



# Garcia MRSEC

Polymers at Engineered Interfaces

SUNY Stony Brook • Polytechnic University • CUNY • North Carolina State University



# Research Scholars Program 2004



This Program is sponsored in part  
by the National Science Foundation.



"The program has no set time limits. Research is a lifetime learning experience, and we hope to remain a resource to our students long after 'graduation'."

- Miriam Rafailovich  
Program Director



Miriam Rafailovich



Jonathan Sokolov

## Research Scholar Program

**The Garcia Center for Polymers at Engineered Interfaces** is a collaboration of eleven academic, industrial, and government laboratories. The Center was founded in 1996 and is named after the late Queens College professor, Narcisso Garcia, a pioneer in the integration of education and research. The Garcia Center is funded by the **National Science Foundation** as part of its Materials Research Science and Engineering Center (MRSEC) program. The goal of the MRSEC is to combine the instrumentation and expertise of the participating institutions into a coordinated research program on polymer interface science. The principal focus areas include thin films, coatings, nanocomposites, self assembled structures, biomaterials, and tissue engineering. These areas address both the fundamental and applied aspects that are relevant to the development of cutting edge enabling technologies in both engineering and medicine. In the community, the mission of the center is to serve as a valuable resource providing easy access for technological assistance to educational and industrial institutions. For information on the numerous programs that are available please see our web site at: <http://polymer.matscieng.sunysb.edu>

**The Research Scholar Program** offers the opportunity for high school teachers and students to perform research on the forefronts of polymer science and technology together with GARCIA faculty and staff. Students work as part of focused research teams and are taught to make original contributions of interest the scientific community. In addition to entering national competitions, the students are encouraged to publish in refereed scientific journals and present their results at national conferences.

Our goal is to convey to the students the excitement we enjoy daily in research. The program has no set time limits. Research is a lifelong learning experience, and we hope to remain a resource to our students long after "graduation".

Miriam Rafailovich  
Professor, Garcia MRSEC

Jonathan Sokolov  
Professor, Garcia MRSEC

# Research Experience For Teachers



Rebecca Isseroff



John Jerome



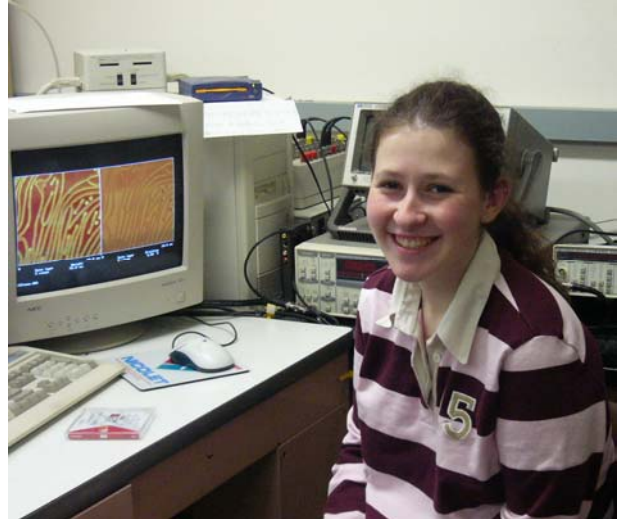
Ronald Occhiogrosso

Not Shown: Tara Sanfilipo

# Research Experience For Undergraduates



Mitchell Fourman



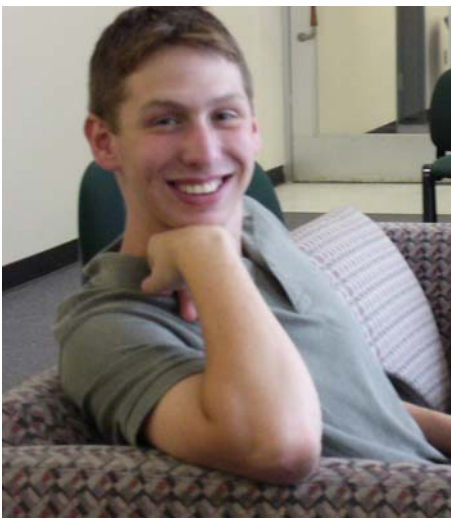
Arielle Galambos



Chananel Gez



Madelyn Ho



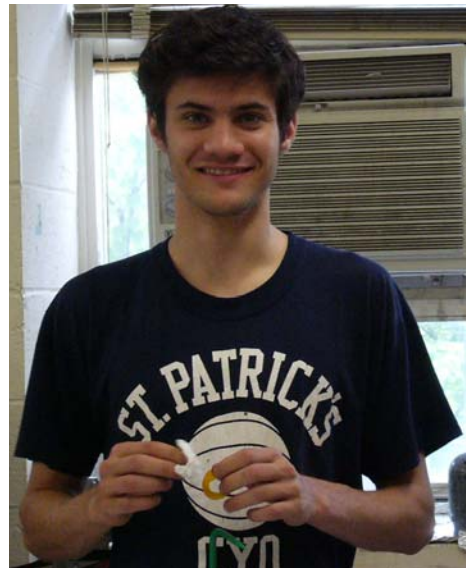
Steven Lubin



Brandy Ma



Aprajita Mattoo



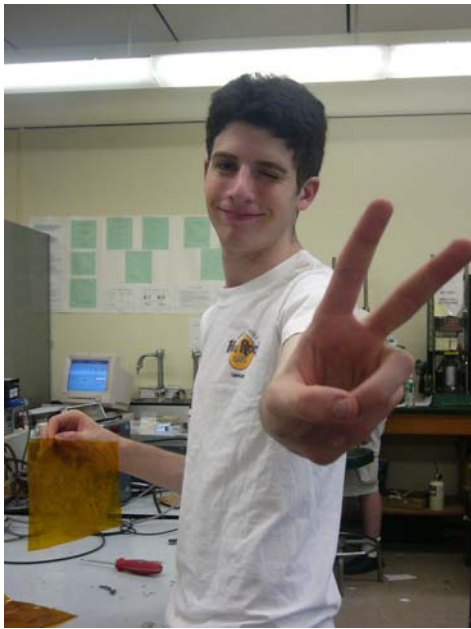
Edmund Palermo



Eric Peterson



Sara Rafailovich-Sokolov



Bradley Schwartz



Lenny Slutsky



Avtar Singh

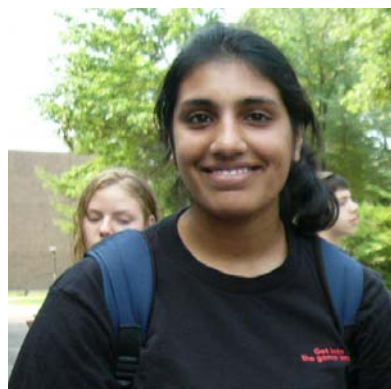


Michael Snow

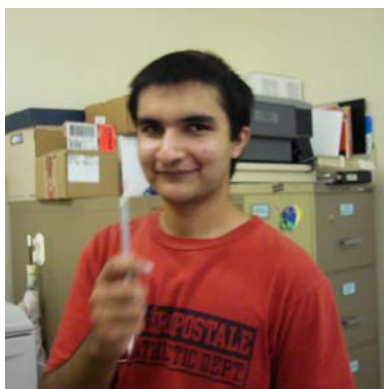


Rivki Perducci

# High School Summer Scholars 2004



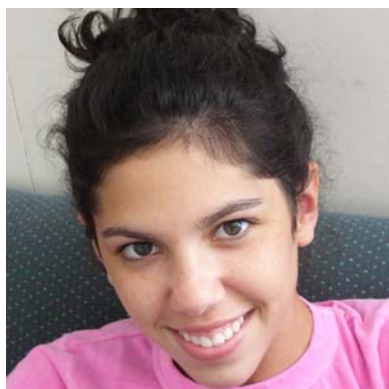
Brinda Alagesan



Ajwad Bajwa



Taylor Bernheim



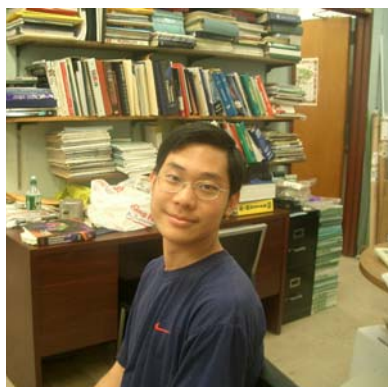
Ayla Bloomberg



Brendan Burns



Jeddy Chen



Alan Chou



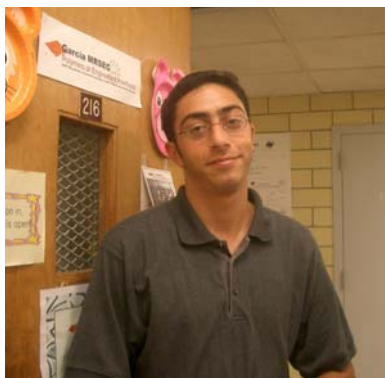
Benjamin Cohen



Victor Daniel



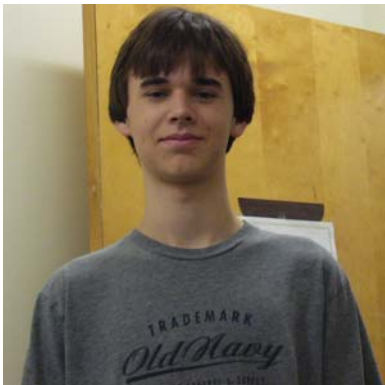
Lynn Dong



Ben Eghbali



Jessica Fields



Dimitri Garbuzov



Jason Goodman



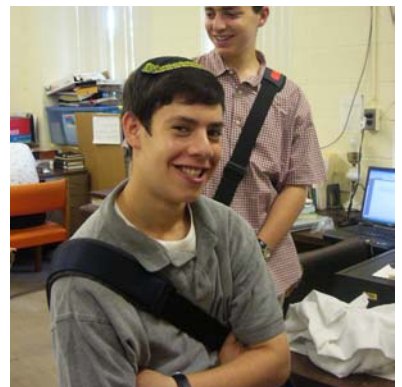
Chelsea Gordon



Daniel Hefter



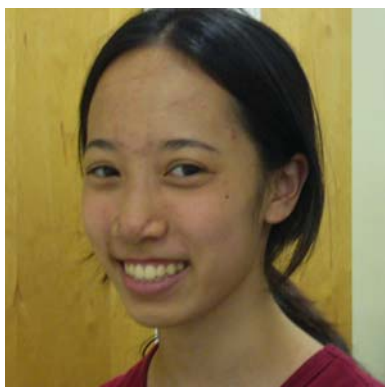
Evan Hertan



Yisrael Herzberg



Joel Herzfeld



Allyson Ho



John Michael Iraci





Ezra Katz



Albert Ko



Stephen Ko



Christopher Mackey



Eric Mansfield



Alan Masand



Amit Mehta



Sagar Mehta



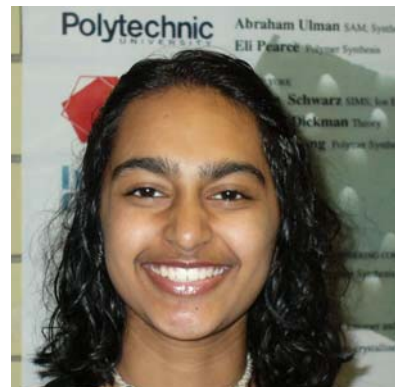
Josh Nissel



Gregory Parnes



Sylvia Qu



Aditi Ramakrishan



Andrew Scheur



Matthew Schlossberger



Jonathan Scholl



Yonatan Schawb



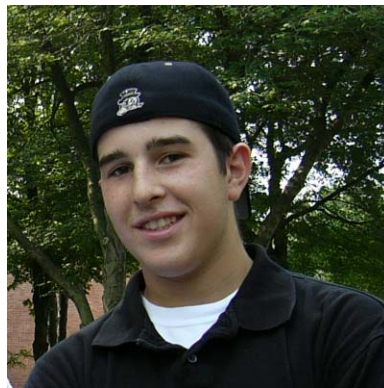
Anna Shneidman



Aryeh Sokolov



Vandana Sood



Tom Strand



Alex Thachara

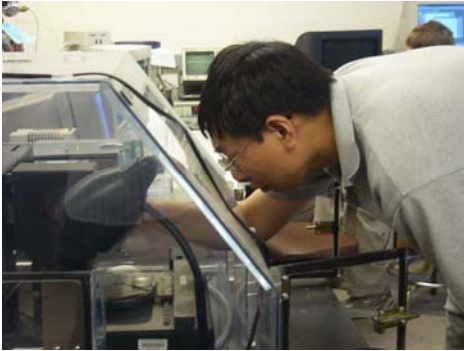


Ming-Jie Wang



Tiffany Yeh

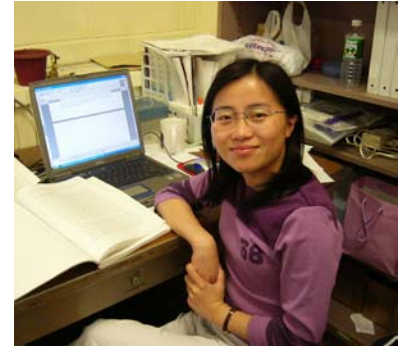
# Staff and Grads



Dr. Shouren Ge



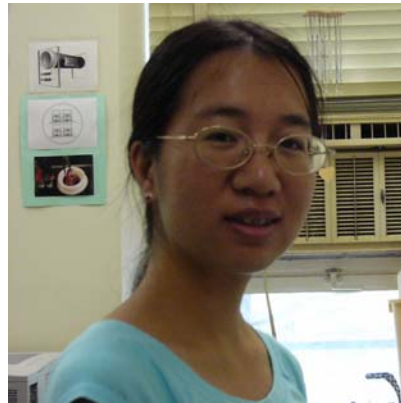
Lourdes Collazo



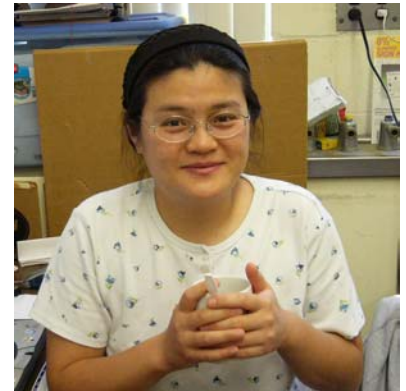
Yuan Sun



Dr. Nadine Pernodet



Yantian Wang



Xiaohua Fang



Harry Xavier



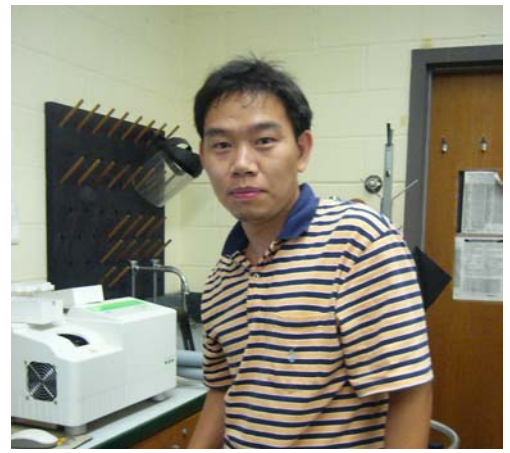
Bingquan Li



Song Feng Li



E Guan



Mayu Si



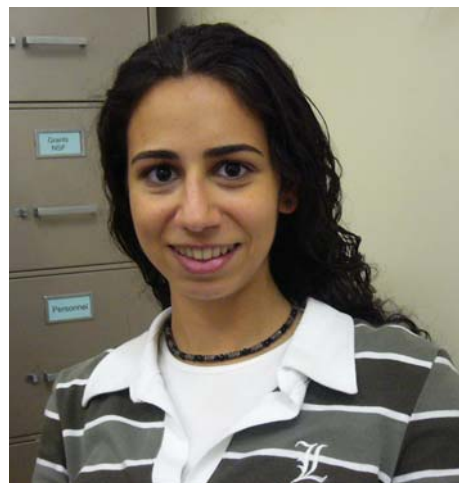
Yuan Ji



Karthikeyan Subburaman



Elaine Lerum



Bracha Peled



# Summer Scrapbook

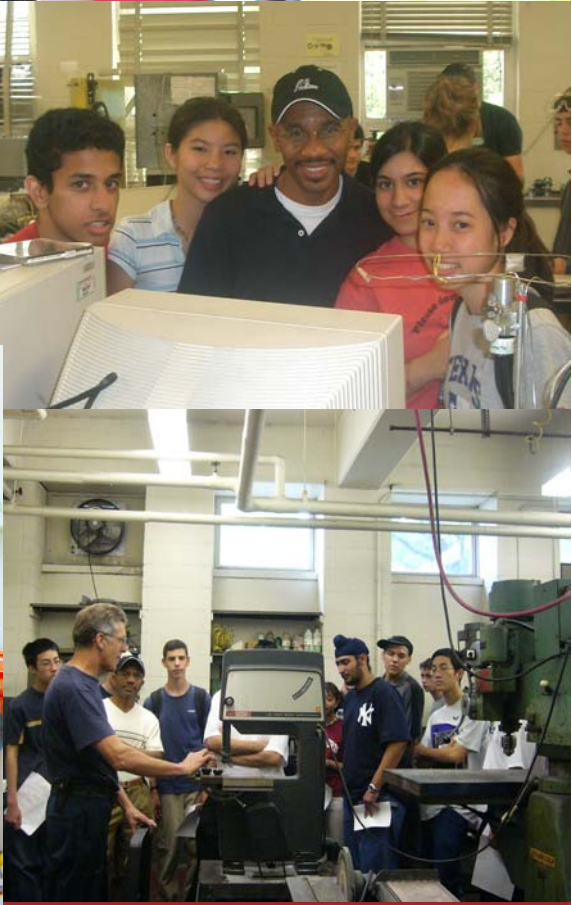
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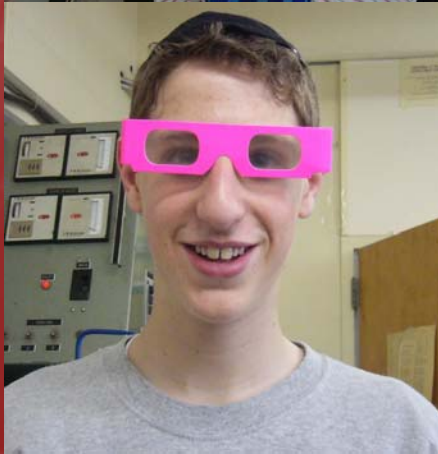
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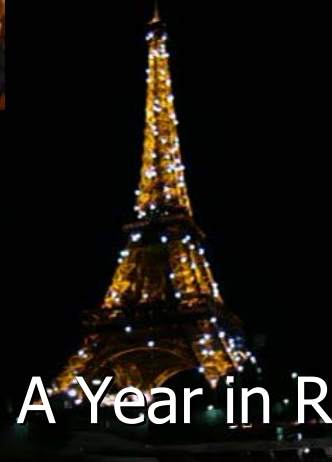
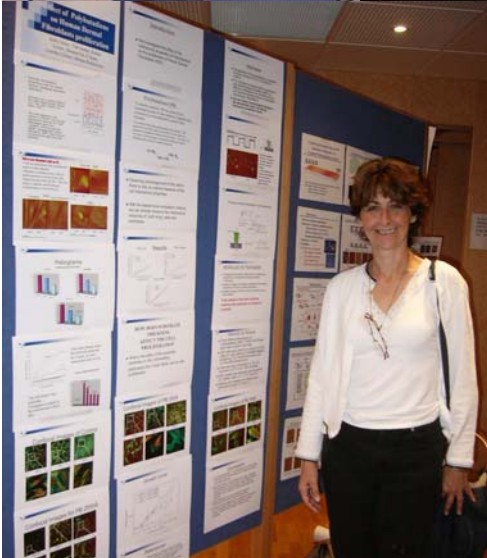




# Eyewear: Garcia Style







A Year in Review

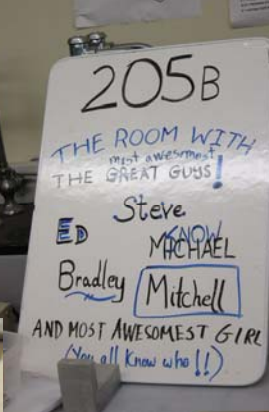
# Interesting Hand Gestures





פרנסה

"Who needs love when You have PIZZA BAGELS?"



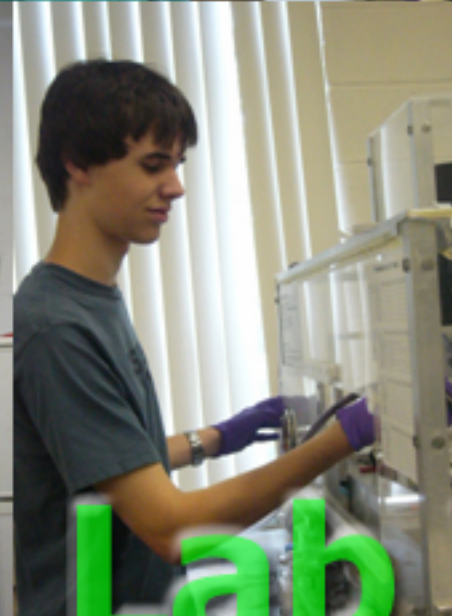
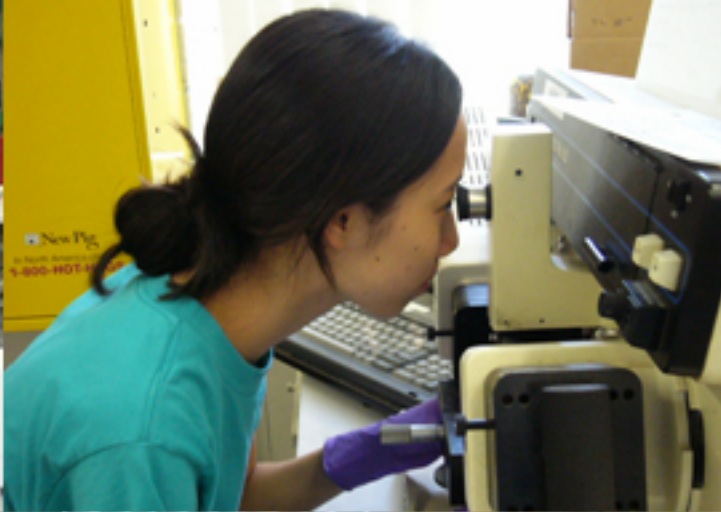
Arielle with the VSM in room 117 in 1998



# Thin Films v. Bulk Softball Game

## Thin Films win by a bulk margin!!





# Lab Work





# Canoe Trip on the Nissequogue River





# Going Insane!





The Garcia Center invites you to attend the

# Annual Summer Symposium

of the  
Research Scholars Program

which will take place

at  
August 16, 2004  
10:00 AM

in the  
Student Activities Center Auditorium

The scientific program will be followed by

a buffet luncheon and artistic program arranged by the students.

