere (65 ± 2% RH and 21±1°C) following CAN/CGSB - 4.2 No.2-M88, prior to contamination. An AATCC standard reference detergent without optical brighteners (WOB) was used as a detergent, and Spray’n wash was used as the only pre-treatment. Specimens having dimensions of 40 X 40 mm were cut on the bias and were randomly assigned to each treatment. Fifty milliliters of oil was spiked with 200 μL of 0.1 mCi/ml tritiated-triolein and was used for the contamination of specimens. The contaminated specimens were aged for three days before being decontaminated.

Decontamination of radiotracer specimens was carried out in a Launder-Ometer. The hardness of the wash water was controlled by using reverse osmosis water. The method used by Crown et al. (2004) was followed with some modifications to the amount of wash water and the amount of detergent. The decontamination process included a 10 min wash cycle at 60°C in the Launder-Ometer. Each Launder-Ometer canister contained five specimens in 400 ml of water, 4 g of detergent and twenty-five steel balls. The wash cycle was followed by two rinse cycles at 30°C for 5 and 3 minutes respectively. The specimens were air-dried as needed.

Each fabric specimen was placed in a scintillation vial and 20 ml of the scintillation liquid was added. ScintiSafe™ Econo F (Fisher Scientific, Canada) was the scintillation liquid used. The specimens were extracted in the scintillation liquid for seven days prior to counting. Radioactivity of the contaminated fabric specimens in terms of counts per minute (cpm) was measured with Packard Tri-Carb 2100 TR liquid scintillation counter. DPM (disintegrations per minute) can be calculated from cpm if the sample counting efficiency (E) is known. DPM represents the amount of radioactivity present in
contaminated specimens in absolute units. Internal standardization was used as the quenching correction due to the reduction of counting efficiency resulting from the discoloration of the scintillation liquid from motor oil. After the specimens were counted, 50 µl of 0.001 mCi/ml tritiated-triolein was added to each specimen vial and was recounted. Sample counting efficiency and the sample activity in dpm were calculated. DPM is positively correlated with the residual oily contaminants present in the fabric. Hence, the residual mass of oil present in fabric specimens was calculated. The percentage decontamination after the first contamination-age-decontamination cycle was also calculated.

Results
Statistical analyses was performed using statistical software, SPSS version 15 with a significance level of p<0.05 for hypothesis testing. Means were calculated for the residual oily contaminants present and the decontamination percentage (percentage of oily contaminants removed) considering each independent variable (fabric type, detergent, pre-treatment, contamination-age-decontamination cycle). Analysis of variance was conducted to determine the differences among FR fabrics, among laundry treatments, among number of decontamination cycles and the interaction effects among fabric, laundry treatment and decontamination cycles for the residual oily contaminants present and the decontamination efficiency.

According to the three-way-ANOVA conducted, significant differences in residual oily contaminants were noted among laundry treatments, and among number of decontamination cycles for all FR fabrics. According to the one-way-ANOVA conducted for each fabric for each decontamination cycle, treatment combination with no pre-treatment or detergent was significantly different from other treatment combinations for one and five contamination cycles for all fabrics. FR cotton/nylon blend fabric retained the highest amount of residual oil compared to aramid and aramid/FR viscose fabrics for all treatment combinations. Aramid fabric retained the lowest amount of residual oil. Accumulation of oily contaminants was noted after five contamination-age-decontamination cycles for all FR fabrics for all treatment combinations. Decontamination efficiency after one contamination-age-decontamination cycle was lowest for the FR cotton/nylon for all treatment combinations.

References
Ultraviolet Protection of Clothing

Ron Postle¹ and Michael T. Pailthorpe²

¹School of Chemistry, University Of New South Wales, Sydney, 2052, Australia
r.postle@unsw.edu.au

²AgResearch Ltd, New Zealand, Po Box 3084, Willougby North, 2068, Australia
mike.pailthorpe@agresearch.co.nz

Textile materials and clothing have been used since antiquity by human beings for the purposes of protection, comfort and adornment. Recent times have witnessed a steadily increasing emphasis on the role that clothing can play to guard against skin cancer and in particular malignant melanoma caused by excessive exposure to ultraviolet solar radiant energy.

It is often believed by the general community that sun creams and light weight summer clothing (including hats and sunglasses) provide total protection from the adverse health effects of solar ultraviolet radiation on the human skin. This presumption, however, is far from the truth in many circumstances.

Recent statistics reveal that in Australia over one thousand people die from skin cancer each year from a population of some twenty million people. In addition, two-thirds of Australians are directly affected by skin cancer of one kind or another during their lifetime. The occurrence of the most dangerous form of skin cancer i.e. malignant melanoma in Australia is very high for both males and females. High incidence rates also occur in other countries such as USA and New Zealand. The Australian statistics represent the highest incidence of skin cancer world-wide. Furthermore, the incidence of skin cancers continues to increase world-wide according to the World Health Organisation (WHO).

The medical dermatology profession recognises that the dominant factor causing these high rates of skin cancer is the cumulative exposure to the sun’s ultraviolet radiation. The requirement for test methods and standards has been recognised to specify the protection provided by clothing from the harmful effects of solar radiant energy, which is generally classified as ultraviolet A (UVA) 315-400 nm wavelength and the more harmful ultraviolet B (UVB) 280-315 nm wavelength.

The two main ways of assessing the UV protection of clothing are in vivo or in vitro test methods. In vivo testing measures the actual protection afforded by the garment from human skin erythema by means of a xenon solar simulator as the source of UVA and UVB radiant energy. For in vivo testing, the sun protection factor (SPF) determines the ultraviolet protection by adopting the minimum erythema on human skin as the end point.

The transmission of ultraviolet radiation through the textile material or garment is measured by in vitro testing using a spectrophotometer or spectroradiometer which actually detects the percentage transmission in wavelength intervals of 5 nm for the 280 to 400 nm wavelength range of the UV spectrum. Both the direct and diffuse UV radiation transmitted through the garment are detected and measured.

The ultraviolet protection factor of clothing (UPF) derived from the in vitro test method is defined in the original Australia / New Zealand standard AS/NZS 4399 (1996), ‘Sun protective clothing – evaluation and classification’. This standard has recently been developed by the International Commission on
Illumination - Technical Report CIE 172: 2006. The UPF provides a single numerical value which is representative of the whole UVA and UVB wavelength energy spectrum. The UPF gives the greatest weighting to the biologically most harmful UVB wavelength band.

Almost all structural parameters of a textile material especially the fabric cover factor or weight, have a direct influence on the fabric ultraviolet protection factor. The most important fabric properties in this context are: fabric cover factor (or weight), fibre type, yarn construction, fabric construction, finishing processes, colour, UV absorbers, wash and wear, fabric stretch and wetting (or hydration). The effects on UPF of these fabric parameters have been studied in detail at the University of New South Wales through research collaboration between the textile technology and medical dermatology professions.

In order to achieve a desired UPF rating for a textile material, it is always necessary to control all the textile parameters which influence the transmission of ultraviolet radiation through the material, especially the fabric cover factor. If we define an ‘ideal’ textile material as one in which the constituent yarns are completely opaque to the transmission of ultraviolet radiation, then the UPF of this ideal fabric is given by:

\[ \text{UPF} = \frac{100}{100 - (\text{CoverFactor})} \quad \text{eqn. (1)} \]

Very small changes in the fabric cover factor give substantial improvements in the UPF of the textile material. It follows that a small increase in the fabric cover factor will produce a substantial improvement in ultraviolet protection of clothing.

In order to produce high UPF ratings for textile materials, it is necessary for textile designers and manufacturers to maintain stringent quality control systems which enable textile materials to be produced uniformly in a narrow range of cover factor. It is also noteworthy that highly UPF rated textile materials having high cover factor are generally less permeable to air and water vapour.

Therefore, a high fabric UPF rating should be balanced by considering the comfort properties of summer weight clothing. There is considerable scope for innovative fabric structures and finishing processes (including the incorporation of UV absorbers) in order to achieve these aims set by consumer demand.
A Dynamic Mannequin for Virtual Performance Testing of Functional Clothing

Colby C. Swan*, Matthew Rasmussen, Rob Williams, Xiaolin Man, and Salam Rahmatalla
The University of Iowa

In this presentation, we will demonstrate the latest advances in a long-term effort to develop a computational framework for virtual performance testing of functional clothing. First, we will present and discuss a new animated mannequin. To utilize the animated mannequin, a laser body scan is performed on a human subject to capture the body surface in a specific pose. This body-surface mesh is then decomposed into individual limb segments which are in turn driven in time and space by motion capture data and rigid body kinematics. Smoothing of the body surface meshes is necessary at the interfaces between the limb segments (See Fig. below). The final animated mannequin is a fairly realistic moving body-surface onto which mathematical clothing models can be draped and performance tested.

Fig. Dynamic mannequin in different stages of motion.

Having established this dynamic virtual mannequin, a realistic finite element clothing model of a standard issue military chemical protection suit is then draped onto it as it undergoes a prescribed series of motions. Details of the material models and the

* Contact author: E-mail colby-swan@uiowa.edu; Tel: 1 (319) 335-5831; Surface mail: The University of Iowa, Dept. of Civil & Environmental Engineering, 4120 Seamans Center, Iowa City, Iowa 52242.
constitutive behaviors of the fabrics that comprise the suit will be discussed as will be the treatment of frictional sliding between the body and the garment. The forces that the clothing exerts on the human body are then integrated in space to yield joint resistance torques on the main body joints, and the products of these torques and rotational velocities are integrated in time to produce the resistance work that the garment performs on the human body undergoing prescribed motions.

Although this framework is presented here for a specific garment type and a specific human body surface, it is ultimately expected to be very general so that the virtual performance testing can be done with any garment and any human body.
SESSION 3A

FIBERS WITH NANOTUBES AND NANOPARTICLES
Carbon Nanotube Reinforced Recombinant Spider Silk for Tissue Engineering Scaffolds

Milind R. Gandhi¹, Frank K. Ko² and Costas Karatzas³

¹: School of Biomedical Engineering, Sciences and Health System, Drexel University, Philadelphia, PA
²: AMPEL, Department of Materials Engineering, University of British Columbia, BC, Canada
³: Nexia Biotechnologies, Quebec, Canada

Introduction
Silk is an ideal candidate for biomedical applications because of its unique mechanical properties. The most extensively used silk for various applications are those from silkworm silk; Bombyx mori and spider silk; Nephila clavipes. Bombyx mori silk is available in abundant amount by sericulture but it is not equitable to grow spiders in the farm due to the cannibalistic nature of spiders. Dragline silk from Nephila clavipes is made up of two segments, MaSp1 (Major Ampullate Spidroin 1) and MaSp2 (Major Ampullate Spidroin 2) coded by different genes [1, 2]. Nexia Biotechnologies Inc., in 1999 introduced an innovative technology of using transgenic approach to produce recombinant spider silk. They introduced spider silk DNA into goat to produce recombinant spider silk, Biosteel® [3, 4]. They have successfully generated both MaSp1 and MaSp2 in their goat system. These individual components, in different ratios (1:0, 1:1, 1:3, 3:1, 0:1) were successfully electrospun to obtain nanofibers. Masp1 was used to generate aligned nanofibers. We incorporated carbon nanotubes (CNT) in MaSp1 component of spider silk to improve the mechanical and electrical properties of fibers. To explore the feasibility of the spider silk as tissue engineering scaffolds bovine osteoblasts were cultured on the nanofiber mats of MaSp1 with and without CNT.

Materials and Methods
The morphology and fiber diameter distribution of various samples were examined by ESEM. The structure and composition of nanofibers were characterized by FTIR and the presence of CNT in MaSp1 was determined by Raman spectroscopy. The cell proliferation was measured using Alamar Blue dye assay. The differentiation was evaluated by measuring alkaline phosphatase (p-NPP method), osteocalcin (Enzyme linked immunoassay) and calcium (o-cresolphthalin complexone method) levels.

Results and Discussion
Concentration was found to be a dominant factor determining the spinability as well as diameter of fibers. 12% concentration of MaSp1 at 10 cm spinning distance and charge density of 3kV/cm produced continuous uniform fibers with diameter 100.7± 36.43 nm. MaSp2 by itself was not spinnable at any conditions producing droplets instead of fibers. 3:1 ratio of MaSp1 to MaSp2 at 12% concentration, 10 cm spinning distance and charge density of 3kV/cm produced fibers with diameter of 81.1± 29.73 nm. 1:1 ratio at 10% concentration and similar distance and electric field generated 63.3± 25.17 nm size fibers and 1:3 ratio at 6% concentration delivered fibers with the diameter of 57.4± 25.75 nm. The aligned fibers were used to calculate mechanical properties. Aligned fibers fabricated from MaSp1 had the average fiber diameter of 96± 34.87 nm. MaSp1 was reinforced with 1% CNT. The fiber diameter of aligned MaSp1 fibers having CNT was 97± 29.57 nm. Incorporation of 1% CNT in MaSp1 significantly increased the modulus and strength of aligned fibers. There was ~10 time increase in the modulus and ~5 time increase in the tensile stress (Figure 1). Analysis with FT-IR spectroscopy proved electrospinning did not change the chemical composition of spider silk. Raman spectroscopy results
proved that CNTs were in the nanofibers. Cell-matrix interaction showed better proliferation and differentiation on MaSp1 nanofibers compared to MaSp1 with CNT. But the morphology of cells remained same on both the scaffolds.

![Graph](image)

Figure 1: Effect of CNT on the tensile properties of aligned MaSp1 nanofiber

References
Preparation and Characterization of Polymer-Carbon Nanotube Fibers

Brett Ellerbrock, Konstantin G. Kornev, Phil Brown, Kate Stevens

School of Material Science and Engineering
Clemson University, Clemson, SC 29634
E-mail: hellerb@clemson.edu, kkornev@clemson.edu

Wet spinning is one of the most basic but effective techniques to generate fibers with a high carbon nanotube loading. It is known that the fibers produced from single-walled carbon nanotubes (SWNT) with a polymer binder consist of an interwoven structure of nanotubes and polymer chains. This makes them unique and distinguishable from any composite materials where the reinforcing elements are incorporated into a polymer matrix forming islands-in-a-sea-type structures. The fibers can be freely stretched, twisted, knotted, or bent. It has been shown that carbon nanotubes have a Young’s modulus of 1000 GPa, as opposed to conventional carbon fibers which range between 200-800 GPa. Also, the carbon will experience plastic deformation under excessive tensile strain, meaning strain energy is released before tubes fracture. Therefore, the idea to produce new materials by incorporating SWNTs into a polymer network at the macromolecular level looks very attractive from the materials science prospective. We report on wet spinning of SWNT-polymer fibers. Various tests have been conducted to study this highly promising system. Such characterizations include mechanical, thermal, morphological, and SWNT ordering analyses. Finally, we will discuss some potential applications of these fibers.

Figure 1. Roughened polymer surface due to SWNT loading. Magnified insert shows SWNT bundle bridging between surface crack.
1. Introduction

Fiber reinforcement using particles is a well known method in textile and composite industries not only for enhancing the properties but also for synthesizing a new material having unique properties. The success in the fabrication of ultrafine fibers with nanoparticles will greatly expand the functionality of particulate filled composites. This will enable new applications including filters, sensors, scaffolds for tissue regeneration, wound dressing, flexible structure, enhanced mechanical properties, customizable electrical and optical properties, high sensitivity etc.

Taking advantage of the exciting new developments in the areas of nanomaterial fabrication, three type of particle reinforced nanofibers will be demonstrated in this study. The three nancomposite systems including 1) polyethylene oxide (PEO) and Quantum dots (QDs), 2) Polyvinylidene fluoride (PVDF) and titanium dioxide (TiO2) and 3) PVDF- tetrafluoro ethylene (PVDF-TeFE) copolymer and iron oxide are fabricated and characterized. These 3 systems were chosen to illustrate the special functions the nanoparticle will create. For example QDs are known for their optical and electrical properties; TiO2 for anti-bacterial induced by photo catalytic effect and iron oxide for electric and magnetic properties.

This study showed that co-electrospinning is effective one step process capable of producing nanoscale composites fibers with a broad selection of functional materials and high productivity resulting in a new family of nanofiber based multifunctional materials, thus providing a bridge between nanoscale materials and macro level performance.

2. Materials and Methods

Cds-PEO (Fluorescence Nanofiber)

An environmentally friendly and low-cost synthesis procedure for aqueous CdS QDs has been developed. Without the drawbacks of organometallic method, aqueous QDs are prepared in one-step reaction by using simple inorganic precursors. As an example, the aqueous CdS QDs are produced in water by the reaction between cadmium nitrate [Cd(NO3)2] and sodium sulfide [Na2S] with 3-mercaptopropionic acid [MPA] as the capping molecules. The resultant clear aqueous QDs suspension remained stable for more than 12 months at 4°C away from light. 5% PEO (Mw 600,000, purchased from Sigma) by weight were dissolved into 1.6mM, 6.4mM and 12.8mM of as prepared aqueous cadmium sulfide (CdS) quantum dot solutions by magnetically stirring for 24 hours to prepare spinning dope for electrospinning.

Fe3O4 /PVDF-TeFE (Magnetic Nanofiber)

Optimization carried out on Iron Oxide/PVDF-TeFE system suggested that 20% of PVDF-TeFE in 75/25 MEK/DMF was required at spinning distance of 20cm and field strength of 20 kV in order to obtain continuous, uniform and nanoscale fibers. 5 % and 10 % of Fe3O4 nanoparticles (purchased from Sigma) by weight were dispersed in the prepared polymer solution then electrospun at similar condition as described previously.

TiO2/PVDF Nanofiber (Photocatalytic Nanofiber)

Optimization study was carried out for TiO2-PVDF system similar to that in the preparation of the magnetic nanofiber. It has been found that 20% of PVDF in 75/25 MEK/DMF was required at spinning distance of 10cm and filed strength of 15 kV to obtain uniform and nanoscale fibers. 1 %, 3 % and 5 % by weight of TiO2 were mixed into PVDF solution for electrospinning.

The prepared solutions were then transferred into a glass syringe containing 18-gauge needle to electrospun. A high voltage power supply was connected to the metallic needle nozzle of the solution container. The 10cm by 10cm metallic grounded target was placed 20cm away vertically The distance between the nozzle to target and the voltage applied were fixed to 20cm.
3. Results and Discussion

The average diameter of the fibers with combination of different CdS solution concentration were 271 nm, 226 nm and 225 nm from 5 wt % of PEO dissolved in 1.6 mM, 6.4 mM and 12.8 mM of CdS solution respectively. When higher concentration of CdS solution was used the fiber diameter decreased. Photoluminescence spectroscope was used to characterize the electrospun fibers for fluorescence properties. As expected lower level of emission intensity was observed on the fibers having lower level of CdS concentration.

![Figure 1. Morphology of PEO-CdS nanofibers(a) and Photoluminescence of CdS-PEO solution and electrospun fiber(b)]](image)

As shown in Figure 2, uniform fibers were obtained from 20 % of PVDF-TeFE. When magnetic particle were mixed and electrospun, the fiber diameters decreased from 600 nm to 400 nm with 10 % of Fe$_3$O$_4$ addition. The magnetic moment of nanofiber were measured by applied field from -100K to 100K Oe at room temperature (300K). The result showed that typical superparamagnetic properties of iron oxide nanoparticle with great susceptibility to external magnetic field suggesting this can be an excellent candidate for magnetic sensor application.

![Figure 2. Fe$_3$O$_4$/PVDF-TeFE Electrospun Fibers and Magnetic Response]](image)

To demonstrate the photocatalytic effect and to explore new applications of TiO$_2$ composite nanofibers, antibacterial activity and cell proliferations were observed. It was found that over 3% of TiO$_2$ additions enabled electrospun fiber membrane to become an effective bactericidal membrane on *E.coli* under the fluorescence light. When bovine osteoblasts were seeded on electrospun TiO$_2$ membrane, increased cell proliferations were observed with higher content of particles contributed by increased roughness on the fiber surface.

4. References


Many routes have been developed for the synthesis of carbon nanotubes, but their assembly into continuous fibres has so far been achieved only through post-processing methods. In this work, carbon nanotube fibres were obtained by directly spinning an aerogel of carbon nanotubes formed during chemical vapour deposition synthesis (1). Typically a mixture of ethanol, ferrocene and thiophene is injected into a hot hydrogen atmosphere (1150 °C) and these compounds rapidly react to form the carbon nanotubes. The carbon nanotubes then interact to form a continuous sock-like aerogel that travels down the reaction zone without sticking on the furnace walls. The sock is then spun into a fibre using a variety of different spindle orientations. Overall, this process can be split broadly into three stages; the initial chemical vapour deposition reaction, the formation of sock and the drawing and properties of the fibre. Each of these processes will be addressed in the talk.

Different hydrocarbons have been used for the reaction, with the yield and products being found to vary greatly with the feedstock used. These products were characterised using Raman spectroscopy and electron microscopy. The presence of small amounts of oxygen was found to be enhance sock formation and hence spinning of the fibre. Also, the process parameters were found to have a strong effect on whether multi-walled or single-walled nanotubes are produced.

Physical properties of the fibres were also assessed, with special emphasis on tensile strength and electrical conductivity. Tensile strengths are greatly dependant on process conditions and therefore, the different microstructures observed. On average, values lie in the range of 0.7 ± 0.2 GPa, with the current maximum tensile strength reaching 1.5 GPa. The electrical conductivity of the carbon nanotube fibre is consistently higher than for carbon fibres, ranging from 2.5 to 8.3 per Ohms per metre. All experimental evidence points out to the fact that very significant improvements in properties can be accomplished by better controlling the synthesis process.

1. Li et al., Science, 304, 276, 2004
SESSION 4A

FIBER FORMATION: PROCESS TECHNOLOGY I
MELT SPINNING OF POLY(ETHYLENE TEREPTHALATE) USING WATER-QUENching BATH PLACED AT EXTREMELY SHORT AIR-GAP LENGTH

Tomoyuki Enya, Hiroshi Ito and Takeshi Kikutani

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-S8-32, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan
e-mail: kikutani.t.ta@m.titech.ac.jp

Abstract. Effect of air-gap length on the occurrence of draw resonance in the water quenching melt spinning process of poly(ethylene terephthalate) (PET) was investigated. It was found that the reduction of air-gap to extremely short length lead to the disappearance of draw resonance behavior. Structure and property of fibers prepared under such conditions were investigated. Analysis on the birefringence variation in the cross-section of the water-quenched fibers revealed that although the birefringence near the fiber surface was high, birefringence in the core part of the fiber is negligibly small in spite of the application of extremely high elongational strain rate during the spinning process. Sheath-core bicomponent spinning using PET and atactic polystyrene as the core and sheath components, respectively, was carried out. The PET fiber obtained after the removal of the sheath component showed high strength and high elongation at elevated temperature.

1. Introduction

In the melt spinning process, periodic diameter fluctuation occurs when the spinline is quenched using a water bath placed at a position close to the spinneret. This phenomenon is known as the draw resonance. It has been reported that the draw resonance can be reproduced by the numerical simulation of the non-steady-state melt spinning process. In addition, under the assumption of the isothermal melt spinning of Newtonian fluid, it was also revealed that the draw resonance starts to occur when the melt draw ratio exceeds 20 (Fisher & Denn 1975).

The theoretical analysis also predicted that the spinline becomes stable when air-gap length, i.e. distance between the spinneret and the water surface, is extremely short. Recently, experimental results concerning the suppression of draw resonance at the conditions of short air-gap length were reported (Ishihara et al 2004), however, spinning conditions adopted was still limited. Therefore, we conducted the melt spinning of poly(ethylene terephthalate) (PET) under a wide-range of spinning and quenching conditions, and experimental results of on-line diameter measurement were compared with the results of numerical simulation. Structure and properties of the water-quenched fibers thus prepared were also investigated.

