

Research Scholar Program 2002





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



Dr. Ronald Occhiogrosso, Research Coordinator **Nancy Rifkind**, Project Coordinator



Miriam Rafailovich



Jonathan Sokolov

Research Scholar Program 2002

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 polymers interface science. The principal focus areas include thin films, coatings, nanostructured materials, and composites. These areas address both the fundamental and applied aspects that are relevant to the development of cutting edge enabling technologies for a diverse group of US industries. 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 encourage 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 lifetime learning experience, and we hope to remain a resource to our students long after "graduation".

Sincerely,

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Miriam Rafailovich Professor, Director, Garcia MRSEC

Jonathan Sokolov Professor, Co-Directtor, Garcia MRSEC

Research Experience for Teachers Research Experience for Teachers

Rebecca Isseroff









Hubert Mantz

Ron Occiogrosso





Gary Ramonetti

Research Experience for Undergraduates Research Experience for Undergraduates



Mordechai Bronner



Michael Goldman



Dina Gewaily

Vinitha Jacob





Eli Hoory

Stephanie Kasbuza



Research Experience for Undergraduates Research Experience for Undergraduates

Rebecca Klein





Pam Li

Dora Chana Sosnowik





Edmund Palermo



Pierre Xavier

High School Summer Scholars 2002 High School Summer Scholars 2002

Christine Ahn





Joseph Barone

Nina Bai



Jacqueline

Brazin







Felicia Chiu



Hye Yeon Choi





Simon Ebrani

School Summer Scholars 2002 High School Summer Scholars 2002

Maanasa





Hatty Hong





Jessica Jiang





- Jonathan

- - - Hefter





Lauren



Rikki Frenkel



High School Summer Scholars 2002 20

Unaza

Kahn



Josh Levine

Vivek Kuncham





Rachel Lavon



Aaron Long





Steven Lubin









Abigail Maller



Sarvajit Patil



High School Summer Scholars 20 High School Summer Scholars 2002

Nikhilesh Ray-Mazumder





Setton Tedi

Joan Rho



Michelle Simpser



Michael Snow



Arvin Thachara



Rouge





Lenny Slutsky

Andrew Song



Sarah Smilow



	GARCIA CENTER High School Summer Scholars 2002			
Christine Ahn	A Comparison of Water to Silicon as a Surface For Fibronectin Fibrillogenesis	Ward Melville High School		
Nina Bai	Synthesis and Characterization of 1-Decanethiol Functionalized Gold Nanoparticles	Plainview-Old Bethpage John F. Kennedy High School		
Joseph Barone	DNA Morphology in an Evaporation Droplet	West Islip High School		
Jacqueline Brazin	Protein Adsorption on Polypropylene Scaffolds and Flat Surfaces	HAFTR		
Neil Chheda	Chheda Synthesis and Characterization of 1-Decanethiol Functionalized Gold Nanoparticles Gr So			
Felicia Chiu	Prevention of Cell Attachment to Vascular Stents Through the Modification of Hyaluronic Acid	The Wheatley School		
Hye Yeon Choi	The Effects of Supercritical CO2 and Ethane Exposure on Contact Angle and Interfacial Width of Polymer Thin Films	Half Hollow Hills High School East		
Amruta Desai	Sonochemical and Thermal Synthesis and Characterization of Polymer Supported Iron Nanoparticles for Selective Catalytic Reactions	Ward Melville High School		
Simon Ebrani	A Universality of Supercritical Phenomena	HAFTR		
Robert Fisher	Improving Plastics Recycling Through the Addition of Modified Organoclays	Hebrew Academy of Nassau County		
Mitchell Fourman	A Comparison of the Effects of Supercritical CO2 and Ethane on PS-PMMA, PMMA-EVA and PMMA-PB Blends	Ward Melville High School		
Rikki Frenkel	Extra cellular Matrix Protein Adsorption on Sulfonated Polystyrene Surfaces	Stella K. Abraham High School for Girls		
Lauren Goldstein	The Effect of Nanofillers on Polymer Thin Films	Stella K. Abraham High School for Girls		
Jonathan Hefter	Increasing Thermal Stability of PMMA Resins by way of Melt Blending with Modified Organoclays	Davis Renov Stahler Yeshiva High School		
Madelyn Ho	Gold Nanopatterns and Fibronectin Adsorption on 28% Sulfonated Polystyrene	Clements High School Bountiful TX		
Hatty Hong	Crystallization Properties of Thin Polymer Films	Manhasset School		