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## Partial List of Symposia

- Flame-Resistant Polymers
- Polymeric Crystals
- Self-Assembled Structures
- Bio-Materials Engineering
- DNA Surface Electrophoresis
- Homeland Security:
- Dynamic Facial Recognition
- Nano Composites
- Supercritical Fluid Processing
- Kinetics, Mineralization, and Self-Assembly
- Cellular Micro-Mechanics, Proliferation, and Dynamics

Guest Speaker

Professor Harry Gafney

Director of CUNY Photonics Program



RSVP on or before August 16

(631) 632-6097

or e-mail

miriam.rafalovich@sunyusb.edu

## Sponsors

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Special thanks to:  
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for summer refreshments



## Garcia MRSEC Polymers at Engineered Interfaces

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Research Scholars Program 2004

## **Garcia Research Scholar Symposium, August 16, 2003**

### **Plenary Lecture: Prof. Harry Gafney , Department of Chemistry, Queens College, CUNY**

#### **Session 1: Cell Proliferation, Adhesion & Dynamics**

**Chairs:** *Madelyn Ho*

Ajwad Bajwa, Ming-Jie Wang	Analysis of Normal Dermal Fibroblast Surface Conformation on SPS and PB Substrates
Ezra Katz, Eric Mansfield	Substrate Optimization of Hyaluronic Acid Hydrogels for Wound Healing Applications
Anna Shneidman	Effects of Aging on Extracellular Matrix and Cytoskeleton Formation of Human Dermal Fibroblasts
Alan Masand, Tiffany Yeh	Growth Modulation of Dermal Fibroblasts by Polybutadiene and Clay Modified Solutions
Lynn Dong	A Novel Technique for Accelerated Tissue Growth using Supercritical Carbon Dioxide

#### **Session 2: Surface Protein Adsorption & Extracellular Matrix**

**Chair:** *Apra Mattoo*

Ayla Bloomberg	The Effect of Glucose on Fibroblasts and Extracellular Matrix Proteins as a Model for Impaired Wound Healing in Diabetics
Stephen Ko	Microcontact Printing of Self-Assembled Monolayers by Means of Polyolefin Stamps
Jessica Fields	Substrate-induced Protein and Cell Organization and the Investigation of Cancer Cells
Christopher Mackey	An Analysis of the Interactions Between the Extra-cellular Matrix Proteins and Glycosaminoglycans Fibronectin, Elastin, and Heparin and the Effects of Biomineralization Through Calcium Carbonate

#### **Session 3: Self Assembled & Nanostructured Films**

**Chair:** *Arielle Galambos*

Taylor Bernheim	Nanopatterns to Control Cell Mechanics
Victor Daniel, Chananel Gez	Croslink Density in Thin Polymer Films
Ben Eghbali, Dmitri Gurbazov	Self Assembled Structures of Poly(styrene- <i>b</i> -ferrocenyldimethylsilane) (PS- <i>b</i> -FS) Blended with PS-PMMA

#### **Session 4: DNA Surface Electrophoresis**

**Chairs:** *Avtar Singh, Eric Petersen*

Brinda Alagesan	An Exploration of the Surface Kinetics of Mega-base Pair DNA
Amit Mehta	Surface Electrical Transport of Mega Basepair-Size DNA Molecules

#### **Session 5: Supercritical Fluid Processing of Thin Films**

**Chair:** *John Jerome*

Brendan Burns, Tom Strand	The Effect of Exposure to Supercritical CO <sub>2</sub> and Confinement on Morphology of Thin-Film Polyethylene
Chelsea Gordon, Sylvia Qu	The Effects of Supercritical Carbon Dioxide on the Segregation of Polymer Blends: A Novel Method of Substance Extraction for Improved Commercial Applications
Allyson Ho, Alex Thachara	The Effects of Nanoparticles (Clay, Gold, Carbon Black, POSS) On Selective Permeability (O <sub>2</sub> , CO <sub>2</sub> , SF <sub>6</sub> ) of Thin Film Membranes Using Supercritical Fluid
Jonathan Scholl	Crystallization of EVA Thin Films Using Supercritical Carbon Dioxide

**Session 6: Polymer Inorganic Nanocomposites**Chair: *Michael Snow*

Vandana Sood, Sagar Mehta	POSS Nanocomposites as Viscosity Modifiers of Polymer Thin Films
Benjamin Cohen, Josh Nissel	Analyzing Adhesion At Polymer Interfaces Containing Filler Mixtures
Matthew Schlossberger	Electrospinning of Polystyrene and POSS Nanofibers

**Session 7: Flame Retardant Nanocomposites**Chairs: *Mitchell Fourman*

Daniel Hefter, Aryeh Sokolov	Creating an Environmentally Healthy Self-Extinguishing Polymer Blend
Evan Hertan	Self-extinguishing Polyolefin Rubber/Organoclay Nanocomposites
Albert Ko, Jeddy Chen	Achieving Fire-Resistance in Polymer Blends by using Clay and Bromine Mixtures

**Session 8: Supercritical Processing of Blends**Chair: *Ed Palermo*

Joel Hertzfeld	The Effects of Supercritical Carbon Dioxide on Biodegradability
John Michael Iraci	Tri-blends: A Novel Procedure to Create Ideal Plastics using Recycled Materials Exposed to Supercritical Carbon Dioxide
Gregory Parnes	Effects of Supercritical Carbon Dioxide on the Mechanical Properties of PB-PS and PS-EVA Blends with Clay Nanocomposites

**Session 9: Biomedical and Miscellaneous Applications**Chair: *Sara Sokolov*

Jason Goodman	Investigations for Facial Recognition through Digital Image Speckle Correlation
Alan Chou	The Relationship Between Cells Traction Forces and their Growth Rate
Andrew Scheur	NY Orionis: The Nature of an EXor Star

**Session 10: Nanoparticles, Synthesis & Side Effects**Chairs: *Rebecca Isseroff*

Aditi Ramakrishnan	Cytotoxicity of Citrate Covered Gold Nanoparticles in Dermal Fibroblasts
Yonatan Schwab, Yisrael Herzberg	Synthesis of Palladium Nanoparticles for Embedding in a Polymer Matrix (for Use in Catalysis and Hydrogen Storage)

**Luncheon****Musical program: John Jerome****Video Program: Sylvia Qu**

# Session 1: Cell Proliferation, Adhesion, & Dynamics

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***Chairs: Madelyn Ho, Apra Mattoo***

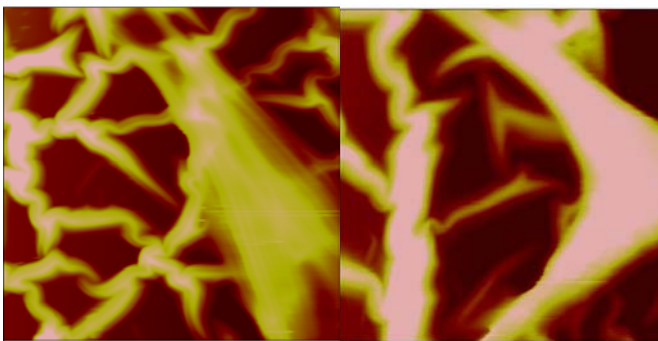
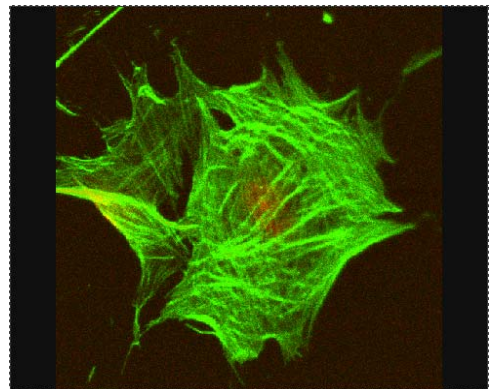
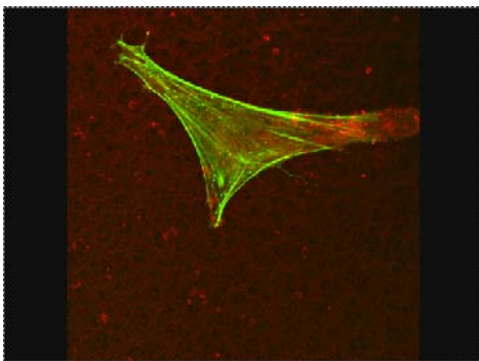
Ajwad Bajwa, Ming Wang

Ezra Katz, Eric Mansfield

Anna Shneidman

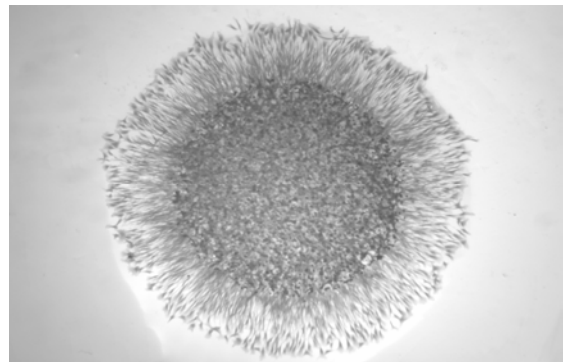
Alan Masand, Tiffany Yeh

Lynn Dong



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# Substrate Optimization of Hyaluronic Acid Hydrogels for Wound Healing Applications

Eric Mansfield, Smithtown High School

Ezra Katz, Mestiva Ateres Yaakov

Every year, over twelve million people suffer from chronic wounds characterized by impaired tissue formation and remodeling. Previous treatments for acute wounds have failed to address the complexity of chronic wounds. In order to construct an appropriate biomaterial for the healing of chronic wounds, the material must be able to support successful tissue repair and regeneration, which is partially determined by the viscoelastic properties of the hydrogel [1]. Therefore we propose to use thiol functionalized hyaluronic acid (HA-DTPH) conjugated with recombinant fibronectin functional domains (rFNfd) as a scaffold to facilitate the healing of chronic wounds [2]. The thiol groups are covalently crosslinked with poly(ethylene glycol) diacrylate. By varying the ratio between the number of free thiols and acrylate groups of the crosslinker molecule, the rigidity of the hydrogel can be controlled. Thus we derived three crosslinking densities: 2 to 1, 6 to 1, and 12 to 1. The functional response of adult human dermal fibroblasts (AHDFs) was investigated as a function of crosslinker density using six assays: migration, proliferation, tractional force, cell rigidity via AFM, spreading and arrangement of actin cytoskeleton.

In the migration assay, a relationship was seen that AHDF migration was enhanced as the substrate stiffness increased. Additionally, the proliferation assay demonstrated that AHDFs prefer the 2-1 hydrogels rather than the 6-1 or 12-1. This was verified by cell counting after 1, 2, 3 and 4 day incubation period. Tractional force applied by the AHDFs was quantified using the “DISC” method; images of spread and relaxed AHDFs used for DISC analysis were acquired using a Leica Confocal microscope as a function of hydrogel deformation. Extent of hydrogel deformation was determined through the movement of fluorescent 40 nm beads embedded in the HA hydrogel. Levels of isometric tension within the living AHDFs were measured using AFM under the Shear Modulation Force Microscopy (SMFM). In the cell spreading assay the AHDFs had optimal spreading on the more rigid substrate indicating that the cells prefer a stiffer substrate. Arrangement of actin cytoskeleton was determined viewing the organization of the Actin fibers under the Confocal microscope. Data from all the functional assays indicate that increasing mechanical properties is important for the AHDFs to retain their normal morphology and function. Ultimately, this data will provide insight into the optimal mechanical properties of hyaluronic acid hydrogels capable of sustaining invasive cell migration in chronic wounds.

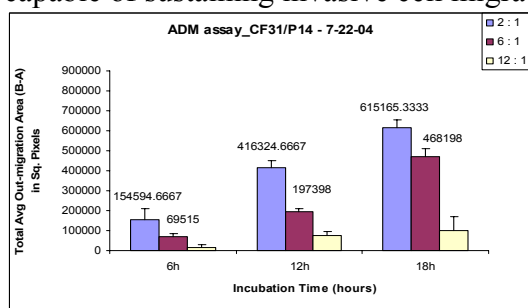


Figure 2: Chart of Human Dermal Fibroblast Migration

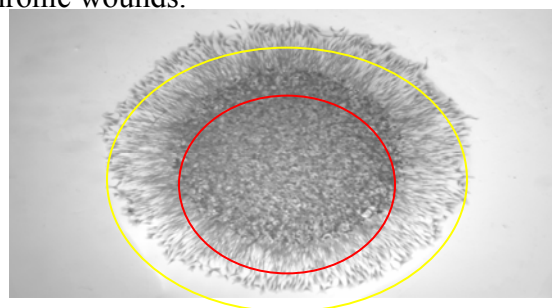


Figure 2: Image where the red area indicates original location of cells compared to the yellow area which is the position of the cells after migration

<sup>1</sup> Ingber et al. Models of cytoskeletal mechanics of adherent cells. Biomechan Model Mechanobiol. 2002

## Analysis of Normal Dermal Fibroblast Surface Conformation on SPS and PB Substrates

Ming Wang, John Glenn High School

Ajwad Bajwa, Half Hollow Hills High School West

Madelyn Ho, Nadine Pernodet and Dr. Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

The extracellular matrix (ECM) is a network of protein and polysaccharide macromolecules that provide signaling cues used to regulate cell behavior and direct functions related to tissue formation. The composition of the ECM controls cell shape, motility, growth, survival and differentiation. It has been previously shown that cells adjust to these mechanical surface properties as closely as possible, and we are testing this ability for normal and cancer cells. Moreover, we want to follow the ECM formation in Sulfonated Polystyrene as it is closely related to cell mechanics. An important protein within the ECM, fibronectin, is involved in cellular migration during wound healing and development. Fibronectin can be used to promote attachment, spreading, and proliferation of cells. N. Pernodet et al. have found that a fibronectin matrix can be grown on a Sulfonated Polystyrene (SPS) surface.<sup>1</sup> It has been proposed that cancer cells cannot conform to surfaces and maintain tensegrity as normal cells do.<sup>2</sup> We know little about mechanics of cells in general and even less for cancer cells. In order to answer this question, we used Polybutadiene (PB) films, spun at varying thicknesses giving mechanical properties to the surfaces. As the thickness increases, the surface becomes softer.

A prepared solution of SPS was spun cast onto hydrophilic silicon wafers cleaned using the shiraki method. Solutions of varying concentrations of PB were spun cast onto hydrophobic silicon wafer. Polybutadiene wafers were annealed in the vacuum oven for 24 hours at 170 degrees Centigrade. SPS wafers were annealed for 24 hours at 150 degrees Centigrade. Following dewetting normal dermal fibroblasts were plated onto each of two wafers for each polymer concentration and incubated. After incubation, the cells were stained and observed under the confocal microscope for signs of ECM development.

PB films were spun at 350 angstroms, 450 angstroms, 850 angstroms, 1,500 angstroms, and 3,400 angstroms and annealed overnight. SPS surfaces were spun at 30 mg/ml concentration at 208 angstroms and were also annealed. Normal dermal fibroblasts were plated on the surfaces and incubated at 37 degrees Celsius at 100% humidity and 25% CO<sub>2</sub>.

Later, we will observe cancer cell surface conformation on polymer substrates as compared to normal cells. We hypothesize that mechanical response from cancer cells will be different, as well as their actin organization.

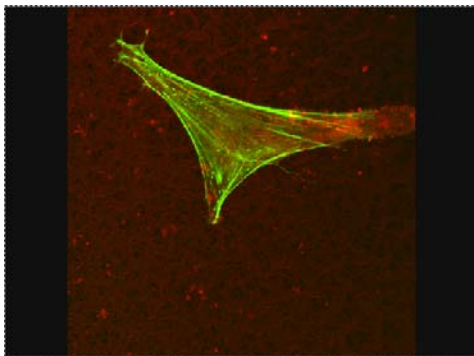


Figure 1: Normal Dermal Fibroblast on SPS; Actin Fibers can be observed.

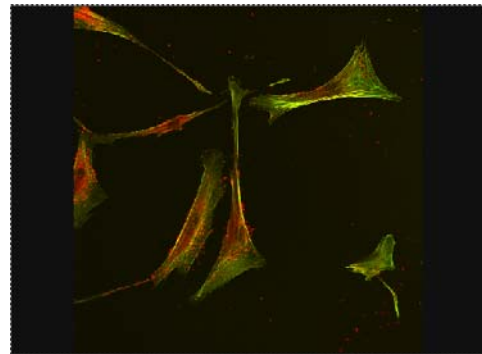


Figure 2: Group of Normal Dermal Fibroblasts on PB

<sup>1</sup> Pernodet, N.; Rafailovich, M.; Sokolov, J; Xu, D.; Yang, N. L.; Mcleod, K. "Fibronectin fibrillogenesis on sulfonated polystyrene surfaces." *Journal of Biomedical Materials Research* **2003**, 4, 684-692

<sup>2</sup> Ingber, D. "Tensegrity I. Cell structure and hierarchical systems biology." *Journal of Cell Science* **2003**, 116, 1157-1173.

## Effects of Aging on Extracellular Matrix and Cytoskeleton Formation of Human Dermal Fibroblasts

Anna Shneidman, Academy for the Advancement of Science and Technology  
Madelyn Ho, Harvard University

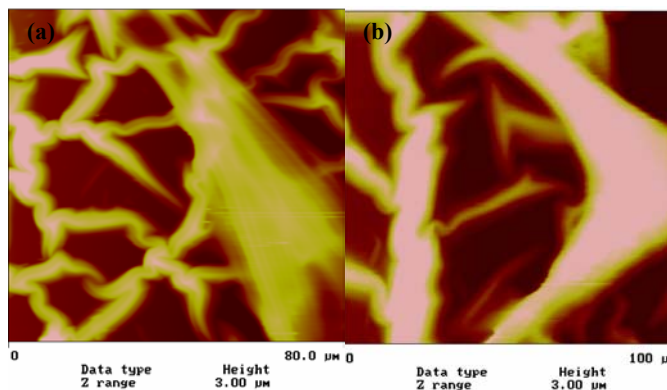
Karthikeyan Subburaman, Nadine Pernodet, Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

In face of a shortage of available tissues and adverse patient immune response to grafts<sup>1</sup>, an alternative to tissue grafts is desirable. The tissue engineering at hand seeks to mimic the natural extracellular matrix (ECM) that provides a supportive framework for tissue cells, directs cell mechanics through the cytoskeleton (cell morphology), and controls cell proliferation, adhesion, propagation, differentiation, and apoptosis.<sup>2</sup> Naturally, many factors, such as aging, pollutants, glucose concentration, etc., influence ECM functionality and cytoskeleton arrangement. In our research we study age-related alterations in the ECM and cytoskeleton as well as the possibility to control ECM by varying polymer thickness on a silicon substrate.

Labat<sup>3</sup> suggests that the aging process modifies ECM proteins such as fibronectin and elastin, and consequently alters the actin organization in the cytoskeleton<sup>4</sup>. Specifically, the uncontrolled non-enzymatic reaction of sugars and proteins (glycation) and protein crosslinking increase with aging.<sup>2</sup> As human longevity increases,<sup>5</sup> it is necessary to understand the effects of glycation and crosslinking on protein hardness and arrangement in the ECM and cytoskeleton. The results of these studies may clarify symptoms associated with the aging process and lead to novel methods of determining cell lifespan.

In our research we investigate age-related protein modification and cell response to different polymer thickness using atomic force (AFM) and confocal microscopies. Silicon wafers with spin-cast 28% sulfonated polystyrene (SPS) were incubated for 24 h with female human dermal fibroblasts 24, 31 (young) and 85 (old) yrs. Upon starvation, the cells produced a rich ECM, which was observed using AFM. The topographical and lateral force data were used to compare the complexity and rigidity of the ECM (fig.1). Furthermore, the cells were stained with Alexa Fluor 488, an actin-specific fluorescent dye to detect variations in actin organization of different ages by confocal microscopy. To study substrate response, Si wafers with spin-cast Polybutadiene (PB) of 200 and 2000 Å were incubated with young and old cells. Young vs. old cell adjustment to polymer hardness was observed with the AFM.

Lifespan predictions for a given cell based on comparative studies with middle-aged and malignant cells are forthcoming. Applications in tissue engineering and healing for the understanding of pathological tissue formation will enable the creation of viable tissues and medicines to counter the effects of aging and other malignancies.



**Figure 1.** AFM topographical images show that 31 year old cells (a) are shorter than 85 year old cells (b) and are surrounded by a more complex matrix.

<sup>1</sup> Kimball, J. "Organ Transplants" *Kimball's Biology Pages*. July 20, 2004. <<http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/T/Transplants.html#problems>> 2004.

<sup>2</sup> Pernodet, N.; Rafailovich, M.H.; Sokolov, J.; "Protein Self-Organization on Patterened Surfaces."

<sup>3</sup> Labat-Robert, J.; "Cell-matrix interactions in aging: role of receptors and matricryptins." *Ageing Research Reviews*. **2004** Vol. 3, Issue 2. 233-247

<sup>4</sup> Reed, M.J. "Impaired Migration, Integrin Function, and Actin Cytoskeletal Organization in Dermal Fibroblasts from a Subset of Aged Human Donors." *Mechanisms of Ageing and Development*. **2001** Vol. 22, Issue 22. 1203-1220.

## Growth Modulation of Dermal Fibroblasts by Polybutadiene and Clay Modified Solutions

Alan Masand, Locust Valley High School

Tiffany Yeh, Syosset High School

Eleanor Lerum, Apra Mattoo, Lourdes Collazo, & Miriam Rafailovich  
Department of Materials Science and Engineering, Stony Brook University

Dermal fibroblasts play an active role in the wound healing process. They secrete an extracellular matrix rich in collagen, a protein fiber that closes wounds by activating the clotting mechanism and allowing for new tissue to form and regenerate. However, excessive production of collagen can lead to undesirable keloids and hypertrophic scars.<sup>1</sup> Polybutadiene (PB), an elastic polymer, is a compatible surface for fibroblast cell growth. The addition of water soluble clay, natural montmorillonite (Cloisite Na<sup>+</sup>), improves cellular conditions by accelerating the spontaneous conversion of fatty acids into vesicles<sup>2</sup>. In order to regulate collagen production, fibroblasts were plated onto polymer thin films of polybutadiene and various clay solutions.

Different concentrations of PB were dissolved in toluene in order to spin polymer thin films at various thicknesses.<sup>3</sup> These samples, spun cast onto glass, were annealed in the oven for 15 hours at 170° C, then plated with dermal fibroblasts. This procedure was repeated with the montmorillonite particles in the media and PB-Cloisite 6A nanocomposites. Cell counts were conducted for each condition and analyzed through growth curves. The samples were also observed under the confocal microscope to determine the cells' adherence and reaction to the thin polymer films. As seen in Figures 1 and 2, the fibroblasts' cytoskeletons were stained green with Alexa Flour and the nuclei were stained red with propidium iodide in order to visualize cell structure on the surfaces.