2. Experimental

High molecular weight PET supplied by Toyob Co., Ltd. with the intrinsic viscosity of 1.0 dl/g was used in this study. Single component spinning of PET as well as the bicomponent spinning of sheath-core fibers using PET as the core component and atactic polystyrene (PS) (Idemitsu Kosan Co., Ltd.) as the sheath component were conducted at the extrusion temperature of 300 °C using a spinning nozzle of 1 mm diameter. Throughput was set to 6.0 g/min for the single component spinning of PET. For the PET/PS bicomponent spinning, throughput of PET/PS (g/min) of 6.0/0.5, 5.5/0.5, 6.0/1.0 and 4.0/3.0 were selected. A water quenching bath was installed immediately below the spinneret. Air-gap and take-up velocity were varied from 0.2 to 20 cm and from 0.3 to 1.0 km/min, respectively. On-line measurement of diameter variation was carried out using a back illumination type diameter monitor (Zimmer OHG, 460/A10). Numerical simulation of the non-steady-state melt spinning process was performed using a program developed in our group.

Structure and properties of the as-spun fibers were analyzed through the measurements of wide-angle X-ray diffraction (WAXD) patterns, and birefringence distribution in the cross section of the fibers. Drawing behavior of water quenched PET fibers prepared by removing the sheath component from the PET/PS bicomponent fibers using carbon tetrachloride was also analyzed.

Figure 1 Variations of diameter with time measured in the water-quenching melt spinning process of PET for air-gap lengths of 0.2 and 0.5 cm.
3. Results and Discussion

Time-course variations of spinline diameter for the air-gap lengths of 0.2 and 0.5 cm measured at the take-up velocity of 0.4 km/min and throughput of 4 g/min are compared in Figure 1. A significant and periodic diameter fluctuation was observed when the air-gap length was 0.5 cm, whereas the spinline stabilized when the air-gap length was reduced to 0.2 cm. Through this experiment, stabilization of the spinning process even at the melt draw ratio of 90 was confirmed.

Through the measurements of refractive index distribution in the cross-section of water-quenched fibers, it was found that the fibers had significant orientation variation in the cross-section in that birefringence near the surface has a high value, whereas that in the core part is negligibly small. The core part occupies the volume of about 60 %. On the other hand, WAXD patterns of as-spun fibers are shown in Figure 2. It was found that the water-quenched fibers show the weak but distinct reflections of highly oriented crystals. The crystalline reflections became stronger with decreasing air-gap length, increasing take-up velocity, and decreasing throughput.

Mechanism for the development of such structure can be speculated as follows. Even though the spinline was quenched in the water, development of high stress, which is due to extremely short air-gap length, caused the significant molecular orientation and significant increase of crystallization rate. Accordingly, there can be a chance of crystallization and maintaining of a certain level of orientation in the course of cooling from the filament surface. Orientation of the core part can be relaxed because of slower cooling.

After the bicomponent spinning of PET/PS fibers consisting of PET and PS as the core and sheath components, sheath part was removed using solvent. Birefringence distribution in the cross-section of the resultant PET fiber was homogeneous and its value was negligibly small. Stress-strain curve of this fiber and the fiber obtained at the condition of ordinary low speed spinning were measured at 90 °C. The results are compared in Figure 3. Although strain hardening of these fibers started at a similar strain level, elongation and tensile strength of the water-quenched PET fiber was found to be significantly high.

References

![Figure 1](image1.png)

![Figure 2](image2.png)

![Figure 3](image3.png)
DEVELOPMENT OF HIGH-STRENGTH PET FIBERS USING SPIN-LINE-DRAWING SYSTEM

Kensuke Nakahara* and Takeshi Kikutani**

* R & D Division, Japan Chemical Innovation Institute (JCII)
3-29-8, Kitasenzoku, Ohta-ku, Tokyo, 145-0062, Japan, e-mail nanonaka@abox2.so-net.ne.jp
**Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,
Tokyo Institute of Technology
2-12-1, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan, e-mail kikutani.t.aa@m.titech.ac.jp

Abstract Melt spinning process of poly(ethylene terephthalate) was modified installing a hot roll and a quenching nozzle in the spinning line, which will be called Spin-Line-Drawing (SLD) system. In this system, thermal and stress histories of polymer melt can be actively controlled by varying the velocity and temperature of hot roll, and the position of quenching nozzle. Application of the SLD was found to improve the true strength of as-spun fibers. In addition, the fibers obtained by drawing and annealing of the as-spun fibers prepared using the SLD system showed high tensile strength and high toughness.

1. Introduction
About 70% of the annual production of chemical fibers in the world, which is about 30 million tons, is occupied by poly(ethylene terephthalate) (PET). This percentage is still increasing because of its excellent fiber properties and low price. On the other hand, even though various types of high-strength fibers have been developed during these one or two decades, tensile strength of the commercialized PET fibers is still limited at around 1 GPa. Therefore, development of high-strength PET fibers with reasonable cost is highly desired. Important two factors for achieving high strength are known to be the application of high-molecular-weight polymer and the alignment of those molecules along the fiber axis. However, larger number of entanglement in individual chain of high molecular weight makes it difficult to stretch fibers to high draw ratios. For this reason, development of high-strength PET fibers was not successful even in laboratory scale except for the application of solution spinning technology (Huang et al 1994, Tate et al 1996). In this research, we attempted to control the structure and properties of as-spun PET fibers by installing a hot roll and a quenching nozzle into the melt spinning process as shown in Fig.1. We named this process Spin-Line-Drawing (SLD) system.

2. Experimental
Melt spinning of PET with intrinsic viscosity of 1.0 dL/g was carried out using a twin screw extruder, a metering pump and a monohole spinneret. A hot roll was set 100 cm below the spinneret. The extruded filament was passed through the hot roll and a quenching nozzle and wound up using a winder. Temperature and velocity of the hot roll, and the distance between the hot roll and quenching nozzle were varied. Thus prepared as-spun fibers were subjected to continuous drawing and annealing processes for the development of fiber structure with high molecular orientation and high crystallinity. Mechanical properties and thermal shrinkage of the as-spun fibers and the drawn and annealed fibers were measured. In addition, structural analysis of as-spun fibers was also performed.

3. Results and Discussion
Stress-Strain curves of as-spun fibers prepared at various take-up velocities with and without the application of SLD are shown in Fig.2. Fibers obtained at 250 m/min with SLD were found to show higher mechanical properties with improved tensile strength and elongation at break in comparison with those for fibers prepared at 250 – 1000 m/min without SLD. True stress-true strain curves of as-spun fibers prepared with and without SLD are shown in Fig.3. True stress at break, which also represents the toughness, for all fibers prepared without SLD were around 0.9-1.0 GPa, while the fibers prepared with the SLD apparently showed higher value.

To investigate the mechanism for the improvement of toughness, network structure of each fiber was evaluated (Long & Ward 1991). Obtained master curves are significantly different from each other as shown in Fig.4. This result clearly suggests the change of network structure by the application of SLD.
Mechanical properties of drawn fibers of various draw ratios prepared from the as-spun fibers are compared in Fig. 5. Along with the improvement of attained highest tensile strength, there was a shift of the tensile strength versus elongation at break relation to the upper right direction when the SLD was installed in the melt spinning process. In other words, application of SLD was found to improve the toughness of drawn fibers. The highest tensile strength of drawn fibers reached 1.44 GPa.

References
B. Huang, M. Ito, T. Kanamoto (1994), Effects of draw conditions on deformability and draw efficiency of high molecular weight poly(ethylene terephthalate) fibres, Polymer, 35, (6), 1329-1331
S. Tate, S. Chiba, K. Tani (1996), Melt viscosity reduction of poly(ethylene terephthalate) by solvent impregnation, Polymer, 37, (19), 4421-4424
Polymer blends have been used in fiber extrusion for many decades, but most previous studies have been focused on the use of miscible polymer blends for enhancing fiber properties. Melt extrusion and spinning of highly immiscible polymer blends is fundamentally challenging, because the two size scales, namely the phase size and the filament diameter, may be of a similar size scale, thus prohibiting the production of a uniform morphology. It is also known in the fiber spinning industry that melt spinning of immiscible blends, such as PP/nylon blends, is difficult since the coarse phase structure in the molten filament frequently results in an unstable spinning process and thus unexpected filament breakage. On the other hand, the phase separation mechanism in combination with some processing strategies may be used for the development of innovative fiber products. From some experimental evidences in the literature, e.g., (Karami and Balke 2000), (Afshari et al. 2005), (Afshari et al. 2002), (Li et al. 2000), (Grof et al. 1992), (Liang et al. 1983), dependent on the material formulation and processing conditions, island-and-sea and sheath-and-core structures may be produced. In other cases, filaments with a co-continuous morphology may be generated.

The authors have conducted experimental work on filament extrusion of immiscible polymer blends for fabrication of highly porous fibers with continuous and size adjustable porous structures. The two polymers used in the blend were polycaprolactone (PCL), a biocompatible and biodegradable polymer, and polyethylene oxide (PEO), a biocompatible and water soluble polymer. PCL and PEO have similar melting temperatures and desired rheological properties for forming a co-continuous polymer blend. To produce highly porous PCL fibers with continuous porous structures, the two polymers at a mixing ratio of 30%wt-PCL and 70%wt-PEO were first blended in a batch mixer, then co-extruded, and finally selectively dissolved in water and dried. Some as-extruded filaments were also annealed at 80°C for a period of time. It was found that this post annealing process can be effectively used to control the phase structure and thus the porous structure of the PCL filament after dissolution of the PEO phase. Selected morphologies from this process are shown in Figure 1.

With the change of the mixing ratio of the PCL/PEO blend, different filament morphologies can result. It appears that although the formation of a sheath-and-core morphology is favored by the minimal energy principle, e.g., (Karami and Balke 2000), (MacLean 1973), (Goldsmith and Mason 1967), the actual formation of such a morphology is difficult under the normal fiber extrusion condition. Instead, in a high-shear process with shear rate reaching 10³ s⁻¹ performed on an injection setup, a sheath-core morphology was observed, even for thick flow cross-sections, as shown in Figure 2. Computer simulations were used to study the favorable conditions for the formation of such a morphology. If successful, this single-extruder process can be used to replace the more expensive bi-component fiber spinning process.
References:

VARIATION OF DRAWABILITY WITH STORING TIME FOR MELT-SPUN POLY(ETHYLENE TEREPTHALATE) FIBERS

Akira Hamano* and Takeshi Kikutani**

* R & D Division, Japan Chemical Innovation Institute (JCII)
3-29-8, Kitasenzoku, Ohta-ku, Tokyo 145-0062, Japan, e-mail: nanohama@abox.so-net.ne.jp
**Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,
Tokyo Institute of Technology
2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan, e-mail: kikutani.t.a@titech.ac.jp

To obtain high strength fibers using high-molecular weight poly(ethylene terephthalate) (PET), optimization of drawing condition is crucial. In this study, variations of stress-strain curves, thermal and thermo-mechanical behaviors and maximum draw ratios for as-spun PET fibers of two different molecular weights were analyzed as a function of storing time after spinning. Those changes occurred more slowly in high molecular weight PET.

1. Introduction

Poly(ethylene terephthalate) (PET) fiber is widely used as industrial fibers, especially as tire codes. Although PET fibers have an advantage in terms of the cost per strength than other high-performance fibers such as aramid fibers, its maximum strength is limited at around 1 GPa, which is about a half of the strength of aramid fibers. Because of this reason, significant efforts have been devoted for the development of PET fibers of high strength. To maintain the merit of low cost, it is considered that the preparation of high-strength PET fibers utilizing the melt spinning process is inevitable.

Application of high molecular weight polymer is known to be one of the key factors for achieving high strength, however it is also known that the drawing of as-spun high-molecular weight PET fibers to high draw ratios is difficult. Therefore, improvement of drawability through the optimization of melt spinning conditions and the selection of appropriate drawing conditions is considered to be the important subject for obtaining high-strength PET fibers.

On the other hand, properties of as-spun PET fibers including drawability changes with time after spinning. However detailed analysis on the effect of molecular weight on such behavior has not been reported yet. In this research, variations of stress-strain curves and thermal properties as well as the drawability of the as-spun fibers of two different molecular weight PETs were analyzed to obtain fundamental knowledge concerning the optimization of drawing conditions.

2. Experimental

Melt spinning of two types of PET with different molecular weight was performed at the extrusion temperature of 330 °C and take-up velocity of 500 m/min. Weight average molecular weights of the resultant fibers were 13000 (Fiber A) and 26000 (Fiber B), respectively. To investigate the change of the properties of fibers after spinning, fibers were stored at 23 °C and subjected to characterization after 1, 2, 5, 10, 20, 50, 100, 200 and 500 hours. For the characterization of fibers, drawability evaluation, tensile test, and thermal and thermo-mechanical analyses were performed. Drawability was estimated by evaluating the maximum draw ratio in the continuous two-step drawing process. In this process, drawing of the first step was performed at 80 °C and at the draw ratio 1.1 times higher than the natural draw ratio of the as-spun fibers. In the drawing of second-step, temperature was set at 140 °C, and the draw-ratio was gradually increased until the fiber breakage occurred to determine the maximum draw ratio. For the preparation of drawn fibers, draw ratio was set at 0.7 to 0.9 times of the maximum draw ratio. Stress-strain behavior of the as-spun and drawn fibers was measured using a tensile testing machine (Autograph AG-11, Shimadzu corp.) at the strain rate of 100 %/min. Thermal behavior near the glass transition temperature (Tg) including enthalpy relaxation was measured by modulated differential scanning calorimeter (M-DSC, TA instruments Corp.) at the heating rate of 2 K/min, and modulation period and amplitude of 60 s and 0.32 K. Dynamic visco-elasticity measurement for single filament was performed using a dynamic mechanical analyzer (DMA, A&D corp.) at the heating rate of 1 K/min and frequency of 3.5 to
110 Hz. The DMA measurement for Fiber A was difficult because of its low modulus. Thermal shrinkage force was measured using a shrinkage force meter exclusively designed for fibers (Fig. 1, Kanebo Corp.). The heating rate was set to 150 K/min.

3. Results and Discussion

Stress-strain curves for Fiber A and Fiber B measured after different storing time are shown in Fig. 2. Elongation at break decreased slightly with time. It should be noted here that the maximum draw ratio evaluated separately in the continuous drawing process also decreased similarly with time. After 500 hours, Fiber A broke at the first yielding point, while Fiber B still kept high elongation. On the other hand, there was a significant change in necking deformation behavior, which could be approximated from the characteristics of the stress-strain curves. The end point of necking deformation became clearer and shifted to higher elongation with time. Reduction of the elongation at the end point of necking and the maximum draw ratio proceeded more rapidly in Fiber A than in Fiber B. Despite the changes in the necking behavior, latter part of the stress-strain curves did not change much except for the point of breakage.

Changes in thermal properties were also confirmed. In the M-DSC measurement, peak of enthalpy relaxation appearing immediately below Tg shifted to higher temperature. The peak corresponding to glass transition in the DMA measurement also shifted to higher temperature. These results coincide with those previously reported in some papers, while effect of molecular weight on these behaviors was clearly confirmed in this research.

Significant changes were also confirmed in the thermal shrinkage force measurement as shown in Fig. 3. One or two hours after spinning, a peak (Fiber A) or a shoulder (Fiber B) was clearly observed at a temperature slightly lower than Tg in the shrinkage force measurement, however, the peak or shoulder disappeared after 500 hours. Disappearance of the peak or shoulder proceeded from the lower temperature side, and therefore they appeared to be shifted to higher temperature and finally be absorbed to the main peak existing at Tg. As in the cases of the variations of necking behavior and maximum draw ratio, the shift of peak in Fiber A proceeded more rapidly than that of shoulder in Fiber B.

Figure 2 Variation of stress-strain (s-s) curves with time for Fiber A and Fiber B. The s-s curves are shifted vertically for clearer indication of difference.

Figure 3 Variations of shrinkage force with increasing temperature for Fiber A and Fiber B which were stored for different periods after melt spinning. The curves are shifted vertically for clearer indication of difference.
1. Abstract
The history of the carbon-fiber industry has been a series of surplus-scarcity cycles as new demand is balanced against new production. Recently, this cycle has had a period of approximately 10 years. The current condition is a state of fiber scarcity, and is likely to remain this way for a number of years into the future. As such, many fiber consumers must investigate non-traditional fiber sources; such as warehousing fibers whenever possible, or purchasing from other consumers. All such approaches run the risk that the fibers will be beyond the traditional shelf-life when put to use.

This work examined the aging phenomena of one popular carbon fiber – M55JB. Eight fiber lots were examined, spanning a manufacturing period (DOM) from April 1997 through June 2006. Examined were: 1) the stability and chemical activity of the fiber sizing; 2) the oxidation state of the carbon surface; 3) the dry fiber handling characteristics; and 4) the mechanical shear strength of the fiber in an epoxy matrix. From this work it was determined that the two year shelf life can be confidently extended to at least nine (9) years.

2. Materials
The fiber studied herein is M55JB-6K from Toray, a 72 Msi tensile modulus, PAN-based carbon fiber with a proprietary sizing agent ("Type 5", believed to be a long-chain epoxide-urethane-aliphatic) on the surface. The studied fiber spools were removed from the warehouses at Sigmatex and YLA Inc, both of Benecia, CA. The spools were stored in the original shrink wrap under ambient conditions (typically 73°F and 50% Rh), without any special consideration given to protecting the fiber from moisture, oxygen, or other airborne chemicals. A list of the fiber lots studied, and the tests applied to each lot, are provided in Table 1.

3. Test Methods
Multiple analytical methods were brought to bear in order to analyze these fibers.

Inverse Gas Chromatography (SMS-iGC 2000) evaluated the dispersive surface energy, specific free energy, and acid-base number of each fiber in order to assess the chemical reactivity of the sizing.

TGA (TA Instruments Q-500) evaluated the ratio of fiber sizing to carbon. This was used to compare fibers across all evaluated lots, as well as a check against a pyrolysis method of determining the same ratio.

HPLC (Waters 1525 pump & 2996 photodiode detector, Agilent Zorbax RX-C18 column) evaluates the sizing obtained from an acetonitrile extraction. Using 227 nm light (~UV), the molecular-weight constituents of the sizing was obtained. An identical HPLC trace would indicate that the sizing had not changed over time, either from evaporative or reactive mechanisms.

FTIR also evaluates the acetonitrile-extracted sizing; however, at > 1000 nm frequency (IR).

➢ TGA + HPLC + FTIR is a powerful test combination: if the total sizing quantity (TGA) remains constant with age, and the molecular constituents (HPLC, FTIR) remain proportional with age, it is very likely that the system has remained static over time.

ESCA (Perkin Elmer Phi 5400) evaluates the atomic composition of a surface exposed to high-energy photons (X-Ray). By analyzing ejected electrons, the chemical constituents (atoms and molecules) can be generally determined. In this study, the fiber sizing was removed prior to testing such that only the fiber surface was being evaluated.

Interlaminar Shear Strength (ASTM D 2344, "ILSS") evaluates the shear strength of the fiber-to-sizing bond and/or the sizing-to-matrix bond, through a 3-point flexure test of CFRP laminates fabricated from each fiber. Failure
occurs when one of the interface fractures, thus providing an indicator of the chemical reactivity between either the fiber and sizing, or the sizing and matrix.

Handling (Sigmatex & YLA Inc.) evaluates the less tangible characteristics of the fibers through the eyes of the technicians who are responsible for converting the raw fiber into usable fabrics and prepregs. Sigmatex ran aged fiber through the weft-direction of a weaving machine, and YLA assessed the ability of aged fibers to be threaded through unidirectional prepregging equipment.

4. Results

iGC: The iGC results are notes in Table 1. Based on the experiences of the SMS testing facility, the three tested fiber lots are statistically identical. As noted by SMS, "… there is no evidence of any surface chemistry changes occurring to the carbon fibers [authors - the sizing] over the time scale and conditions measured."

TGA: In this experiment it was seen that the sizing mass ratio of the four lots tested remained essentially unchanged with age. The values were compared against the original Toray values obtained via pyrolysis. Three of the four lots were also retested by Toray for direct correlation. The results are all basically consistent with the originally reported Toray values, and seen in Table 1.

HPLC: Figure 1 shows the HPLC chromatographs of each sample overlaid. It can be seen that the time peaks match across all samples, indicating that the number of sizing constituents remained constant with age. One lot was run multiple times with the minor variations matching that seen between multiple lots.

FTIR: Figure 2 shows the FTIR traces of each sample overlaid. Similar to the HPLC, it can be seen that the frequency peaks match across all samples, indicating that no loss of any key components occurred with age.

Combined, the iGC, TGA, HPLC, and FTIR discerned no change in chemical reactivity, constituents, or overall mass. This gives strong confidence to the conclusion that the sizing can remain stable over at least nine years of warehouse storage.

ESCA: As a test of the fiber, this data (Table 1) is inconclusive since there is no baseline value, nor lot-to-lot variation, against which to compare the results. However, examining the fiber surface oxygen/carbon atomic concentration ratio across all lots provides some information. It can be seen that while there is a significant amount of scatter in the results, there is not a trend which correlates with fiber age. As such, a reasonable conclusion is that the variations are normal lot-to-lot variations and not assignable to aging.

ILSS: Three lots of fiber were submitted to Toray for re-certification, which included fabrication of unidirectional laminates to test the shear performance. The iCG results indicate that the sizing should remain fully capable of forming a strong chemical bond to the resin, while the ESCA results indicate that the fiber should remain fully capable of forming a strong chemical bond to the sizing. As such, no loss of shear strength was anticipated. Indeed, the results given in Table 1 demonstrate that the chemical bonds appear to develop as fully with nine years of aging as they did at the day of manufacture.

Handling: Engineering and technical staff at both Sigmatex and YLA Inc. examined the aged fibers for manufacturing suitability. Sigmatex ran a trial weaving cycle with the aged fiber in the challenging weft position. YLA handled multiple fiber lots for handling comparison, and Toray actually produced prepreg and laminates from the aged fibers. In the case of Sigmatex and YLA, written observations noted that the aged fibers "... looked and felt like any other M55JB-6K fiber." Per Sigmatex, the fiber "... performed in the weft with no problem, and did not appear 'cracky' or stiff." Handling at Toray was apparently uneventful also as demonstrated through the reported tensile moduli; which, due to their exact comparison with the original certification values, indicate that the handling damaged none of the fibers. The tensile moduli are reported in Table 1 for reference.