Maanasa Indaram	DNA Electrophoresis on Modified Silicon Surfaces in the Presence of Electro-osmotic Flow	The Wheatley School
Jessica Jiang	Synthesis and Characterization of 1-Decanethiol Functionalized Gold Nanoparticles	Ward Melville High School
Unaza Kahn	The Effects of Alkyl Ammonium Ions on DNA Droplets	East Islip High School
Vivek Kuncham	Crystallization Properties of Thin Polymer Films	The Wheatley School
Rachel Lavon	Testing the Mechanical and Adhesive Properties of Hyaluronic Acid For Use on Vascular Stents	Great Neck North Senior High
Joshua Levine	Characterization of Ventricular Fibroblasts and Myocyte Cells on PB and PDMS Thin Films	Ramaz School
Aaron Long	The Effects of Supercritical CO2 and Ethane Exposure on Contact Angle and Interfacial Width of Polymer Thin Films	Locust Valley High
Steven Lubin	Optimizing the Properties of a PB-EVA Blend	West Islip High School
Abigail Maller	The Effect of Nanofillers on Polymer Thin Films	Stella K. Abraham School
Varun Mehta	Making a High Performance Polystyrene-EVA Blend	Sachem High School North
Eric Petersen	DNA Electrophoresis on Flat Surfaces	Ward Melville High School
Sarvajit Patil	The Modeling of the Interactions of Polymers Adsorbed onto Clay Surfaces	Half Hollow Hills West
Nikhilesh Ray-Mazumder	The Synthesis and Characterization of 1-decanethiol Functionalized Gold Nanoparticles	Ward Melville High School
Joan Rho	DNA Electrophoresis on Modified Silicon Surfaces in the Presence of Electro-osmotic Flow	The Wheatley School
Evan Rouge	Controlled Release of Drugs by Surface Micelles	Sachem South High School
Tedi Setton	Characterization of Ventricular Fibroblasts and Myocyte Cells on PB and PDMS Thin Films	Plainview-Old Bethpage John F. Kennedy High School
Michelle Simpser	Extra cellular Matrix Protein Adsorption on Sulfonated Polystyrene Surfaces	Stella K. Abraham High School for Girls
Lenny Slutsky	Gold Micro patterning and Fibronectin Adsorption on 28% Sulfonated Polystyrene	Ward Melville High School

Sarah Smilow	Determining the Mechanical Properties of Rat Skin	Smithtown High School
Micheal Snow	Improving Adhesion at Polymeric Interfaces Containing Filler Mixtures	Rambam Mesivta High School
Andrew Song	Increasing Thermal Stability of PMMA Resins by Way of Melt Blending with Modified Organoclays	Jericho High School
Arvin Thachara	The Prevention of Cell Attachment to Vascular Stents Through the Modification of Hyaluronic Acid	The Wheatley School

	GARCIA CENTER Research Experience for Undergraduates			
Mordechai Bronner	Improving Adhesion at Polymeric Interfaces Containing Filler Mixtures	Yale University		
Dina Gewaily	DNA Electrophoresis on Modified Silicon Surfaces in the Presence of Electro-osmotic Flow	Brown University		
Michael Goldman	Melt Blending of Acrolate Resins and Elastomers	Harvard University		
Eli Hoory	Measurement of Electro-Osmotic Flow With a Confocal Microscope	SUNY Stony Brook		
Vinitha Jacob	DNA Electrophoresis on Modified Silicon Surfaces in the Presence of Electro-osmotic Flow	Princeton University		
Stephanie Kasbuza	Fibronectin Fibrillogenesis on Sulfonated Polystyrene	University of Virginia		
Rebecca Klein	The Effect of Nanofillers on Polymer Thin Films	Columbia University		
Pam Li	Gold Nanopatterns and Fibronectin Adsorption on 28% Sulfonated Polystyrene	MIT		
Edmund Palermo	Supercritical Fluid Technology	Cornell University		
Dora Chana Sosnowick	The Effect of Nanofillers on Polymer Thin Films	Michlelet Mevaseret Yerushalayim		
Pierre Xavier	Improving Plastics Recycling Through the Addition of Modified Organoclays	Stevens Tech		

	GARCIA CENTER Research Experience for Teachers	
Chirakkal Krishnan	The Effect of Alkylammonium Ions on DNA Droplet. Synthesis and Characterization of Alkane Thiol Functionalized Gold Nanoparticles.	East Islip High School
Rebecca Isseroff	The Characterization of Octadecane Thiol Functionalized Gold Nanoparticles	Stella K. Abraham High School for Girls
Hubert Mantz	The Effect of Nanofillers on Polymer Thin Films	University of Ulm, Germany
Ronald Occhiogrosso	Supercritical Fluid Technology and Effects on Polymer Films and Composites	HAFTR High School
Gary Ramonetti	Protein Adsorption with Respect to Surface Type and Pattern	John Glenn High School