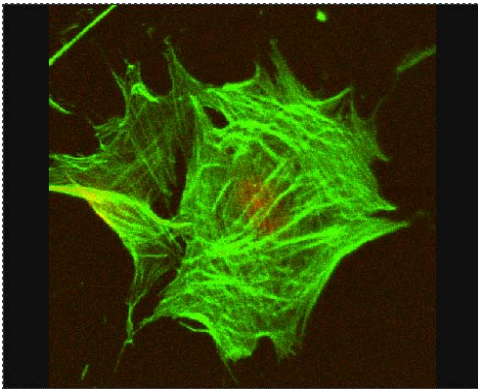


Figure 1: Dermal fibroblasts on glass substrate

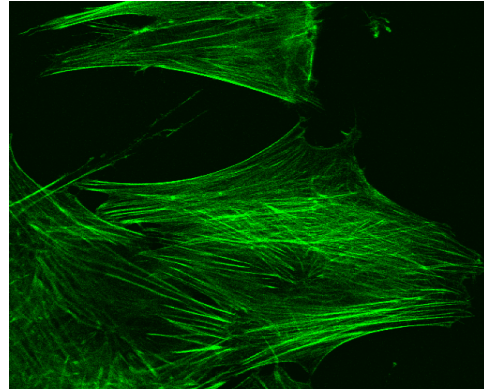


Figure 2: Dermal fibroblast on PB film of 800 Å on day 7

<sup>1</sup> Risbud, M.; Hardikar, A.; Bhonde, R. *Growth Modulation fibroblasts by chitosan-polyvinyl pyrrolidone hydrogel: Implications for wound management?* 2000. *J. Biosci.* Vol 25:1. Pgs 25-31.

<sup>2</sup> Hanczyc, M.; Fujikawa, S.; Szostak, J.; *Experimental Models of Primitive Cell Components: Encapsulation, Growth, and Division.* 2003. *Science.* Vol 302. Pgs 618-622.

<sup>3</sup> Li, J.; Singh, A.; Shapovalov V.; Bhupinder, S.; Isakova, M.; Schwarz, S.A.; Rafailovich, M.H.; Sokolov, J. *Measurements and Model for the Thickness of Spin Coated Polybutadiene and Polystyrene Films.* 2003.



# A Novel Technique for Accelerated Tissue Growth using Supercritical Carbon Dioxide

Lynn Dong, Locust Valley High School

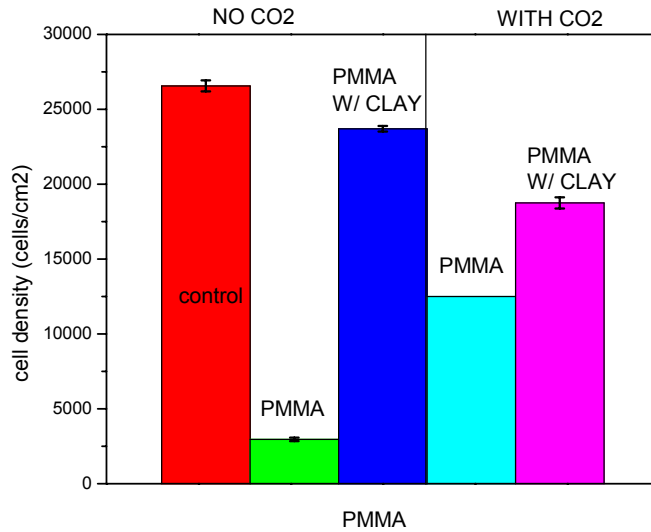
Aprajita Mattoo, Columbia University

Mitchell Fourman, Miriam Rafailovich, Lourdes Collazo, Stony Brook University

The advent of supercritical fluids as universal co-solvents has opened up new avenues of materials and cell research. Used industrially for decaffeination of coffee beans, extraction of cocoa butter, and dry cleaning, supercritical carbon dioxide has also been shown experimentally to increase the interfacial width and thus the compatibility of polymer blends<sup>1</sup>. Koga et al. have also shown that porosity increased due to the swelling of polymers in the supercritical medium<sup>2</sup>. Here we show that supercritical carbon dioxide aids in the substantial increase in cell growth on Poly(methyl methacrylate) (PMMA) spun cast thin films.

In addition we also experimented with the addition of Cloisite 6A clays. We found that they dramatically increase the cell proliferation on PMMA, but have only minimal difference when the clay nanocomposite films are exposed to ScCO<sub>2</sub>.

Samples of pure PMMA and PMMA/clay (Cloisite 6A) were spun cast onto cover slips and annealed at 170 °C. Some of the samples were then exposed to supercritical carbon dioxide (SC CO<sub>2</sub>) at 36 °C and 1450 psi(g), along the density fluctuation ridge. Mouse osteoblasts were plated and the cells were counted after 3 days. The results are shown in table 1, where we can see that the cell count is nearly five times as high when clays are added in the substrate and three times as high when exposed to ScCO<sub>2</sub>. On the other hand, exposure to ScO<sub>2</sub> slightly decreases the cell count on the PMMA/Clay films. These results are applicable to modification of the polymer used in hip implant surgery.



**Table 1:** Histogram of cells incubated for 3 days on PMMA substrates with different treatments.

<sup>1</sup> Fourman, M. Palermo E. Lubin S. Si M. Rafailovich M. Sokolov J. *Increasing the Compatibility of Polymer Blends using Supercritical Fluids* APS March Meeting (Abstract), 2004.

<sup>2</sup> Koga, T. Seo Y-S. Hu, X. Shin, K. Zhang, Y. Rafailovich, M H. Sokolov, J C. Chu, B. Satija, S K. *Dynamics of Polymer Thin Films in Supercritical Carbon Dioxide* Europhys. Lett., 60(4), pp. 559-565 (2002)

# Session 2: Surface Protein Adsorption & Extracellular Matrix

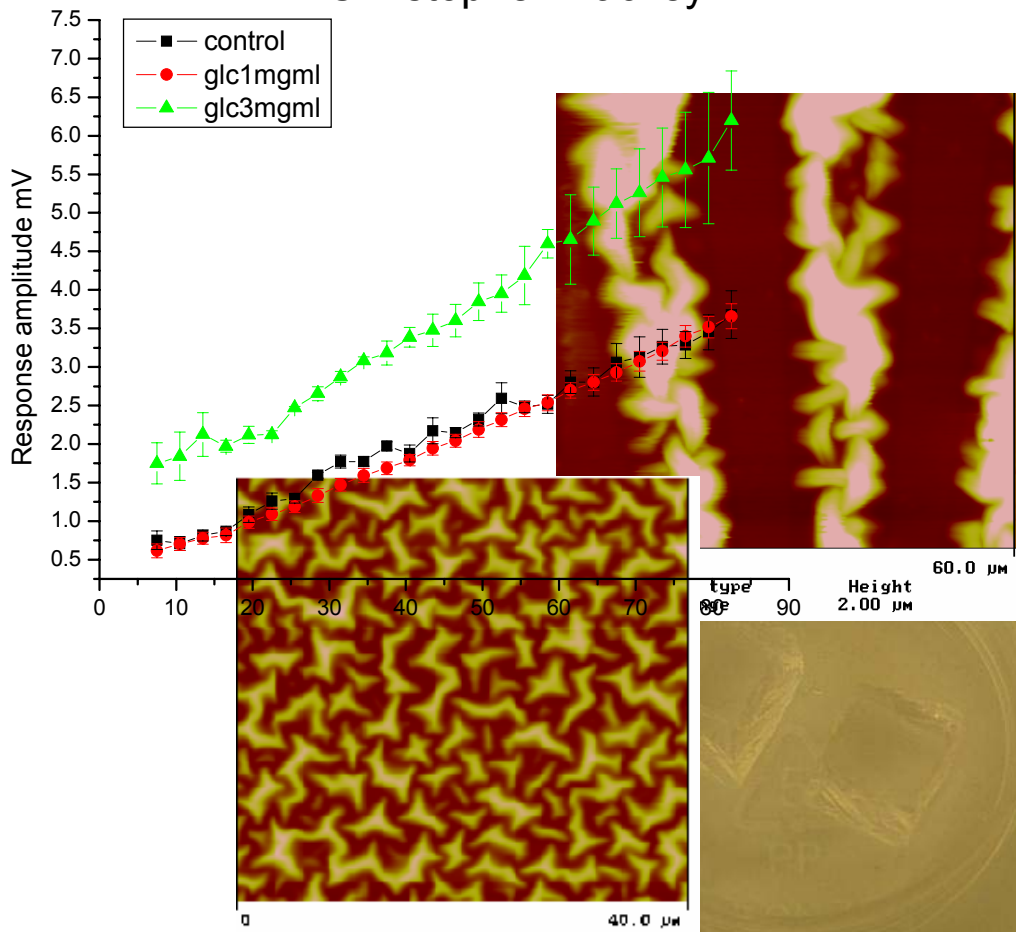
**Chair: Apra Mattoo**

Ayla Bloomberg

Jessica Fields

Stephen Ko

Christopher Mackey



## The Effect of Glucose on Fibroblasts and Extracellular Matrix Proteins as a Model for Impaired Wound Healing in Diabetics

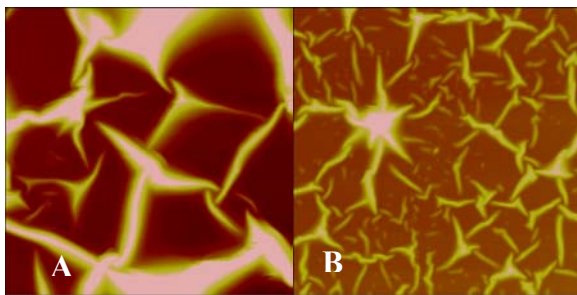
Ayla Bloomberg, Northport High School

N. Pernodet, M. Rafailovich, S. Ge, M. Ho, X. Fang, Karthikeyan Subburaman, Department of Materials Science and Engineering, Stony Brook University

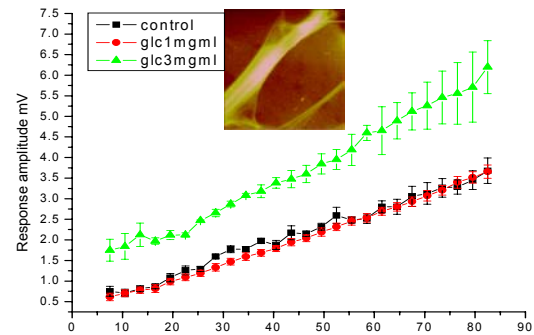
It is known that normal wound healing involves the interaction of ECM proteins, such as fibrinogen, with fibroblasts.<sup>1</sup> Fibrinogen, produced by the liver, is a plasma protein that is converted into an insoluble fibrin gel following a cut. This interaction not only results in the formation of a clot that will reduce blood loss but also appears to play a critical role in the tissue repair necessary to heal a wound. Each stage of wound healing in diabetics is impaired. The reasons for these impairments in diabetic wound healing are presently unclear. The objective of this research is to observe the effects of glucose on the human fibroblasts and their extra cellular matrix (ECM). In diabetics, excess glucose causes glycosylation, a reaction between glucose and the ECM, specifically its proteins, causing non healing wounds. Therefore, the structure of the fibroblast, as well as the ECM, at the sight of the wound is believed to change as a result of this reaction.

An in-vitro model of an ECM can be reproduced by spinning sulfonated polystyrene (SPS) 28% onto a silicon (Si) wafer.<sup>22</sup> Since diabetes mellitus is diagnosed when levels of blood glucose are constantly 2 mg/ml or higher than normal physiologic levels, the effect of glycosylation on fibroblasts, fibrinogen, and the natural ECM can be studied by adding various concentrations of glucose to the solution (0, 1, 2, and 3 mg/ml).

At the 3 mg/ml glucose concentration, fibroblasts had a higher lateral response as measured by the AFM, indicating that these samples became softer than the control (Graph with inset). The samples of fibrinogen at the 3 mg/ml glucose concentration hardened after the second day of incubation (Figure 1). However, as the incubation period increased, the fibers became softer as a result of excess glucose absorbing on the surface. In conclusion, it is apparent that glycosylation is hardening proteins. Similarly, excess amounts of glucose significantly changed the mechanics of the cell. These mechanical differences might be responsible for impaired wound healing in diabetes.



**Figure 1:** (a)Fibrinogen control (b) Fibrinogen and glucose 3mg/ml [AMF images have a scale of (100um)]



**Figure 2:** Lateral response of cells and glucose [inset: fibroblast control]

<sup>1</sup> Makogonenko, Evgeny, Tsurupa, G., Ingham, K., Medved, L. *Interaction of Fibrin(ogen) with Fibronectin: Further Characterization and Localization of the Fibronectin-Binding Site.* Biochemistry 2002;41:7907-7913.

<sup>2</sup> Pernodet N, Rafailovich M, Sokolov J, Xu D, Yang NL, McLeod K. *Fibronectin fibrillogenesis on sulfonated polystyrene surfaces.* J Biomed Mater Res. 2003; 15:64A(4):684-92.

## Microcontact Printing of Self-Assembled Monolayers by Means of Polyolefin Stamps

Stephen Ko, Ward Melville High School

M. Rafailovich, J. Jerome, Department of Materials Science and Engineering, Stony Brook University

Microcontact Printing ( $\mu$ CP) is an experimentally simple and cost-effective method of creating micrometer structures on surfaces. It can serve as a simpler method of producing micro-sized or even nano-sized devices such as circuitry for electronics.  $\mu$ CP has the ability to organize microcrystals or produce microstructures on surfaces.

The procedure for  $\mu$ CP is shown in Figure 1. An elastomeric stamp is created through a master made through standard photolithography. Using this stamp, normally made from poly(dimethylsiloxane) (PDMS) (Shown in Figure 2), self-assembled monolayers (SAMs) can be deposited on a surface. One such application is the stamping of alkanethiols on a gold surface to create microstructures of gold on silicon.<sup>1</sup>

This study discusses the use of polyolefin plastomers (POPs), a relatively new class of materials, as a replacement of PDMS in  $\mu$ CP of alkanethiols on a gold surface. POP stamps have already been shown to be an effective replacement for PDMS when stamping proteins or block copolymers and have shown superior performance to that of PDMS stamps.<sup>2</sup>

A comparative study on quality of printing will be run between the new POP stamps and the conventional PDMS stamps when  $\mu$ CP on gold surfaces. POP stamps will also be tested for use of submicrometer-printing with alkanethiols.

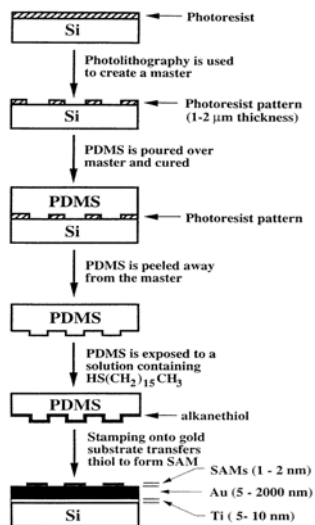


Figure 2: Two conventional PDMS stamps made by  $\mu$ CP.

<sup>1</sup> Whitesides, George M. Microcontact printing of self-assembled monolayers: applications in microfabrication. *Nanotechnology*, **1996**, 7, 452-457.

<sup>2</sup> Csucs, Gabor; Künzler, Tobias. Microcontact Printing of Macromolecules with Submicrometer Resolution by Means of Polyolefin Stamps. *Langmuir*, **2003**, 19, 6104-6109.

\*Figure 1 taken from <sup>1</sup> Whitesides, George M. Microcontact printing of self-assembled monolayers: applications in microfabrication. *Nanotechnology*, **1996**, 7, 452-457

## Substrate-induced Protein and Cell Organization and the Investigation of Cancer Cells

Jessica Fields, Jericho High School

Nadine Pernodet, Miriam Rafailovich, Department of Materials Science and Engineering,  
Stony Brook University

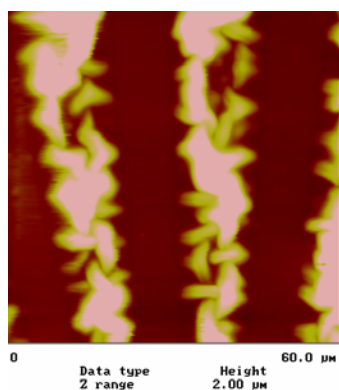
Madelyn Ho, Harvard University

Lenny Slutsky, Duke University

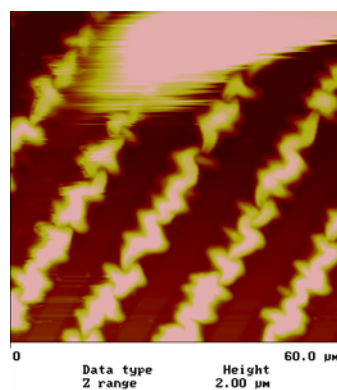
Control of the organization of cells and proteins is critical to future advances in the field of tissue engineering.<sup>1</sup> Such advances in the control of the growth and proliferation of living cells will ultimately lead to cell layers that can function as tissues, which can be employed to replace or repair damaged or diseased tissue in the human body.

The technique of micropatterning, also known as the Whitesides microprinting method<sup>2</sup>, was employed to organize proteins and cells on surfaces to produce a defined architecture and scaffold for the future creation of tissues. Substrate platforms are crucial to protein organization and cell physiology and proliferation. This investigation employed Au/Si micropatterned chips as well as gold, silicon, copper, and platinum substrates to assess optimal organization and biocompatibility as well as the substrate influence on protein and cell organization. A clear comparison of the extracellular matrix (ECM) proteins was examined in both starved human dermal fibroblasts versus pure Fn on micropatterns. Atomic force, optical, and confocal microscopy were utilized.

Preliminary results indicate that, through the use of micropatterning, natural ECM proteins and cells can be organized effectively on Au/Si chips, Si, and Cu. Proteins change their original and natural conformation when Si domains become smaller. Mechanical data suggested that this organization change is also associated to hardness of proteins. Further, examination of cancer cell protein organization and study of differential cancer cell growth may provide implications for the future harnessing of treatment modalities.



**Figure 1:** Natural ECM on Au/Si micropatterned chip



**Figure 2:** Natural ECM on Au/Si micropatterned chip with cell

<sup>1</sup> Wang YC, Ho CC. *FASEB J.* 2004 Mar; 18(3): 525-7. Epub 2004 Jan 08.

<sup>2</sup> Y. Xia, G. M. Whitesides, *Angew. Chem.* 110, 568 (1998).

# An Analysis of the Interactions Between the Extra-cellular Matrix Proteins and Glycosaminoglycans Fibronectin, Elastin, and Heparin and the Effects of Biomineralization Through Calcium Carbonate

Christopher Mackey, South Side High School  
Brandy Ma, Rice University

Karthikeyan Subburaman, Nadine Pernodet, Miriam Rafailovich, Department of Materials Science and Engineering Stony Brook University  
Elaine Dimassi, Brookhaven National Laboratory

One of the primary goals of bioengineering has been the creation of artificial tissues. However, there are many impediments such as reconstructing the extra-cellular matrix (ECM). Early studies involved the observation of ECM proteins in their globular form<sup>1</sup> or in the presence of cells, but more recent studies have revealed ways to observe proteins more efficiently by allowing them to undergo spontaneous unfolding and fibrillogenesis without the use of cells but only in the presence of a charged surface<sup>2</sup>. Using such methods allow one to study natural protein organizations. The goal of this investigation is to study the interactions between proteins such as Fibronectin and Elastin but also glycosaminoglycans such as Heparin as well as biomineralized protein mixtures.

28% Sulfonated Polystyrene (SPS) was spun-cast onto hydrophilic Silicon wafers. SPS is used to create a high charge density, which, as proven by previous experiments, is the major factor in creating and influencing the process of fibrillogenesis<sup>2</sup>. Samples were then annealed for 12 hours. Resulting wafers were placed in solutions of desired proteins or minerals and kept in an incubator at 37°C and 100% humidity. Surfaces were observed and imaged under an Atomic Force Microscope (AFM). Readings of the modulus as well as measurements of the height and width of protein fibers were also taken using the AFM. Networks of plain Fibronectin, Elastin and Heparin appeared to reflect fibers such as those seen in Fig. 1 or in Fig. 3 in the case of Heparin. The mixtures, however, organized differently. The combination of Fibronectin and Elastin displayed a pattern more intricate than the separate proteins while the Heparin and Fibronectin mixture showed a very different organization. Fig. 2 shows mounds of protein that are not connected in a matrix. This leads one to believe that the binding of Fibronectin to Heparin interferes with the binding of Fibronectin to itself. When the modulus was observed, fibronectin displayed a hard rigid property while both Heparin and Elastin were much softer. It appears as if neither of the soft Elastin or Heparin affected the modulus of the Fibronectin greatly when mixed. When biomineralized, the modulus of the Fibronectin and Heparin mixture was lowered resulting in an even harder material. These results are visible in Fig. 4. In addition to the examination of such images and moduli, Fibronectin and Elastin were followed as a time dependence, thus providing further information on the interaction between these two proteins. Though inferences can be drawn based on the data received, it is necessary to obtain more data before and set conclusions are drawn.

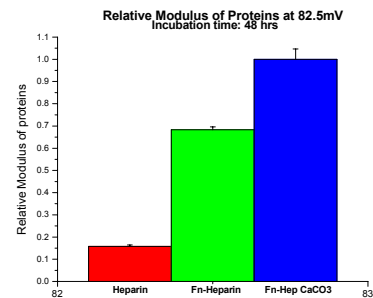
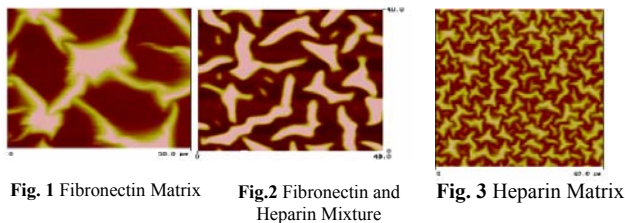


Fig. 4 Relative Modulus of Proteins

<sup>1</sup> Redfield, C. (2004). Using nuclear magnetic resonance spectroscopy to study molten globule states of proteins. *Methods* 34(1): 121-32.