5. Conclusion

Eight separate lots of M55JB-6K carbon fiber were evaluated - spanning nine years of aging in uncontrolled warehouse storage. Seven different evaluation methods were employed to assess the sizing chemistry, fiber surface chemistry, handling characteristics, and translation to laminate mechanical performance. As demonstrated, the results across all fiber lots and all evaluations generate the same conclusion - these fibers do not have any aging phenomena which is discernible over this nine year period.
6. Tables & Figures

Table 1: Fiber Lots, Tests & Results

<table>
<thead>
<tr>
<th>LOT #</th>
<th>DOM</th>
<th>mJ/m²</th>
<th>kJ/mol</th>
<th>gC</th>
<th>FTIR</th>
<th>Surface Chemistry</th>
<th>Mechanical Retention</th>
<th>Handling</th>
</tr>
</thead>
<tbody>
<tr>
<td>637041</td>
<td>04 / 1997</td>
<td>35.10</td>
<td>9.41</td>
<td>12.97</td>
<td>7.52</td>
<td>9.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>637082</td>
<td>02 / 1998</td>
<td>34.60</td>
<td>9.69</td>
<td>9.30</td>
<td>8.06</td>
<td>8.55</td>
<td>1.2%</td>
<td>1.3%</td>
</tr>
<tr>
<td>630111</td>
<td>02 / 2001</td>
<td>34.67</td>
<td>9.86</td>
<td>9.40</td>
<td>8.09</td>
<td>8.69</td>
<td>1.3%</td>
<td>1.2%</td>
</tr>
<tr>
<td>635021</td>
<td>06 / 2006</td>
<td>1.1%</td>
<td>1.14%</td>
<td>1.13%</td>
<td>Fig 1 Fig 2</td>
<td>10.9</td>
<td>89.1</td>
<td>0.122</td>
</tr>
</tbody>
</table>

Figure 1: Overlaid HPLC Chromatographs

Figure 2: Overlaid FTIR Traces

7. Acknowledgements

The authors would like to extend their thanks to Dr. Daniel Burnett of Surface Measurement Systems for conducting iGC testing, Michigan State University for ESCA testing, Steve Smith of YLA and Kathy Pollard of Sigmatex for handling evaluations, and Toray for recertification testing.
Self-Assembly Fabrication and Applications of Functional Graded Fibers, Films, and Particles

Katsuo ORIHARA, Satoru TAKANO, Noriko ASANO, Aki ANDO, Ken ITAWA, Neidi TAN, Hajime SUZUKI, Takashi SASAKI, Daisuke KIMURA, Takahisa UCHIDA, Akie OIKAWA, Yahui DAI, Takahiko HIROKA, Katsuhiko AOKI

Department of Functional Macromolecular Science and Technology, Faculty of Engineering, Yamagata University
*4-3-16 Jonan, Yonezawa-city, 992-8510 Japan  Tel:0238-26-3081 Fax:0238-26-3410
e-mail: san_son@ms5.omn.ne.jp

Functionally graded fiber, film, particle, and engineering plastics are fabricated self-assembly. The new fabricating method was developed by applying particular phase separation phenomena of “layered structure” that had been discovered previously [1,2,3] in the polymer blend. Each basic phase separation structure of uniform sea-island, graded and step are as shown in Fig.1 schematically. In the Fig.1, the first model a is a conventionally applied structure but the second one b is a new structure and had been not yet applied. The last one c is similar to laminated film, but just different.

![Fig.1 Three kinds of cross-section structure appearing in membranes, plastics, fibers and particles.](image)

Especially the second model b of graded composition structure is hardly to be fabricated by conventional non-self-assembly method. It needs many kinds of process. On the other hand, the self-assembly method make the process very simple. This
character is expected to present the saving energy, saving labor and decreasing surrounding load in the manufacturing process.

Each structure a, b, c in the Fig.1 was formed from uniform mixture of polymer blend solution or melt without any artificial technique. The processing condition selected for forming each structure of (a), (b), (c) in the Fig.1 needs not to be changed during the processing in lapsed time if you want. For example, constant drying condition in casting process or constant temperature condition in the melt processing of spinning or molding are enough for forming each structure.

In the conference, each applications of skin-core graded new fiber, graded membrane, particle or plastic products, electrostatic removal and electronic devices and the principle of the self-assembly phenomena will be discussed.

References:
SESSION 6A

FIBERS AND YARNS
ANALYSIS OF THE TENSILE BEHAVIOR OF LOW-TWIST STAPLE FIBER ASSEMBLIES

Xin Shao(1), Yiping Qiu(2), and Youjiang Wang(1)

(1) School of Polymer, Textile & Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA
(2) College of Textiles, Donghua University, Shanghai, China

Introduction

Unlike high-twist yarns for which the main failure mechanism is fiber rupture, low-twist staple yarns show significant fiber slippage and fiber pull out during the rupture process. In studies of staple yarn mechanics reported in the literature, attention has generally been paid to the prediction of the yarn modulus and strength. Few studies go beyond these aspects to investigate the breakage and failure response of yarns, and the whole stress-strain curve. Also, little attention has been paid to the yarn behavior under cyclic loading conditions. However, it is well known that yarn breakage is an important issue in textile manufacturing processes. The cyclic response of staple yarns is another important aspect since the fibers and yarns are more likely to be subjected to repeated cyclic loads in applications and in textile processes such as yarn spinning, knitting and weaving. A clear understanding of the above problems is critically important in order to efficiently improve the manufacturing processes of fibrous assemblies and to obtain high quality yarns.

This study focuses on the progressive deformation mechanisms of low-twist staple yarns subjected to tensile loading. A theoretical model is developed to predict the entire load-extension response in tension, and under cyclic tensile loading. Comparison between experimental data and theoretical predictions shows that the predicted yarn behavior (monotonic and cyclic behavior) is in reasonable agreement with the experiment results.

Theoretical Modeling

The approach undertaken in this study involves the following steps. First, a stress analysis is performed on a fiber in staple yarn which is subjected to tensile loading condition based on short-fiber composite theory. Then, finite element analysis is used to investigate the distribution of fiber shear stress and tensile stress under tensile loading and unloading conditions. A fiber pull-out analysis is conducted to study the yarn post-peak response. Finally, a model of yarn tensile behavior is established through which yarn strength, the complete load-extension curve and yarn cyclic response can be obtained.

It is observed that the behavior of a low-twist staple yarn under tensile loading can be described by the following two stages: (1) an initial uniform straightening and stretching of the fibers throughout the yarn length up to the peak load, and (2) then a non-uniform stretch due to fiber slippage in a failure zone which lead to the breakage of the yarn. The yarn is separated into two pieces.

Figure 1 is an illustration of the typical yarn response, a physical yarn model, and an idealized yarn model used in this analysis. The local extension $\delta_2$ captures the yarn deformation due to fiber slippage at the local failure section. The above two phases of deformation are considered to predict the full load-extension curve. The contribution of yarn stress in the first phase is due to the sum of forces acting on the fibers which are being stretched. The yarn deformation at the “crack plane” $\delta_2$ is assumed to be zero in this phase. In the second phase, both the global fiber stretching and local separation at the crack plane take place simultaneously. From force equilibrium, the tensile force along the yarn is a constant, determined by the weakest section, where fiber slippage takes place. Considering only the local separation of fibers, the frictional forces between the fibers to resist fiber slippage determine the strength of the yarn. The combined effect of fiber stretching, fiber re-orienting, and local separation determine the yarn behavior in this phase.
The deformation of the yarn before peak load is mainly due to the elastic deformation of fibers. Also fiber movement changes fiber orientation. At peak load, yarn failure is initiated after which extensive fiber slippage takes place in a local section (“crack plane”). The deformation in this stage consists of basically two parts: fiber separation at the crack plane and the elastic deformation of the yarn away from the crack plane. Assuming there is no fiber breakage when the low twist yarn ruptures, the tension of the yarn is determined by the frictional forces acting on fibers undergoing a slippage motion. An equation to relate yarn tension to the distance of fiber pull out (“crack opening”) can thus be established. Combining the results for yarn response at both pre-post peak stage and post peak stage, we can obtain the entire load-extension relation. The monotonic tensile response and cyclic loading response of a cotton roving from experiments are compared with the theoretical predictions (Figure 2). Good agreement is observed. Effect of fiber types, twist levels, linear densities, and fiber friction coefficients on yarn behavior is analyzed by theoretical and experimental studies.

Figure 1. Typical yarn tensile response (top left), post-peak yarn deformation (top right), and idealized model (bottom).

Figure 2. (a) Experimental cyclic loading response of cotton roving, (b) predicted cyclic loading response of cotton roving, and (c) experimental and theoretical results for monotonic tensile response of cotton roving.
Fiber length is one of the most important cotton properties that need to be measured physically. It can affect yarn strength, evenness, and the efficiency of the spinning process, and therefore is a determinant factor in assessing fiber quality and price. Currently, there are three instrumental methods for cotton length measurements. Based on the fibrograph method, the High Volume Instrument (HVI) is the USDA’s classing methodology that provides fiber upper half mean (UHM) length and uniformity index for American upland cotton [1]. Fibers are caught at random points along their lengths to form a beard. The beard is scanned photoelectrically from base to tip, and the amount of light passing through the beard is used as a measure of the number of fibers that extend various distances from the comb. Although HVI offers rapid length measurements, it does not provide information on the entire fiber length distribution [2] (e.g., SFC--short fiber contents). The accuracy of the measurements relies on the calibration and the stability of the light source. Advanced Fiber Information System (AFIS) is another commonly used system in the industry for length measurements. AFIS individualizes fibers mechanically and transports single fibers aerodynamically through an optical sensor that produces signals when the fiber blocks the light path. The duration of the signal pulse reflects the length of the fiber. The curvature of the fiber in the air stream can cause an underestimation of fiber length [3], and substantial fiber breakage in the high-speed opening roll of AFIS can skew the data [4]. Recently, various imaging systems were adapted for fiber length measurements [3,5,6]. Although they all demonstrated effectiveness of accurate length measurements, these methods require extensive preparations (often manually) for individualizing fibers so that folding and entangling of fibers can be avoided. Therefore, they are not suitable for high volume measurements.

In this paper, we introduce a novel method to measure the number-length distribution of cotton fibers using image technology. The test samples are combed to form a tuft web or a beard. The beard is cut into a number of sections of specific length by a fiber amputator. The snippets in different cut sections are collected and distributed on separate black glassy papers, and then are digitized in order by a regular scanner into a computer for image analysis. The scanning order indicates the distance of each section from the cutting base line, and the number of the snippets on a paper is the frequency of fibers present in the current section. A specially designed image analysis program is used to trace all snippets in a scanned image so that the number of snippets can be calculated. After all the images were analyzed, the fiber numbers in different length sections can be summarized. From these number-length data, the distribution, maximum length, mean length, and short fiber content can be calculated.
CONTRIBUTION TO THE STUDY OF THE ELONGATION OF THE COTTON FIBER

H. Benzina ¹,², O. Harzallah ¹, J. Y. Drean ¹, E. Hequet², N. Abidi²

¹LPMT UMR 7189 CNRS-UHA, ENSISA 11 rue Werner 68093 Mulhouse cedex; email: o.harzallah@uha.fr
²International Textile Center and Dept. of Plant & Soil Science, Texas Tech University Lubbock Texas 79403-5019, USA

Due to the lack of calibration standards, High Volume Instruments (HVI) does not provide consistently accurate fiber elongation data. In this study, cotton fibers bundle elongation and tenacity were measured using a modified Testometric instrument to which Pressley clamps (1/8” gage length) were adapted [1]. Thirty two cotton genotypes with a range of bundle tenacity and elongation were carefully selected based on their distinct physical properties. The work of rupture was calculated from the curves Load versus Elongation for each cotton. Results demonstrated the importance of fiber bundle elongation in the work of rupture of fiber bundles, which is critically important to processing performance. This study lays a foundation for future efforts to calibrate the HVI elongation measurements and to breed new cultivars with improved work of rupture. This should result in lower fiber breakage when the cotton fibers are submitted to different mechanical stresses (ginning, carding, spinning, and weaving) [2].

The second part of this work consists of developing a mechanical model for six selected cottons by studying the results obtained from the creep and the relaxation tests. These tests were performed using the Universal fiber testing.

REFERENCES


SESSION 3B

INNOVATIVE USES AND ENHANCEMENT I
Modifying the Surface Properties of Specialty Polyolefin Elastomer Based Elastic Nonwovens through additives

Raja Dharmarajan, Smita Kacker, Vincent Gallez, A.D Westwood and C.Y. Cheng (consultant)

ExxonMobil Chemical Company
5200 Bayway Drive
Baytown, TX 77520

Vistamaxx™ specialty elastomers are a new generation of metallocene catalyst based specialty polyolefin elastomers (SPE) that can be processed in conventional spunmelt equipment to produce elastic nonwoven fabrics. For applications as elastic components in the hygiene absorbent products market, the touch and aesthetic properties of the SPE based nonwoven are important.

This paper examines modification of the surface properties of spunmelt SPE nonwovens through the use of additives that can be added in-line during melt spinning. The additives considered are conventional slip additives such as erucamide, and other surface modifying additives such as high melt flow polypropylene, polyolefin waxes, as well as inorganic particulates and combinations of slip with surface modifying additives. The slip, which is formulated as a masterbatch in the SPE carrier is added to provide an effective concentration between 3,000 to 6,000 ppm in the elastic nonwoven. The slip additive either by itself or in combination with the other polyolefin surface modifiers provides a touch that is markedly different from the base SPE touch that has been described as "rubbery", without sacrificing the intrinsic elastic property of the SPE nonwoven.

The elastic properties of the modified SPE nonwovens are measured using cyclic testing to an extension of 100 % strain and return to zero load. The permanent set, load loss and mechanical hysteresis are measured after the first and second cycle. The surface chemistry and morphology of the nonwoven fibers is characterized using an array of surface sensitive analytical techniques such as Atomic Force Microscopy and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Addition of slip and low molecular weight polyolefins show a distinct migration tendency to the fiber surface due either to viscosity mismatches relative to the SPE resin, or due to a thermodynamic incompatibility with the SPE resin, thereby imparting a touch that is different from the unmodified SPE.

The addition of surface modifying additives is an effective way to adjust the surface features of the elastic nonwoven, resulting in the ability to tailor the surface feel of the nonwoven. Further custom tailoring by various combinations of the modifiers is an extension of this effort that can be conducted by the nonwoven manufacturers.
TOWARDS A PHOTOCATALYTIC FIBER FOR DEGRADATION OF MALODOR

Felix A. Reifler †, Axel Ritter †, Giuseppino Fortunato †, Andri Vital ‡, Kranthi K. Akurati ‡ and Rudolf Hufenus † *

† Empa - Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Advanced Fibers, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland.
‡ Empa - Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland.
* E-Mail: rudolf.hufenus@empa.ch

Many textiles have a distinct ability to adsorb odors from the surrounding air and act as a sink for volatile substances (Figure 1) (Jørgensen et al., 1993). This can be a problem when there are unpleasant odors leaving the textile through desorption. To meet this issue, odor control textiles are developed.

In most cases, a finishing based on the adsorption-desorption abilities of cyclodextrins (Buschmann et al., 2003, Szejtli, 1998) is applied on the textile fabric. Cyclodextrins have a cage-like structure which can act as a "host" taking up "guest"-molecules. Hence, the odor control effect is based on such host-guest complexes with the volatile substances, thus leading to their delayed desorption. In an ideal case, the volatiles would not desorb during the use of the odor control textile (1 to 3 days) and only be released during the next washing process.

Regarding the practical use of odor control textiles, this can lead to unwanted side effects: the release of adsorbed volatiles is retarded, but can last much longer than with untreated textiles. This is an inherent drawback of the adsorption-desorption odor control technology. Furthermore, this odor control technique can only be applied for textiles which are regularly washed.

A far more attractive way is the degradation of the malodor itself at the surface of the odor control material through, e.g., photocatalytic processes on TiO2 based photocatalysts (Fujishima et al., 2000, Kaneko and Okura, 2002, Mills and LeHunte, 1997). Malodor reduction with bactericidal or bacteriostatic agents is not targeted at odors coming via the gas phase but to prevent the evolution of odors from initially odorless substances and will not be treated here.

The goal of the presented work is a PET-based fiber with photocatalytic activity for the degradation of malodor in air (Hufenus et al., 2006). The photocatalytic particles shall be incorporated directly into the fiber.

Photocatalytic TiO2 nanoparticles with high degree of crystallinity and surface area were obtained by flame synthesis (Akurati et al., 2007) (Figure 2). The synthesis of nanoparticles with the general formula TiO2-xNx was conducted through a new process route (pat. pend.). Such nitrogen doped nanoparticles are known to show a good photocatalytic activity in the wavelength range between 400 nm and 500 nm and open the opportunity to realize photocatalytic fibers operating even under indoor conditions (artificial light) or in an automotive interior (behind laminated glass) (Sakthivel et al., 2004).
For particle incorporation and fiber manufacture experiments (monocomponent and bicomponent fibers), Degussa P25, a commercially available photocatalytic TiO$_2$, was used. Pretreatment of the P25 particles helped to facilitate the compounding step and to prevent agglomeration problems.

Analytical procedures play a central role during the fiber development; e.g., for the assessment of the photocatalytic activity and malodor degradation (Reifler and Ritter, 2006), for gaining insight into the size and the dispersion of the incorporated particles, and for the assessment of the resistance of the fibers to UV light. New methods have been developed to enable the assessment of the photocatalytic activity of a broad range of samples (particles, fibers, fabrics) using light with various spectral distributions.

Fibers containing P25 were subjected to formaldehyde decomposition tests to evaluate photocatalytic activity. The results indicate that malodor degradation can be expected. Method development to verify the degradation of other malodors is ongoing. The fibers mentioned were also subjected to artificial weathering. Their degradation behavior was not severely inferior to the fibers without P25.

References


A method for forming an electrically charged split films consisting of a high molecular weight nonpolar semi-crystalline polymeric materials was invented by van Turnhout in 1976 in Netherlands (1, 2). This method includes blown film process, uniaxial drawing, uniaxial stretching, splitting, charging and winding. These highly corona charged fibrillated materials are called “Electret.”

Figure 1 shows the filaments from highly uni-axially stretched thin films. The thickness of this film was down to 0.6 micrometers and width of these split films ranged from 3 to 250 micrometers. This figure shows the fine filaments formed from uni-axial drawing and stretching.

The nearly amorphous polymer film showed similar fibrillation behavior after highly uniaxial drawing and stretching processes. Even this material showed the ductile failure. Figure 2 shows the fibrils from a split uniaxially stretched polystyrene thin film. The size of these fibrils is about 1 micrometer (3).
The process for producing highly porous materials was invented by Gore (4, 5) with polytetrafluoroethylene (PTFE) materials in 1976. Gore-Tex is well known in lightweight sports jackets that are breathable and waterproof. The expanded PTFE multi-axially fibrillated ultra thin materials produce through sequential stretching processes. The filament size is about 100 nanometers (see Figure 3).

References
Understanding coordination polymerization and its value to producing stereoregular and chiral polymers

Navzer D. Sachinvala, Ph.D., MBA
2261 Brighton Place Harvey, LA 70058

Following a brief review of the state of the art with regard to designing and preparing stereo-regular polymers with metal containing auxiliaries, in this presentation I will discuss how carbohydrate-derived organometal complexes could be used to make stereo-regular and perhaps chiral polymers. The discussion will then lead into designing sugar derivatives that afford a left and right handed bias towards the approach of reagents and monomers to yield chiral materials. Finally, I will present how saccharide derivatives could be exploited to afford ligands that only permit trans geometries at metal centers and their as yet unknown potential in preparing stereo-regular polymers.
SESSION 4B

INNOVATIVE USES AND ENHANCEMENT II: CHEMICAL
Homogeneous Modification of Cellulose with Chloro-2-Hydroxypropyl Trimethylammonium Chloride

Khaled El-Tahlawy and Renzo Shamey

Fiber and Polymer Science Program, Box 8301, North Carolina State University, Raleigh, NC 27695-8301. email: kfeltahl@ncsu.edu; rshamey@ncsu.edu

1. Introduction

Cellulose is the most abundant natural polymer in the world. It is the main source of a number of agricultural crops and products, such as wood, cotton, flax, and jute, to name but a few. The production and characterization of cellulosic fibers has therefore been the subject of immense interest for the researchers over the last few decades. In the last decade, however, due to increasing environmental awareness and associated legislations, significant research was required to develop environmentally benign technologies. This has involved investigating fiber production techniques that use natural polymers as an alternative to the petroleum-based synthetic polymers with a potentially wide range of applications in the industrial as well as consumer end use products. The low cost and availability of wood pulp is an attractive prospect in this regard for the development of new functional cellulosic derivatives for industrial and technical applications. One of the main goals of this research is to produce novel modified cellulosic fibers using wet spinning techniques. This would enable the production of modified fibers with an increased number of functional groups.

2. Modification of Cellulose

A 20 ml of a mixture of N,N-dimethylacetamide (DMAc) and lithium chloride (LiCl, 9 %) has been used as a stable, colorless, and effective solvent for cellulose wood pulp [1]. This solvent has been used to dissolve 1.62 g (10 mequivalent) of cellulose wood pulp (DP: 600) without instigating a noticeable degree of polymer degradation [2]. In this study the cellulosic pulp was allowed to react with chloro-2-hydroxypropyl trimethylammonium chloride (1.881 g, 10 mequivalent) using different types of catalyst such as pyridine, triethanol amine, and sodium hydroxide at different temperatures ranges varying between 80-140 °C. The reaction efficiency was evaluated using FTIR, NMR, TGA and elemental analysis.

3. Results and Discussion

Chemical modification of cellulose using a homogeneous system is an excellent way for introducing cationic groups along the structure of cellulose in a well defined manner. This will allow the primary hydroxyls of cellulose to react with 3-chloro-2-hydroxypropyl trimethylammonium chloride in the presence of different alkaline catalysts. The catalysts examined in this study included pyridine, triethanol amine, and sodium hydroxide at different temperatures ranges varying between 80-140 °C. The reaction efficiency was evaluated using FTIR, NMR, TGA and elemental analysis.

Although a higher nitrogen content was obtained when pyridine was used as a catalyst, sodium hydroxide was chosen as the catalyst since it provides a more eco-friendly modification route. Results
showed that increasing the sodium hydroxide concentration is accompanied by a clear increase in the reaction efficiency, expressed in nitrogen content percentage of the modified product. Increasing the concentration of sodium hydroxide results in a modified structure which facilitates subsequent reactions. Increasing the reaction temperature from 80 to 140 °C is also accompanied by an increase in the nitrogen content of the modified cellulose.

Structural characterization of modified cellulose was performed using a Hitachi S-3200N scanning electron microscope. The samples were coated with platinum to a thickness of 10 nm to make them conductive. Results revealed promising characteristics.

Table 1, Elemental Analysis of Modified Cellulose Using a Variety of Catalysts.

<table>
<thead>
<tr>
<th>Catalyst Used</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% C</td>
</tr>
<tr>
<td>Unmodified cellulose</td>
<td>41.61</td>
</tr>
<tr>
<td>Pyridine</td>
<td>36.19</td>
</tr>
<tr>
<td>Triethanol amine</td>
<td>41.78</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>39.9</td>
</tr>
</tbody>
</table>

4. Conclusions

Wood pulp was dissolved in dimethyl acetamide / lithium chloride (9 %) and then chemically modified with 3-chloro-2-hydroxypropyl trimethylammonium chloride in the presence of an alkaline catalyst. Although the nitrogen content of modified cellulose was the highest when pyridine was used as a catalyst, sodium hydroxide was selected as a convenient catalyst to provide a more eco-friendly modification route. Elemental analysis and subsequent SEM characterization of the product treated with sodium hydroxide are promising. Further work is currently underway to assess the properties of modified cellulosic structures and determine the performance of the modified fiber with specific imparted functionalities.

5. References

2) Matsumoto, T., Tatsumi, D., Tamai, N., Takaki, T., Cellulose, 2002, 8, 275.7
The parallel surface grooves on so-called deep-groove fibers offer new applications in many areas such as medical devices to allow guided cell growth along the grooves [1], liquid absorbent materials [2, 3], liquid transport [4, 5], chemical separation [6], and filtration [7]. Conventional round PP fiber has been widely used for fabrics and composites [8], however, the hydrophobic nature of PP and the lack of surface functionality limit its applications. Surface modification is required to meet certain end uses. Photografting is well known for its easy operation, mild reaction conditions, and permanency of the surface modification. This technique usually involves two UV irradiation steps: first to form radical sites on the substrate, and then to polymerize monomer from these reactive sites [9]. It has been extensively applied to films to achieve specific surface properties [10-13], but there are no reports on its use to modify deep-groove fibers.

This paper presents photografting as a surface modification method to provide permanent wettability improvement to deep-groove polypropylene (PP) fibers. We also describe approaches to evaluate the wettability of these fibers and the wicking performance of fiber bundles when polyacrylamide (PAAm) was grafted onto the fibers. In this study, the concentration of the monomer and the UV-exposure time were altered to examine the effects of those variables on fiber hydrophilicity. Results showed lower water contact angle and improved wicking capacity upon modification with PAAm.

References

4. M. Ogle, T. Hinnenkamp, U.S. Pat. 2005021152
13. L. Ng, D. Nguyen, S. Adeloju, Polymer International (2005), 54, 202-8
Green Chemistry for Fibers and Textiles

Ian R. Hardin, the University of Georgia

The Green Chemistry movement started in the early late 1990’s and had picked up enough momentum by the middle of that decade to generate a Presidential Green Chemistry Award, first given in 1995. The guiding principle of green chemistry is to reduce or eliminate the use of hazardous substances in the design, manufacture and use of products of a chemical nature. The obvious environmental advantage in textiles is the reduction of major costs associated with cleanup of many wet processes. The emphasis in the UGA labs has been on a “green chemistry” approach in fabric preparation, in treatment of dye wastewater and in recycling of used carpet and carpet waste. Much of this work involves the use of enzymes to accomplish what is normally done by conventional chemicals. This involves both laboratory and pilot plant scale up. Screening of enzymes for future use possibilities is also an active area of research. Experimental results from continuing research is discussed, as well as industrial interest in applications of the principles explored in our research.
DEVELOPMENT OF TEXTILE FIBERS WITH A CONDUCTING METAL CORE

Stephen A. Fossey¹, Thomas Godfrey¹, and James Brang²

¹US Army Natick Soldier RD&E Center, 15 Kansas Street, Natick, MA 01760-5020 USA. email: Stephen.Fossey@us.army.mil, Thomas.Godfrey@us.army.mil

²Hills Inc. 7785 Ellis road, W. Melbourne, FL 32904 USA. Email: JBrang@hillsinc.net

1. Fiber Spinning.
We have used melt spinning to spin fibers with a polymer sheath and a metal core. The metal core is a low melting point nontoxic metal. While only two different metal alloys and ten different polymers (including different grades of the same polymer) were spun the process appears to be influenced by both the energetics of the surface interactions and the physical forces of the spinning process.

1.1 Stability of the flow of the metal core.
An analysis of the metal core as a fluid jet indicates that the jet is unstable and breaks into droplets after only a few millimeters at most. The length (i.e. distance the fluid column travels before breaking into droplets as a result of surface tension effects), \( L^* \), of a Newtonian liquid jet is given by (Middleman 1977).

\[
L^* = 13UD^{3/2} \left( \frac{\rho}{\sigma} \right)^{1/2} \left( 1 + \frac{H}{(\rho D \sigma)^{1/2}} \right)
\]

Where:
\( \rho \) is the density
\( U \) is the jet velocity
\( \sigma \) is the surface tension
\( \mu \) is the viscosity

The breakup length for a 0.05 mm diameter jet of indium metal (Culpin 1957 and following websites) in air, being extruded at 100 m/min is approximately 0.4 mm.

In general, the fibers are formed as hollow fibers and a metal drop is drawn within the fiber. The continuous length of the metal core is then limited by the size of the initial droplet and the dimensions of the core. However, under at least some conditions for certain combinations of metal and polymer we have been able to spin fibers with what appears to be a nearly continuous (> 3 meters) metal core. Typical fibers were 150 – 200 microns in diameter with a metal core of 10 to 30 % of the cross-sectional area.

The fibers were produced without being drawn. Small segments of fiber were subsequently drawn in an oven using a tensile testing apparatus. In addition, we will discuss measurements of the electrical resistivity of the fibers and preliminary work to interconnect yarns made of these fibers.

References:


1. Introduction
Conductive polymers are used in a variety of applications where a material is required that is both electrically conductive and mechanically compliant. Recently, interest in conductive polymeric fibers has been motivated by electronic textiles applications, such as the integration of sensors and signal/data transmission lines into military combat clothing. The goal is to eliminate traditional cables now in use; such cables pose snag hazards and reduce the agility and mobility of the soldier. One avenue being pursued is a composite fiber approach, where a sufficient concentration of suitable conductive filler (e.g., graphite platelets) in the polymer provides a percolating conductive network. Ideally, such fibers should be durable and exhibit little change in electrical resistance during extension. To understand the changes in conductivity of composite fibers produced by extension, we investigate the effect of multi-axial direct strain on the electrical conductivity of particle filled polymer composites in the framework of concentration driven percolation. This work forms part of a broader study of the basic mechanical and electrical behavior of conductive fibers and fibrous assemblies for potential electronic textile applications.

2. Simple Effective Volume Fraction Model
Kirkpatrick (1973) demonstrated that random resistor networks follow a percolation conduction law of the form

$$\sigma \propto (p - p_c)^\mu$$

where in, say, the simplest case of nearest neighbor bond percolation, $p$ is the probability that a given bond in the lattice is conductive, and $p_c$ is the percolation threshold value of $p$. The conductivity exponent has a value of about 2 for three-dimensional networks (Stauffer & Aharony 1994), and, as with critical exponents in percolation phenomena generally, it is sensitive to the dimensionality of the system, but not the specifics of the lattice. The probabilities model the concentration of the conductive phase in a mixture or composite, so $p$ and $p_c$ may be replaced with volume fractions $V$ and $V_c$ or area fractions $A$ and $A_c$ for three- and two-dimensional systems, respectively. Experiments on many mixed conductor/insulator systems have demonstrated the validity of Eq (1) with the aforementioned substitution (Coutts 1976).

Consider a composite comprised of low aspect ratio rigid conductive particles in a compliant polymer matrix (RCPCPM) deformed homogeneously by direct strains $\varepsilon_x, \varepsilon_y, \varepsilon_z$. We hypothesize that Eq (1) may be rewritten as follows to model the strain dependence of conductivity in such composites,

$$\sigma \propto \frac{V_0}{(1+\varepsilon_x)(1+\varepsilon_y)(1+\varepsilon_z)} - V_c$$

The first term in Eq (2), the effective volume fraction of the conductive phase in the deformed composite (where $V_0$ is the original particle volume fraction), takes its simple form due to the assumed rigidity of the particles. We present an argument suggesting that Eq (2) provides a good representation of the piezoresistivity of such composites under general 3D direct strains provided the composite’s deformation is approximately affine. Note that Eq (2) implies that conductivity of the composite remains isotropic despite any degree of directional bias in the 3D strain state.

3. Random Resistor Network Simulations
Consider again the RCPCPM composite. The material is originally macroscopically isotropic, therefore the bond probabilities of a corresponding cubic lattice resistor network model are identical in the $x$, $y$, and $z$ lattice directions. As the composite is deformed, bond probabilities will vary with the effective volume fraction of the conductive particles, if the deformation is affine. Approximately affine deformation will arise if particle displacements closely match the prescribed global deformation of the composite. If, however, particles tend to agglomerate, deformation will not be nearly spatially homogeneous and affine; instead particle clumps or rafts will form with much of the deformation occurring in localized bands between clumps. It is natural to expect particle connectivity to be affected most significantly along the most severely strained directions in the composite. For example, in the case of uniaxial
extension of the composite, particle-to-particle connections will be preferentially broken along the strained direction, leading eventually to the development of a pattern of microcracks in particle connectivity largely perpendicular to the direction of extension. Similarly, for uniaxial compression of the composite, new particle-to-particle connections are created along the direction of compression at a rate higher than in proportion to the increase in particle volume fraction. Lateral particle-to-particle connections (y or z direction) are affected to a lesser degree by x-axis extension or compression because the global deformation tends to place less stress on these connections. To assess the importance of this possible directional bias, random resistor network models are used to study the conductivity of uniaxially strained composites. Results for x-direction uniaxial compression of a composite with \( V_0/V_c = 1.08 \) are given in Fig. 1, where the x- and y- direction conductivities (nondimensional) are indicated, and the “power law” curve is calculated using Eq (2). For conservative assumptions on the severity of the bias in bond probabilities, network conductivities exhibit approximately isotropic, concentration driven behavior for moderate strains (4 %), supporting the predictive utility of the simple percolation conduction-effective volume fraction approach.

4. Comparison with Experiments
The modeling results here are compared with experiments by Beruto et al (2005, 2006) on compression of thin disc-like specimens of a graphite platelet / silicone elastomer composite. Results for the 32% graphite composite (\( V_0/V_c = 1.032 \)) are exhibited in Fig 2 along with simulation results and the effective volume fraction power law, Eq (2). Conductivity is normalized to one for the zero strain reference state, which actually represents a 2 % pre-compression necessary to ensure percolation. The model results are seen to be in good agreement with experiment through about 4 % strain, providing further corroboration of Eq (2).

5. Concluding Remarks
The piezoresistive response of conductive composites comprised of rigid conductive particles in a compliant polymeric matrix has been shown to be fairly well approximated by a simple power law derived from concentration driven percolation. Ongoing work involving the application of these results to composite fibers, and experiments on the conductivity of mixed conductor/insulator powders under compression, will be discussed in the presentation.

References
Antimicrobial, Elastomeric Fibers and Films via Halamines

Hasan Kocer1, Fatma Kilinc-Balci1, Roy M. Broughton1, Jr., S. D. Worley2, and T.S. Huang3

1. Department of Polymer and Fiber Engineering
2. Department of Chemistry
3. Department of Nutrition and Foods

Auburn University, Auburn, AL 36849
Contact information: royalb@eng.auburn.edu  Phone 334 844 5460

Previous efforts in our laboratory have resulted in numerous approaches to the attachment of halamines onto fibers and fabrics (1-5). Inclusion of halamine precursors has also been accomplished in fibers through blending of polymers in the manufacturing process (6,7). Obviously, other laboratories have worked in the same areas (8-11). Some have produced antimicrobial fibers through copolymerization of appropriate monomers into fiber forming polymers (8).

Previous attempts to incorporate halamine materials into latex elastomers failed presumably because the active chlorine was in close proximity to and reacted with the residual unsaturation of the rubber. An antimicrobial elastomer was produced by addition of a halamine onto the styrene repeating unit of a styrene/butadiene block copolymer, but the method was judged impractical for industrial use (12). There is an obvious need in the medical community for antimicrobial, elastomeric materials, particularly in the form of gloves and other molded soft materials. Antimicrobial elastomeric fibers would also be of interest. There are few literature references to antimicrobial elastomers where the antimicrobial moiety is linked to the elastomer (13).

We have begun to incorporate halamine precursors into elastomeric polymers which lack the residual unsaturation of natural and synthetic rubber. As a result, the major reaction of these materials with sources of active halogen is the formation of the halamine, and the halamine does not react with the base polymer. These elastomeric materials have been formed into fibers and films. The formed materials can be chlorinated without severe degradation and active chlorine retained on the film surface is about $2 \times 10^{17}$ atoms of Cl per cm$^2$. Previous work on solid surfaces has also yielded similar chlorine retention results, perhaps indicating that a fully “saturated” surface can hold about that concentration of Cl atoms. Previous work on halamine loaded surfaces also indicate that increasing the specific surface area – as when making smaller and smaller fibers – increases the chlorine retention, almost in direct proportion to the specific surface area of the material (7). Taking advantage of this effect is particularly important for hydrophobic materials, where the penetration of chlorine charging agent is restricted.

The manufacture of antimicrobial elastomeric films and fibers will be described, their physical properties discussed, and data will be presented on their antimicrobial effectiveness. Their potential applications will also be discussed.
References


8. Wang, Liuyang; Gu, Lixia; Xie, Juan; Xiao, Ru; Sun, Gang. Method for preparing antibacterial polyacrylonitrile fiber. *Faming Zhuanli Shengqing Gongkai Shuomingshu* (2006),


SESSION 6B

FIBER / FABRIC CHARACTERIZATION
Effective Thermal Conductivity of Fibrous Materials

Moran Wang and Ning Pan

Nanomaterials in the Environment, Agriculture and Technology (NEAT)
UC Davis, CA 95616

Porous fibrous materials have extended their applications beyond the consumer products because of their easy fabrication, relatively low cost and superior mechanical and thermal properties. In general, thermal properties of a fibrous material depend on: (i) thermal properties of each phase (fiber and air), (ii) fiber size and volume fraction, and (iii) structural characteristics of the system. A number of analytical models have been proposed to predict the thermal conductivity of short fiber composites, however most of which only considered factors (i) and (ii). To our knowledge, there is no method yet that can predict, with acceptable accuracy, the effective thermal conductivity of fibrous materials while taking into account the material structure.

To achieve a reliable prediction, one needs to work on two aspects: an acceptable description of structural details, and an efficient method for the solution of energy equations through fibrous structures. It is extremely difficult to describe in reasonable accuracy the internal structure of a fibrous medium due to its complex and stochastic nature. One has to bridge between the microscopic stochastic nature and the macroscopic statistic characteristics. The structural complexities also bring in two big challenges when the governing equations are to be solved numerically: the inter-phase conjugate heat transfer and the requirement of grid refinement for complex structures, both demanding great computational efforts.

The objective of this work is to develop a robust computer simulation model for predicting the effective thermal conductivity of fibrous materials including the structural characteristics. The model will enable parametric simulations to investigate the effects of related factors on the effective thermal conductivity.

To achieve such an objective, we first develop a random generation-growth (RGG) method for reproducing stochastic microstructures into our model based on macroscopic statistical information, and then introduce the lattice Boltzmann approach, increasingly adopted by many for its higher efficiency, auto-conservation characteristics and easy implementations at complex boundary conditions, for solving the energy equations through a multiphase structure.

The flowcharts of the numerical methods are shown in Fig. 1. The macroscopic statistical parameters including the fiber number density, fiber length and diameter, fiber orientation and distribution, and the fiber volume fraction are given as the inputs to generate the system microstructure on a set of grid system. Random numbers are used in every step of the generation so as to account for the stochastic features and variations in the structure. The proposed lattice Boltzmann method is then applied to analyze the system thermal behaviors.

With proposed numerical methods, we first investigate the influences of fiber shape, orientation and volume fraction on the effective thermal conductivity using a two-dimensional numerical set, and predict the connections between the system effective thermal conductivity and the fiber volume fraction, and fiber orientation shown in Fig. 2 as examples. We also compare our numerical predictions with available experimental data in three-dimensional cases for a carbon fiber-in-oil suspension and a phase change material containing carbon fibers as seen in Fig. 3, respectively.

No any empirical parameters are needed in our method so that it is useful for design and optimization of new materials, beyond just for prediction and analysis of existing ones.
Initialize the temperature evolution scalar in each node and each direction

Spread/evolve the temperature along each direction between neighbors

Interact with interfaces

Relax for each time step and update the new scalar in each node

Judge the error limit

No

Yes

Output the results

(a) Flow chart of the generation of fibrous structures generation

(b) Flow chart of the Lattice Boltzmann model

Fig. 1 Flow charts of the algorithms

![Flow chart of the generation of fibrous structures](image1)

![Flow chart of the Lattice Boltzmann model](image2)

Fig. 2  Thermal conductivity of 2D fibrous materials against the fiber orientation and the volume fraction. (a) \( c_d = 0.0025, d = \delta \), \( l = 50 \delta \); (b) \( \theta_{\text{lim}} = \pi / 4, d = \delta \), \( l = 100 \delta \).

Fig. 3  Predicted thermal conductivity of 3D fibrous materials compared with available experimental data. (a) Phase change materials containing carbon fibers, \( k_f = 180 \text{ W/m K}, k_m = 0.47 \text{ W/m K} \); (b) Carbon fiber in oil suspensions, \( k_f = 2000 \text{ W/m K}, k_m = 0.1448 \text{ W/m} \).
VALIDATION OF A NEW DEVICE FOR TACTILE CHARACTERIZATION OF FABRIC

Manal Issa, Laurence Schacher and Dominique Adolphe

ENSISA, Laboratoire de Physique et Mécanique Textiles UMR-7189, CNRS, UHA
11, rue Alfred Werner – 68093 Mulhouse Cedex – FRANCE. m.issa@uha.fr, l.schacher@uha.fr
, d.adolphe@uha.fr

Abstract

The textile fabrics are often characterized by a particular parameter called “hand”. This parameter evaluates the tactile characteristics and the transformability of fabric for a specific end-use. In our laboratory, we developed a sensory tool for tactile characterization, called “panel”, which allows us to obtain sensory textile fabric profiles. This tool, using the human being as instrument is pertinent, but the obtained data are currently difficult to be included in specifications. An original experimental device has been developed in order to imitate, up to a certain point, the deformation generated during handling by the panel. Several sets of fabrics have been characterized by this device. The correlations between the most common descriptors and the physical and/or mechanical parameters obtained have been established.

1. Introduction

The sensory analysis approach gives sensory profile of product which is close up to a certain point to the feeling of consumers. Unfortunately, this method and these data are quite difficult to be included in the specification sheets due to the methodology involved. The instrumental measurement will give us data directly linked with physical and mechanical parameters (mono dimensional data) of the tested textile goods; however, these data couldn’t be easily linked with the consumer’s requirements. So, to include the sensory specification into the specification sheets, it seems important to develop a new apparatus that will be close to the sensory evaluation procedure and to instrumental devices methodology. A new apparatus has been developed in our laboratory (Issa, 2007). The precedent study has highlighted that the most frequent used sensory descriptors are supple/rigid, falling, thin/thick, soft, crease and responsive. (Issa et al.2005). Our developed device allows us two types of tests, with and without rotation, and provides 15 parameters. The aim of the present study is the validation of this new device by the selection of the parameters presenting a good correlation with the most frequent sensory descriptors. For this purpose, correlations studies (sensory profile – new apparatus parameters) have been carried out.

3. Validation of the New Device

3.1 Description (Issa, 2007)

The figure 1 presents the principal parts of our system. This one has to be inserted onto a tensile machine ((MTS® 20/M)) which provides the sample vertical displacement and the force displacement curve recording. The rotation of the cylinder is given by a CC engine which allows a speed variation from 0 to 3000 RPM. A transparent cylinder has been selected, in a first time, in order to be able to observe and film the deformations of the fabric during the test.

3.2 Results and Discussion

The figures (2) and (3) show the general shape of the curves obtained in both test’s cases, respectively, without and with rotation. Characteristic elements of these curves are also presented in both cases.

3.3 Correlations Sensory Descriptors/Parameters of Developed Device

Using the Principal Component Analysis (PCA), the following correlations have been studied:
- correlation between the extraction parameters without rotation and the sensory descriptors;
- correlation between the extraction parameters with rotation and the sensory descriptors.

We found that the correlations obtained between the selected sensory descriptors and the instrumental parameters with rotation are better than those of the test without rotation (more important coefficients of correlation), moreover, the correlations in this case are more numerous. For this reason, we retained the instrumental parameters obtained from extraction test with rotation and we chose only those which have a coefficient of correlation ≥50 with the studied sensory descriptors. So, the chosen parameters are \( w_1, w_2, f_1, f_{\text{mo}}, f_{\text{max}}, v \) and \( p \).
4. Conclusion and perspectives

The following conclusions can be carried out:
- Our developed device allows establishing good correlations between the most frequent sensory descriptors (supple/rigid, falling, thin/thick, soft, crease and responsive) and some parameters of this device one;
- The analysis of these parameters showed the importance of the rotation of the tube in this instrumental evaluation method, for this reason \( w_1, w_2, f_1, f_m, f_{max}, v \) and \( p \) have been chosen as the parameters of the new device;

A study of:
- The influence of the parameters and the conditions of measurement on the obtained results;
- Comparison with others devices as KES-F (Kawabata et al. 1982) and Griff-Tester (Strazdienė et al. 2003);

will be the subject of future studies, in order to highlight the advantage and the disadvantage of the developed device.

5. References


The bending and recovery behavior of woven fabrics affects many end-use characteristics such as crease recovery and pleat retention of garments. In the paper, a viscoelastic model is used to study the bending and recovery behavior of wool/polyester fabrics. The mechanical properties of the fabric are described by a three-element linear-viscoelasticity model, as shown in Fig. 1. The fabric strip is assumed to have a racetrack shape when it is compressed for the convenience of calculations. The bent portion of the fabric strip forms two semicircles, and the upper and lower portions of the fabric contacting with the plates are straight. The radius of the semicircles decreases gradually and some of the bent fabric strip is straightened and comes into contact with the plates in the compression process.

If a fabric is bent such that the rate of change of curvature ($\rho$) is a constant, the bending moment $M$ is given by

$$M(t) = \frac{E_1E_2}{E_1 + E_2} \rho t + \frac{E_1^2}{(E_1 + E_2)^2} \rho \eta (1 - e^{-t/c})$$

Therefore, the total bending moment can be obtained as

$$M = M_v + M_f$$

Assuming that the frictional bending moment $M_f$ is a constant, from Equations (1) and (2), it can be obtained

$$M(t) = at - be^{-t/c} + M_f + b$$

where $a = -\frac{E_1E_2}{E_1 + E_2} \rho$, $b = \frac{E_1^2}{(E_1 + E_2)^2} \rho \eta$, and $c = \eta/(E_1 + E_2)$. In a compression test, the initial separation of the plates is $T_0$ when $t=0$, $v$ is the speed of the upper plate moving upwards and downwards, and $T$ is the separation of the plates at time $t$. They are related by

$$t = (T_0 - T)/v$$

From Equations (3) and (4), the total bending moment can be recast as

$$M(t) = -\frac{a}{v} T - be^{-t_0/cv} e^{\gamma/cv} + (M_f + b + \frac{aT_0}{v})$$

where $\alpha = -a/v$, $\beta = be^{-T_0/cv}$, $\gamma = -1/cv$ and $\omega = M_f + b + aT_0/v$. The relationship between the separation of plates and the force either in the bending compression process or in the bending recovery process can be obtained from experimental data of tests using the KES (Kawabata Evaluation System) compression tester. The model parameters $\alpha$, $\beta$, $\gamma$ and $\omega$ can be calculated by Equation (5).

Four fabrics with different characteristics are chosen. The fabrics are cut into strips 2 cm wide, 6 cm long, with their longer edges parallel to the warp or weft direction of the fabrics. The shorter edges of the strip are joined together to form a loop. In the experiments, a fabric loop is placed between the two parallel plates mounted on the KES compression tester. The initial separation of the plates $T_0$ is equal to 4.16 mm, and the upper plate is moved downwards at a rate of $v=0.04$ mm/s. When a preset force is reached, the upper plate will instantaneously reverse its travel direction, while the force and the
separation between the plates are recorded. All fabric samples are preconditioned at 65%±5% RH and 20°C±1°C for 24 hours and tested in the same conditions. The values of the calculated parameters are listed in Table 1.

Comparisons of the theoretical calculations based on Equation (5) and the experimental results for samples No. 1 and No. 2 are shown in Fig. 2 and Fig. 3. It can be seen that good agreement exists between the theoretical and experimental results for these fabric samples. It indicates that the bending and bending recovery of fabrics can be described by a linear viscoelastic model. It is noted that these experiments are under low-stress, and the permanent deformation is relatively small. With the increase of the creasing force, nonlinear and permanent deformation will emerge, leading to significant large differences between the calculated and experimental values.