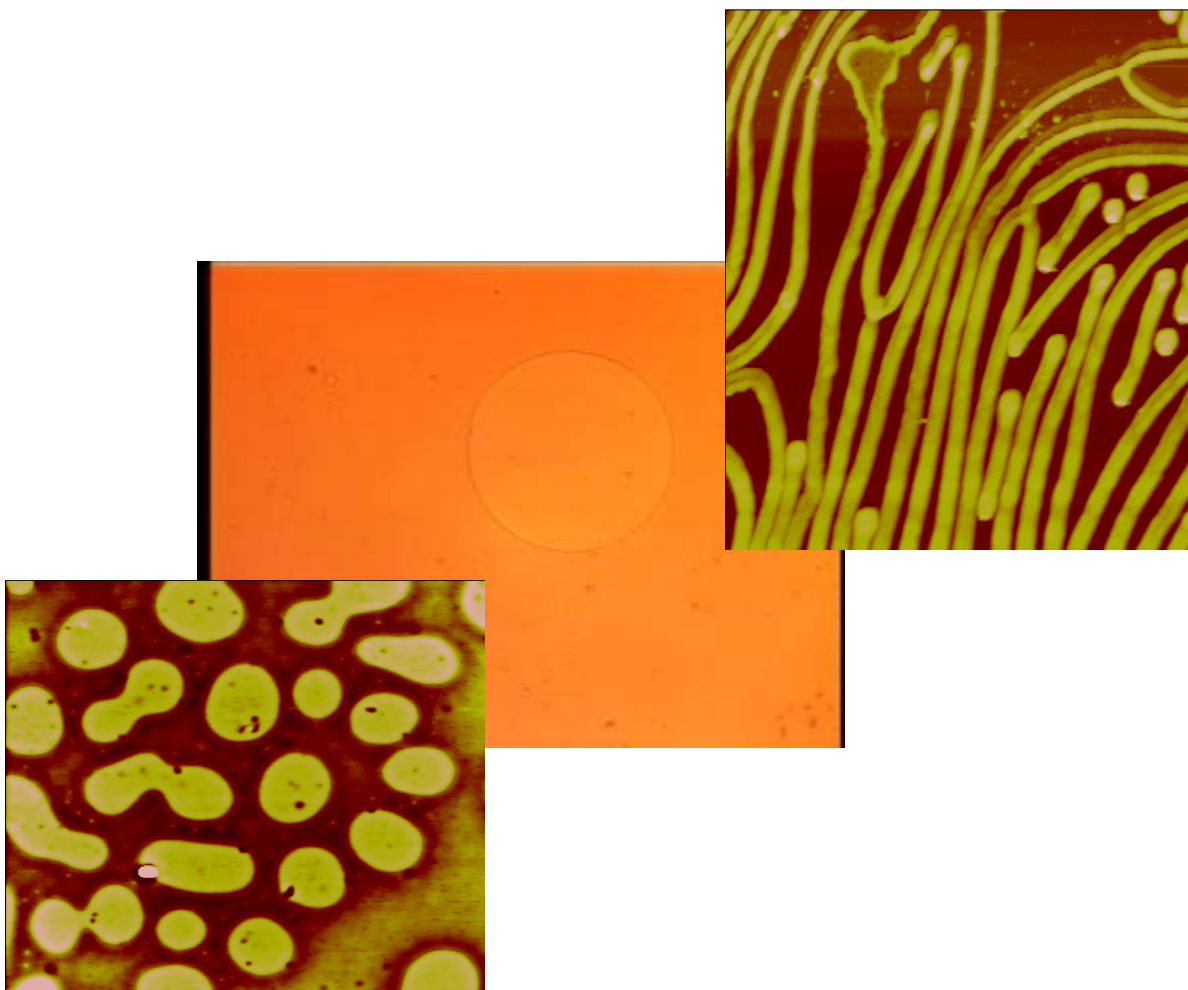
<sup>2</sup> Pernodet N, Rafailovich M, Sokolov J, Xu D, Yang NL and McLeod K.(2003). Fibronectin fibrillogenesis on sulfonated polystyrene surfaces. *Journal of Biomedical Materials Research*, 64(4), 684-692.

# Session 3: Self Assembled & Nanostructured Films

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***Chair: Arielle Galambos***

Taylor Bernheim,  
Victor Daniel, Chananel Gez  
Ben Eghbali, Dmitri Gurbazov



## Self Assembled Structures of Poly(styrene-*b*-ferrocenyldimethylsilane) (PS-*b*-FS) Blended with PS-PMMA

Benjamin Eghbali, DRS H.S

Dmitri Garbuzov, Princeton H.S.

Arielle Galambos, Wellesley College

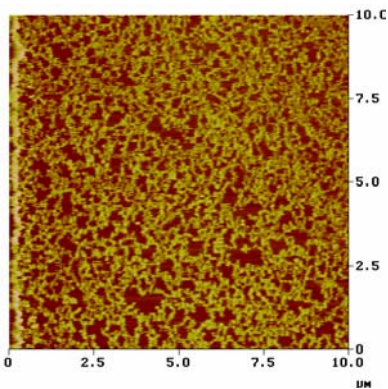
Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

Self-assembling polymers present a possible solution to the growing demand for miniaturization of nanostructures. Techniques using self-assembling polymers can circumvent the problems facing older processes such as lithography by building structures from the molecular level up. By avoiding etching the material, surface defects associated with using lithography at increasingly smaller scales can be prevented.

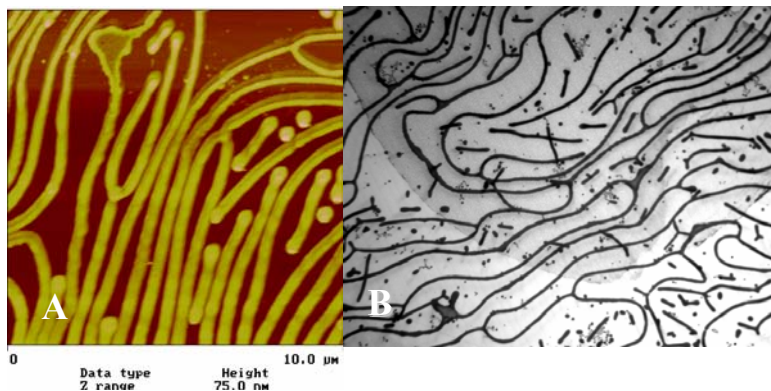
In our experiment we used PS-*b*-PMMA, a polymer whose ordered arrangement produces a favorable structure as part of a blend and the organometallic polymer Poly(styrene-*b*-ferrocenyldimethylsilane), a self-assembling polymer containing Fe that greatly increases its potential for applications however with an ineffective morphology.

Using the Langmuir-Blgett trough we ran individual isotherms (pressure in terms of area) of solutions of PS-*b*-PFS and PS-*b*-PMMA to identify each of their onset points and then deposited samples of each on a hydrophilic silicon wafer and observed their structures using Atomic Force Microscopy and Transmission Electron Microscopy.

We then made a 1mg/ml solution of a 5:1 blend of PS-*b*-PFS and PS-*b*-PMMA and spread it on the LB trough. The sample observed had an increasingly regular morphology. The air/water interface allowed these polymers to self-organize and form structural patterns that would otherwise be difficult to produce. Due to the difference in hydrophobicity of the blocks of PS-*b*-PMMA, the polymer formed micelles that, at greater pressures fused into channels<sup>11</sup>. In the future, we hope to use ion etching to study the orientation and location of the different polymers in the channel. We also plan to alter the morphology of the blend by applying an electric field to the solution before it is deposited.



**Figure 1:** AFM image of an LB Film of PS-*b*-PFS (100µl of a 1.0 mg/ml solution) spread onto a hydrophilic Si wafer. The image has a z range of 50.0nm



**Figure 2:** LB Films of a blend of PS-PMMA and PS-*b*-PFS in a 1:5 Ratio with a total polymer concentration of 1.0 mg/ml (100µl spread). (a) AFM image of the LB Film with a z range of 75.0 nm. (b) Transmission Electron Microscope image of the LB film on a TEM grid of a 1.0 mg/ml solution.

<sup>1</sup> Young-Soo Seo, K. S. Kim, Arielle Galambos, R. G. H. Lammertink, G. J. Vancso, J. Sokolov, and M. Rafailovich. *Nano Letters* **2004**, 4, 483.



## Crosslink Density in Thin Polymer Films

Chananel Gez, Mestiva Manhattan Beach

Victor Daniel, Haborfields Highschool

Clive Li, J.H. Xavier, J. Sokolov, and Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

The formation and growth of holes in free standing films has been studied recently<sup>1,2,3</sup>. For films at low temperature, linear growth of hole diameter vs time has been observed, changing to exponential growth at higher temperature. Visco elastic properties can be determined from the hole growth measurement. We have studied hole opening in cross linked polymers, where the elastic behavior can be varied. Free standing polystyrene thin films with molecular weight of 400kg/mol, were crosslinked with Co60 gamma irradiation at a rate of 800 krad per hour at different time intervals were flattened by pre-amealing at 90C for two hours. A small hole with diameter of about 20um was nucleated at the center of the free standing film by poking with a sharp needle. These samples were then annealed under vacuum at 132C<sup>0</sup> to allow nucleated holes (figure 1.) magnification of 20 X. We measured that the dynamics of hole growth in the melt state as a function of gamma radiation exposure time. Rates of hole growth decreased with increasing gamma ray exposure, reflecting the increasing crosslink density and elastic modulus. Independently, crosslink density is measured by swelling experiments on bulk samples exposed in the same cells as the thin films.

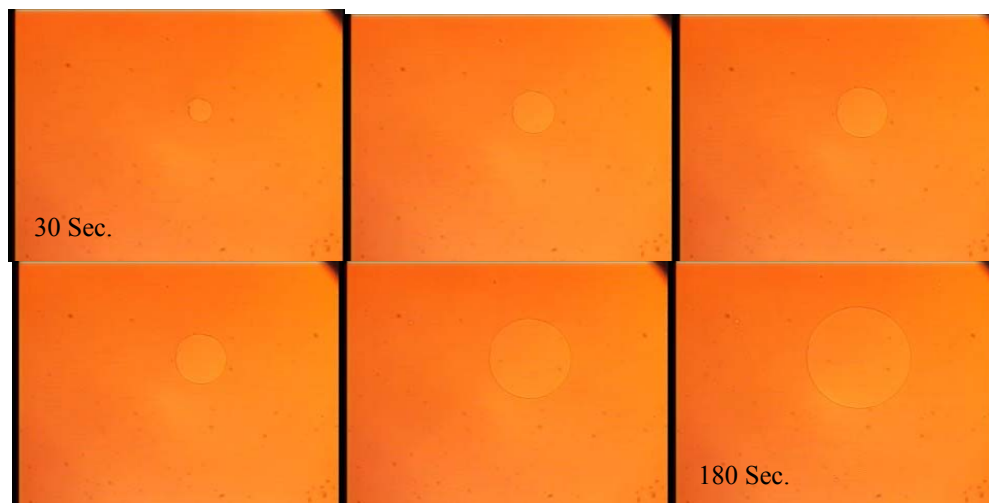


Figure 1. 400k sample annealed at 132°C

<sup>1</sup> Debregeas, G.; Martin, P.; Brochard-Wyart, F. Phys. Rev. Lett. 1995, 75, 3886

<sup>2</sup> Danolki-Veress, K.; Nickel, B. G.; Roth, C.; Cutcher, J. R. Phys. Rev. E B1999, 59, 2153

<sup>3</sup> J.H. Xavier, Y. Pu, C. Li, M.H. Rafailovich, and J. Sokolov Macromolecules 2004, 37, 1470-1475

## Nanopatterns to Control Cell Mechanics

Taylor Bernheim, Ramaz Upper School

Madelyn Ho, Harvard University

Nadine Pernodet, Miriam Rafailovich, Sharon Ge, Department of Materials Science and Engineering, Stony Brook University

Although cells are on the micro-scale, our hypothesis is that nano-scale patterns will significantly affect cell behavior through their mechanics and their extra cellular matrix (ECM) organization. Curtis has reported that cells are extremely sensitive to their nanoenvironment and that it should be taken into consideration when designing next-generation tissue engineering materials.<sup>1</sup> In accordance with this, we have to set up several environments to reproduce the cell organization of tissues as well as the ECM. The goal of our research is to determine the best, most regular nanopattern for cells to adhere and observe their mechanical properties in order to create tissues and organs in the future.

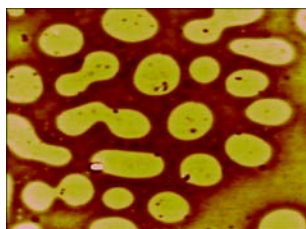
A blend of polystyrene (PS) and poly(methylmethacrylate) (PMMA) is used to create a recurring pattern, due to phase segregation because of their hydrophilic and hydrophobic traits.<sup>2</sup> The two polymers polystyrene and poly-bromo-styrene (PBrS) are also immiscible, thus phase segregate. In search of finding the most regular pattern, solutions of the two blends in varying ratios of 1:1, 1:9, 9:1, 3:7, and 7:3, were spun-cast on silicon wafers, with some annealed and some unannealed. Each sample was imaged under the Atomic Force Microscopy (AFM) and five of the twenty were distinguished as having the best patterns, as shown in Figure 1 and Figure 2.

The ion mill was used to sputter the samples, in order to etch the nanopattern of the copolymer blend into the silicon. PS/PMMA samples were sputtered at intervals of one minute and PS/PBrS samples were sputtered at three minute intervals, to determine sputtering rate, as seen in Figure 3.

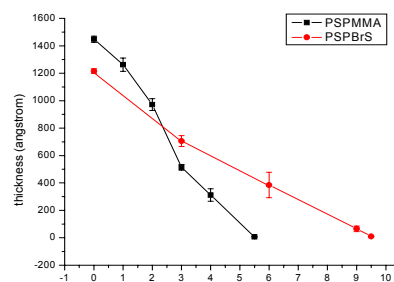
Polybutadiene (PB) and sulfonated polystyrene (SPS) were spun-cast on the sputtered surfaces, and plated with cells to investigate whether the cells would adhere and organize on surfaces with varying mechanical properties as well as protein organization.



**Figure 1.** Annealed PS/PMMA 1:9 under the AFM (scale:15  $\mu\text{m}$ )



**Figure 2.** Annealed PS/PBrS 1:1 under the AFM (scale:15  $\mu\text{m}$ )



**Figure 3.** Graph depicting sputtering rates of PS/PMMA and PS/PBrS

<sup>1</sup> Curtis, Dalby; Gadegaard; Riehle; Wilkinson. *International Journal of Biochemistry and Cell Biology* **2004**, 36(10), 2015-25.

<sup>2</sup> Morin, C.; Ikeura-Sekiguchi, H.; Tylliszczak, T.; Cornelius, R.; Brash, J.L.; Hitchcock, A.P.; Scholl, A.; Nolting, F.; Appel, G.; Winesett, A.D.; Kaznatcheyev, K.; Ade, H. *Journal of Electron Spectroscopy and Related Phenomena* **2001**, 121, 203-224.

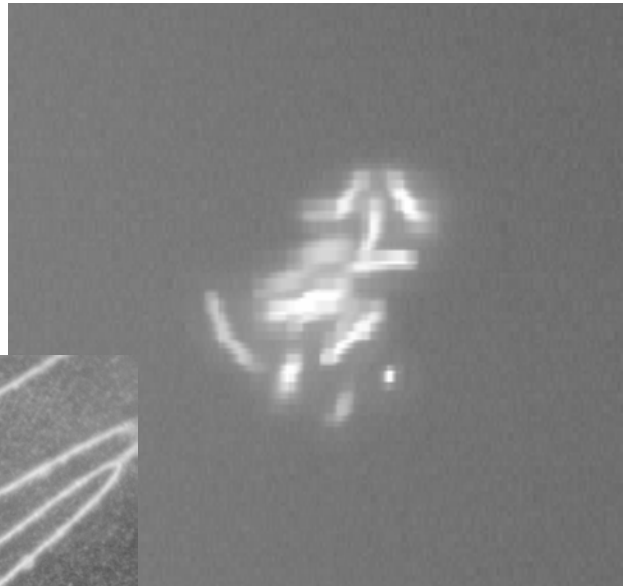
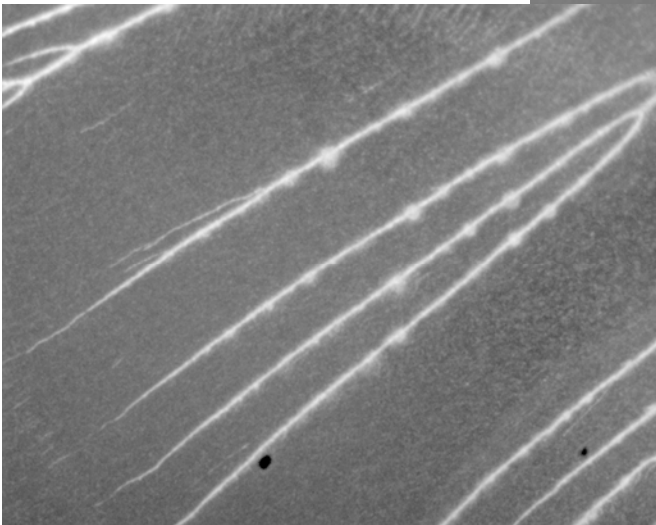
# Session 4: DNA Surface Electrophoresis

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***Chairs: Avtar Singh, Eric Peterson***

Brinda Alagesan

Amit Mehta



# Surface Electrical Transport of Mega Basepair-Size DNA Molecules

Eric Petersen: Harvard University

Amit Mehta: St. Anthony's High School

Avtar Singh: Cornell University

Brinda Alegason: Manhasset High School

Bingquan Li, Vladimir Samuilov, Jonathan Sokolov, Miriam Rafailovich: Department of Materials Science and Engineering, SUNY Stony Brook  
Benjamin Chu: Department of Chemistry, SUNY Stony Brook

Conventional methods of DNA fractionation, such as pulsed field gel electrophoresis, have great difficulty handling large molecules, because they easily become trapped in the pores of the gel. Recently, a method of fractionating DNA on a surface was proposed by Pernodet et al [1] and Seo et al [2]. In these studies, bacteriophage DNA in the 10-100 kilobase pair range was separated on a flat silicon surface.

In this work, we attempt to understand the dynamics of Mega base pair size DNA molecules during surface electrophoresis. *Escherichia Coli* (5.4Mbp) and *Thermotoga Neopolitana* (1.8Mbp) DNA were used for these experiments. The mobility of DNA across a surface was measured via laser induced fluorescence detection. The interaction of DNA with the surface was imaged with a confocal microscope in laser scanning mode with a CCD camera. Surfaces of gold, silicon, and two-dimensional gold-silicon micropatterns [FIG 1] were used for these experiments. Micropatterns of alternating gold and silicon strips were created by the Whitesides microcontact printing method [3].

Results indicate that the micropattern retards the mobility of the DNA relative to the mobility on an unpatterned gold [FIG 2] surface when the period size of the gold striped pattern is less than the natural chain length of the DNA (approximately  $67\mu\text{m}$ ). Furthermore, when the pattern spacing falls below approximately two-thirds the natural chain length of the DNA molecule, a further decrease in pattern size will not affect the mobility. This suggests that the DNA is feeling the size of the pattern, and when the pattern becomes much smaller than the DNA, the chains cannot sense this change and their mobility across the patterned surface is unaffected.

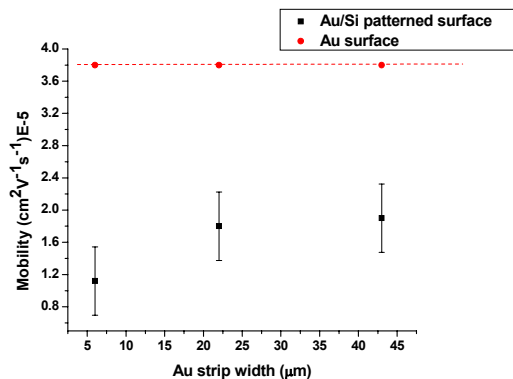


FIG 2: *TN* DNA mobility on patterned and unpatterned surfaces

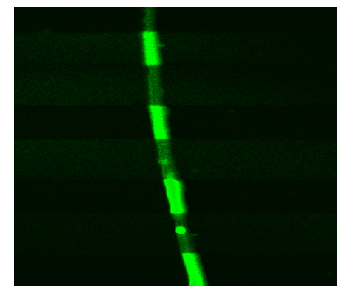


FIG 1: DNA adsorbed onto micropatterned surface. Laser scanned confocal image, 100X oil immersion lens

1. N. Pernodet et. al., *Phys. Rev. Lett.* 85, 5651 (2000).
2. Y. Seo et. al., *Electrophoresis* 23, 2618 (2002).
3. A. Kumar and G.M. Whitesides, *Appl Phys Lett* 63, 2002 (1993).

## An Exploration of the Surface Kinetics of Mega-base pair DNA

**Eric Petersen**, Harvard University

**Avtar Singh**, Cornell University

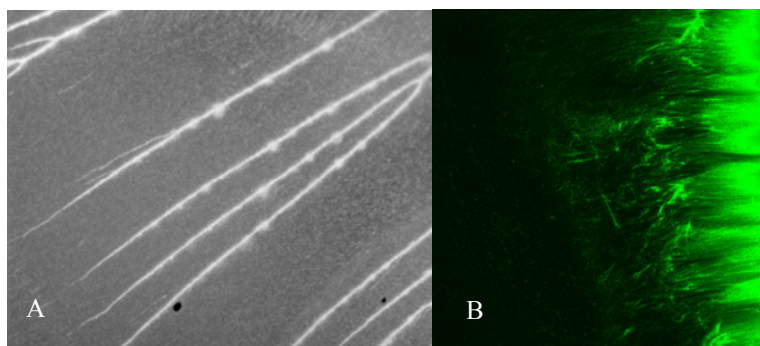
**Amit Mehta**, St. Anthony's High School

**Brinda Alagesan**, Manhasset High School

Miriam Rafailovich, Jonathan Sokolov, Vladimir Samuilov, Bingquan Li, Xiaohua Fang,  
Department of Materials Science and Engineering, Stony Brook University

Flat-surface electrophoresis of DNA is a novel concept that relies on surface interactions between the polyelectrolyte chains and the substrate as a fractionation mechanism.<sup>1</sup> These interactions provide a mechanism for characterization of unique molecules. Previously, studies of the evaporation kinetics of droplets containing  $\lambda$ -DNA revealed a high concentration of the genetic material to be located in the outer ring of the dried droplet, with a “combed” arrangement of the molecules.<sup>2</sup> Variables included the molecular weight of the DNA used, the surface itself and the concentration of DNA within the droplet.

While flat-surface electrophoresis has demonstrated its potential in the realm of short genomes, its application to longer chains remains of particular interest to an age concerned with genomic sequencing and medical innovation. Droplets of *Thermotoga neopolitana* and *Escherichia coli* were examined using confocal microscopy as well as a contact angle machine. Furthermore, human genomic DNA was observed from a gel medium and “stretched” with an electric field within TBE (Tris-borate EDTA) buffer to investigate the relaxation properties of such molecules.(Figure 1) The location of individual chains of human DNA within an agarose gel provided a stable environment for examining the DNA while an electric field was applied. One critical prospect is a transfer of the DNA from the gel to the surface, through either melting the gel or a greater manipulation of the system altogether.



**Figure 1(a):** *Thermotoga neopolitana* DNA on hydrophobic silicon (63x) **(b):** Human DNA extricated from agarose gel after the application of a 5 V/cm electric field

<sup>1</sup> N. Pernodet et. al., *Phys. Rev. Lett.* 85, 5651 (2000).

<sup>2</sup> Y. Seo et. al., *Electrophoresis* 23, 2618 (2002).

# Session 5: Supercritical Fluid Processing of Thin Films

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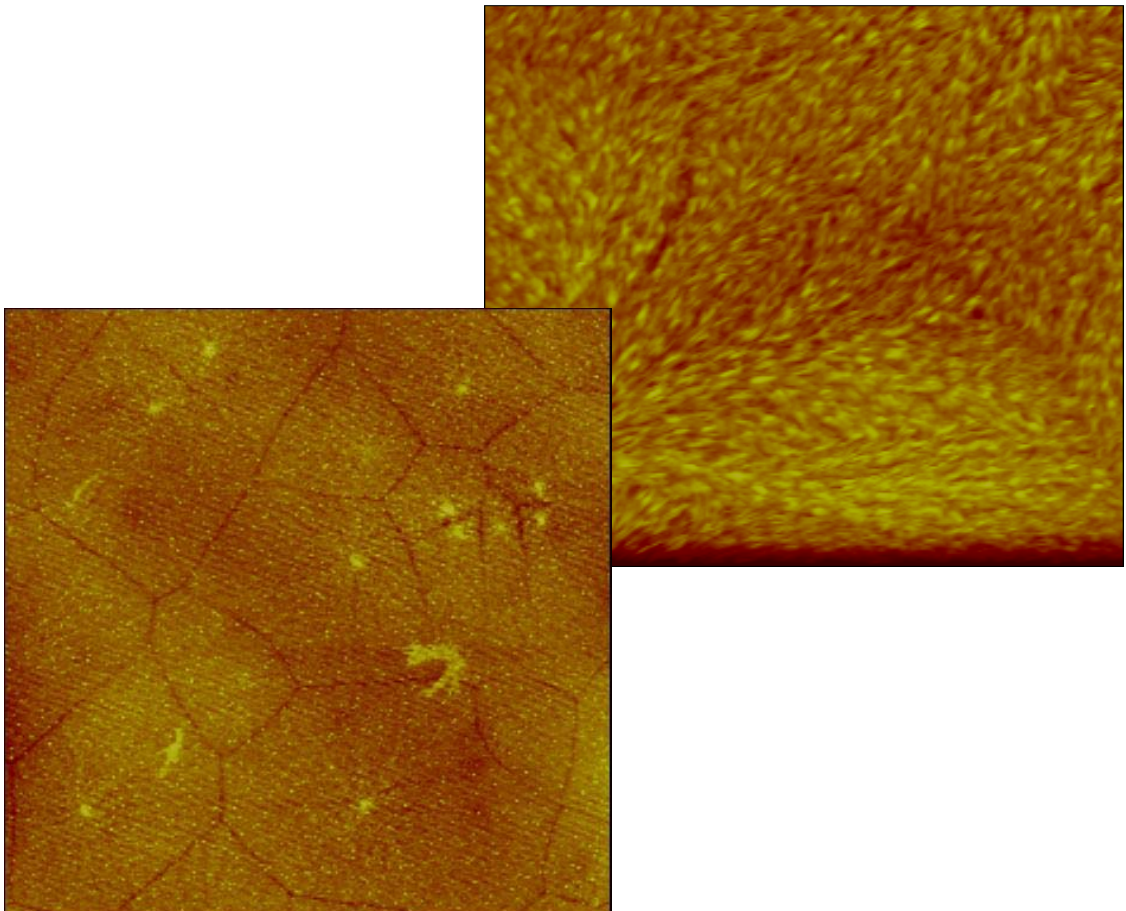
***Chair: John Jerome***

Brendan Burns, Tomas Strand

Chelsea Gordon, Sylvia Qu,

Allyson Ho, Alex Thachara

Jonathan Scholl



# The Effects of Supercritical Carbon Dioxide on the Segregation of Polymer Blends: A Novel Method of Substance Extraction for Improved Commercial Applications

Sylvia Qu and Chelsea Gordon, Half Hollow Hills High School East

John Jerome, Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

Supercritical fluid (SCF) technology has emerged as a novel method of substance extraction in industry. Temperature and pressure induced density fluctuations give SCFs properties that are between those of a gas and a liquid, thus making them ideal solvents.<sup>1</sup> Here we focus on the effects of supercritical carbon dioxide (scCO<sub>2</sub>) on surface segregation in polymer blends. Present techniques for polymer separation require exposure to high temperatures for long periods of time, which causes sample degradation.<sup>2</sup> SCFs have the ability to extract substances at lower temperatures and with greater speed.

We wanted to determine the effects of supercritical fluids on polystyrene and deuterated polystyrene (PS/dPS) blends after exposure to four different pressures (800, 1200, 1450, and 2000 psi) at two different temperatures (36°C, 50°C). Under these conditions, we expected the polymers to phase segregate without any degradation of the polymer blend. The two polymers were dissolved in toluene and diluted to four different concentrations. Samples were exposed to scCO<sub>2</sub> and segregation was examined via Secondary Ion Mass Spectrometry (SIMS). In addition, the degree of dPS mobility was determined through bilayer PS/dPS samples.

SIMS data revealed that segregation of dPS from PS occurred at the silicon substrate rather than at the surface. The control deuterium profile was flat (Figure 1), whereas after 24 hours a peak was distinctly visible (Figure 2), indicating that segregation had occurred. Bilayer deuterium profiles also indicated dPS mobility. The data suggests that dPS migration occurs more readily at 50°C than 36°C, and most effectively along a 1450 psi isobar. Future work will involve an investigation as to how scCO<sub>2</sub> affects segregation in polyethylene (PE)/dPS blends, as well as in PE/trans fatty acid blends. Future project applications involve a novel method to extract trans fatty acids from specific foods using SCFs in the hope that one day these foods can be consumed without the fear of contamination by hazardous fatty substances.

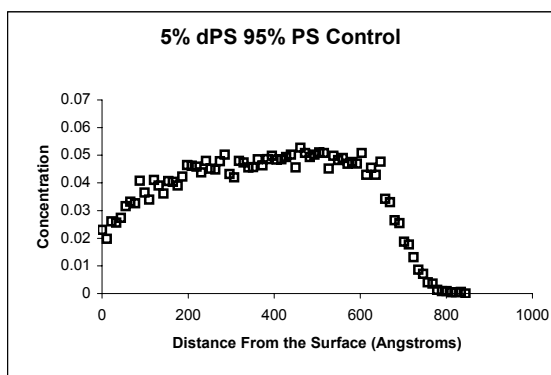


Figure 1: Deuterium profile of control sample

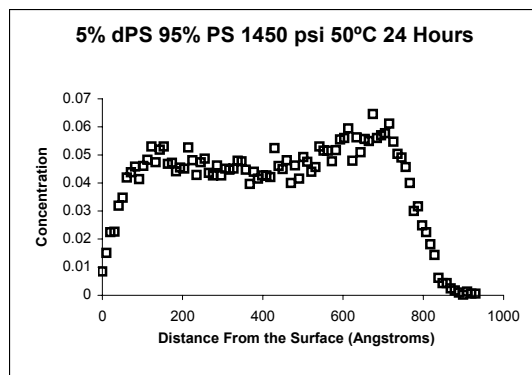


Figure 2: Deuterium profile of exposed sample (1,450 psi, 50°C)

<sup>1</sup> Huang, Ai-Yin. The Effect of Supercritical Fluids and Supercritical Carbon Dioxide to Homogeneous Organometallic Catalysis System. <http://cm.utexas.edu/academic/courses/Fall1997/CH380L/student.papers/ah.html>.

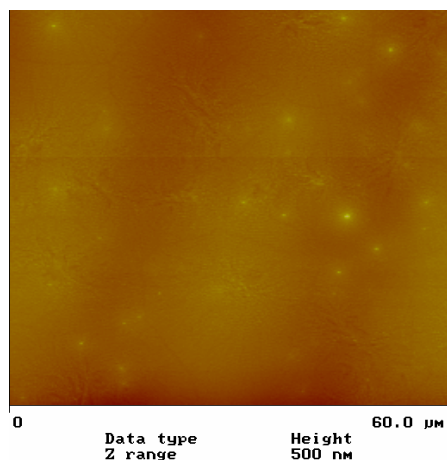
<sup>2</sup> Kumar S., Yethiraj A., Schweizer K., Leermakers F. *The Effects of Local Stiffness Disparity on the Surface Segregation From Binary Polymer Blends*. Journal of Chemistry and Physics. Volume 23.

# The Effect of Exposure to Supercritical CO<sub>2</sub> and Confinement on Morphology of Thin-Film Polyethylene

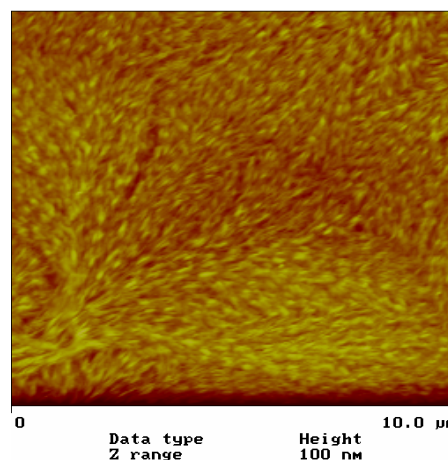
**Brendan Burns** and **Thomas Strand**, Locust Valley High School

John Jerome, Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

There are two types of polymer structures: crystalline and amorphous. Amorphous polymers are soft and easy to manipulate, while crystalline polymers are the complete opposite. Studies have shown that when a polymer is confined the presence of interfaces greatly affects the morphology of the polymer.<sup>1</sup> At the interface, the nature of the interaction between the polymer molecules and molecules of the confinement material determines the reaction of the polymer.<sup>2</sup> This study focused on the effects of supercritical CO<sub>2</sub> and confinement of polyethylene (PE) to determine if the morphology of PE could be altered. To observe the effects of confinement, PE of varying thickness was spun-cast and annealed on silicon and platinum substrates. Atomic Force Microscopy (AFM) was used to see the morphology of the annealed PE and the samples that were exposed to supercritical CO<sub>2</sub> (Figures 1 and 2). After exposure of half the samples to sc CO<sub>2</sub> a silicon oxide layer was deposited over the polymer for confinement. Then, following the vapor deposition, the samples were annealed for three days and then immersed in hydrofluoric acid (HF) to remove the oxide layer. The results showed that not only did the morphology of the polyethylene change, but the melting point increased as well due to both the sc CO<sub>2</sub> exposure and confinement.



ape01.01  
**Figure 1:** 500 Å of annealed PE on a Si wafer prior to exposure



c02ape01.01  
**Figure 2:** 500 Å of annealed PE on a Si wafer after exposure to supercritical CO<sub>2</sub>

<sup>1</sup> Y. Wang, S. Ge, M. Rafailovich, J. Sokolov, Y. Zou, H. Ade, J. Luning, A. Lustiger, G. Maron. "Crystallization in the Thin and Ultrathin Films of Poly(ethylene-vinyl acetate) and Linear Low-Density Polyethylene." *Macromolecules*, 2004, 37, 3319-3327.

<sup>2</sup> K. Dalnoki-Veress, B.G. Nickel, and J.R. Dutcher. "Dispersion-Driven Morphology of Mechanically Confined Polymer Films." *Physical Review Letters*, 1999, 82, 7, 1486-1489.



**The Effects of Nanoparticles (Clay, Gold, Carbon Black, POSS)  
On Selective Permeability (O<sub>2</sub>, CO<sub>2</sub>, SF<sub>6</sub>) of Thin Film Membranes Using Supercritical  
Fluid**

**Allyson Ho**, Clements High School, **Alex Thachara**, The Wheatley School  
L. John Jerome, Miriam Rafailovich, Department of Materials Science and Engineering,  
Stony Brook University

The use of nanocomposite polymer films has increased greatly over the last few years. The addition of inorganic nanoparticles to these films can have numerous beneficial effects on their lubrication, strength, and UV resistance<sup>1</sup>. Since nanoparticles are rigid, they do not conform completely to the molecular order of the film. Hence nanometer-sized voids may be formed. Thus the introduction of nanoparticles into polymers may cause increased porosity to gases. This may be used to engineer selectively permeable membranes. Different nanoparticles were mixed with Polystyrene (PS) and Poly(methyl methacrylate) (PMMA) to examine the causes for this increased porosity and its dependence on polymer structure as well as the interaction between the polymer and the nanoparticles.

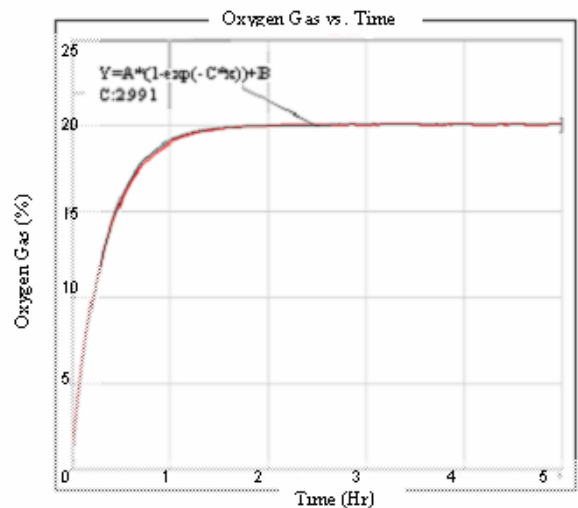
We observed the effect of various nanoparticles (gold-1%, clay-10%, 20%, carbon black, and POSS) on the permeability of O<sub>2</sub>, CO<sub>2</sub>, and SF<sub>6</sub>. Figure 1 shows the typical curve for a sample. The black line is the inverse exponent fit. The equation:

$$Y = A * (1 - \exp(-C * x)) + B$$

determines the value C, which is the permeability of the membrane. Table 1 shows the values of C-1 and C-2 where C-1 is the C value for samples not exposed to scCO<sub>2</sub> and C-2 is the C value for samples exposed to scCO<sub>2</sub>. From the table we see that Lucentite SPN, synthetic clay, increases permeability as compared to 20A, natural clay, which sometimes decreases permeability. Furthermore, an exposure to scCO<sub>2</sub> increased the permeability of gases. When clay was added to PMMA solutions, the result would always be an increase in permeability. Samples containing 20% clay that were exposed to scCO<sub>2</sub> were found to significantly increase in gas permeability.

Solution	C (unexposed)	C (exposed to scCO <sub>2</sub> )
100% PMMA	1.491	2.991
10% 20A 90% PMMA	2.591	3.474
20% 20A 80% PMMA	2.091	3.389
10% SPN 90% PMMA	5.329	2.091
20% SPN 90% PMMA	2.191	4.589
100% PS	3.779	
10% 20A 90% PS	1.691	2.391
20% 20A 80% PS	1.391	
10% SPN 90% PS	6.944	5.529
20% SPN 80% PS	5.849	8.349

**Table 1: C Values**



**Figure 1: 100% PMMA (exposed to scCO<sub>2</sub>)**

<sup>1</sup> Chabert, E, et al. Filler- Filler Interactions and Viscoelastic Behavior of Polymer Nanocomposites. Materials Science and Engineering A. Volume 381, Issues 1-2 , 15 September 2004, Pages 320-330 43, 509-514.

# Crystallization of EVA Thin Films Using Supercritical Carbon Dioxide

Jonathan Scholl, The Wheatley School

Yantian Wang, John Jerome, and Miriam Rafailovich,

Department of Materials Science and Engineering, Stony Brook University

Crystallized polymer thin films have a variety of benefits over their amorphous counterparts, ranging from increased hardness to better chemical resistance to special optical properties. To attain this crystalline state, several procedures are currently used involving annealing the polymer samples above their melting points at low pressure and allowing either slow cooling or quenching the samples to room temperature.<sup>1</sup> Supercritical carbon dioxide (scCO<sub>2</sub>), serving as a solvent, has also been shown to increase the degree of crystallinity in bulk samples.<sup>2</sup>

Three types of ethylene vinyl acetate (EVA) polymer were used for crystallization: Elvax 770, 550, and 265, in order of increasing vinyl acetate weight-percentage. The ethylene is partially crystalline, while the vinyl acetate remains amorphous, and thus increasing its percentage reduces the degree of crystallinity of the sample as a whole. The samples were spun-cast on silicon wafers in thicknesses ranging from 15 to 120 nm and exposed to scCO<sub>2</sub> along the density fluctuation ridge (36C, 1200 PSI and 50C, 1450 PSI) or the high temperature annealing procedures or both. The resulting thin films' thicknesses were compared using an ellipsometer, their surface morphologies were examined with an atomic force microscope (AFM), and their melting points were measured by shear modulus force microscopy (SMFM).

EVA film swelling was observed after scCO<sub>2</sub> exposure but not after the annealing processes. Both sets of samples developed spherulite structures with lamellae extending from the crystal nuclei, but they were even more pronounced in thicker films and in the supercritical samples (figure 1). Finally, samples that were exposed to the scCO<sub>2</sub> displayed higher melting points than the annealed and as-cast controls, again indicating a higher degree of crystallinity (figure 2).

Fourier transform infrared spectroscopy (FTIR) is used to determine the degree of crystallinity of the thin films spun on Copper (Cu) and Gold (Au) by comparing the signal emission ratios. Small angle x-ray scattering (SAXS) is used to determine lamellar spacing.

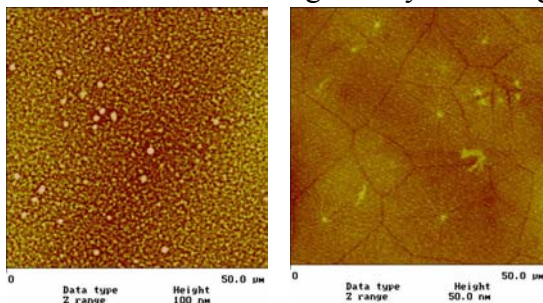


Fig. 1: AFM images before and after scCO<sub>2</sub> exposure

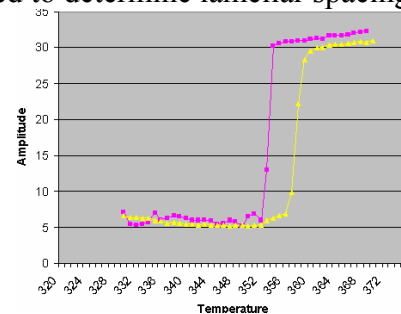


Fig. 2: Graph of melting points of same samples

<sup>1</sup> Wang, Y.; Ge, S.; Rafailovich, M; Sokolov, J.; Zou, Y.; Ade, H.; Luning, J.; Lustiger, A.; Maron, G. *Macromolecules* **2004**, *37*, 3319.

<sup>2</sup> Shieh, Y.; Lin, Y. *Journal of Applied Polymer Science* **2003**, *87*, 1144.

# Session 6: Polymer Inorganic Nanocomposites

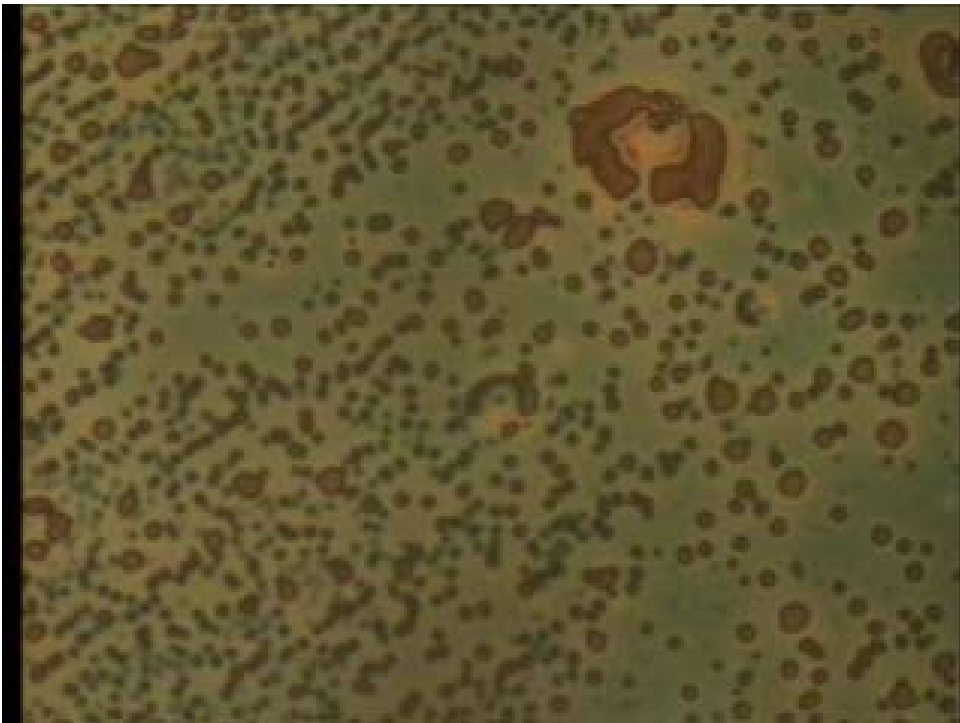
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***Chair: Michael Snow***

Vandana Sood, Sagar Mehta

Benjamin Cohen, Josh Nissel

Matthew Schlossberger



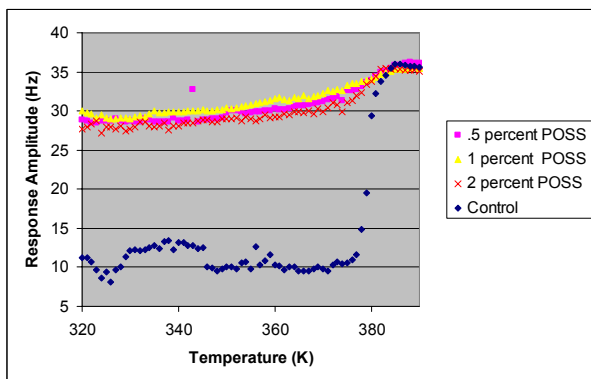
## POSS Nanocomposites as Viscosity Modifiers of Polymer Thin Films

Sagar Mehta, The Wheatley School

Vandana Sood, Syosset High School

Xavier J.H., Li C., Rafailovich M., Department of Materials Sciences & Engineering, Stony Brook

Controlling the viscosity of polymer thin films is of considerable interest because of their use as coatings and lubricants. The dispersion of nanoparticles to a polymer matrix can impact the material properties of the polymer.<sup>1</sup> We are studying the dewetting dynamics of PMMA/PS bilayers with the addition of the nanocomposite POSS (Polyhedral Oligomeric Silsesquioxane). Based on the rate of hole growth, the viscosity of the bottom layer can be determined using the Brochard-Wyart theory of liquid/liquid dewetting.<sup>2</sup> 50K PS films of approximately 1400 Å were spun cast onto clean silicon wafers with various concentrations of POSS. A 353K PMMA layer of approximately 300 Å was floated on top of the PS layer. The samples were annealed in a vacuum oven 175°C to initiate dewetting. The diameter of dewetting holes was measured after each annealing time interval to determine the rate of hole growth. Atomic Force Microscopy (AFM) was used to study the surface topography of the samples and Shear Modulation Force Microscopy (SMFM) was used to determine the glass transition temperature of the samples with various concentrations of POSS. The viscosity calculated from dewetting experiments will be compared with the viscosity calculated from diffusion coefficients determined using Secondary Ion Mass Spectrometry (SIMS). The addition of POSS significantly lowered the T<sub>g</sub> of PS (Figure 1). POSS nanoparticles also seem to significantly alter the elastic properties of the surface even below the T<sub>g</sub>. Dewetting experiments and SIMS experiments are still in progress (Figure 2).