Table 1 Calculated parameters from experimental data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameters of compression equation</th>
<th>Parameters of recovery equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parameters of compression equation</td>
<td>Parameters of recovery equation</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td>β</td>
</tr>
<tr>
<td>1# warp</td>
<td>-468.2</td>
<td>-834.0</td>
</tr>
<tr>
<td>1# weft</td>
<td>-498.3</td>
<td>-796.4</td>
</tr>
<tr>
<td>2# warp</td>
<td>-429.5</td>
<td>-873.4</td>
</tr>
<tr>
<td>2# weft</td>
<td>-442.0</td>
<td>-708.2</td>
</tr>
<tr>
<td>3# warp</td>
<td>-304.2</td>
<td>-285.4</td>
</tr>
<tr>
<td>3# weft</td>
<td>-511.8</td>
<td>-1004.5</td>
</tr>
<tr>
<td>4# warp</td>
<td>-525.1</td>
<td>-822.3</td>
</tr>
<tr>
<td>4# weft</td>
<td>-480.9</td>
<td>-913.6</td>
</tr>
</tbody>
</table>

Fig. 1 three-element linear-viscoelasticity model

Fig. 2 Comparison of theoretical and experimental results for sample 1

Fig. 3 Comparison of theoretical and experimental results for sample 2
SESSION 7A

FORMATION / FABRICATION / CHARACTERIZATION AND MODELING
Multiweave - Multiaxial Technical Fully Interlaced Woven Fabric and Prototype Weaving Machine

Mário Lima, University of Minho, Department of Mechanical Engineering, Guimarães, Portugal, mlima@dem.uminho.pt
Raul Fangeiro, University of Minho, Department of Textile Engineering, Guimarães, Portugal
António Costa, P & Maia Lda, Guimarães, Portugal
Christian Rosipelen, Institut für Textiltechnik der RWTH Aachen (ITA), Aachen, Germany
Válter Rocha, IAITI, Instituto Agilus de Inovação em Tecnologia de Informação, S.A., Matosinhos, Portugal

Keywords: Technical textiles, Multiaxial weaving, Multiweave

Motivation and objectives
Technical textiles are products for applications where technical performance is more important than aesthetics, such as the reinforcement of composite materials. In this case, the possibility to reinforce in several directions is of paramount importance for a wide range of applications, such as aircraft fuselages, boat hulls, etc. The aim of this work was to investigate the feasibility of a multiaxial 2D woven structure able to provide specified strengths in four different directions and develop a manufacturing process for its production. Therefore, the main objectives of this research were:

1. The design and development of a Multiaxial Weaving Machine incorporating mechanisms, systems and components for guiding bias yarns, warp yarns and weft yarns toward a multiaxial fabric formation area;
2. The resulting product, the multiaxial fabric.

Applications
The use and impact of the multiaxial fabric may be found in two different products:

1. Technical textiles, such as composites for car and aircraft industry, conveyor belts, inflatable boats, sails, boat hulls, air inflated houses, geotextiles, wall coverings, sport devices, tarpaulins, tents, grinding and lapping disks and many other applications on products that still use traditional technology of gluing together several layers of fabrics, differently oriented.
2. Garments designed to be resistant to tear, with an original texture, easily conformable and dimensionally stable could have a big impact on very different articles such as military and protective clothing. Although the application on conventional clothing looks considerably out of the way, possible applications on tennis and other sports shoes and some sportswear seems a possibility to further explore.

The model
A multiaxial woven fabric can be obtained by interlacing 4 sets of yarns, the warps (blue), the wefts (green) and other two sets of bias yarns at +45 and -45 degrees (red) as shown in figure 1.

Fig. 1 – Geometric model of a multiaxial woven fabric
The development prototype

The main specifications for the design of the limited scale Multiweave development prototype were established early in the project according to the available technical capabilities. The resulting Multiweave machine comprises the following elements: Bias yarns feeding system; Mechanism for the criss-cross insertion of the bias yarns; Warping system; Shedding system, incorporating the heddle; Weft insertion system; Beating-up mechanism, incorporating the reed; Fabric taking-up system.

Working principle

The working principle of the Multiweave development prototype is as follows: The bias yarns are feed from two bias beams through a tension compensation device and stepwise moved in two very close and parallel layers in opposite directions by means of an appropriate mechanism. The heddle and the reed are in their lower and backward positions, out of the plane of the bias yarns, allowing their free criss-crossing. The heddle rises forming the shed and the warps interlace with the bias. The shed is formed between the warp and the two very close parallel layers of the bias yarns. A first (false) beating takes place to clear the shed; this was found necessary as when the warp yarns are raised by the heddle, they are partially held up by the criss-crossing effect of the bias, preventing from obtaining a clear shed which caused difficulties for the insertion of the weft yarn; The weft yarn is then inserted across the shed to be interlaced with the warps and bias yarns as shown in figure 2; A second (real) beating operation takes place which pushes the weft forward and compacts the fabric, at the same time that the heddle moves down to its rest position closing the shed and holding the weft. The taking-up mechanism advances one step and the fabric is wound-up.

![Fig. 2 – Multiweave – detail of shed and weft insertion](image)

During the development process, all synchronization has been achieved mechanically to help getting to a working prototype faster. Therefore, all movements are mechanically driven from a main shaft with the help of cam and intermittent mechanisms.

Conclusions

The multiaxial concept was embodied in a development prototype which proved the feasibility of the concept. The most significant innovation of this idea is concerned with the characteristics of the fabric structure where there is crisscrossing between all sets of yarns, which increases the capability for supporting more severe mechanical loads without failure, namely without delaminating. Simultaneously, the strength-weight ratio is expected to increase, which, for applications such as in the aircraft and car industries, can be very advantageous. Other important applications are in marine textiles, such as composites for boat and shipbuilding, which are products submitted to severe stressing conditions. The Multiweave prototype developed within this work is being used to produce different types of DOS, Directionally Oriented Structures, using various types of fibres (HT polyester, aramide, carbon and glass) and yarn counts.
MODELING RADIATIVE HEAT TRANSFER IN MULTIFILAMENT FIBER MELT-SPINNING

Young-Pyo Jeon1 and Christopher L. Cox2

For semicrystalline polymer melt-spinning, crystallization during solidification is closely tied to final fiber properties. Particularly for high-speed melt spinning, flow-induced (stress-induced) crystallization occurs as a result of high tensile stress in the fibers. Crystallization and orientation also depend heavily on fiber temperature, so that the quench process plays a significant role in controlling fiber properties affected by orientation and degree of crystallization, including mechanical properties. Several models have been developed to describe crystallization during the spinning process, including models which combine crystallization kinetics with the Newtonian constitutive equation for the polymer melt. Other models incorporate crystallization with strain-softening and strain-hardening associated with nonlinear viscoelastic effects which produce a necking phenomenon.

Most models to date lack sufficient details to adequately describe the melt-spinning process at industrial scales. Many models focus only on a single filament, and multifilament models often fail to capture complexities in the spinning process such as nonlinear constitutive behavior. In addition, most models ignore radiative heat transfer, which may become significant in high temperature melt-spinning. For that reason, more accurate and flexible models are required due to the growing diversity of spinning materials and the need for fibers with desired properties. Therefore, the purpose of this paper is to develop a multifilament spinning model which includes radiative heat transfer in order to accurately describe semicrystalline behavior in a nonisothermal multifilament setting. A secondary goal is to develop a model which will run on a desktop computer in reasonable time (e.g. 1 to 2 hours).

In most fiber spinning models, radiative heat transfer has often been ignored in the calculation because of complexities in modeling and its relative importance compared to convective heat transfer. Fiber properties, however, are very sensitive to temperature especially with respect to crystallization and orientation phenomena: a few degrees difference in fiber temperature may result in fibers with different properties. Therefore, radiative heat transfer should not be ignored in multifilament spinning models, especially for higher temperature processes such PET (Polyethylene Terephthalate) or PEEK (PolyEtherEtherKetone) fiber spinning.

The current model, extending the work in Zhang (Zhang 2004), combines the flow-enhanced crystallization (FEC) model by McHugh’s group (Shrikhande et al. 2006) with a generalization of Dutta’s multifilament model (Dutta 1987). We include the comprehensive formulation of air drag effect, which is usually neglected, but should not be ignored at higher fiber speeds, and unlike Dutta’s model, the current model has variable air density. Radiative heat transfer among fibers, the spinneret, and the background is simulated by a Monte Carlo method calculating the overall heat transfer coefficient ($h = h_c + h_r$), and the overall heat transfer coefficient is applied in the FEC model to more accurately calculate the fiber properties.

The proposed model calculates the interdependent quench air cross velocity and temperature distributions among fibers modeled by the radiative heat transfer calculation added to the 1-D FEC model which describes crystallization using Avrami crystallization kinetics. The crystalline phase is treated as growing and orientating rigid rods, and the amorphous phase is described by a modified Giesekus fluid model, a realistic viscoelastic model with finite chain extensibility. Compared to the convection-only model, the model with convection and radiation predicts a difference of as much as 10°C in fiber temperature depending upon process conditions.

To test the model, we make comparisons with the Dutta’s model prediction for low-speed spinning of PET. The results show a qualitative match with Dutta’s multifilament calculation, with differences due to our application of the FEC model, inclusion of radiative heat transfer, and variable density.

1 Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634. email: ypjeon@clemson.edu
2 Department of Mathematical Sciences, Clemson University, Clemson, SC 29634. email: clcox@ces.clemson.edu
Developing a model with high accuracy and flexibility to describe and predict the real process is an essential component of this effort. The long-term goal is to provide an advanced framework for modeling of the fiber spinning process, with ease of extension to more complex (e.g. higher-dimensional) fiber spinning models.

References
Zhang, Z. (2004), A Model For Radiation Heat Transfer In Multifilament Fiber Spinning, M.S. project manuscript, Department of Mathematical Sciences, Clemson University.
YARNS TENSION DISTRIBUTION AND RAPTURE MECHANISM IN NARROW STRIP OF
PLAIN WEAVE FABRIC UNDER BIAS STRESS

MEHDI KAMALI DOLATABADI, RADKO KOVAR
Kamalimehdi@yahoo.com, Radko.kovar@tul.cz
Technical University of Liberec Halkova 6, 46117, Czech Republic

Abstract: Mechanical property of a fabric in diagonal direction is important as principal directions in some fabric applications. The tensile strength and flexibility of a fabric in bias direction are higher than the main directions due to different stress distribution and deformation of a fabric under bias direction. Dealing with rapture mechanism and yarns tension distribution of a plain weave fabric are the scopes of this paper. For this purpose, a combinational deformation includes of pure shear and complex shear deformation is considered based on previous works. The relationship between compression force and yarn packing density in each contact place of fabric structure is assumed with regard to Van Wyk's theory and Neckar's modifications. The yarns tension distribution is found as a function of yarn strength and critical width, which it is independent to Van Wyk's constant and coefficient of friction. In this paper, proposed model is a new approach to predict the rapture force and rapture mechanism of a plain weave fabric by general data of a fabric. The predicted values by this model are evaluated by an empirical work and it is demonstrated that the model is responsible for assessing rapture mechanism and tensions analysis of plain weave fabric under bias direction stress.

\[ P[Pa] = k[Pa] \frac{\mu^3}{(1 - (\frac{\mu}{\mu_m})^3)^3} \]

where

\[ F_N(n_i) = \begin{cases} (P_S - P_0)A_S & \text{if } n_i > n_c \\ \frac{P_S A_S - P_0 A_W}{n_c - 1} (n_i - 1) + (P_0 - P_0)A_W & \text{if } n_i \leq n_c \end{cases} \]

\[ i \in \{1, 2, 3, ..., m\} \quad n_i \in \{1, 2, 3, ..., n_{IT}\} \]

\[ m_c \quad \text{the number of broken warp yarn in rapture area.} \quad m \quad \text{the total number of warp yarns in rapture area.} \quad n_i \quad \text{the sequence number of contact in } j^{th} \text{ warp yarn.} \quad n_c \quad \text{the contact number of the broken yarn in critical width.} \quad n_{IT} \quad \text{the total sequence number of contact in } j^{th} \text{ yarn situated in rapture area.} \quad P_0 \quad \text{pressure in structure of original yarn before weaving process.} \quad W_S, W_C \quad \text{the arbitrary width and critical width that could be determine by empirical work.} \quad P_S \quad \text{pressure in structure of yarn under pure shear.} \]

$$T(n_i) = \sum_{n_i=1}^{n} F_i(n_i), \quad F(n_i): friction force, T(n_i): yarn tension in cross over point(n_i)$$

$$T(n_i) = C_s \sum_{n_i=1}^{n} \left( \frac{P_w A_s - P_w A_w}{n_i - 1} \right) (n_i - 1) + (P_w - P_0) A_w n_i, \quad C_s: coefficient of friction$$

$$T(n_i) = C_s \left( \frac{(P_w A_s - P_w A_w)(n_i - 1) n_i}{2(n_i - 1)} \right) + (P_w - P_0) A_w n_i, \quad \text{if } n_i \leq n_c$$

$$T(n_c) = T_s = C_s \left( \frac{(P_w A_s - P_w A_w)n_c}{2} \right) + (P_w - P_0) A_w n_c, \quad T_s: tension of yarn at break$$

$$X = \frac{\mu_0^3}{(1 - \mu_0^3)} A_w, \quad Y = \frac{\mu_w^3}{(1 - \mu_w^3)} A_w, \quad Z = \frac{\mu_s^3}{(1 - \mu_s^3)} A_s$$

$$T(n_i) = \frac{n_i T_b}{n_i (Z + Y - 2X)} \left[ \frac{(Z - Y)(n_i - 1)}{(n_i - 1)} + 2(Y - X) \right], \quad \text{if } T(n_i) = T(n_c) \text{ if } n_i > n_c$$

Fig. 3 Force requirement to rapture of polypropylene fabric: experiment and predicted values.

Fig. 4 Force requirement to rapture of cotton fabric: experiment and prediction values.
BIOSYNTHESIS AND APPLICATION OF COLORANTS FROM MICROORGANISMS FOR USE ON TEXTILE MATERIALS

Farzaneh Alihosseini (fhosseini@ucdavis.edu) and Gang Sun (gysun@ucdavis.edu)

Textiles and Clothing Department, University of California Davis, Davis, CA, 95616

1- Introduction

In recent years, there has been a growing interest in biosynthesis of colorants for food and textile applications. The use of non-renewable resources produced economically beneficial synthetic colorants, but also harmful by-products to human health and environment. In addition, dependence of dye production on oil resources leads to an increased consumption of nonrenewable energy and feedstock. Using bio-resource is believed as an alternative to the use of non-renewable resources and reduce the deleterious effect of chemical synthetic processes into the environment (Mapari et al 2005). Plants could produce natural colorants but in low eco-efficiency and yields (Raisanen et al 2002). For this reason, the dyestuff industries have started searching new renewable resources that are environmentally friendly and can be considered as the best alternative for the existing synthetic colorants. We consider microorganisms such as fungi and bacteria as an interesting source of manufacturing colorants because (1) these fungal species are rich in stable colorants such as carotenoid, flavenoid, quinones, and monascus; and (2) the microbial production of colorants have the advantage of producing higher yield than plant growing techniques(DurAn et al 2002). Thus, working on microbiologically produced colorants may be valuable in the quest to find highly interesting economical pathway in the textile industry. Some studies suggest that colorants isolated from fungi without modification provide good alternative solution to synthetic colorants. It is also possible to modify these natural colorants chemically to produce new bio-based colorants for textile products(Hobson & Wales 1998). Besides, some of the natural colorants especially the anthraquinone-based compounds have recently been shown to possess remarkable antibacterial activity. Human beings are commonly exposed to microbes in their daily lives. If antibacterial colorants were used in the textile materials it could be a beneficial factor to the human health.

2- Experimental

A marine bacterium related to Vibrio gazogenes was cultivated on yeast extract and tryptone media. The immobilized cells were easily extracted by using methanol. The extract was filtered and concentrated under reduced pressure. The extract was further purified on silica gel with chloroform and methanol as solvents. The pigmented fractions was analyzed and identified by UV-visible spectrophotometer, HPLC, The liquid chromatography- electro spray ionization- mass spectroscopy (LC-ESI-MS), Fourier Transform Mass Spectrometry (FT-MS) and H-NMR(CDCl3) δ 14.02(2H,s), 7.24 (1H, m), 6.98 (1H, s), 6.94 (1H, m), 6.7(1H, d,), 6.36 (1H, m), 6.1 (1H, d,), 4.01 (3H, s), 2.56 (3H, s), 2.39 (2H, m), 1.54 (2H, m),1.31 (4H, m), 0.91 (3H, m).

Dyeing was attempted by immersing the multi-fiber test cloths in the colorant solution under normal and basic pH conditions. The antibacterial properties of the dyed fabrics were examined against Escherichia coli K-12 (E. coli, UC Davis Microbiology Laboratory, 10^2 -10^6 CFU/ml) following an AATCC test method 100-1999.

3- Results

A novel marine bacterium strain, which by 16S rDNA analysis related to the category of bacteria Vibrio gazogenes, was found to produce a bright red colorant. The colorant was extracted from a large scale culture by methanol. The extract was dried over anhydrous magnesium sulfate and concentrated. Further purification was done on TLC by chloroform and ethyl acetate as solvent system. The extracted colorant was analyzed by LC-MS/MS spectrometry, showing a major peak at 11 min in the total ion chromatogram with m/z: 324 [M+H]^+, which indicating an odd number of nitrogen atoms in the molecule (figure1a). The 1H-NMR result showed that pigment has unsaturated C-C double bonds. Signals in the very low magnetic field in 1H-NMR spectrum (14ppm) showed the existence of pyrrole ring. The accurate molecular mass of m/z: 323.19975 by FT-MS and COSY- NMR data (figure2) confirmed the structure of prodigiosin (C20H25N3O) by 3.6 ppm accuracy. The UV-Visible spectra of methanol solution has absorption wavelength at λmax 530nm which is in agreement with the maximum absorption of prodigiosin from serratia marcescens at 537nm(Castro et al 1959). (Figure1-c)
The preliminary dying test showed that this colorant can dye the wool, silk, nylon and acrylic fabrics and has similar characteristic to basic and disperse dyes. Dyeing process was applied in high temperature, so the stability of colorant in boiling point is critical. For that reason, a dyeing process was applied only with the colorant solution without fabric. The result showed 15% reduction in colorant content. Since prodigiosin have good antimicrobial activity in solution, their antimicrobial activity on dyed fabric (wool) was tested as well. The wool samples dyed with colorant were used as model system. The results showed that dyed fabric have ability to kill all the E-COLI bacteria within 18hours.

References

Novel pH-Sensitive Hydrogel Fibers Based on Hydrolyzed-Polyacrylonitrile and Soy Protein

Liwei Yu\textsuperscript{a}, Gang Sun\textsuperscript{a,b}, Lixia Gu\textsuperscript{a}

\textsuperscript{a}The State Key Laboratory For Chemical Fibers and Polymer Materials, Dong Hua University, Shanghai, 200051, China

\textsuperscript{b}Division of Textiles and Clothing, University of California, Davis, California, 95616, USA

ABSTRACT: Novel pH-sensitive hydrogel fibers were prepared from a blend of hydrolyzed-polyacrylonitrile (H-PAN) and soy protein (SP). The chemical structure of H-PAN was analyzed with element analyzer and infrared spectroscope. The dynamical and static elongation/contraction behaviors of the fibers were studied. It was discovered that H-PAN/SP hydrogel fibers consisted of a multi-porous structure by a scanning electron microscope. With an increase in the content of SP, the hydrogel fibers exhibited excellent reversible pH-sensitive behavior. When the weight ratio of H-PAN to SP was 4:6, the hydrogel fibers showed the best response times at 1.35s (elongation) and 0.63s (contraction). Discontinuous volume phase transitions and hysteresis loops of the hydrogel fibers induced by changes in pH value were found. These results were found to be explicable in terms of the surface morphology and polyampholytic properties of H-PAN/SP hydrogel fibers.

Contact Information
Liwei Yu, E-mail: shaiyaren@yahoo.com.cn
Gang Sun, E-mail: gysun@ucdavis.edu
Lixia Gu, E-mail: gulx@dhu.edu.cn
POSTER

PRESENTATIONS
ENZYMATIC FORMATION OF COLORANTS

Rosary Stephen and Gisela Buschle-Diller*

Auburn University, Department of Polymer and Fiber Engineering, 115 Textile Building, Auburn, AL 36849.
email: stephra@auburn.edu and buschgi@auburn.edu

1. Background

Interest in green processing technologies and sustainable products has increased dramatically over the past decade. Biocatalysts together with lower use of energy and milder reaction conditions are more and more important for synthesis reactions of chemical, pharmaceutical and polymeric products. Thus it is not surprising that the potential industrial use of enzymes for processes typically performed with conventional chemicals is being exceedingly explored and expanded.

Oxidoreductases are enzymes capable of catalyzing oxidation and reduction reactions that can result in either the polymerization or degradation of a substrate depending on the reaction conditions. For example, it is well-known in the pulp and paper industry that laccases, in conjunction with other oxidoreductases, are involved in the depolymerization of lignin (Camarero et al 2007), (Bajpai 2004); these reactions often require mediator systems (Call & Mucke 1995). Further, a mixture of laccases with peroxidases has been successfully applied for the treatment of dye effluents (Wesenberg et al 2003). On the other hand, laccases can also perform one-electron oxidations on small organic compounds resulting in the formation of either relatively long-lived or rapidly regenerated radicals (see Figure 1). In subsequent enzymatic or non-enzymatic reactions larger molecules can be formed. Potential compounds include mono-, di- or polyphenols, phenolic acids, aromatic amines and aminophenols, many of which are components of colorant systems.

A recent review of laccase catalysis involving fiber materials and including polymerization and grafting reactions can be found in (Kenealy et al 2006). Polymeric products based on 8-hydroxyquinoline have been produced with horseradish peroxidase (Liu et al 1985) and laccase catalysis (Ncanana & Burton, 2007). Laccases have been implicated in the production of melanin and conidial pigmentation and are used in nature by fungi to create pigments (Mayer & Staples 2003). Coloration of wool fibers by enzymatic phenolic polymerization, based on a patent on enzymatic hair coloring (Aaslyng et al 1998), has also been reported (Shin & Cavaco-Paulo 2001). The researchers used laccases and horseradish peroxidase.

2. Enzymatic formation of colorants

Based on experience from previous research involving pulp fibers (Buschle-Diller et al 2003) and (Kenealy et al 2003), the objective of this research has been to synthesize colorants from small phenolic fragments by means of laccase catalysis with or without the involvement of free or bound lignin. These colorants have been applied to fibrous and non-fibrous polymers, thus offering an alternative, “green” coloration route. Guaiacol, resorcinol and other phenolic substrates were

![Figure 1. Reaction scheme of laccase catalysis.](image1)

![Figure 2. Enzymatic color formation with time.](image2)
used in presence or absence of lignin or suitable mediators. The time-dependent development of the colored compound in solution was followed by UV-vis spectroscopy as shown in Figure 2 for the laccase-catalyzed color formation using guaiacol as substrate. The addition of lignin during the reaction clearly influenced the color and the yield of the product. It was possible to create colored compounds that could be used for wash-fast shades of red, brown and purple on linen containing approximately 5% lignin. By column separation it was also possible to isolate water-insoluble pigments in sufficient yield that could be used for coloration of biodegradable films made from cellulose derivatives and polyvinyl alcohol. An attempt was made to identify the chemical composition of the obtained compounds by FT-IR, GC-MS and NMR analysis.

3. References

1. Abstract
Gas transmission through microporous membranes was investigated experimentally and a molecular-level probabilistic model was constructed to evaluate the effect of various parameters on the gas flow. Air transmission experiments were conducted on PET, nylon and PP microporous membranes at different pressure values, using a volumetric air permeability tester according to ASTM D 1434 standard. Gas transmission experiments were simulated utilizing the proposed model, and results were compared to experimental data and to macro-level gas transmission models available in literature.