**Figure 1:** T<sub>g</sub> measurement of PS with varying concentrations



**Figure 2:** Dewetting Sample of PMMA/PS with .5% POSS

<sup>1</sup> Starr F, Douglas J, Glotzer S. *Origin of Particle Clustering in a Simulated Polymer Nanocomposite and its Impact on Rheology*. The Journal of Chemical Physics 2003 Jul: Vol 119(3):1777-1788.

<sup>2</sup> Wyart F, Martin P, Redon C. *Liquid/Liquid Dewetting*, Langmuir 1993 Sep: 9: 3682-3690.

# Analyzing Adhesion At Polymer Interfaces Containing Filler Mixtures

Josh Nissel, DRS Yeshiva High School

Ben Cohen, HAFTR High School

Michael Snow (Cornell University), Miriam Rafailovich

Department of Materials Science and Engineering, Stony Brook University

The purpose of this study was to determine the effects of fillers on the adhesion at polymeric interfaces and to control this adhesion. The Symmetric Double Cantilever Beam Model (SDCBM) was used to determine the quantitative strength of the samples, due to the filler additions. However, in order to analyze the effect, the optimal annealing time must first be determined. Using the SDCBM, the sample strength or fracture toughness ( $G_c$ ) is measured. When the  $G_c$  plateaus, this is the optimal annealing time. The reason for this is that the fracture toughness is directly related to the interdiffusion of the polymer chains. The strongest sample occurs when the polymer chain has fully diffused through the interface. Therefore, a plateau of the  $G_c$ , indicates an equilibrium in the polymer chain dynamics. We tried to determine what fraction of a polymer chain needs to diffuse in order to obtain the max  $G_c$ . Max  $G_c$  occurs when you have a solid material without an interface. Using the Fickian Equation for Diffusion,

$$\text{Equation 1: } \Delta X = \sqrt{4Dt}$$

we determined the fraction of polymer needed for max  $G_c$ <sup>1,2</sup>.  $\Delta X$  is the width of the interface,  $D$  is the Diffusion Coefficient which is equal to  $1 \cdot 10^{-20} \text{ m}^2/\text{s}^3$ , and  $t$  is the annealing time. the square root of 4 times the diffusion coefficient and the annealing time. In order to find the distance the polymer must diffuse, the  $\Delta X$  is divided by the length of the polymer chain,  $R_g$ . The data shows that only .41 diffusion of the  $R_g$  of PMMA is necessary to reach optimal fracture toughness (*Table 1*). In order to test the effect of nano-composites on adhesion, Polymethyl methacrylate (PMMA) (Aldrich Chemical, Mw = 120k) powders were cast into molds and then hot pressed at 160°C for 15 minutes to form slabs of PMMA. The polymer slabs were then annealed for different times at 160°C and 1.5 tons of pressure to form adhesive bonds. The resulting sample was then tested by means of the SDCBM. In this test a razor is inserted at the interface at a rate of 10 $\mu\text{m}$  per second<sup>4</sup>. By measuring the length of the propagating crack we can obtain the  $G_c$  (*Figure 1*). A twin-screw extruder was used to create PMMA/clay mixtures of varying concentrations at 170°C for 10 minutes. The resulting mixtures were then fit into an aluminum mold and hot pressed at 160°C for 15 minutes to produce PMMA/clay slabs. The PMMA/clay slabs will then annealed together at 1.5 tons pressure for 7 minutes which was found to be the optimal time for annealing. The resulting annealed PMMA/clay sample will be tested using the SDCBM.

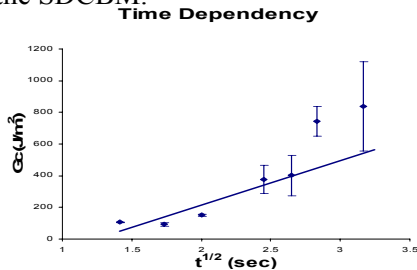


Figure 1: PMMA time dependency

$\Delta X/R_g$	$\Delta X$ (m)	t(sec)	$G_c$ (J/m <sup>2</sup> )
0.22	2.19E-09	120	106.12
0.27	2.68E-09	180	92.13
0.31	3.1E-09	240	151.02
0.38	3.79E-09	360	329.10
0.41	4.1E-09	420	389.26

Table 1: Ratio of interface width to radius of gyration, interface width, annealing time and fracture toughness.

<sup>1</sup> Frank, J.; *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, 1975

<sup>2</sup> Frank, J.; Park, G. S. *Diffusion in Polymers*, Academic Press, 1968

<sup>3</sup> Shin, K. et al; Silicon Oxide Surface as a Substrate of Polymer Thin Films, *Macromolecules*, Vol. 34#14, 2001, 4993-4998

<sup>4</sup> Brown, H.R. et al., Adhesion between polymers, *IBM Journal of Research and Development*, Vol. 38# 4, 1994, 379-389

## Electrospinning of Polystyrene and POSS Nanofibers

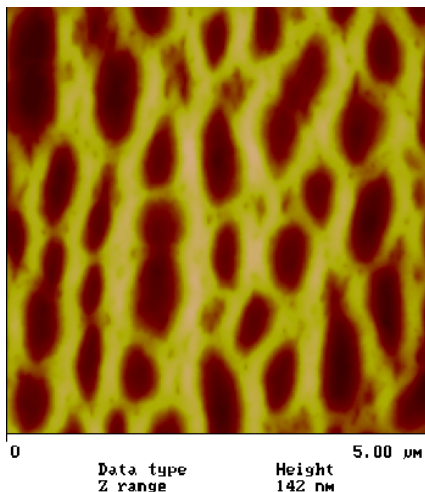
**Matthew Schlossberger**, Plainview Old Bethpage John F. Kennedy High School

Yuan Ji and Dr. Miriam Rafailovich

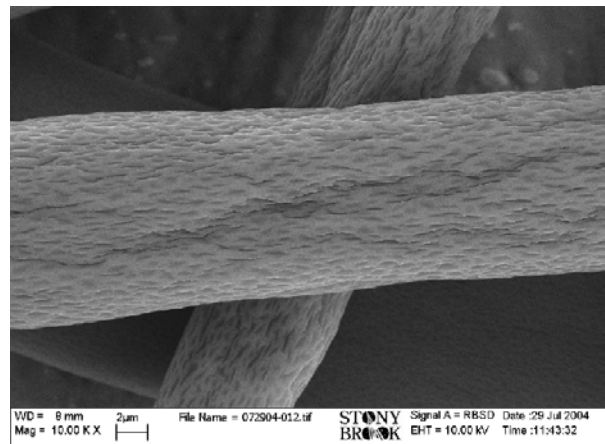
Department of Materials Science and Engineering, Stony Brook University

Nanofibers are being researched for their beneficial properties of high mechanical strength, high porosity, and large surface to volume ratio.<sup>1</sup> In technology, electrospun nanofibers could be used to create filters on the order of nanometers that can filter out small particles. In addition, they can be used to perform chemical or biological reactions at a high rate due to their large surface to volume ratio.

Electrospinning has been a rediscovered process that originated in the early 1900's.<sup>2</sup> It uses an electric field to induce a jet of polymer solution to split into many nanofibers. This experiment uses various concentrations of a polymer called polystyrene and a nanoparticle called POSS to form the optimum nanofiber. First, solutions are created by dissolving polystyrene and POSS in a solvent called tetrahydrofuran. Then the solutions are electrospun onto aluminum foil and silicon wafers on a flat surface, the fibers are annealed for one day in a vacuum oven, and they are observed using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The fiber in the AFM image shows a honeycomb morphology which indicates a high number of pores in the fiber. (Figure 1) This increases the surface area of the fiber and this would allow a high rate of reaction to occur. The SEM image shows a fiber of uniform diameter that is about ten microns wide. (Figure 2) Even though this fiber is thicker than a nanofiber, it is hoped that the fiber will have superior mechanical properties due to the lack of beading on the fiber. Future work with this project includes electrospinning with a rotator. These fibers will be compared to the fibers formed from electrospinning onto a flat surface. The electrospinning with a rotator will also allow the tensile strength of the fibers to be tested.



**Figure 1:** AFM image of 15% polystyrene and 4% POSS showing morphology of a fiber



**Figure 2:** SEM image of 30% polystyrene and 4% POSS showing image of fiber diameter

<sup>1</sup> Frenot, A.; Chronakis, I. S. *Polymer Nanofibers Assembled by Electrospinning* **2003**, 8, 64-75.

<sup>2</sup> Fong, H.; Chun, I.; Reneker, D. H. *Beaded Nanofibers Formed During Electrospinning* **1999**, 40, 4585-4592.

# Session 7: Flame Retardant Nanocomposites

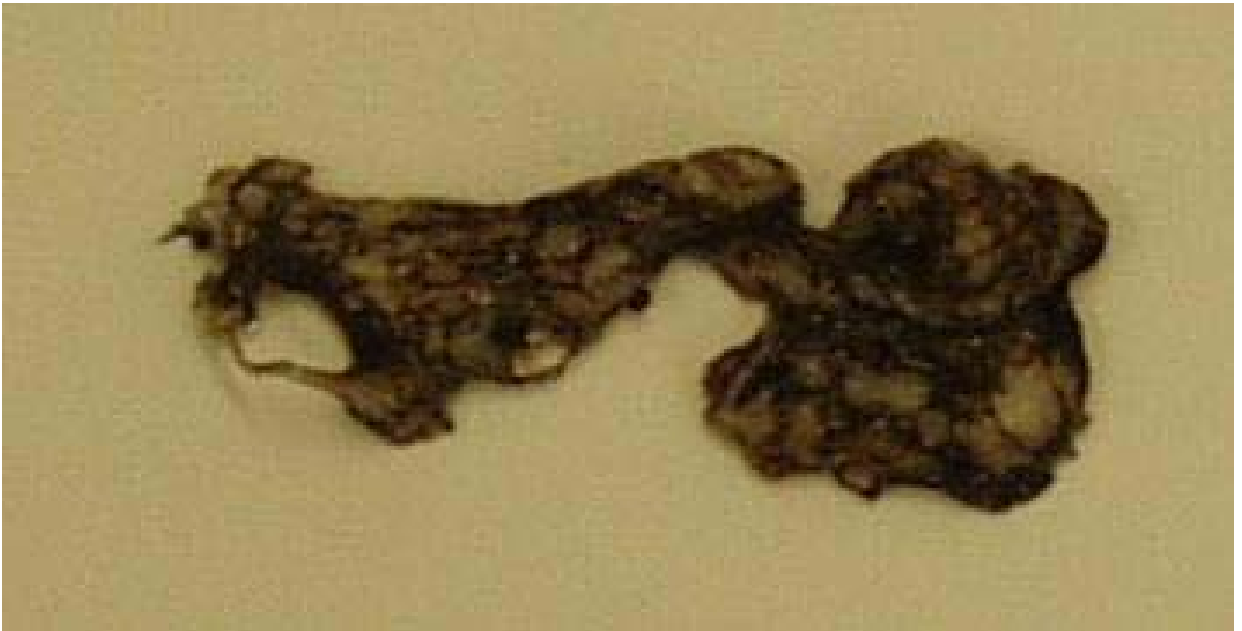
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*Chairs: Mitchell Fourman*

Daniel Hefter, Aryeh Sokolov

Evan Hertan

Alber Ko, Jeddy Chen



## Creating an Environmentally Healthy Self-Extinguishing Polymer Blend

Daniel Hefter, Davis Renov Stahler High School

Aryeh Sokolov, HAFTR High School

Myu Si, Charlie Shin, and Miriam Rafailovich, Department of Materials Science and Engineering,  
Stony Brook University

Self-Extinguishing polymer blends are mixed materials which when ignited will create their own reaction to extinguish the flame. Different materials create different reactions when putting out fires. Some bond H and OH to create water vapor, while others take away the oxygen from a fire suffocating it. One of the more popular fire retardant agents and this project's fire retardant choice was Bromine. Fire runs on three main components; fuel oxygen and heat. If one of these were to be removed, the fire could no longer last. Bromine molecules absorb large quantities of heat rapidly causing the flame temperature to drop and the fire to go out. Bromine also bonds with free Oxygen molecules leaving the fire with nothing to burn on causing it to extinguish.<sup>1</sup>

We mixed the compositions listed in table 1 in a Brabender at 170C. The samples were then molded into slabs approximately two inches by half an inch. The slabs were suspended vertically and flame tested according to UL-V0 protocols. Namely; we applied a blowtorch onto the tip of our samples for ten seconds. We then slowly removed the sample from the flame and timed how long it took for the sample to self extinguish. The procedure was repeated at least four times for each sample with identical results.

The results are listed in table 1. From the table we can see that neither polymer is intrinsically self extinguishing. In the case of Elvax, and Elvacite the standard formula which for the addition of 22% Pentabromophenyl ether and 6% Exploit AP750 results in a self extinguishing polymer. From the table we can see that the addition of clay allows us to drastically decrease the more toxic Pentabromophenyl ether and Exploit AP750 components.<sup>22</sup> Furthermore, clay increases the modulus above Tg and suppresses dripping of the sample.

Our attempts to substitute Exploit AP750 for the Pentabromophenyl ether was unsuccessful. The addition of clay only prevented dripping, but did not improve the flame retardance.

Polymer	Pentabromophenyl ether	Exploit AP750 (Phosphorous)	Sb <sub>2</sub> O <sub>3</sub> (antimony)	Cloisite20-A	UL-V0 candidate
Elvax					
72%	22%	0%	6%	0%	YES
70%	20%	0%	5%	5%	YES
77%	10%	0%	3%	10%	YES
87%	10%	0%	3%	0%	YES
100%	0%	0%	0%	0%	NO
75%	0%	20%	0%	5%	NO
80%	0%	20%	0%	0%	NO
85%	0%	10%	0%	5%	NO
95%	0%	0%	0%	5%	NO
Elvacite					
70%	20%	0%	5%	5%	YES
75%	20%	0%	5%	0%	NO
100%	0	0	0	0	NO

**Table 1:** List of polymer nanocomposites produced by mechanically mixing in a Brabender.

<sup>1</sup> Kiddie Fire Protection. Home page. <http://www.kfp.co.uk/GetFile/A50EEADF333195E380256D19002b94b2/fm200.pdf> Accessed 13 August. 2004

<sup>2</sup> Bolle, Paola Costa, Lucio G. Evandri, Maria G. Mastrangelo, Sabina. "In vitro assessment of mutagenicity and clastogenicity of BDE-99, a pentabrominated diphenyl ether flame retardant." . 10 February. 2003. European Union; Grant Number: QLK4-CT-1990-01562. 13 August. 2004 <<http://www3.interscience.wiley.com/cgi-bin/abstract/104553508/ABSTRACT>>.



## Self-extinguishing Polyolefin Rubber/Organoclay Nanocomposites

Evan Hertan, Yeshivah of Flatbush High School

Mayu Si, Hsinchou Chu, Miriam Rafailovich, Jonathan Sokolov, Department of Materials Science and Engineering, Stony Brook University

Polyolefin rubbers, ethylene-propylene rubber and ethylene-propylene-diene-methylene (also called EP rubber and EPDM), are the most widely used and fastest growing synthetic rubbers having specialty and general-purpose application due to their excellent resistance to heat, oxidation, ozone and weather aging. But when exposed to a flame, polyolefin rubbers are easy to ignite and the flame spreads rapidly. As the usage of polyolefin rubbers increases, flame retardancy has become a pressing issue. Traditionally the flame-retardancy of polyolefin rubbers can be improved by compounding with conventional flame retardant (FR) agents such as decabromodiphenyl ether (DB) and antimony trioxide (AO).<sup>1</sup> Due to the corrosivity and suspected smoke toxicity of halogen-containing FR chemicals, an environment friendly FR agent for polyolefin rubbers is necessary, which will improve or maintain the properties of the original flammable polymer.

EP Rubber and EPDM were melted and then blended with varying concentrations of DB, AO and Cloisite 20A using a brabender. The combustion behavior of the sample was investigated by mimicking the UL 94 V-0 test. Testing began with a high concentration of DB, decreasing it while increasing the concentration of clay to allow us to find the optimal clay concentration and the minimal DB concentration(as shown in table 1). The addition of clay can effectively avoid dripping (a very common reason for UL-V0 failure) and decrease the burning speed during burning test, which makes it possible that the sample achieve UL 94 V-0 standard. The mechanical properties of the new FR polyolefin rubbers were measured by using the dynamic mechanical analysis (DMA) and the results show the introduction of clay improved the modulus by 200 % compared to pure rubber and rubber containing DB and AO.<sup>2</sup> Addition of the DB and AO did not have a significant effect on the mechanical properties and does not prevent dripping during burning.

The optimal formula was found for the self-extinguishing polyolefin rubbers, which contains minimum DB and AO. Future work will investigate the FR mechanism with the addition of clay by using thermal gravimetric analysis (TGA), cone calorimeter and limiting oxygen index (LOI).

Sample #	EP Rubber	EPDM	Decabromine	Antimony Trioxide	Cloisite 20A	PP-Ma	Phosphorus	UL-V0 Candidate
1	73%	--	16%	4%	5%	2%	--	Yes
2	73%	--	12%	3%	10%	2%	--	Yes
3	77%	--	12%	3%	5%	3%	--	No
4	68%	--	12%	3%	15%	2%	--	No
5	83%	--	12%	3%	--	2%	--	?
6	76%	--	--	--	7%	2%	15%	No
7	78%	--	8%	2%	10%	2%	--	No
8	--	77.5%	10%	2.5%	10%	--	--	Yes
9	77.5%	--	10%	2.5%	10%	--	--	Yes
10	75%	--	12%	3%	10%	--	--	Yes
<b>EP</b>	<b>100%</b>	--	--	--	--	--	--	<b>No</b>
<b>EPDM</b>	<b>100%</b>	--	--	--	--	--	--	<b>No</b>

**Table 1:** List of polymer nanocomposites blended in the brabender.

<sup>1</sup> Marco Zanetti, Giovanni Camino, Domenico Canavese, Alexander B. Morgan, Frank J. Lamelas, Charles A. Wilkie, "Fire Retardant Halogen-Antimony-Clay Synergism in Polypropylene Layered Silicate Nanocomposites" *Chemistry of Materials* 14 (1), 189 -193, 2002

<sup>2</sup> Jeffrey W. Gilman, "Flammability and thermal stability studies of polymer layered-silicate clay nanocomposites". *Applied Clay Science* 15 1999.

## Achieving Fire-Resistance in Polymer Blends by using Clay and Bromine Mixtures

Jeddy Chen, Albert Ko, Ward Melville High School

Mayu Si, Charlie Chu and Dr. Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

The poor thermodynamic properties of a polymer have always been a problem; their low melting points and ease of combustion make them susceptible to deformation and burning. Mixtures of traditional fire-retardants decabromodiphenyl ether<sup>1</sup> and clays<sup>2</sup> have been studied for their ability to enhance the polymer's thermodynamic properties.

Five different concentrations of clay, bromine, and polymers have been studied. The polymers we chose were polystyrene (PS) and poly(methyl methacrylate) (PMMA) because of their naturally low resistance to thermal decomposition. The mixtures were analyzed with an ignition test to see their flammability; a dynamic mechanical thermal analysis (DMTA) to see their modulus and strength; and were observed by Transmission Electron Microscopy (TEM) to see the particle interactions.

Without clay or bromine (Figure 1), the polymers have no fire retardant properties. We have seen that the presence of only one fire retardant, clay (Figure 2) or bromine (Figure 3), in a PS/PMMA mixture has little effect on the thermal dynamic properties. While with a combination of both substances (Figure 4), the polymer becomes very fire resistant and has the ability to self extinguish. From this we can conclude that this combination of two fire retardants could make normally non-fire resistant polymers more resistant to thermal decomposition.

With the DMTA, we hope to find the effects on the mechanical properties of the polymer blend with the introduction of clay and bromine particles. We also hope to find the interaction between the bromine and clay, which allows it to have such fire retardant properties. Other tests, such as the TEM, are also being performed on the materials to find out why bromine and clay make them more fire retardant.



**Figure 1:** PS and PMMA burned



**Figure 3:** PS, PMMA, Bromine burned.



**Figure 2:** PS, PMMA and Clay burned



**Figure 4:** PS, PMMA, Bromine and Clay burned.

<sup>1</sup> G. Camino, L. Costa; Luda di Cortemiglia. *Polymer Degradation and Stability*, **1991**, 33, 131-154

<sup>2</sup> Gilman, Jeffrey W. *Applied Clay Science* **1999**, 15, 31-49

# Session 8: Supercritical Processing of Blends

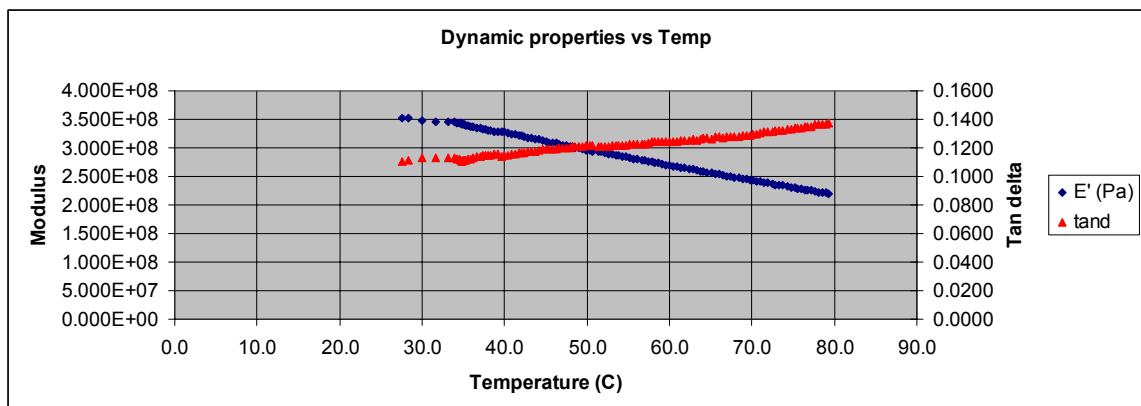
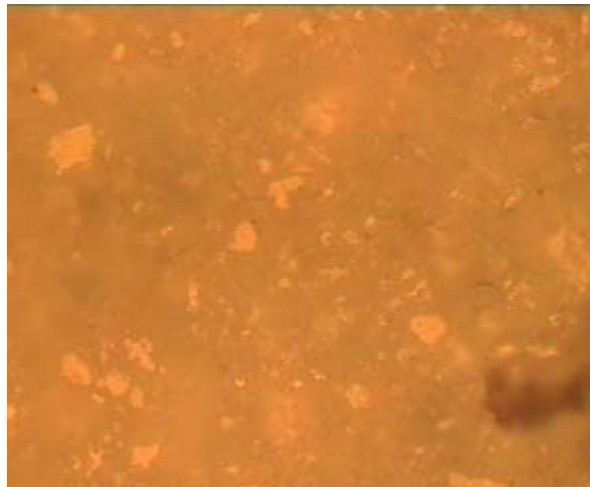
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*Chair: Ed Palermo*

Joel Herzfeld

John Michael Iraci

Gregory Parnes



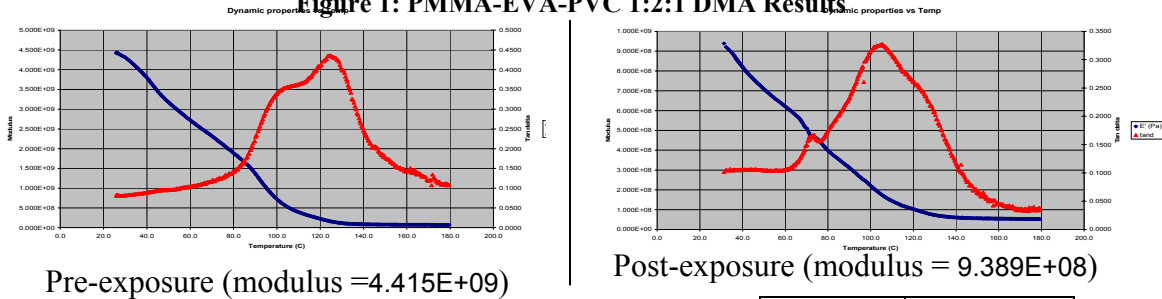
# Tri-blends: A Novel Procedure to Create Ideal Plastics using Recycled Materials Exposed to Supercritical Carbon Dioxide

**John Michael Iraci**, Kings Park High School  
Ed Palermo, Cornell University

Mitchell Fourman, Miriam Rafailovich, Department of Materials Science and Engineering,  
Stony Brook University

In recent decades supercritical fluids have proven themselves as environmentally safe universal co-solvent<sup>1</sup>. When exposed to supercritical fluids (SCF), polymers will exhibit many variations of swelling and enhanced chain mobility<sup>1</sup>. Recycled plastics pose a significant environmental challenge due to their inability to biodegrade or be reprocessed into a usable material. Along with current applications that span from industrial extraction of caffeine from coffee beans to a much more domestic dry cleaning agent, supercritical carbon dioxide has been shown to increase the interfacial width of polymer blends, thus inducing a partial to complete compatibilization within the materials<sup>2</sup>. Here we show that supercritical carbon dioxide induces similar results within recycled polyvinyl chloride (rPVC) when blended with poly(methyl methacrylate) and ethylene vinyl acetate (PMMA-EVA-rPVC). As shown by Dynamic Mechanical Analysis (DMA), these “tri-blends” showed reduced modulus after exposure (10<sup>9</sup> to 10<sup>8</sup> Pa), as well as a more gradual modulus decrease (Figure 1). DMA results also revealed a merging of the relative glass transition temperatures of the polymers. Using the Flory-Fox equation for polymer compatibility (Equation 1), the materials were found to have increased in compatibility as a result of SCF exposure (Table 1). This justifies that Supercritical CO<sub>2</sub> has a unique solvent strength which can revitalize previously unusable PVC. New applications for such materials include cheaper alternatives to current plastics on the market, as well as a new domain for replaceable parts.

**Figure 1: PMMA-EVA-PVC 1:2:1 DMA Results**



**Equation 1: Flory-Fox Equation for Polymer Blend Compatibility**

$$\phi_1 T_{g1} + \phi_2 T_{g2} + \phi_3 T_{g3} = T_{g4}$$

	Pre Exposure	Post Exposure
Φ1	0.25	0.25
Tg1	120	120
Φ2	0.5	0.5
Tg2	60	105
Φ3	0.25	0.25
Tg3	84	75
<b>Tg4</b>	<b>81</b>	<b>101</b>
<b>Actual Tg4</b>	<b>117</b>	<b>117</b>

**Table 1: Results of Flory-Fox Equation**

<sup>1</sup> D. L. Tomasko, H. Li, D. Liu, X. Han, M. J. Wingert, L. James Lee, and K. W. Koelling. *A Review of CO<sub>2</sub> Applications in the Processing of Polymers* Department of Chemical Engineering, The Ohio State University, Columbus, Ohio Ind. Eng. Chem. Res. 42 6431-6456, 2003.

<sup>2</sup> Fourman, M. Palermo, E.. Lubin, S. Si, M. Rafailovich, M H. Sokolov, J C. *Increasing the Compatibility of Polymer Blends using Supercritical Fluids* (Abstract) APS March Meeting, (2004).

# The Effects of Supercritical Carbon Dioxide on Biodegradability

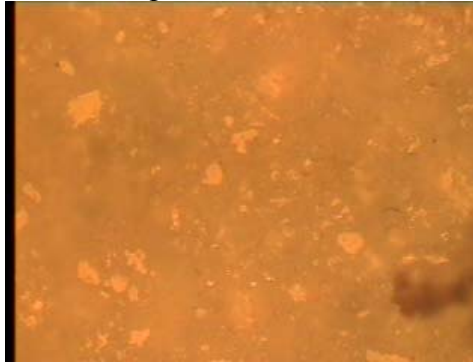
Joel Herzfeld HAFTR High School

Ed Palermo and Dr. Miriam Rafailovich

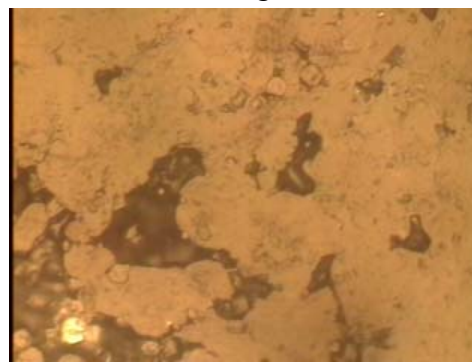
Department of Materials Science and Engineering, Stony Brook University

Today, as xenobiotic mass accumulates in soil, the market for biodegradable polymers is increasing. As the market increases, companies are searching for new sources of cheap biodegradable polymers.<sup>1</sup> One possible future market is in supercritical fluids, namely blending a biodegradable polymer such as starch with a polymer that shows increased mechanical properties upon exposure to the supercritical fluid. Some research shows that when polymers are foamed, one of two things can happen: In the first case, the increased porosity of the polymer blend allowed amylase secreted by bacteria and fungus to gain better access to the amylase in the starch, therefore yielding faster, more efficient biodegradation. In the second case, the porosity inhibited enzymes.<sup>2</sup> In my experiment, I plan to look at the affects of supercritical fluids on starch blends to examine its effect on the rate and efficiency of biodegradation. I hypothesize that the supercritical treatment will increase the rate of biodegradation in starch blends.

For my experiment, a hot press was used to create two groups of samples of different starch blends, namely starch and poly(ethylene oxide) and starch and hydroxypropyl cellulose. Each group contained a 5% and a 10% starch mixture. Dogbone samples were also created for each group to be used for tensile testing. The samples were then examined under an optical microscope as one method of degradation quantification. As seen in figures 1 and 2, the starch is not readily miscible with cellulose. The samples were also weighed. When starch undergoes the enzymatic degradation, it releases hydrogen, which makes weight loss another test to quantify degradation. Other quantification methods are via mechanical testing of samples by dynamic mechanical analysis and tensile testing. Then, I plan to expose my samples to soil for various times and redo all the previous tests. Results will be compared to see if the supercritical treatment had any effect an on the rate of biodegradation.



**Figure 1:** Optical microscope image of 10-90 starch-cellulose blend under 10x magnification



**Figure 2:** microscope image of a 5-95 starch-cellulose blend under 50x magnification.

<sup>1</sup> S.N. Jogdand. "Bioplastics" Biopolymer.net

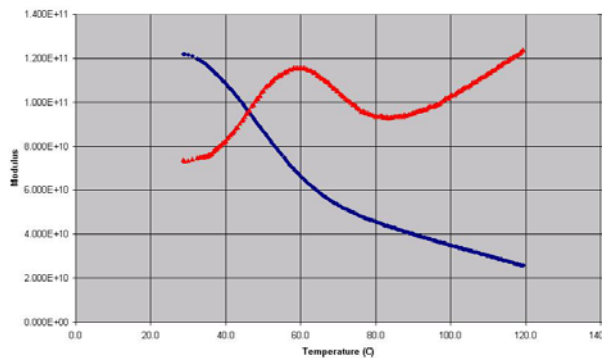
<sup>2</sup> Thakore I.M.; Desai, S.; Sarawade, B.D.; Devi S. "Studies on biodegradability, morphology and thermomechanical properties of LDPE/modified starch blends." *European Polymer Journal*. **2001**, 37, 151-160.

# Enhancing Mechanical Properties of PVC-Polypropylene and PVC-Polyethylene oxide Blends through Exposure to Supercritical Carbon Dioxide

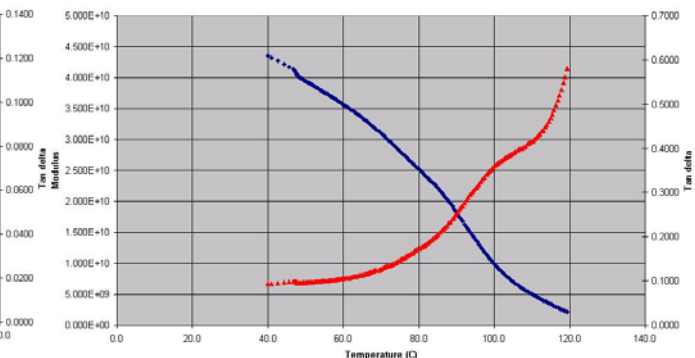
**Bradley Eric Schwartz**, Rennselaer Polytechnic Institute  
Edmund Francious Palermo, Cornell University  
Dr. Miriam Rafailovich, Stony Brook University

Most polymers are not miscible with one another, and so polymers generally do not bind effectively at the interfaces within polymer blends. Supercritical fluids such as supercritical carbon dioxide have been shown to act as general compatibilizers of polymer blends. The gaseous component of supercritical fluids creates pores within blends; it is hypothesized that when the pores displace sections of homopolymers the surface area at which the blended polymers react is expanded, and the polymers are brought into contact with each other more tightly, thus allowing them to mix more effectively. The differences in the mechanical properties of pre-exposed and post-exposed blends of PVC-Polypropylene and PVC-Polyethylene oxide were analyzed in order to gain insight into other reasons for which supercritical fluids compatibilize polymers and to demonstrate further that supercritical carbon dioxide acts as a general compatibilizer for all combinations of polymer blends.

Dynamic Mechanical Analysis was used to compare the elastic modulus of blends as a function of temperature, and the set of damping coefficient data was used to determine the glass transition temperature of each blend. Post-exposed blends were found to have only one glass transition temperature, which suggests that the polymers that compose them compatibilized effectively. Additionally, post-exposed blends had a consistently higher storage modulus as a function of temperature, which shows that mechanical strength was enhanced. Figures 1 and 2 below show elastic/storage modulus vs. temperature for pre-exposed and post-exposed PVC-Polypropylene, respectively. Scanning Electron Microscopy was used to analyze the change in porosity of exposed blends, and Instron was used to compare tensile strength.



**Figure 1:** Pre-exposed PVC-PP



**Figure 2:** Post-exposed PVC-PP

1. Fourman, M. Palermo E. Lubin S. Si M. Rafailovich M. Sokolov J. *Increasing the Compatibility of Polymer Blends using Supercritical Fluids* APS March Meeting (Abstract), 2004.
2. Dowling, Norman E. Mechanical Behavior of Materials: Engineering Methods for Deformation, Fracture & Fatigue. January 1993.

# Effects of Supercritical Carbon Dioxide on the Mechanical Properties of PB-PS and PS-EVA Blends with Clay Nanocomposites

Gregory Parnes, HAFTR High School, Five Towns NY

Mitchell Fourman, E Guan, Miriam Rafailovich, Mayu Si, Dept. of Materials Science and Engineering, Stony Brook University NY  
Edmund Palermo, Cornell University

A supercritical fluid combines the density and viscosity of a liquid and gas, thus creating density fluctuations typical of the phase of matter. When a supercritical fluid is compressed to a liquid-like density, it develops into an ideal co-solvent unseen in any other phase of matter<sup>1</sup>. High impact polystyrene (HIPS) is an inexpensive, lightweight plastic typically used for handling-trays with which accommodate lightweight products. It has marginal resistance to impact and tearing, although it can be modified with a rubber additive to improve its durability<sup>2</sup>. The purpose of this study was to mechanically engineer a material with greater mechanical properties than high impact polystyrene, using supercritical carbon dioxide. Polystyrene-*blend*-Polybutadiene and Polystyrene-*blend*-Ethylene vinyl acetate were used along with the addition of clay nanocomposites (Cloisite 6A) at varying ratios. Polymers were blended, pressed, and exposed to supercritical carbon dioxide to achieve polymer foaming above and below the critical point of 87.3 °C and 1073 psi(a). An increased brittleness was observed with higher contents of clay in the polymer blends. Due to a difference between the melting points of PS and PB, the blends created displayed grain boundaries when they were pressed. These grain boundaries acted as fracture points in the material, and therefore further stress strain testing was not possible. Additionally, a direct relationship was established between exposure pressure and the resulting increase in ductility and tensile strength. Applications of such materials include stronger and more efficient outdoor plastics, shoe materials, car bumpers/chassis, and packaging. The addition of tests such as Transmission Electron Microscopy (TEM), DMA (Figure 1), and polymer cross-sectioning will lead to the possibility of synthesizing prosthetic tendons and ligaments.

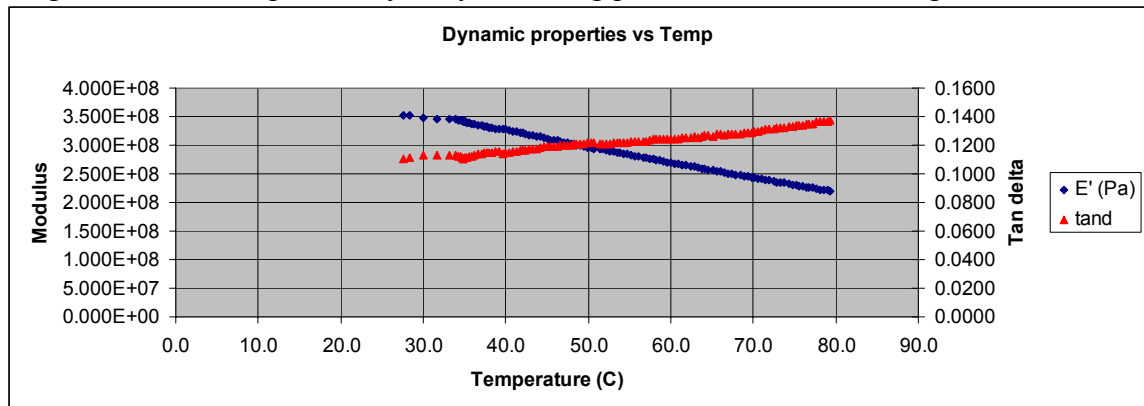


Figure 1: DMA Test- PS-PB control sample-pre exposed- modulus of  $3.5 \times 10^8$

<sup>1</sup> Jerome, J. Koga, T. Seo, Y-S. Rafailovich M.H. Sokolov, J. *Co-Solvent Effect of Supercritical Carbon Dioxide for Immiscible Polymer Interfaces* (Abstract) APS March Meeting, 2003.

<sup>2</sup> The Dow Chemical Company **Technical Library: High Impact Polystyrene**  
<http://www.dow.com/styron/tech/high/product.htm>, 2004.

# Session 9: Biomedical and Miscellaneous Applications

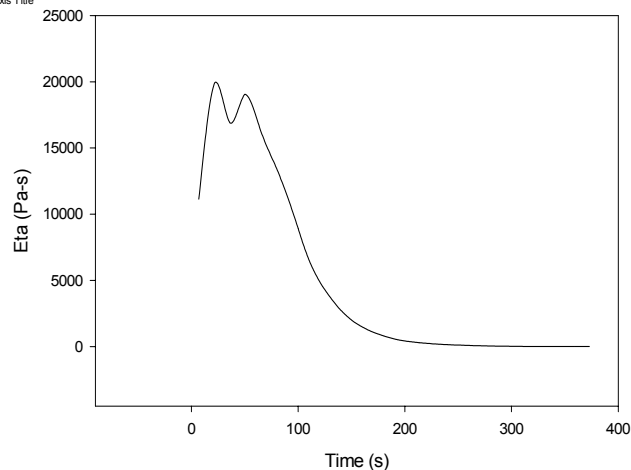
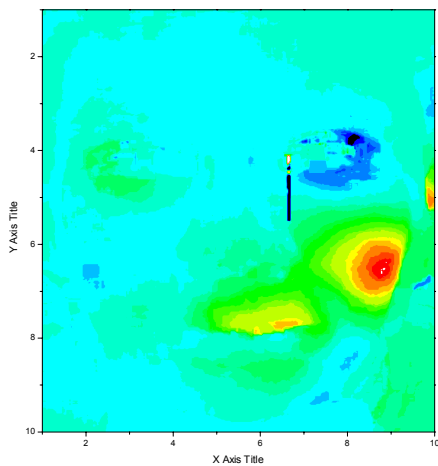
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***Chair: Sara Rafailovich-Sokolov***

Jason Goodman

Alan Chou

Andrew Scheur





## The Relationship Between Cells Traction Forces and their Growth Rate

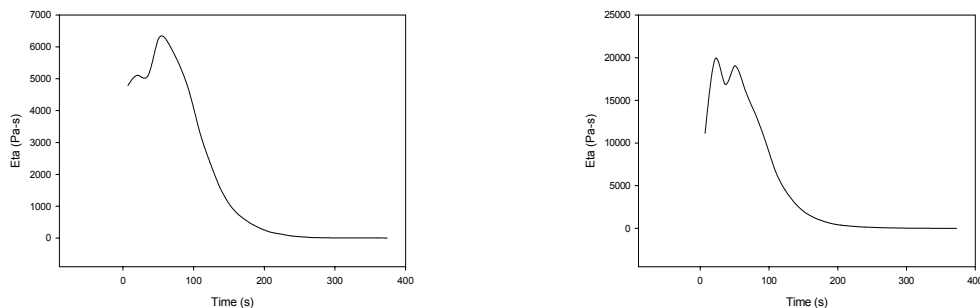
Alan Chou, Great Neck South High School

E Guan, Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

Understanding the intercellular and cell-substrate dynamics is crucial in analyzing biological processes such as tissue engineering, wound healing, and cancer metastases. These physical interactions also govern tissue and cell growth, movement, and migration. The purpose of this study was to relate the growth rate of fibroblasts to their cellular traction forces.

The polymer substrate selected for cell growth was polyoxypropylene-polyoxyethylene block copolymer F127 (Pluronic F127). It forms a gel around 25°C and melts near 4°C rapidly and reversibly, making it ideal for manipulation. In addition to the reversible phase change, Pluronic F127 was shown to be biocompatible and an effective vehicle for protein drug delivery. These properties make Pluronic F127 a likely substrate for controlled cell growth. In this project, the concentrations of Pluronic F127 solutions were varied to alter cell growth conditions. 10%, 20%, 30%, and 40% concentrations were made with either water or D-MEM solution as the solvent. Two kinds of clays, montmorillonite and lucentite, were used in this study to improve the mechanical properties of the aqueous gels. 0.7% of each kind of clay was added to the aqueous solutions. The viscosity of each solution was then measured by a rheometer (Figure 1). The curves show how viscosity, measured in poise, change with respect to shear rate. The solutions also contain nanobeads to help quantify the magnitude of the cellular traction forces.

Current techniques of observing cellular traction forces are limited by the mechanical properties of the substrates such as flexibility. Other techniques, such as using micromachined cantilevers on silicon wafers, are expensive and complex.<sup>1</sup> DISC<sup>2</sup> (Digital Imaging Speckle Correlation), is a tool used to measure deformation. It is an effective instrument to measure and graph cell traction forces.



**Figure 1:** The rheometry curve for Pluronic F127 solutions at 10% concentration (left) and 20% concentration (right).

<sup>1</sup> K.A. Beningo and Y.L. Wang, "Flexible Substrata for the Detection of Cellular Traction Forces," in TRENDS in Cell Biology, vol. 12, no. 2, Feb., pp. 79-84, 2002.

<sup>2</sup> D. Amodio, G.B. Broggiato, F. Campana, and G.M. Newaz, "Digital Speckle Correlation for Strain Measurement by Image Analysis," Society for Experimental Mechanics, vol. 43, no. 4, Dec., pp. 396-402, 2003.

## Investigations for Facial Recognition through Digital Image Speckle Correlation

Jason Goodman, Roslyn High School

E. Guan, Sara Rafailovich-Sokolov, and Miriam Rafailovich, Department of Materials Science and Engineering, Stony Brook University

The Purpose of this study is to explore a novel dynamic approach for facial recognition. To date, most facial characterization techniques utilize still images to extract features of the face (such as the eyes, nose, and mouth). In this research, we suggest that it is possible to uniquely identify faces by analyzing the natural motion of facial features. Because the motion is mostly determined by the facial musculature and skin elasticity, detection of facial dynamics, as opposed to static facial features, is less prone to distortion by lighting condition or be obscured by facial makeup.<sup>1</sup> In order to accomplish this analysis we will use the technique of Digital Image Speckle Correlation (DISC) to detect the facial motion. DISC calculates the facial motion from two pictures taken in a quick succession while the subject is making a facial expression. The resulting vector maps and U/V maps (see fig. 1) will be used as a signature for identification.<sup>2</sup>

To test the accuracy of DISC an identical twin study was performed. Photographs were taken and DISC was used to generate motion maps of each twin. A correlation was then run against the two maps. The result was a .034 coefficient of correlation between the identical twins. This supports the concept that DISC can identify the unique qualities of ones personal musculature development even in the condition of complete genetic similarity.

An investigation into the modulus of human skin as a function of age is also being run. The first approach uses a weighted earring apparatus (see fig. 2). A photograph of the subject is taken with the weighted earring (3.4 grams) and then another after weight is removed. The observed displacement and constant force is used to calculate the modulus. The second approach utilizes surgically removed human skin. Carefully prepared strips (apprx. 4 in x .5 in) of human skin (epidermis and dermis) were stripped of fat and tested for tensile strength in the Instron.