2. Background
Selectively permeable layered systems assembled from a group of microporous membrane layers and fabrics provide a logical premise to be able to obstruct the passage of toxic gases while providing breathability to the skin (Truong et al 2004). The first step to design such an assembly is to understand the process of gas permeation through a single layer of a microporous membrane. The permeation of gas molecules through a pore of a microporous membrane can be studied either at the level of individual molecules or at the level of the molecular population. At the molecular-level, each molecule and its interaction with other molecules and surfaces have to be taken into consideration and maybe studied using a probabilistic technique. At the macro-level, the behavior of the molecular population depends on the gas concentration (Bird et al 2002, Cunningham & Williams 1980). The flow of any gas through a porous system is typically governed by geometric and energetic considerations. The geometric aspects are affected by the ratio of the mean free path of the gas (\(\lambda\)) to the diameter of the pore represented by the Knudsen number (George & Thomas 2001, Fried 1995). Kinetic energy of the molecules with respect to the potential energy of the pore surfaces is also an important factor in gas flow through pores (Shindo et al 1983).

3. Experimental and Modeling Work
In the experimental work, gas transmission rate (GTR) was calculated in mol/(m².s) using the equation

\[
GTR = \frac{10^4 \times p_r \times V_r}{A \times R \times T}
\]

where \(A\) = transmitting area of specimen (mm²), \(p_r\) = ambient pressure (Pa), \(R\) = universal gas constant (\(R=8.314\) L.Pa/(mol.K)) and \(T\) = ambient pressure (K). \(V_r\) is the rate of permeated volume in a specific time (mm³/s).

A probabilistic model was developed utilizing a Monte Carlo approach to simulate gas transmission through microporous membranes. The location and direction of the molecules entering the pores were assumed to be random initially and the molecular trajectory inside the pore was determined. The distance a molecule travels between two points inside a pore (\(\ell_n\)) was assumed to be equal to the mean free path (\(\lambda\)) or less in the case that it hits pore walls. The direction of the molecule after each collision was determined within the boundary limits and the total path of the molecule inside the pore was calculated by following this trajectory and used to determine the time required for a molecule to be transmitted to the other side of the membrane. The number of molecules transmitted through the pore at the same amount of time was calculated using the molecular separation distance at the given temperature and pressure.

Results from the probabilistic model were compared with the Knudsen and viscous models developed by Schofield et al (1990), using the equations below, where \(J_k\)=Knudsen flux, \(J_p\)=viscous flux, \(\varepsilon\)= porosity, \(\tau\)= tortuosity, \(\delta\)= thickness, \(\eta\)= viscosity, \(M\)=molecular weight and \(R\)=gas constant.:

\[
J_k = \frac{2 \times \varepsilon \times 8RT}{3 \times M \times \pi \times \delta} \equiv K_k \frac{\Delta P}{\delta}
\]

and

\[
J_p = \frac{1}{8} \frac{\varepsilon \times MP}{\tau \times RT \times \delta} \equiv K_p \frac{\Delta P}{\delta}
\]
The experimental results for air permeability are shown in Figure 1, for 3 microporous membranes - PET, Nylon and B130 PE/PP copolymer. Experimental as well as modeling results based on the probabilistic model and Schofield et al’s Knudsen-viscous model are shown in Figure 2 for PET.

4. Conclusions
Gas transmission rate through microporous membranes was studied experimentally and theoretically. A probabilistic computer model was developed to analyze the flow of gases at a microscopic level. Results from the model were compared to experimental data as well as to a macro-level analysis. Acceptable correlations were observed between the probabilistic model and the experimental data. Gas transmission rate increases with an increase in pressure and as porosity of the materials increases, the gas transmission rate increases. Knudsen number as well as the relationship between mean free path and pore diameter can be used to predict the flow regime inside the porous media with a reasonable degree of accuracy.

References
MELT-INDUCED GRAFTING OF POLYPROPYLENE WITH N,N-DIALLYLMELAMINE WITH POTENT ANTIMICROBIAL ACTIVITY

Mohammad Reza Badrossamay (mrbadrossamay@ucdavis.edu) and Gang Sun (gysun@ucdavis.edu)

Textiles and Clothing Department, University of California Davis, Davis, CA, 95616

1. Introduction

Among all the synthetic polymers, isotactic polypropylene (PP) is one of the most widely used commercial polymers used in textile, medical, automotive and food industries. The unique characteristics of the superior chemical resistance and the resultant utility besides its low cost make PP one of the best candidates to be used in health care products and medical textiles. In spite of all the advantages of PP, there are some inherent drawbacks such as, nonpolar chemical structure of PP causing its poor adhesion and incompatibility to polar materials, low moisture uptake and poor dyeability that limit its applications. Weak melt strength and melt elasticity of linear PP is another shortfall in some end-use fabrications. These two main disadvantages have been scientifically challenging and industrially important issues since the discovery of PP. The only successful technique to introducing functional polar groups in non-polar chains of PP is using free radical grafting which can be carried out in solution, melt phase or solid-state process (Russell 2002). Melt grafting has several advantages such as absence of solvents and short reaction times and continues processing conditions compared to the other methods. Melt phase chemical reactions, so called reactive extrusion, have been investigated for plastic industry more than 30 years (Moad 1999 & Russell 2002) but have not been applied in manufacturing of functionalized fibers. Although a variety of vinyl and allyl monomers have been grafted onto PP improving dyeability, processability, compatibility and hydrophilicity of PP polymer, there is no published document regarding the melt grafting of melamine derivatives on PP.

The melamine derivatives such as chlormelamine are relatively stable chlorinating agents which show high chlorine content and may be used as antiseptics, disinfectants, oxidizing agents and bleaching agents in water disinfection and textile bleaching process (Wayman et.al 1968). Chlormelamine may be classified as an organic N-halamine. Since N-halamines compounds provide the most durable and rechargeable biocidal properties compare to other antimicrobial agents we were interested in incorporating them into PP materials. To do so, we developed a reactive extrusion process for modification of linear PP to a branched and biocidal polymer by using a melamine derivative, N,N-diallylmelamine (NDAM) as an halamino-azine precursor monomer. The grafted polymer was successfully prepared and converted to sub-micro fibers through melt spinning process (Wang et. al 2007). The active chlorine content and biocidal efficacy of functionalized fibers were studied. Effects of different monomers and peroxide concentrations on rheological properties, grafting efficiency and biocidal activity were further investigated.

2. Experimental

Modification of PP with N,N- diallylmelamine (NDAM) in presence of dicumyl peroxide (DCP) was carried out in a 3-PC Brabender Plasticorder ATR. The grafted samples were purified through dissolving/precipitating process. The purified samples were converted to sub-micro fibers and were bleached by immersing in diluted common chlorine bleach for a short time. Finally, chlorine content of grafted fibers was recorded. The biocidal properties of the chlorinated grafted fibers were examined against Escherichia coli K-12 (E. coli, UC Davis Microbiology Laboratory, 10^6 -10^7 CFU/ml) following an AATCC test method 100-1999. Bacterial reduction is reported according to \((A-B)/A \times 100\) where \(A\) is the number of bacteria counted from virgin samples, and \(B\) is the number of bacteria counted from grafted samples.

3. Results & Discussion

Radical grafting copolymerization of PP includes consecutive processes which firstly initiator thermally decomposed to primary free radicals that can undergo hydrogen abstraction from polymer backbone to form macroradicals. The macroradicals can undergo chain scission (β-scission) or grafting. When the macroradicals react with a monomer molecule, this monomer may react with more monomer molecules forming longer grafting chain on the polymer backbone which brings about long chain branched polymers (LCB). This grafting may be continued by a radical transfer to the same or a different polymer backbone or terminated by radical combinations (Schema 1).
Fig. 1a, b indicates grafting contents of the NDAM in varied concentration of monomer and peroxide. At low monomer concentration, increasing peroxide concentration does not change grafting content which indicates excess peroxide brings about more polymer degradation which was characterized by the reduction in end-torque (Fig. 1c). As the monomer concentration increases, grafted monomer content shows a steady increase, which indicates the competition between chain scission and grafting copolymerization have been balanced and polymer β-scission is no more the dominant reaction. More interestingly, the grafting yield is a monotonic function of the monomer concentration, which is contradicted to radical copolymerization of maleic anhydride on PP [Moad 1999].
DETOXIFICATION OF ORGANOPHOSPHORUS PESTICIDES BY N-HALAMINE PROTECTIVE TEXTILE MATERIALS

Xin Fei† and Gang Sun‡

Division of Textiles and Clothing, University of California at Davis, Davis, USA, email: † xfei@ucdavis.edu, ‡ gysun@ucdavis.edu

1. Introduction

Most conventional protective clothing was made of barrier materials which impose possible heat stress on wearers due to impermeable properties. Breathable fabrics combined with functional detoxifying properties would be desirable for preparing comfortable protective clothing. Thus chemically decontaminating fabrics should have the promising applications on pesticide protective clothing or chemical protective clothing.

N-halamine grafted polymers have demonstrated powerful regenerable anti-bacterial functions against a broad spectrum of microorganic contaminants due to the strong oxidative ability of halamine functional groups. N-halamine polymers are capable of converting alcohols to ketones, sulfides to sulfoxides and sulfones, and cyanides to carbon dioxide and ammonium in water [Bogoczek, R., et al, 1991; Sun, G., et al, 1997; Sato, T., et al, 1979; Takemoto, K., et al, 1997]. Therefore, N-halamine polymers could be one of the hopeful candidates of chemically decontaminating textile materials. In a previous study [Fei, X., et al, 2006], N-halamine grafted cellulose were tested to show reactivity to detoxify some aliphatic thio carbamate pesticides, such as aldicarb. Same as carbamate pesticides, organophosphorus pesticides are also one of the important groups of agricultural chemicals. Due to the wide use of organophosphorus chemicals in agriculture applications, it is necessary to investigate the decomposition results of organophosphorus pesticides by N-halamine grafted polymers, the potential self-decontaminating materials.

Two different N-halamine fabrics were investigated in this study. One is a pure cotton (#400 TestFabrics, Inc.) treated by a finishing solution containing 4%1,3-dimethylol-5,5-dimethylhydantoin (DMDMH), and another one is a polyester/cotton blend (65/35 PET/Cotton, #7436 TestFabrics, Inc.) treated by 4% 1-monomethylol-2,2,5,5-tetramethyl-4-imidazolidin-4-one(MTMIO) aqueous solution. Then both fabrics were chlorine bleached to form N-halamine functional groups. Since N-halamine polymers were extremely effective to eliminate thio containing carbamate, three organophosphorus pesticides with sulfur atoms, malathion, methyl parathion and chlorpyrifos, were selected in this study. The N-halamine fabrics were immersed in the pesticide solutions. The pesticide concentration changes were measured by HPLC-UV, and the products were identified by mass spectrometer.

2. Results & Discussion

2.1 Reaction kinetics

Almost all malathion was gradually degraded by chlorinated DMDMH treated fabrics. Unfortunately, the peaks of intermediates overlapped with the malathion peak in HPLC-UV spectra. The degradation rates of malathion by N-halamines cannot be calculated. The concentrations of chlorpyrifos were not obviously decreased, or suddenly dropped in initial contact with N-halamine fabrics and then kept unchanged in the following 6 hours probably due to the absorption by fabrics. More than 80% methyl parathion can be eliminated by the chlorinated DMDMH fabrics within 1 hour at room temperature. Even the temperature was lowered to 0 °C, almost all methyl parathion was still eliminated by the chlorinated DMDMH fabrics within 4 to 6 hours. It took a longer time for chlorinated TMIO fabrics to eliminate methyl parathion at room temperature, after 6 hours 20% to 40% pesticide still survived, which means that the oxidative ability of the amine N-halamine groups in MTMIO fabrics was not as strong as that of amide or imide N-halamine groups in DMDMH fabrics.

The reaction between methyl parathion and N-halamine functional groups can be written as Equation (1).

\[ \text{a MeP + b halamine \rightarrow c products} \]  (1)

Here a and b are the orders of the two reactants. Thus the reaction rate of methyl parathion is expressed as the Equation (2)
\[
\frac{-d[MeP]}{dt} = k_r [MeP]^a [\text{halamine}]^b \quad (2)
\]

The concentration of the active chlorine on the fabric was controlled at 356.5 ppm or higher. So the active chlorine / pesticide ratio was at least 20:1 and could reach as high as 100:1. It means that the active chlorine on the fabric is much more excessive than the pesticide in the reaction systems. Since the consumed halamine is negligible due to the highly excessive active chlorine, concentration of halamine on the fabrics [halamine] could be regarded as a constant for Equation (2). Furthermore, if a is equal to 1 (first order reaction in terms of methyl parathion),

\[
\ln[MeP] - \ln[MeP]_0 = - k_{obs} t \quad (3)
\]

\[
k_{obs} = k_r [\text{halamine}]^b.
\]

Then, \(\ln[MeP]\) was plotted versus contact time resulted in linear profiles (Figures 1 and 2). This means a pseudo-first-order reaction for methyl parathion with excessive active chlorine.

---

Based on the Arrhenius Equation, the activation energies for oxidation of methyl parathion by chlorinated DMDMH fabrics were in the range of 5.47 to 7.36 kcal/mole.

### 2.2 Oxidation products

Products of both malathion and methyl parathion reacted with N-halamine grafted polymers were identified as their corresponding oxon forms. Generally the oxon forms show stronger anti-cholinesterases activity than that of their corresponding phosphorothionate pesticides. But on the other hand, the oxon products are more susceptible to hydrolysis than the original organophosphorothionate pesticides [Wolfe, N. L., 1980]. Thus the solution for the potential self-decontaminating materials is to impart the OP hydrolysis promoting functions onto the N-halamine grafted polymers.

### 3. Conclusions

The reaction between methyl parathion and N-halamine grafted polymers were pseudo-first order as the prediction. The activation energy of oxidizing methyl parathion is 5.47 to 7.36 kcal/mole. Except Chlorpyrifos, the other two OP pesticides, malathion and methyl parathion, could be oxidized to their oxon forms by N-halamine grafted polymers. Though the oxon products are more toxic than the parent pesticides, the high hydrolysis rates of oxon forms indicate a new solution for preparing novel chemically decontaminating textile materials.

### 4. References


FIBER FORMATION OF POLY(TETRAFLUOROETHYLENE) FROM ITS EMULSION

1) Hideki Yamane, 2) Yoshito Takagi, 3) Takashi Wano and 3) Daisuke Kitagawa

1) The Center for Fiber & Textile Science, Kyoto Institute of Technology, Kyoto 606-8585, Japan. (Email: hyamane@kit.ac.jp)
2) Graduate School of Science and Technology, Kyoto Institute of Technology, Kyoto 606-8585, Japan.

1. Introduction

Poly(tetrafluoroethylene) (PTFE) has been known to have various superior properties such as thermal stability, chemical resistance, weather resistance, and a low friction coefficient. However, the spinning of PTFE fiber is rather difficult since it has a high melting point and the viscosity of the melt is very high. One of the processes to obtain PTFE fiber is to wet spin the viscose rayon filled with PTFE powder and to pyrolyze the cellulose component after spinning. Another process is to obtain PTFE film by casting PTFE emulsion and sintering. Split yarn can be obtained from the film. In either way, the process is rather complicated. Recently, we found that the applying high shear flow to the PTFE emulsion gives PTFE paste and it can be processed into strands. Since this thick strand is composed of the aggregation of PTFE fine particles similarly to the structure of the metal, fine PTFE filaments may be obtained by the wire drawing process, in which a rod is drawn through a tapered orifice of a die.

In this study, the mechanical property, micro and higher-order structure of PTFE filaments prepared by the wire drawing process were investigated.

2. Experimental

A strand of PTFE paste, about 2 mm in diameter, was used in this study. This strand contains about 50 wt% of water and some surfactant. Plastic dies with orifices with inner diameters of 0.75, 0.98, 1.2, 1.4, and 1.7 mm and the opening half angle of 6.5° were used for wire drawing at 90°C. The drawing speed was set at 4.7 m/min. A metal die with an orifice with an inner diameter of 0.5 mm and an opening half angle of 30° was used at higher temperatures. The drawing speed was set at 0.8 m/min. The mechanical property and the thermal property were evaluated by the tensile tests and DSC, respectively. Morphology and the higher-order structure were determined with SEM and WAXD, respectively.

3. Results and discussion

PTFE particle showed a Tg at 22.7°C and a Tm at 345°C as revealed by DSC measurement. Since the PTFE strand is composed of the aggregation of particle, it has a very low mechanical property (Table 1) and the simple uniaxial drawing was not possible. The strand of PTFE paste with 50 wt% water content was drawn stepwise through 5 plastic dies, a fine filament with a diameter of 0.75 mm was obtained. This fine filament kept its original particulate structure as shown in Fig. 1 and the mechanical property was still low. After the drawing through a metal die at 330°C, the filament tended to have a fibrillar structure and some crystalline orientation was observed in the WAXD pattern as seen in Figs. 2 and 3, respectively. The filament tended to have a much dense structure and the higher crystalline orientation after drawing at a temperature higher than Tm of PTFE up to 380°C. The mechanical property of the filaments increased with the drawing temperature. Drawing at much higher temperature resulted in the breakage of the filament.

Table 1 Mechanical properties of PTFE strand and fibers.

<table>
<thead>
<tr>
<th></th>
<th>Diameter (mm)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE strand</td>
<td>2.0</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>PTFE filament</td>
<td>0.75</td>
<td>8.0</td>
<td>62</td>
</tr>
<tr>
<td>PTFE fiber (330°C)</td>
<td>0.36</td>
<td>36</td>
<td>801</td>
</tr>
<tr>
<td>PTFE fiber (380°C)</td>
<td>0.1</td>
<td>502</td>
<td>13,200</td>
</tr>
</tbody>
</table>
CONTRIBUTION TO THE DEVELOPMENT AND THE INDUSTRIALISATION OF A THREE-DIMENSIONAL NONWOVEN SYSTEM FOR AUTOMOTIVE INTERIOR APPLICATIONS

Nicole Njeugna†, Dominique Adolphe† and Laurence Schacher†
Jean-François Moret‡ and Olivier Demangeat‡

† ENSISA, Laboratoire de Physique et Mécanique Textiles (LPMT), UMR 7189 CNRS-UHA, 11, rue Alfred Werner, 68093 Mulhouse CEDEX France. Email: nicole.njeugna-yotchou@uha.fr
‡ N.Schlumberger, 170, rue de la République, 68502 Guebwiller CEDEX France.

1. Introduction
The new European directives concerning sustainability in particular in the automotive sector, lead to redefine the requirements that automotive manufacturers have to reach. In order to satisfy these new requirements, the automotive OEMs focus their researches tasks towards new innovating products. The development of these new products will have to be marked by:

- The development of mono material products;
- The increase of the recycling rate to reach 85% at January 1, 2015;
- The improvement of the performances of the product (physical, mechanical and insulation properties);
- The improvement of interior comfort.

To answer to these new automotive requirements, the research is turned towards new innovating products in order to replace the current existing ones. In the case of the complex textile used in the field of upholstery, solutions of substitution of the polyurethane foam by textile products are under development. Our suggestion is to develop a tri dimensional nonwoven, which will be manufactured with a vertical lapping. This development represents a research project named vertilap.

2. Presentation of the vertilap program
The vertilap project has been labelled by the competitiveness cluster « Vehicle of the Future » in July 2006 and supported by the regional founding in November 2006. It is composed of 7 partners: 5 Industrialists and the LPMT Research Laboratory, as the project leader of the program.

Based on the expectations previously noted, the aim of the vertilap project is to develop a tri dimensional nonwoven, which will present a low density and the maximum resilience. This tri dimensional nonwoven will exhibit good insulation properties, as well as thermal and acoustic properties. It will also be easy to recycle. This new textile product will allow:

- To substitute the classical used polyurethane foam in the flexible (example: car seat) and semi-rigid linings car (example: door pillar);
- To improve the sensory comfort (touch, sight) of the passenger by increasing the cocooning effect;
- To improve the insulation properties.

3. Approach of the work

3.1 Presentation and Characterisation of the vertilap 3D nonwoven
The vertilap 3D nonwoven is manufactured with a vertical lapping unit for nonwovens. It could be made any kind of raw material but the preferred one are of polyester and/or polypropylene material. The density of the vertilap 3D nonwoven can vary from 10 to 110 kg/m³ according to the thickness of the nonwoven, the number of pleats per centimetre and the weight of the textile material input. Its thickness can vary from 2 to 50 mm.

The characterisation will consist in evaluating the physical, the mechanical and the insulation properties of the 3D nonwoven. Methods of characterisation will be developed or adapted from the existing ones in order to determine the characteristics of the 3D nonwoven. These first trials are under progress and the first results are presented bellow.

3.2 Experimental modelling of the manufacturing process of the vertilap 3D nonwoven
The whole characteristics of the 3D nonwoven should allow us to carry out an experimental model. The purpose is to predict the characteristics of the 3D nonwoven, at least for the most important properties, according to the adjustment parameters of the industrial process and the material input characteristics.
3.3 Comparison of the vertilap 3D nonwoven and the polyurethane foam

It aims at evaluating the differences and/or the similarities of these two types of products. It will also enable the evaluation of the efficiency of the substituted textile product.

The study has been started through the characterisation of the compression behaviour. This one has been performed thanks to the Kawabata Evaluation System, KES-FB3 Compression Tester (Kawabata 1980). A 10 cm x 10 cm sample has been compressed with a speed of 0.2 mm/sec on a 2 cm² circular surface with a maximum pressure of 5 kPa. The first curves of the compression behaviour (see Figure 1. & Figure 2.) show a similarity in the compression behaviour of the two products.

The curve (see Figure 1.) is characterised by two parts: a linear elastic deformation and a constraint plateau. This behaviour is typical for polyurethane foams (Bouchou et al 1999). In the elastic zone, the enclosed air in the cells of the foam is released due to the effect of compression. The cells break down when the whole air is released and then a constraint plateau is observed. A third area, called the densification zone can be observed for loads higher than 5 kPa. The same type of compression behaviour is reproduced with our 3D nonwoven.

The curve (see Figure 2.) represents the compression behaviour of the 3D nonwoven. It can be noticed that the previous remark can be applied to this curve. A linear elastic zone is observed corresponding to the bending of the pleats. Then, an unpronounced constraint plateau is observed due to the crushing of the structure. This hypothesis, which has to be confirmed, could be explained by the bending stiffness and the buckling of the filaments. The densification part of the curve will be visible for loads higher than 5 kPa. This densification will represent the crushing of the lap.

4. Conclusions and Perspectives

This work is at its very beginning, the first trials on the characterisation of this new product have to be refined and customized to the properties, limits and constraints generated by this new material. The first tests have shown some similitude between the compression behaviour of the classical foam used in automotive industry and our vertilap 3D nonwoven. Further investigations will be carried out in order to confirm the first results already obtained there and to reach the aim exposed in the introduction.

References


Drean, E., (2006), Contribution au développement de capteurs piézoélectriques pour la caractérisation mécanique des étoffes, Thèse de doctorat de l’Université de Haute Alsace (UHA), Mulhouse, France.

The effect of wool fibers on thermal effects related to moisture sorption and desorption was measured for several wool fabrics, pile fabrics, and wool blend materials. Commercially successful polyester pile fabrics are undergoing further development to add wool fibers into one or more of the pile faces to take advantage of the natural thermal and water vapor regulation properties of wool. Wool clothing actively generates heat when moved from a warm and dry indoor environment to cold and wet outdoor conditions. This is due to the readjustment of water vapor content within wool fibers to maintain equilibrium with the local microclimate.