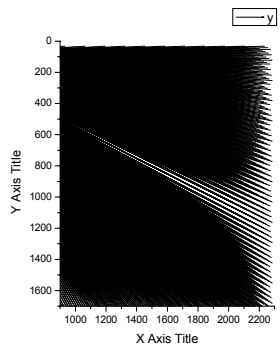


Figure 1: Vector map and U/V map (respectively)



Figure 2: Earring Apparatus with weight

<sup>1</sup> Nash LG, Phillips MN, Nicholson H, Barnett R, Zhang M. *CLINICAL ANATOMY* 2004, 287-293, 17

<sup>2</sup> E. Guan, Sarah Smilov, Miriam Rafailovich, Jonathan Sokolov: Determining the Mechanical Properties of Rat Skin with Digital Image Speckle Correlation. *Dermatology*: 2004;208:112-119.

## NY Orionis: The Nature of an EXor Star

**Andrew Scheur**, Long Beach High School  
Professor Frederick M. Walter  
Department of Physics and Astronomy, SUNY Stony Brook

EXors, named after prototype EX Lupi, are highly active Classical T Tauri stars that periodically undergo UV-optical outbursts. The accrual of matter onto the star from a circumstellar disk is understood to provoke these outbursts.<sup>1</sup> Typically, EXors are associated with nebulosity and recognized in the vicinity of star-forming regions.<sup>2</sup> The outbursts of an EXor star seldom experience periods of inactivity and often cover their entire display of variation, rapidly brightening and fading, in less than a few days.

IDL (Interactive Data Language) software was utilized for differential photometric and spectroscopic observations of EXor star, NY Orionis. Data in the form of images was received and analyzed from the SMARTS Telescope Consortium located at Cerro Tololo, Chile between the years of 2003 and 2004. The brightness of NY Orionis was compared to that of an A-Star on the same exposures. The profound light variations observed were acquired and evaluated on timescales of days in an endeavor to clarify the nature and origin of the phenomenon.

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<sup>1</sup> Stringfellow G. S., Kato, T., Nogami D., Landolt A., Calzetti D., and Laurent-Mueheisen S. "Recent Outbursts of EXors." *American Astronomical Society*, 1998, 30, 934.

<sup>2</sup> Walter F., Stringfellow G., Sherry W., Pollatou A. "V1647 Ori (IRAS 05436-0007) in Outburst: the First Three Months." 2004.

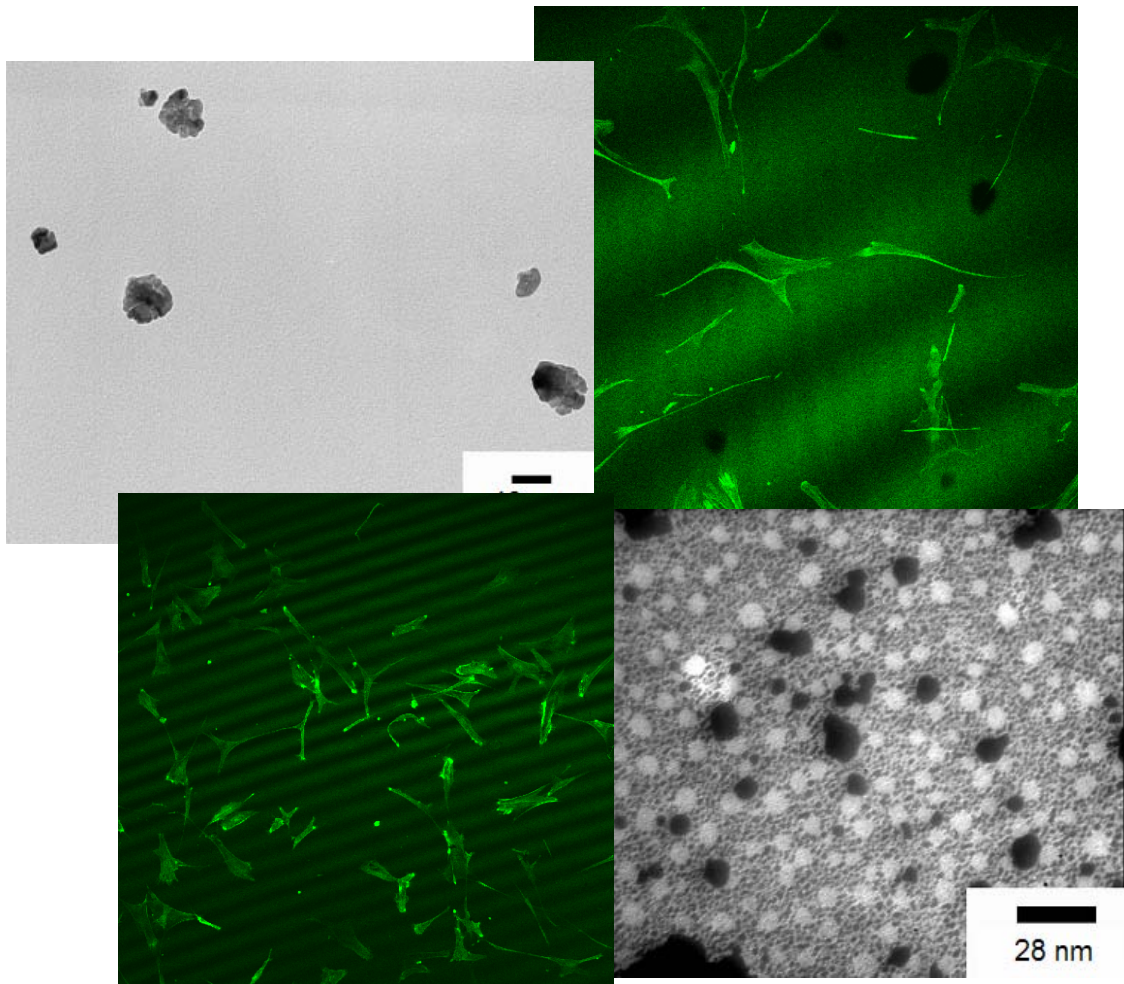
# Session 10: Nanoparticles, Synthesis & Side Effects

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***Chair: Rebecca Isseroff***

Aditi Ramakrishnan

Yonatan Schwab, Yisrael Herzberg



## Synthesis of Palladium Nanoparticles for Embedding in a Polymer Matrix (for Use in Catalysis and Hydrogen Storage)

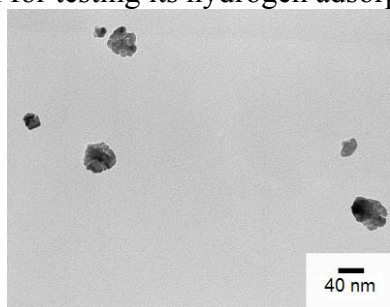
Yisrael Herzberg, Yonatan Schwab, Rebecca Isseroff, Rambam Mesivta  
Yuan Sun, Department of Materials Science and Engineering, Stony Brook University

Palladium nanoparticles are of great interest for their catalytic activity and are well known for their hydrogen adsorption properties. There is much study of the relationship between particle size and catalytic activity. An increase in the surface-to-volume ratio, i.e. a smaller nanoparticle, should have more effective catalytic activity. Our goal was to produce palladium nanoparticles of uniform size and shape, embed them in a polymer matrix uniformly (without clumping) to act as a support, and assure that the nanoparticles would still be readily accessible to reactants for catalysis.

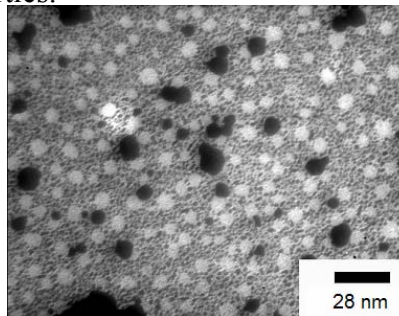
We synthesized palladium nanoparticles using the following method<sup>1,2</sup>: 54.8mg PdCl<sub>2</sub> were sonicated with 6.6ml 1N HCl and added to 325ml of distilled H<sub>2</sub>O. 50ml of this PdCl<sub>2</sub> solution, 100 ml of a 1% NaCit in H<sub>2</sub>O solution, and 100ml distilled H<sub>2</sub>O were added to a 500ml three-neck reaction cell together with a stir bar. The reaction cell was immersed in a silicone oil bath atop a magnetic stirring hot plate and heated to a temperature ranging from 130°C -145°C, thereby boiling the reaction mixture for six hours, by which time it became light brown in color.

Similarly, we combined  $2.775 \times 10^{-4}$  moles (0.091g) of K<sub>2</sub>PdCl<sub>4</sub>,  $2.04 \times 10^{-3}$  moles (0.600g) of NaCit, each dissolved in 10 ml of distilled H<sub>2</sub>O, with an additional 130ml distilled H<sub>2</sub>O. After refluxing for six hours, there was no visible change in the light yellow mixture, and it was left to cool overnight. The next day, the reaction mixture was acidified with 10ml 0.6M HCl. Upon heating again, the color darkened to an amber color and was refluxed for two additional hours. A 50ml aliquot of this mixture was concentrated by roto-evaporation. Samples of the original and concentrated solution were viewed under the TEM. Analysis of the particles in the dilute solution (Fig. 1) showed aggregates ranging from 40nm to 120nm in diameter. In the TEM image of our concentrated solution (fig. 2), we hypothesize that the different colors are aggregate (black, ranging from 25-50nm in diameter), individual Pd nanoparticles (gray, averaging 6nm in diameter), and citrate crystals (white). 2ml aliquots of each solution were then mixed with PEO (25mg/ml) to form films for X-ray diffraction.

Future work will be to expose the polymer nanoparticle films to supercritical CO<sub>2</sub> and hydrogen for testing its hydrogen adsorption properties.



**Fig. 1** TEM image of dilute Pd nanoparticle solution at 100k magnification



**Fig. 2** TEM image of concentrated Pd nanoparticle solution at 145k magnification

<sup>1</sup> G. Kim, J. Turkevich. "Palladium: Preparation and Catalytic Properties of Particles of Uniform Size." Science, Vol. 169, 873-879.

<sup>2</sup> G. Schmid, H. West, H. Mehles, A. Lehnert. "Hydrosilation Reactions Catalyzed by Supported Bimetallic Colloids." Inorg. Chem, 1997, 36, 891-895.

## Cytotoxicity of Citrate Covered Gold Nanoparticles in Dermal Fibroblasts

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Department of Materials Science and Engineering, Stony Brook University

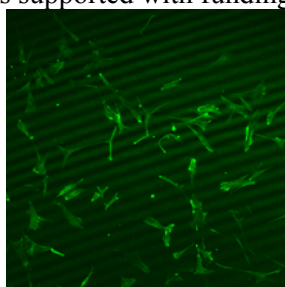
During the past ten years, nanotechnology has blossomed into an intricate field, connecting diverse areas of science such as medicine, electronics, and recently, cosmetology. Companies such as L'oreal are interested in using nanoparticles in makeup because they reflect light in such a way as to create unique pigments. Nanoparticles can be used in sunscreens because they deflect Ultra Violet rays and they can carry vitamins past the epithelial layer<sup>1</sup>. However, there has been no systematic study of the cytotoxicity of nanoparticles. In this study we investigated whether nanoparticles are dangerous for dermal fibroblasts.

We chose to study how particle size and various concentrations of nanoparticles affect dermal fibroblasts. In order to create makeup and drug delivery systems which utilize "safe sizes", it is critical to discover what size is cytotoxic and how size affects cytotoxicity. We also investigated how various concentrations of nanoparticles affect fibroblasts. We experimented with two different sizes of citrate coated gold nanoparticles: 15 nm and 36.3 nm. Gold was used because it is inert and FDA approved, and citrate is present in the Krebs cycle to produce energy for cells. The nanoparticles were delivered to cells in solution at various concentrations: 0 ul/ml, 50ul/ml, 100ul/ml, 150ul/ml, and 200ul/ml.

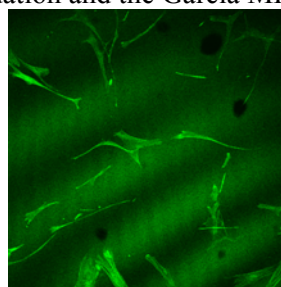
Through taking confocal microscopy images of these cells, we showed that as the concentration of 15 nm particles increased, more nanoparticles accumulated within the cell. The accumulation of nanoparticles was lower when the cells were in 36.3 nm particle solutions, indicating that these larger particles could not easily enter the cells. Even though a particular makeup may have a low concentration of nanoparticles, if applied regularly, this minute concentration will accumulate within cells. Additionally, we found that the cell area (Fig 1, 2) and cell number were dramatically affected by the 15 nm particles, and so were the number of actin fibers in these cells. Knowing that the actin fibers, which create the cytoskeleton, and the extracellular matrix proteins regulate cell functions such as gene transcription, adhesion, proliferation, and differentiation<sup>2</sup> (Alberts et al. 1994, 972) it is clear that nanoparticles can be dangerous for our health.

Further studies will include researching how palladium nanoparticles of different sizes affect cells, thus addressing the chemistry of nanoparticles, how nanoparticles *in vitro* can affect extracellular matrix proteins such as fibronectin, and the mechanisms by which nanoparticles enter cells.

This work was supported with funding from the Simons Foundation and the Garcia MRSEC program.



**Fig 1:** Dermal Fibroblasts in a 15 nm solution  
200 ul/ml, 144 hrs



**Fig 2:** Dermal Fibroblasts in a 36.3 nm solution  
200 ul/ml, 144 hrs



<sup>1</sup> Boseley, Sarah. Toxic Chemicals and Nanoparticles in Conventional Cosmetics Threaten Public Health. *The Guardian*. 8 May 2004.

<sup>2</sup> Alberts, Bruce et al. 1994. *Molecular Biology of the Cell*. New York: Garland Publishing Inc.

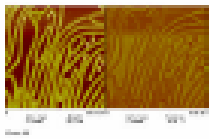
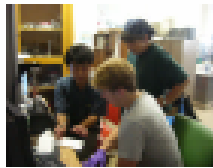
## Summer Scholar Program Schedule of Activities

EVERY DAY STARTS WITH A GROUP MEETING IN 2<sup>ND</sup> FLOOR LOUNGE

# CHECK SCHEDULE DAILY!

	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
<b>Week of 7/5</b>		<p><b>6 10:00 Opening Day- Welcome &amp; Orientation</b></p> <p>10:30 How Small is Small? Intro to Nanotech. Prof. Poros Gouma 12-12:30 LUNCH 12:30-2:00 SEM, AFM, Confocal Demos. <b>Jana Quinn, Nadine Peroulet, Maddie De</b> 2-3:00 Keeping a lab notebook, Presentation of lab notebooks, books, supplies. <b>Dr. Ockhigross</b> 3-3:30 Web of Science, Pub med <b>Michael Foreman, Erik Peterson</b></p>	<p><b>7 10:00 Daily meeting</b></p> <p>10:15 Vacuum technology. Prof. <b>Jonathan Sokolov</b> 11:00 Lab Safety and chemical handling <b>Robert Hoffmann EHS</b> 12:00 LUNCH 12:30 Disposal of Chemicals, Lab Tour. <b>Louise Collins</b> 1:30-2:30 Test-Vacuums, chemicals, disposal, lab safety 1:50-3:00 Group demo of rapid prototype <b>J. Quinn</b> 2:50-3:00 Polymer Dynamics <b>Prof. Dmy Gerasim</b> 3:00-4:00 Journal Club Prep</p>	<p><b>8 10:00 Daily meeting</b></p> <p>10:15 Protecting intellectual property. <b>Dennis Tuzunicko</b> Starting a high tech business <b>David Adams</b> 11:30-12:30 Experiment 1: Coherence of Light <b>Prof. Heary</b> <b>White</b> 12:30-1:30 Lunch 1:30-2:30 Spinning thin films, viscosity, rheology <b>Prof. Steven Schwarz</b> 2:30-4:00 Eboard tutorial <b>Michael Snow, Dr. Ockhigross</b></p>	<p><b>9 10:00 1<sup>st</sup> General Group Meeting- summary of weeks activities</b></p> <p><b>Marie-Guyot</b>, Siemens Foundation: <i>Spinning to the Moon</i> <b>Mr. Herbert Carter</b>, Siemens Foundation: <i>The Siemens Paragon</i> <b>Competition</b> <b>Catalin Luchian</b> <b>Lenny Slutsky, Maddyn H.</b> Participating in the Siemens Competition <b>Kira Katz, Erik Mansfield</b>: Being in the Stratosphere <b>A Scaffold for wound healing</b></p>
<b>Week of 7/12</b>	<p><b>12 10:00 Daily meeting</b></p> <p>10:30 Cell Biology <b>Dr. Nadine Peroulet</b> 11:30 Cell Culture Techniques <b>Louise Collins, Room 143</b> 12:00 Lunch 12:30-1:30 Lunch 1:30 Silicon Wafer cleaning &amp; spinning Tutorial <b>Prof. M. Rafailovich</b> 1:50-3:30 Cleaning Si Wafers (<b>Song Li, Harry Xavier, E. Guan, Chinghua Li, John Jerome</b>)</p>	<p><b>13 10:00 Daily meeting</b></p> <p>10:30 <b>Dr. Eli Harel</b>, Gold spring Harbor "Understanding the Human Genome" 12:00 Lunch 1:00 Spin Coating Films: a method of recycling polymers (<b>Song Li, Harry Xavier, E. Guan, Chinghua Li, John Jerome</b>)</p>	<p><b>14 10:00 Daily meeting</b></p> <p>10:30 <b>Dr. Lance Haworth</b> Director, MRSEC programs "What is the NSF?" 11:30-12:30 Statistics 1 <b>Prof. Miriam Rafailovich</b> 12:30-1:30 Lunch 1:30-4:00 Spin Coating cont. (<b>Harry Xavier, E. Guan, Chinghua Li, John Jerome</b>)</p>	<p><b>15 10:00 Daily Meeting</b></p> <p>10:30 <b>Dr. Joseph Intel</b>, "Technology in Homeland security" Brookhaven National Laboratory 11:30 <b>Prof. Miriam Rafailovich</b> "Statistics II-Propagation of Error" 12:30-1:30 Lunch 1:30-4:00 Spin Coating cont. (<b>Harry Xavier, E. Guan, Chinghua Li, John Jerome</b>)</p>	<p><b>16 10:00 2<sup>nd</sup> General Group Meeting</b></p> <p><b>10:30 Dr. Elaine DiLauro</b>, "Biomedicalization of Marine Life" Brookhaven National Laboratory 11:30 <b>Ms. Katherine Siskin</b> "The Science Talent Competition," Intel Foundation 12:30-2:00 <b>Cake of Luncheon and student presentations</b> <b>Chelsea Gordon and Sybil Qi</b>: BSEP and Polymer Brushes <b>Sara Sokolov</b>: Homeland Security and Facial ID <b>Mitchell Foreman</b>: Supercritical Fluid Processing: Theory <b>Steven Lubin</b>: Blending in Supercritical Fluids</p>
<b>Week of 7/19</b>	<p><b>19 10:00 Daily Meeting</b></p> <p>10:30 <b>Prof. Shrikumar</b> Estimation of Nanocomposite Materials 11:30 Journal Club I 12:30-1:30 Lunch 1:30 Discussion of projects and meeting with Mentors  START PROJECTS</p>	<p><b>20 10:00 Daily Meeting</b></p> <p>10:30 <b>Prof. Jonathan Sokolov</b> Discussion of Projects 11:30 Journal Club II 12:00 Lunch 1:00 Meet with Mentors  START PROJECTS</p>	<p> <b>21 10:00 TRIP to Suffolk County Forensic Laboratory</b> <b>Box Lunch</b> Civil at Sports Plus</p>	<p><b>22 10:00 Daily Meeting</b></p> <p>10:30 <b>Professor Cindy Lee</b>, "Strengthening Under the Sea," School of Marine Sciences 11:00 <b>Prof. Rafailovich</b> "Statistics III - Plotting and Homework assignment" 12:00-12:30 Journal Club 12:30-1:30 Lunch  1:30 WORK ON PROJECTS</p>	<p><b>23 3rd General Group Meeting</b></p> <p>10:30-11:00 Group Presentations: Flame Retardant Groups, Protein Adsorption Groups 12:30-1:30 Lunch 1:30 WORK ON PROJECTS</p>
<b>Week of 7/26</b>	<p><b>26 10:00 Daily Meeting</b></p> <p>10:30 <b>Prof. Ed Weil</b>, Brooklyn Polytech. <i>Fluorene retardant polymer competition</i> 11:30 Journal Club III 12:30-1:30 Lunch 1:30 Discussion of projects and meeting with Mentors  Continue PROJECTS</p>	<p><b>27 10:00 Daily Meeting</b></p> <p>10:30 <b>Heinz-Berndt Minko</b>, HMI, Berlin "EGANs from Semi-conductor nanocrystals" 11:30 Work on Projects</p>	<p><b>28 10:00 Daily Meeting</b></p> <p>10:30 Independent Work on Projects</p>	<p><b>29 10:00 CANOE TRIP &amp; Picnic Nissequoque</b></p> <p></p>	<p><b>30 4th General Group Meeting</b></p> <p>10:30-12:00 Group Presentations: crystalline thin films, wound healing 12:30-1:30 Lunch 1:30 WORK ON PROJECTS</p>

<p><b>Week of 8/18/16</b></p>	<p>21. 11/18/16 (Sat) (presenting)</p> <p>from example</p>	<p>22. 11/18/16 (Sat) (presenting)</p> <p>from example</p> 	<p>23. 11/18/16 (Sat) (presenting)</p> <p>from example</p>	<p>24. 11/18/16 (Sat) (presenting)</p> <p>from example</p>	<p>25. 11/18/16 (Sat) (presenting)</p> <p>from example</p> <p>26. 11/18/16 (Sat) (presenting)</p> <p>from example</p> <p>27. 11/18/16 (Sat) (presenting)</p> <p>from example</p> 
<p><b>Week of 8/19</b></p>	<p>28. 11/19/16 (Sun) (presenting)</p> <p>from example</p> <p>29. 11/19/16 (Sun) (presenting)</p> <p>from example</p> 	<p>30. 11/19/16 (Sun) (presenting)</p> <p>from example</p> <p>31. 11/19/16 (Sun) (presenting)</p> <p>from example</p> 	<p>32. 11/19/16 (Sun) (presenting)</p> <p>from example</p> <p>33. 11/19/16 (Sun) (presenting)</p> <p>from example</p> 	<p>34. 11/19/16 (Sun) (presenting)</p> <p>from example</p> <p>35. 11/19/16 (Sun) (presenting)</p> <p>from example</p>	<p>36. 11/19/16 (Sun) (presenting)</p> <p>from example</p> <p>37. 11/19/16 (Sun) (presenting)</p> <p>from example</p>
<p><b>Week of 8/20/16</b></p>	<p>38. 11/20/16 (Mon) (presenting)</p> <p>from example</p> 			<p>39. 11/20/16 (Mon) (presenting)</p> <p>from example</p> 	





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