Step changes in humidity were used to maximize the thermal effects due to water vapor sorption and desorption. A gas humidifying system that can change relative humidity of the gas flow in a step-wise fashion was used to pass a gas flow over the surface of the fabric sample. A non-contact infrared thermocouple mounted above the sample observed the change in fabric surface temperature. A heat flux meter mounted underneath the sample on a flat rubber sheet recorded the actual heat flow from the fabric into the sheet. The rubber sheet was meant to simulate human skin thermal properties. A second thermocouple mounted on the rubber sheet near the heat flux sensor recorded the temperature change underneath the fabric. The exposed fabric sample area was 10 cm². Relative humidity step changes from 1% to 99%, as well as different gas flow rates, were used to maximize the apparent temperature differences and heat flow. All tests were done in an environmental box at a controlled temperature of 30°C. All samples were initially tested with the wool side towards the “body” side (directly contacting the heat flux sensor).

A series of gas flows were cycled between 1% r.h. and 99% r.h. Each condition of humidity and gas flow rate lasted for one hour. Three gas flow rates were used, varying from 2 liter/minute to 0.5 liters/minute gas flow past the surface of the sample.

Figure 1. Test cell setup to observe temperature and heat flow for fabrics subjected to a step change in relative humidity. Fabric sample is placed on top of the sensor, and humidity-controlled gas flows through the top portion of the flow cell. The heat flux sensor is oriented so that a heat flow from the environment to the body will show as negative, and a heat flow from the body to the environment will show as positive.

An example of the measured heat flux, surface temperature, and humidity change from three samples varying in wool fiber content is shown in Figure 2. The heat flux units in Figure 2 are given in METs (average amount of body heat produced by a sedentary human). A MET is the amount of body heat produced by a sedentary human, and is averaged over the standard body surface area of 1.8 m². (1 MET = 58.2 W/m² = 18.4 Btu/hour-ft²). This body heat is assumed equivalent to the heat flux that must be transferred to the environment to maintain thermal equilibrium.
Figure 2. Heat flux, temperature, and humidity measurements from flow cell under step changes in relative humidity.

Figure 2 shows that the fabric with the highest percentage of wool fiber content also shows the highest heat flow to the body. It can also be noted that the polyester fabric control also shows a measured heat flux. This is probably due to the change in energy content and temperature of the gas stream as its humidity is changed from 1% to 99%, and is also affected by water vapor sorption of the heat flux sensor materials themselves.

An approximate calculation of the relative difference in heat flows between the different cases can be made by integrating the area under the sorption curves (setpoints #2, #4, #6) (negative heat flow only) and subtracting off the area under the curve with no sample in place. Under this example of an extreme step change in relative humidity, the Wool/PLA blend sample will provide about twice the energy transfer to or from the body as the wool/polyester blend sample.

The corresponding temperature and humidity plots show the same trends for the fabrics. The fabric with the highest wool content shows the largest temperature changes due to water vapor sorption and desorption, as well as the longest buffering of humidity change due to sorption of hygroscopic fibers. Humidity buffering correlates with fabric wool content, and the buffering period lasts more than an hour for some conditions.

Further results to be presented show that factors such as the presence or absence of a water repellent treatment or the orientation of the wool component toward or away from the body have minimal impact for thin fabrics, but become more important as fabric thickness increases.
Numerical Analysis of Energy Absorption Mechanism in Multiply Fabric Impacts

Tae Jin Kang and Ju Hyun Kim

School of Materials Science and Engineering, Seoul National University, Sillim-dong, Gwanak-gu, Seoul, 151-744, Korea. Email: taekang@snu.ac.kr

1. Introduction

Numerical modeling of fabric impacts began decades ago and the progress has been made through numerous researches. But, the design process is mainly dependent on extensive ballistic tests. The reasons why the experimental approaches are preferred is that the actual fabric being used is usually layered multi-ply that the modeling becomes complicated and computationally expensive. In analysis of the impact behavior of multi-ply fabrics, computational time is the most critical factor because contact conditions between layers should be checked in every time step. Another bottle-neck is the difficulties in integrating various fabric features into one numerical model. Here, the fabric features can be yarn slippage on the warp-weft crossovers, crimp effect, slippage on the clamped boundaries, yarn pullout, bending phenomena, inelastic collisions and so on. Hence, the majorities of the numerical analysis of fabric impacts have been confined only to one ply fabrics and the models considered only a few fabric features at a time.

2. Numerical Analysis

In this research, multi-ply analysis including the fabric features was performed. The impact problem of multi-ply fabric is modeled as a layered network of crossovers and yarn elements. The multi-ply effect which is the interactions between layers was implemented successfully and the fabric features mentioned above were described reasonably.

The energy analysis method was employed for the understanding of impact behavior of multi-ply plain-woven fabric considering the speed of projectile. Three-element viscoelastic model was used to describe the dynamic behavior of fibers. Yarn slippage on the warp-weft crossovers was considered by updating the element length. Crimp effect was taken into account by assigning some portion of the strain to crimp. Fabric slippage on the clamped area and yarn pullout on the edge of the fabric were also considered. Bending resistance of the fabrics was assumed as the reaction force of a node arising from the curvature of the nodes. The inelastic collision of fabric layers as well as the collision with the projectile was considered. The numerical model describing all of the features was implemented as in-house code. Each of the energy dissipation mechanisms was characterized to clarify the contribution to the total energy absorption and performance of the fabrics against ballistic impacts. Three cases representing no-perforation, mature-perforation and premature-perforation were chosen to explain different energy dissipation characteristics depending on the impact velocity. The difference in reaction of each layer with projectile was also examined.
Figure 1. Simulations for the typical 3 cases of fabric impact

Figure 2. Component-wise energy contribution analysis

References

INFLUENCE OF THE TECHNIQUE OF SIZING WITH PRE-WETTING ON THE MECHANICAL PROPERTIES OF A SIZED YARN

Nejib Sejri 1,2, Omar Harzallah 2, Sami Ben amar 1, Sassi Ben Nasrallah 1, Pierre Viallier 2

1 Laboratoire d’Etude des Systèmes Thermiques et Energétiques, ENIM, 5019 Monastir Tunisie
2 LPMT UMR 7189 CNRS-UHA, ENSISA 11 rue Werner 68093 Mulhouse cedex; email: o.harzallah@uha.fr

The preparation of a warp yarn is an key element of the success of weaving. Under the economic pressure to which is subjected world textile industry, an increased attention is given to the equipment, to the products and the processes used in the preparation of warp yarn for weaving. The yarn, the sizing equipment and the size must be adapted the ones to the others to obtain powerful yarn able to resist to the weaving requests with lower cost.

The objective of this work is to study the mechanical behaviour of sized yarns after a pre-wetting with hot water and the drying of these yarns on the sizing machine. In a first stage we showed that the heat exchange coefficient is the same for a pre-wetted yarn or not. The pre-wetting does not decrease the production. But, although containing less size, the yarn hairiness is reduced compared to a sizing without pre-wetting. The initial modulus yarn sized with pre wetting is higher than that of classically sized yarn and the sized yarn with this new technology of sizing present a more important immediate recoveries. And moreover we studied the influence of a preliminary wetting on the structure of the points of size by using the scanning electronic microscopy (SEM). The examination of cut of sized yarn shows that if the yarn is pre wetted, the points of size are more at the periphery of the yarn. It explains this best mechanical behaviour.
Most of polymers have a very high electrical resistance. On the other hand, polymer materials have to be used to produce some special parts of electronic devices, circuit board or sensors. These applications need the polymer materials having conductive, anti-static electricity or electromagnetic interference shielding ability. A method used to solve this problem is adding conductive metal filament into a polymer filament yarn, getting a composite materials, which can be directly integrated into a textile. However, filaments can be submitted to severe friction stress, during the weaving process for example. The objective of this work is to analyse the friction and wear behaviour of copper reinforced polyethylene terephthalate (PET) filaments.

Pure and copper reinforced (PET) filaments were prepared by melt spinning process. Rheological behavior and crystallinity were investigated by using a plate-plate rheometer and differential scanning calorimetry respectively. Mechanical and viscoelastic properties of filaments have also been quantified (tensile tests and dynamic mechanical analysis). Friction and wear experiments have been performed with a pin on disk tribometer, for different normal loads and speeds. Filaments surfaces have been analysed before and after friction with Scanning Electron Microscope (SEM) and Infra-red spectroscopy. Experimental results show a satisfying wear resistance of filaments, even if friction is able to induce some structural modifications of the polymer surface.
Melting Temperature (T_m) for Single Crystals of Stereoregular Isotactic Poly(acrylonitrile) Prepared by Isothermal Solution Crystallization from Different Organic Solvents

Masatomo Minagawa¹, Takuya Waragaya¹, Ryo Umehara¹, Masaki Tsuji², Nobuhiro Sato³, and Tomochika Matsuyama³

¹) Yamagata University, Graduate School of Science and Engineering, Yonezawa 992-8510; Tel&Fax: +81-(0)238-26-3042; E-mail: minagawa@yz.yamagata-u.ac.jp
²) Kyoto University, Institute for Chemical Research, Uji 611-0011;
³) Kyoto University, Research Reactor Institute, Kumatori 590-0494, JAPAN

Stereoregular poly(acrylonitrile) (PAN) was obtained by urea clathrate polymerization in the solid state at low temperatures. Isothermal solution crystallization for isotactic (~80%) PAN was carried out in different organic solvents. Recovered crystals were each single crystal as evidenced by clear ED pattern. Size of the crystals was determined at low temperatures: Orthorhombic, a=1.11nm, and b=1.19nm (at 4.2K). These crystals showed distinct melting temperature (T_m), which was verified by the appearance of broad exothermic peak in the cooling curve of DSC. When the value of T_m was plotted against T_c (crystallization temperature), two straight lines were obtained. That is, all the experimental data laid on two different straight lines according to the difference of the kind of organic solvents. Correspondingly ED pattern of these samples was different. Structure-properties relationship in single crystals of isotactic PAN is comprehensively discussed.
Moulding Conditions for Seamless Bra Cup

YICK, K.L., NG, S.P. & DENG, Y.M.
Institute of Textiles & Clothing, The Hong Kong Polytechnic University, Hong Kong

Bras are one of the most complicated engineered apparel products with complex pattern design and making-up construction, as well as unique fitting requirements. Conventionally, bra cups are made by many cut components to be sewn together to form a 3D bra cup to fit the women breast anatomy. More recently, seamless moulded bras have becoming more and more popular, representing almost 80-90% of the overall bra market. Moulded bras are not only able to give smooth configuration, but also provide a wide range of designs combined with different levels of softness and support (Loftin 1965). Amongst, a well-known, significant and long standing problem in bra manufacturing is the determination of complicated moulding conditions (viz., temperature, lengths of time and clamping pressure) for particular types of fabric.

Recently, two major types of moulding methods namely contour moulding and bullet moulding are commonly adopted in the intimate apparel industry. Contour moulding requires a pair of aluminum male mould and female mould with conformed shape, which is similar to the anatomical shape of the female breast to mould the bra cup materials (Figure 1). The moulds are then heated so as to soften, heat-set and conform the flat material (usually foam materials) to the desired shape. Bullet moulding is normally used for fabric moulding, which engages a circular cylindrical shaped mould with a parabolic shaped portion at one end as bullet shape (Figure 2), tear drop shape or sloper shape. In order to maintain a more consistent moulding condition, a female mould with a cavity is installed underneath to accommodate the male mould. Both heating tube and thermocouple are inserted in each mould head and they are connected to the control panel of the moulding machine. During the moulding process, the mould heads are heated up to the preset temperature and moulded the fabric according to the preset dwell time. The fabrics used for moulding have to be highly extensible, heat settable and thermoplastic so that fabrics can be deformed and re-set into desired shape according to the contour of the mould head (Thompson 1959). Since polymers have different morphological structures and exhibit different mechanical behaviour under specific temperatures, the moulding conditions therefore must be determined in accordance to the thermal properties of the fabric material so as to achieve precise 3D bra shape with good colour fastness, elasticity, breathability, softness, smoothness, shape retention, but minimum puckering and yellowing (Bhat 2001, Donaghy 1976 & Yu 1996). The control of moulding process has becoming more and more difficult due to a vast number of new fabrics and structures introduced in the market. Furthermore, two fabrics may even be laminated together by using an adhesive film and moulded to produce a natural and smooth breast contour without using polyurethane foams and artificial seam lines (Galitzki 1965 & Abelman 2002).

Figure 1 shows the cup shape and appearance at various moulding temperatures (with dwell time of 45 seconds and mould depth of 70mm) of a polyester/spandex blended fabric that is commonly used for fabric moulding. When the moulding temperature was set between 160-180°C (Figures 3a and 3b), a clear ring mark was observed, the colour of the fabric was changed, the elasticity of the fabric was totally lost and becoming brittle even though a precise 3D bra shape was formed. Thermosetting of soft segments in polymeric fibre occurred and nearly no shrinkage of bra cup depth was observed. In this respect, a lower moulding temperature must be acquired. However, when the moulding temperature fell to 150°C or below (Figure 3c and 3d), the bra shape was not formed as it is well below the softening point of both the polyester and spandex fibres. In this respect, the moulding temperature could be fixed at around 150-160°C. To achieve the desired cup shape, the dwell time and pressure could then
be changed. To some extent, a longer dwell time could be able to compensate for a lower moulding temperature to avoid ring mark, colour changes and even loss of fabric elasticity, however, the production time could become longer. Apart from cup shape and appearance, cup depth is generally regarded one of the major evaluation parameters in fabric moulding. Figure 4 shows some of the cup depth results at various moulding temperatures and dwell times of a nylon/spandex blended fabric. Results indicated that both the moulding temperatures and dwell times not only affect the cup shape and depth of the moulded fabric, but also influence the shape retention and cup depth shrinkage after cooling and/or laundry. A higher moulding temperature with longer dwell time generally resulted in less amount of cup depth shrinkage, provided that it may result in a high incidence of yellowing and loss of elasticity. Amongst various fabrics, cotton/lycra blended fabric resulted in considerably high amount of cup depth shrinkage after cooling. When fabrics are laminated with adhesive film for bra cup moulding, the moulding temperatures and dwell time must be increased considerably in order to achieve a precise 3D cup shape with good retention and appearance.

![Figure 3. Cup Shape and Appearance at various moulding temperatures of a polyester/spandex blended fabric.](image)

![Figure 4. Cup Depth results at various moulding conditions (moulding temperature & dwell time) of a nylon/spandex blended fabric.](image)

As shown above, to meet the long desired objective of determining the complicated moulding conditions for particular types of fabric, it is necessary to investigate the changes of thermal behaviour for different types of mouldable fabrics in relations to temperature changes. When laminated fabrics are used for bra cup moulding, the effects of adhesives, lamination conditions and curing time on the changes of thermal behaviour of fabric composites and their respective performance behaviour and heat setting ability at bra cup moulding should also be investigated.

**References**


Polymers in solution are capable of adopting a great number of conformations. From a rheological perspective, the variations of conformations can significantly alter the flow properties. Moreover, the concentrated polymer solutions and polymer melts can form temporary entanglements and/or intermolecular physical polymeric networks, which are important contributors to the shape of oscillatory shear curves.

In our study, rheological studies of cellulose solutions were carried out to probe the evolving interactions between cellulose and the ethylene diamine (EDA)/salt solvent system. The microstructure of this polymeric system is complex and includes evidence of stretching and alignment of the molecules as well as network formation. Potassium thiocyanate (KSCN) was used as the salt in these studies. Steady shear studies indicated that all solutions exhibited shear-thinning behavior. A transition was observed from shear-independent to shear-dependent viscosity in the steady shear flow curve. Degree of polymerization (DP) measurements showed that the aging times and salt concentrations did not cause cellulose degradation. The viscosity of the system decreased as the sample aged. In contrast, increasing salt concentrations led to an increase in the viscosity. Dynamic shear properties confirmed that the decrease in the viscosity of the solution with time was primarily due to changes in the relaxation behavior of cellulose in...
the solution. The increase in salt concentration increased the number of intermolecular physical crosslinks. The system became a very elastic gel as the salt concentration was increased up to 28.5wt% in EDA. The average relaxation time of cellulose decreased as the sample aged, and increased as the salt concentration was increased. The time temperature superposition (TTS) method was employed to help locate the crossover point of storage modulus (G') and loss modulus (G'') and extend the experimental frequency range of the instrument.

The $^{39}$K and $^{14}$N NMR spectroscopy studies, using cellobiose as a model system, showed a pronounced change in the chemical shift of the $^{39}$K nuclei with increasing cellobiose concentration, but no significant shifts for $^{14}$N nuclei from KSCN and EDA were detected. With ions dissociated, a stronger interaction occurred between the K$^+$ ion and cellobiose than the SCN$^-$ ion.
Nanocomposite Fibers Electrospun from Biodegradable Polymers

Chunhui Xiang and Margaret W. Frey

Department of Fiber Science & Apparel Design, Cornell University, Ithaca, NY 14853

Cellulose nanofibrils were prepared by sulfuric acid hydrolysis and incorporated into dimethylformamide (DMF) by ultrasonication to obtain a stable suspension. The morphology of cellulose nanofibrils was studied by TEM. Nanocomposite fibers were electrospun at elevated temperature from PLA/DMF solutions containing suspended cellulose nanofibrils and collected as randomly oriented non-woven fabrics. Effects of the cellulose nanofibril content on the electrospun non-woven fabrics on the fabric physical properties and morphology were studied. As the concentration of cellulose (on the weight of PLA) increased, the uniformity of the electrospun nanocomposite fibers changed. Crystallinity of the electrospun non-woven fabrics was determined by wide angle X-ray diffraction (WAXD). The thermal properties of the electrospun non-woven fabrics were investigated by a differential scanning calorimeter (DSC). Cellulose nanofibrils retained crystallinity in the electrospun non-woven fabrics.
Chitosan Nanofibers by Electrospinning from Aqueous Solutions

Jian Du and You-Lo Hsieh*
Fiber and Polymer Science, University of California, Davis, CA 95616, USA

1. Introduction

The unique inherent biological and physicochemical characteristics of chitosan have attracted extensive research and development for its potential in biomedical and technological applications [1]. Processing chitosan into fibers has been reported by electrospinning from acid solutions of trifluoroacetic acid [2], formic acid [3], and acetic acid [4]. We have generated higher molecular weight chitosan (Mv=1600kDa) nanofiber by adding PVA from dilute acetic acid [5]. The residual acid in the fibers, however, reduced their biocompatibility, limiting their use in biomedical systems [6]. Therefore, synthesizing water-soluble chitosan derivatives and generating fibers from their aqueous solutions are fundamental to the major challenges that chitosan as a biomaterial. Our laboratory has synthesized water- and organic-soluble chitosan [7]. This paper presents the generation of nanofibers by electrospinning of chitosan derivatives from aqueous solutions. Two water-soluble chitosan derivatives are presented as examples, i.e., carboxymethylated and PEGylated chitosan.

2. Experiment

Carboxymethylated chitosan with varying chain lengths and degrees of substitution (DS) were synthesized by alkalization and carboxylation. Both the yield and the DS of water-soluble CMCS increased with longer reaction times with DS ranging from 0.25 to 1.19 at yields up to 93.6%. The carboxylated products from the 405 kDa chitosan required a DS of 0.72 or higher to become water soluble, whereas lower DSs of 0.36 and 0.25 were sufficient to render the 89 and 40 kDa chitosan water soluble, respectively.

PEGylated chitosan, i.e., PEG-N-chitosan (DS=0.12-0.44) and PEG-N,O-chitosan (DS=0.68 and 1.5), were synthesized via reductive amination and acylation of chitosan (Mv=137 kDa to 400 kDa), respectively. Generally, the extent of PEGylation was higher with shorter PEG lengths (Mn= 550, 2000, and 5000 Da) and lower chitosan molecular weights. All PEGylated chitosan became water soluble, even with a DS as low as 0.2 in the case of PEG-N-CS.

Electrospinning of aqueous solutions of the chitosan derivatives was performed at a 1 mL/h feed rate and ambient temperature. 10–15kV DC voltage (Gamma High Voltage Supply, ES 30-0.1 P) was applied and the distance between the syringe tip and the grounded collector was kept at 15–20cm.

3. Results and discussion

Electrospinning of aqueous solutions of carboxylated chitosans with a wide range of molecular weights (Mv=405 k, 89 k, and 40 kDa) and DSs (0.25 to 1.19) produced only droplets. Mixing several water-soluble PEO, PAAm, PAA, and PVA enabled electrospinning of CMCS (Mv=405kDa, DS=0.82 or 1.14; and Mv=89kDa, DS=0.36) into fibers. For instance, aqueous mixtures of CMCS (Mv=405kDa, DS=0.82) with 70% PEO (Mn=100kDa), equal mass of PAAm mixture (1/10 proportion of 5000kDa to 10kDa PAAm) or PAA (Mw=450kDa) could all be electrospun into fibers. The most uniform fibers were generated from aqueous solutions of CMCS (Mv=405kDa, DS=1.14) and PVA (Mw=124–186kDa, 87–89% hydrolysed) at equal mass (Fig. 1a), a further increase to 60% CMCS was achieved by using the lower Mv of 89kDa CMCS with lower DS at 0.36 (Fig. 1b).

Sprayed droplets were observed with aqueous solutions of all PEG-N-chitosan via reductive amination, even at the highest DS of 0.44. Both acylated PEG-N,O-chitosan (DS=0.68 and 1.50) were soluble in water to higher concentrations than any of the PEG-N-chitosan, yet their electrospun products consisted only large beads.
Compared the electrospinning results, the larger beads appear to be associated with either higher DS, lower PEG lengths or higher PEGylated chitosan concentrations, all associated with better water solubility. Very fine fibers intersticing the beads were observed with those derivatives having lower DS and longer PEG chains. This suggests the important role of long PEG side-chains on chain entanglement, thus fiber formation.

![Image](image1.png)

Fig. 1 Electrospun of CMCS/PVA \((M_w=124–186\text{kDa}, \text{87–89}\% \text{ hydrolyzed})\) bicomponent fibers from aqueous solutions of: a) 50\% CM-CS \((M_v=405\text{kDa}, \text{DS}=1.14)\); b) 60\% CM-CS \((M_v=89\text{kDa}, \text{DS}=0.36)\).

The role of long PEG side-chains on chain entanglement was further studied by comparing chitosan derivatives with the same main chitosan chain length \((M_v=190\text{kDa})\) but the different PEG grafted lengths (PEG5k or PEG550) at a fixed total PEO content of 5.5\%. As Fig. 2a shown, continue and uniform fibers with 125± 20 nm in diameters were generated by electrospinning of the PEG5k-N-CS190 with longer PEG chains but lower DS (0.31). The PEGylated chitosan (PEG550-N-CS190) with shorter chains (PEG550) and higher DS (0.48) produced large numbers of beads and few fibers with tens nanometers (Fig.2b).

![Image](image2.png)

Fig. 2 Electrospinning of 10wt\% PEGylated chitosan: a) PEG5k-N-CS190 (DS=0.31) and b) PEG550-N-CS190 (DS=0.48) from aqueous solutions with 5.5\% PEO \((M_n=600\text{kDa})\) and 0.5\% Triton X-100.

4. References

Layer-by-Layer Polysaccharidic Self-assemblies on Cellulose Nanofibers
Bin Ding, Jian Du and You-Lo Hsieh
Fiber and Polymer Science, University of California, Davis, CA 95616, USA

1. Introduction
The electrostatic layer-by-layer (LBL) self-assembly involves alternating adsorption of oppositely charged electrolytes or particles on solid supports, typically flat surfaces or films [1]. Multilayer LBL self-assemblies have been shown to have well-defined and nanoscale precision of thickness, composition, and structures that are desirable for applications such as catalysis, super-hydrophobic surfaces, dye-sensitized solar cells, medical diagnosis, etc. Fibrous templates, specifically nanofibrous membranes, should expand the potential of LBL self-assemblies by taking advantage of the high specific surfaces of nanofibers. To date, only inorganic LBL has been reported. For instance, controlled thickness of alternating TiO$_2$ nanoparticle/polyacrylic acid and poly(allylamine hydrochloride)/polyoxometalate (H$_4$SiW$_{12}$O$_{40}$) LBL assemblies have been reported on the 3D structured nanofibrous mats of cellulose acetate (CA) to demonstrate their catalytic performance for toxic gases [2].

This goal of this work was to explore the feasibility of generating polysaccharidic LBL assemblies on previously reported cellulose nanofibrous templates [3]. A natural cationic polysaccharide (CPS) with one amino and two hydroxyl groups in the repeating units, and anionic polysaccharide (APS), were selected to construct the LBL self-assembly. The CPS has been coupled with poly(styrene sulfonate) on flat template of poly(D,L-lactic acid) films for medical applications [4]. The APS has exhibited desirable properties for hemodialysis devices and anti-adhesive agents [5]. This exploration opens up novel options of fabricating wholly natural nanofibrous devices of polysaccharidic LBL self-assemblies on cellulose nanofibrous materials. Potential applications of such LBL on cellulose nanofibers include new anti-bacterial and anti-adhesive materials.

2. Experimental methods
Cellulose (CELL) nanofibers were fabricated by the alkaline hydrolysis of CA (M$_n$=30 kDa) nanofibers prepared by electrospinning 15 wt% CA solutions in a 2:1 w/w acetone/N,N-dimethylacetamide at a 1 mL/h feeding rate, a 15 kV applied voltage, and a 22 cm distance. Hydrolysis of the CA fibrous mats was performed in 0.05 M NaOH aqueous and ethanol solutions to yield hydrolyzed CA template fibers with 2.45, 1.14, 0.2 degree of substitution (DS) and CELL template fibers. The surface charges of template fibers were determined by titration using polyelectrolytes.

The CPS (M$_v$=190 kDa) and APS (M$_w$=500 kDa) were alternatively deposited on negatively charged CELL template fibers by the electrostatic force. The deposition of LBL films were performed by first immersing the various fibrous mats into CPS solution (1 mg/mL, pH 5) for 20 min followed by three 2-min rinses in water, each fresh bath. The mats then were immersed into the APS solution (1 mg/mL, pH 6) for 20 min followed by identical rinsing steps. The ionic strengths of CPS, APS, and rinsing solutions were regulated by adding NaCl at 0, 0.25, and 0.5 mol/L concentrations. The adsorption and rinsing steps were repeated until the desired number of bilayers was obtained.

3. Results and discussion
During hydrolysis, the nucleophilic substitution of the acetyl group led to negatively charged fiber surfaces. The
CA2.45, CA1.14, CA0.2, and CELL template fibers were determined to carry negative surface charges of 1.32, 1.56, 2.15, and 2.05 mmol/g, respectively. The FTIR of the hydrolyzed samples showed a consistent decreasing trend in the carbonyl peak at 1740 cm\(^{-1}\) with the decrease of DS. The template fibers of varying DS appear similar except for the more loosely packed nanofibers mat morphology and the thinnest diameters of the CA2.45 fibers.

![Fig. 1. SEMs of: (a) CA2.45, (b) CA1.14, (c) CA0.2, and (d) CELL template fibers.](image)

SEM images of (CPS/APS)\(_{5}\) LBL deposited at 0.25 M NaCl on various template fibers are shown in Fig. 2. The non-uniform deposition of polysaccharides LBL films on the CA2.45 nanofibrous mats showed them to be unsuitable for the electrostatic LBL deposition, likely due to its low fiber surface charge. The uniform LBL deposition of alternating CPS/APS layers was observed for CA1.14, CA0.2, and CELL fibers. The average thickness of each CPS/APS bilayer was calculated to be less than 10 nm. The FTIR of the LBL covered fibers showed higher relative intensity ether to carbonyl ratios than that of the templates at around 1640 cm\(^{-1}\). Peaks at 820 and 1530 cm\(^{-1}\) was observed showing the existence of S-O-S vibrations and the possible presence of intramolecular hydrogen bonding. Without NaCl in the solutions, the strong repulsive forces among the polyelectrolytes obstructed their subsequent adsorption, limiting the quantity of CPS/APS LBL that can be detected by FTIR. With increasing NaCl concentrations, the quantities of CPS/APS LBL gradually increased while the specific surface gradually decreased. Additionally, the number of deposited bilayers greatly influenced the morphology of the LBL modified nanofibrous templates and depended on the inter-fiber spaces.

![Fig. 2. SEMs of (CPS/APS)\(_{5}\) LBL (0.25 M NaCl) on: (a) CA2.45, (b) CA1.14, (c) CA0.2, and (d) CELL template fibers.](image)

**References**


Polyacrylamide Hydrogel Nanofibers by Electrospinning
Ping Lu and You-Lo Hsieh
Fiber and Polymer Science, University of California, Davis, CA 95616, U.S.A.

Hydrogels are three-dimensional hydrophilic macromolecular networks that are capable of expanding in volume and retaining water many time of their mass [1]. Polyacrylamide-based hydrogels are highly versatile and have found extensive applications in wastewater treatment, pulp and paper, mining and mineral processing as well as protein separation and immobilization. While cross-linked PAAm has been fabricated into various forms of beads, rods and films, there has been no report on fibrous materials. Linear PAAm which is water-soluble has been processed into fibers by electrospinning [2]. The electrospun fibers are much finer and have the advantage of much higher specific surfaces and porous structures over the traditional fibers. To enable these ultra-fine PAAm fibers to function in aqueous environment, they must be rendered water-insoluble. However, the inert structure of linear PAAm makes its electrospun nanofibrous membrane hard to be stabilized [3].

The objective of this project is to study the feasibility of fabricating PAAm hydrogel nanofibers. The viscosities of polymer solution increased with increasing the polymer concentrations. Non-ionic PAAm (Mw=5,000-6,000 kDa) was fabricated into fibers with average diameters about 267 nm by electrospinning of 2.5 wt % aqueous PAAm solution. With the addition of varied proportions of a shorter chain PAAm (Mw=5,000-6,000 kDa), fibrous products with diverse diameters from 270 to 2836 nm (Table 1) and interesting morphologies including round fibers, branched fibers, and ribbons (Figure 1) were afforded.

Table 1. Frequency distribution of fibers electrospun from PAAm aqueous solutions

<table>
<thead>
<tr>
<th>Total polymer concentration (wt %)</th>
<th>Other composition (besides 2.5 wt % 5,000-6,000 kDa PAAm)</th>
<th>Average diameter (nm)</th>
<th>Standard deviation</th>
<th>Fiber morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>no</td>
<td>267</td>
<td>105</td>
<td>round</td>
</tr>
<tr>
<td>2.5</td>
<td>0.5 wt % Triton X-100</td>
<td>263</td>
<td>38</td>
<td>round</td>
</tr>
<tr>
<td>5.0</td>
<td>2.5 wt % 10 kDa PAAm</td>
<td>270</td>
<td>77</td>
<td>round and branched</td>
</tr>
<tr>
<td>7.5</td>
<td>5.0 wt % 10 kDa PAAm</td>
<td>440</td>
<td>106</td>
<td>round, membrane, and ribbon</td>
</tr>
<tr>
<td>12.5</td>
<td>10.0 wt % 10 kDa PAAm</td>
<td>542</td>
<td>75</td>
<td>round and ribbon</td>
</tr>
<tr>
<td>17.5</td>
<td>15.0 wt % 10 kDa PAAm</td>
<td>1109</td>
<td>375</td>
<td>ribbon</td>
</tr>
<tr>
<td>22.5</td>
<td>20.0 wt % 10 kDa PAAm</td>
<td>2836</td>
<td>824</td>
<td>round</td>
</tr>
</tbody>
</table>

Figure 1. SEM micrograph of (a) round fibers (b) branched fibers and (c) ribbons.
The PAAm nanofibrous membranes were cross-linked with glutaraldehyde (GA) in the presence of 4 wt % of HCl. The cross-linking reaction successfully stabilized the fibers against deformation in water and organic solvents up to 72 h without any noticeable structural change. In addition, the nanofibrous membrane showed excellent thermal stability below 250 °C, small weight loss under prolonged water immersion (Figure 2), high water up-take (up to 28 g water/g membrane) (Figure 2), controllable hydrophilicity (contact angle from 0 to 25 °), and increased mechanical strength (up to 6 times of the uncross-linked membrane) (Figure 3).

![Figure 2. Effects of GA concentrations on water solubility and uptake of cross-linked PAAm (in EtOH with 4 wt % HCl at 120 °C for 60 min)](image)

![Figure 3. Stress-strain curves of electrospun PAAm nanofibrous membranes crosslinked with GA at varying concentrations](image)

The mechanism of the cross-linking reaction was proposed and confirmed by FTIR. The ultra-high specific surface nanofibrous membranes and the significant swelling capacities of PAAm hydrogels have wide potential applications in separation, filters, oil recovery, soil conditioning, water treatment, agriculture, and biomedical applications.

**References**


Controllable Biotinylated Poly(Ethylene-co-Glycidyl Methacrylate) (PE-co-GMA) Nanofibers to Bind Streptavidin-Horseradish Peroxidase (HRP) for Potential Biosensor Applications

Dong Wang a, Gang Sun a,*, Bei Xiang a and Bor-Sen Chiou b

a Fiber and Polymer Science, University of California, Davis, CA 95616 email: gysun@ucdavis.edu
b Bioproduct Chemistry and Engineering, USDA/WRRC/ARS, 800 Buchanan Street, Albany, CA 94710

Abstract

Poly (ethylene-co-glycidyl methacrylate), a commercial thermoplastic, possesses active epoxy groups, which can serve as reactive sites to hydroxyl and amino groups. Such modifications will enable the polymer to be used in a wide range of biological applications, such as biosensors, high density gene-array, protein extraction and DNA carriers. However, there are only several reports on poly(glycidyl methacrylate) spherical micro-particles as support materials. Gamze et al. synthesized latex poly(glycidyl methacrylate) microparticles for enzyme immobilization. Kodaka et al. reported the fabrication of bifunctional latex beads with hydroxyl and epoxy groups for immobilizing pyruvate kinase. So far, no reports on the fabrication of poly(ethylene-co-glycidyl methacrylate) nanofibers have been published. Although electrospinning is the most popular method to produce nanofibers, it could not make thermoplastics such as PE-co-GMA into nanofibers.

A novel process of preparing thermoplastic nanofibers with high productivity was recently developed in our group, which can produce PE-co-GMA, polyolefin and polyester nanofibers in continuous yarns and controllable sizes. The prepared PE-co-GMA nanofibers with different average diameters ranged from 100 to 400 nm, as shown in Figure 1. Inspired by the successful fabrication of thermoplastics nanofibers, in this study the potential biosensor applications of the PE-co-GMA nanofibers were explored, as shown in Scheme 1. The surfaces of the PE-co-GMA nanofibers were aminated and biotinylated. Figure 2 show the successful amination and the biotinylation. The streptavidin-horseradish conjugate (HRP) was then immobilized onto the biotinylated surfaces of the PE-co-GMA nanofibers via a rapid, specific and strong binding between biotin and streptavidin. The HRP, a model biologically functional molecule, is widely used as a label for immunoglobulins in many different immunochemistry applications and is used to detect a wide variety of chromogenic hydrogen donors in the presence of hydrogen peroxide. The activity of the streptavidin-HRP immobilized PE-co-GMA nanofibers was presented in figure 3. The streptavidin-HRP immobilized PE-co-GMA nanofibers showed high activity, efficiency, sensitivity as well as good reusability. The results demonstrated PE-co-GMA nanofibers prepared could be a promising candidate as solid support materials for potential biosensor applications.

References

Scheme 1 Synthesis route of the streptavidin-HRP immobilized PE-co-GMA nanofibers

Figure 1 Morphology of PE-co-GMA nanofibers

Figure 2 FTIR-ATR Spectrum of (a) PE-co-GMA nanofiber; (b) Aminated nanofibers; (c) Biotinylated nanofibers.

Figure 3 Streptavidin-HRP activity assay of streptavidin-HRP immobilized PE-co-GMA nanofibers in colorless reagent mixture [phosphate buffer, phenol (PhOH), 4-aminoantipyrine (4-AAP, colorless dye) and H₂O₂].
ANALYSIS OF ELECTROSPINNING PROCESS DYNAMICS AND RESULTING NANOFIBER DIAMETER DISTRIBUTIONS

M.A. Gevelber and Xuri Yan

Boston University, Manufacturing Engineering Department, 15 St. Mary’s st. Brookline, MA, 02446, USA
email: gevelber@bu.edu, xryan@bu.edu

In many emerging, high value electrospinning applications, the fiber diameter distribution affects the fiber’s performance and production economics (production rate and material utilization of expensive feedstock in some biomedical applications). However, the current state-of-the-art electrospinning process is run open-loop, which in many cases, results in broad distributions that vary over time. This paper addresses issues for developing a real-time electrospinning control system that can enable greater control over nanofiber diameter distributions. The fundamental process dynamics are identified, and the relationship between measurable process states and the resulting fiber-diameter distribution is examined.

A well instrumented and computer based actuator control system has been developed. The sensing schemes (Fig. 1) include: a) measurement of the dynamic Taylor cone volume for determination of the flow rate entering the jet, $Q_{jet}$, b) length of the upper jet $L_{uj}$ since it reflects the local force balance related to the onset of whipping, c) angle of the whipping region, $\theta$, as well as the motion in the upper whipping region since it reflects a region where there is a major reduction in fiber diameter, and d) high precision fiber current measurement which gives the charge amount embedded in jet/fiber.

Stable operating conditions were determined (Fig 2) for two, 400K molecular weight PEO concentrations of 6% and 8%. For high voltages, a narrow tapered Taylor cone was observed (image 3 at point 3 in Fig. 2), while for low voltages, a larger volume was observed (image 2 for point 2 in Fig. 2). Finding the stable operating condition for some material solutions can be small (eg. 6% PEO, low flow rate).

Fig. 3 shows the dynamic variations of these variables for condition 1 while Fig. 4 shows the resulting fiber diameter distribution. These experiments reveal that large variations of measured variables are correlated to the resulting large variations in fiber diameter, suggesting that implementing real-time control can provide an enhanced...
ability to control diameter distributions. While for all of the conditions evaluated, there are variations in all variables, these variations remain bounded, and the process is operating in a bounded stable state, since while there are variations, they do not grow without bound. Note, condition 1, which has large variations, is considered only marginally stable, in that it produced continuous fibers, but the large variations in state (current, cone volume, etc) resulted in large variations in fiber diameter.

Fig. 5 and Fig. 6 shows the Fourier power spectral decomposition of charge density, upper jet length, and measurement of the whipping region in terms of interference with a laser beam that crosses the whipping region for one operating point. All three reveal that there are dominant low frequency modes of variation (on the order of 6 Hz and less), but that the laser measurement system is picking up important higher frequency modes that are expected to have a significant impact on variations.

To examine the need for control, five, 30 minute runs of the same condition were conducted in order to mimic the process variations that occur when the electrospinning system is cycled on and off. Several interesting variations are observed: a) there are large transient excursions (spikes that are over twice the volume level), but they are slow enough (10 sec) to be controlled, b) the final steady-state condition varies from run to run even though the same input conditions are achieved (a 17% variation in steady-state current), and c) there is a long initial transient period (25% of the run time changing the states by 25%). Similarly, Fig. 7 shows the drift that was observed over 11 days, requiring a 14% change in inputs to maintain the same process window. These results indicate the desirability of a closed loop system in order to minimize run-to-run variation.

To aid in designing a real time control algorithm, we have conducted system characterization experiments. A step change in the power supply voltage is made to observe the dynamic response characteristics in terms of the steady state gain (indicating how large the output value changes for a change in input) as well as how fast the process responds when a potential control input is changed. Fig. 8 shows the current has a large overshoot, while change density (I/Q jet) has characteristic right-half-plane dynamics, and both have dynamics on the order of 2 seconds. These dynamic characteristics pose issues that need to be considered in designing the control algorithm.

Lastly, a low order model is presented to provide insight into the relation of process dynamics to the operating condition.
Development of thermoplastic polyurethane vascular prostheses using solvent-electrospinning methods

Chung Hee Park1, Yun Kyung Kang2, Hak Chang3, Chan Young Park3

1Department of Clothing and Textiles and Intelligent Textile System Research Center, Seoul National University, Seoul, Korea (junghee@snu.ac.kr)
2Department of Clothing and Textiles, Seoul National University, Seoul, Korea (kpig@snu.ac.kr)
3Department of plastic & reconstructive surgery, Seoul National University Hospital, Seoul, Korea

In this study, optimum electrospinning conditions of ether-based thermoplastic polyurethane/N,N-dimethylformamide solution were searched. Applying this conditions, vascular prostheses for using artificial blood vessel (inside diameter was 3mm) was produced by electrospinning. And various properties of this specimen were measured.

The optimum electrospinning conditions of polyurethane solution were 12wt% of concentration, 11.0 kV of voltage and 15cm of tip to collector distance at room temperature 27°C and humidity 80%R.H. Thermal behavior of vascular prostheses from differential scanning calorimeter showed that this polyurethane electrospun web was thermally stable in range of body temperature. Enzyme hydrolysis of polyurethane electrospun web was carried out by using Protease and Lipase. The ratios of degradation were less than 1%. All of the polyurethane specimens were rarely degraded by exposing active enzyme. So, it was expected that the polyurethane electrospun vascular prostheses would be performed as non-degradable blood vessels in the body system.

The possibility of making thrombi when it was grafted in body was tested by platelet adhesion observation. Electrospun web showed less adhesion of platelet than polyurethane bulk film. The pore size range of polyurethane electrospun vascular prostheses was 0~3.5μm. The tensile strain was about 80% and the tensile strain was about 8~9MPa. Hence, the tensile properties were equal with the existing vascular prostheses made by polyester and ePTFE.
The Fiber Society
2007 Officers and Committees

Officers

President
You-Lo Hsieh
University of California at Davis
ylhsieh@ucdavis.edu
2007

Vice-President
Michael Ellison
Clemson University
ellisom@clemson.edu
2007

Secretary
Subhash K. Batra
North Carolina State University
subhash_batra@ncsu.edu
2008

Treasurer
Stephen Michielsen
North Carolina State University
stephen_michielsen@ncsu.edu
2007

Past-President
Phil Gibson
US Army Natick Soldier Center
phillip.gibson@us.army.mil
2007

Governing Council Members

H. Young Chung
Donaldson Co., Inc.
hychung@mail.donaldson.com
2007

Gajanan Bhat
University of Tennessee
gbhat@utk.edu
2007

David Salem
Charged Injection Technologies, Inc.
dsalem@chargedinjection.com
2008

Dominique C. Adolphe
University of Mulhouse
dominique.adolphe@uha.fr
2008

Tom Theyson
Tens Tech
tenstech@earthlink.net
2009

Anil Netravail
Cornell University
ann2@cornell.edu
2009

JEFF Editor (Permanent Member)
Michael Jaffe
New Jersey Institute of Technology
jaffe@adm.njit.edu
**Finance and Administration Committee**
Kay Obendorf (Chair)
Cornell University
sko3@cornell.edu
2008

William (Bill) Haile
Missing Octave Insights
hailefamily@chartertn.net
2007

Phil Gibson
US Army Natick Soldier Center
phillip.gibson@us.army.mil
2009

You-Lo Hsieh
University of California at Davis
ylhsieh@ucdavis.edu
2010

Stephen Michielsen, Treasurer
North Carolina State University
stephen_michielsen@ncsu.edu

**Nominating Committee**
Phil Gibson (Chair)
US Army Natick Soldier Center
phillip.gibson@us.army.mil
2007

David Salem
Charged Injection Technologies, Inc.
dsalem@chargedinjection.com
2007

You-Lo Hsieh
University of California at Davis
ylhsieh@ucdavis.edu
2008

Ian Hardin
University of Georgia
ihardin@fcs.uga.edu
2009

**Membership Committee**
Subhash K. Batra (Secretary)
North Carolina State University
subhash_batra@ncsu.edu

**Publications Committee**
Michael Ellison (Chair)
Clemson University
ellisom@clemson.edu

Urs Meyer
Swiss Federal Institute of Technology
prof@texma.org

Kee Jong Yoon
Dankook University
keeyoon@dku.edu

Raymond Naar
Consultant, Fibers and Polymers
Industries
rnaar@nycap.rr.com

Seshadri Ramkumar
Texas Tech University
s.ramkumar@ttu.edu

Donggang Yao
Georgia Institute of Technology
dong.yao@ptfe.gatech.edu

Janice Gerde
Department of Homeland Security
janice.r.gerde@dhs.gov

Cheryl Gomes
Foster-Miller, Inc.
cgomes@foster-miller.com

**JEFF Steering Committee**
Representative for the Fiber Society
Heidi Schreuder-Gibson
US Army Natick Soldier Center
heidi.schreudergibson@us.army.mil
**Distinguished Achievement Award Committee**

Gajanan Bhat (Chair)
University of Tennessee
gbhat@utk.edu
2007

Jin-tu Fan
Hong Kong Polytechnic University
tcfanjt@inet.polyu.edu.hk
2008

Xungai Wang
Deakin University
xungai.wang@deakin.edu.au
2009

Garth Carnaby
G.A. Carnaby & Associates, Ltd
carnaby@xtra.co.nz
2010

**Founder's Award Committee**

Phil Gibson (Chair)
US Army Natick Soldier Center
phillip.gibson@us.army.mil
2007

Mary Toney
Albany International Research Company
mary_toney@albint.com
2007

Richard Gregory
Old Dominion University
rgregory@odu.edu
2008

Moon Suh
North Carolina State University
moon_suh@ncsu.edu
2009

**Student Paper Competition and Award Committee**

Julie Chen (Chair)
University of Massachusetts at Lowell
julie_chen@uml.edu
2007

Dominique Adolphe
University of Mulhouse
dominique.adolphe@uha.fr
2008

Haskell Backham
Georgia Institute of Technology
beckham@gatech.edu
2009

Suresh Shenoy
Case Western Reserve University
suresh.shenoy@case.edu
2010

**Honorary/Emeritus Membership Committee**

Bhuvnesh Goswami (Chair)
Clemson University
gbhuven@clemson.edu
2007

Yash Kamath
TRI/Princeton
ykkamath1@aol.com
2008

Bhupender Gupta
North Carolina State University
bs_gupta@ncsu.edu
2009

Stan Ross
stanleyeross@bellsouth.net
2007
Lectureship Committee
Kay Obendorf (Chair)
sko3@cornell.edu
2007

Phil Gibson
US Army Natick Soldier Center
phillip.gibson@us.army.mil
2008

You-Lo Hsieh
University of California at Davis
ylhsieh@ucdavis.edu
2009

Fiber Society Secretary (ex-officio)
Subhash K. Batra
North Carolina State University
subhash_batra@ncsu.edu

2007 Lecturers
Cheryl Gomes
Foster-Miller, Inc.
cgomes@foster-miller.com

Michael Jaffe
New Jersey Institute of Technology
jaffe@adm.njit.edu