2002 Summer Scholar Program Schedule of Activities

	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
Week of 7/1	July 1 10:00 Welcome Meeting 11:00 Melanie Krieger Science Competitions 2:00 Group 1 Godlind Johnson Library orientation Melville Library Classroom A 3:15-4:15 Group 2 same as above 2:00 Web of Science Intro to Polymers Room 112	2 10:00-11:30 Laboratory Safety Room 301 11:30-12-00 Jim Quinn Laboratory Orientation Lourdes Collazo Chemical Disposal 1:00-3:00 (2 Sessions) Excel- Data Taking Room 112 3:00 SUNY Shirley KennyWelcome	3 10:00 Sarika Sharma Spin Casting of Films Intro to Polymers 10:00 Adv.Excel Lecture, Web of Science Room 112 1-4 Henry White Research Orientation Lecture Room 301	4 HAPPY 4 th of JULY	5 10:00 Weekly Group Meeting 11:00 Sarika Sharma Spin Casting
Week of 7/8	8 10:00 Jonathan Sokolov Vacuum Systems Spin Casting	9 10:00 Perena Gouma Electron Microscopy	10 10:00 Dilip Gersappe What's a Polymer? Theory and Computation 12:00 Journal Club Brown Bag Lunch	11 1:30-3:00 Excel Cont. Room 112	12 10:00 Weekly Group Meeting Statistics Lecture
Week of 7/15	15	16	17 12:00 Journal Club Brown Bag Lunch 1:00 Krishnan Wiz-Bang Chemistry! Chemistry Bldg.	18 10:00 Mel Cowgill/ Carl Czajkowski BNL 10:30 Excel M _n M _w Room 112	19 10:00 Weekly Group Meeting <i>QUIZ</i> Sarika Sharma Room 301 2:00 Chris Berndt Material Science and Surface engineering Room 301
Week of 7/22	22	23 10:00-2:00pm FIELD TRIP Dayton T Brown Lunch Provided Depart SAC circle 10:00am depart	24 12:00 Journal Club Brown Bag Lunch Lab notebook collection #1	25 2:00 Isaac Cohen, Esteé Lauder Room 301 Lab notebook collection #1	26 10:00 Weekly Group Meeting Lab notebook collection #1
Week of 7/29	29	30	31 12:00 <i>Journal Club</i> <i>Brown Bag Lunch</i>	Aug 1 10:00am departure *Canoe Trip* on the Peconic River	2 10:00 Weekly Group Meeting
Week of 8/5	5	6 2:00 Dr. Richard Rifkind, Memorial Sloan Kettering Cancer Center Room 301	7 12:00Journal Club Brown Bag Lunch	8	9 10:00 Weekly Group Meeting
Week of 8/12	12 Lab notebook collection #2	13 Lab notebook collection #2	14 Lab notebook collection #2	15	16 Final Research Presentations and Luncheon SAC auditorium Special Guest Mr. Albert Hoser Siemens

Summer 2002 Scrap Book



Entenmanns feeds the scientific mind!



Dayton T Brown Field Trip We could tell you what they do here but then we would have to shoot you!!



SUNY Pres. Shirley Kenny meeting with the High School Research Scholars

















Summer 2002 Scrap Book Summer 2002 Scrap Book











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Research Scholars Program 2002

- High School Summer Scholars
- Research Experience for Undergraduates
- Research Experience for Teachers

Creating Fibronectin at the Air-Water Interface

Christine Ahn- Ward Melville High School, Prof. Miriam Rafailovich, Young Soo Seo, Dept. Materials Science and Engineering, SUNY Stony Brook

The protein fibronectin creates a matrix when grown on a surface coated with the polymer sulfonated-polystyrene. However, the process of preparing the fibronectin before spreading requires at least three days. In order to create a more efficient process, the purpose of my experiment was to create an environment in which fibronectin created a matrix without having to be incubated on a surface for three days. In the experiment designed, a Langmuir-Blodgett trough is used (1). With this equipment, our goal is to create a lattice at the air-water interface, and then dip a clean silicon wafer horizontally onto the surface, and theoretically there should be fibronectin on the wafer when seen on the AFM (atomic force microscope). To achieve this, we created a solution of PSS that would be less dense than water, in order to sit on the surface of the water rather than mix with it (2). The most common solution used is a DMF solution, which is very miscible with water. However, a combination of chloroform and methanol was used. After spreading these on the surface, the solution is allowed to sit before dipping the surfaces.

The preliminary conclusions have shown that after dipping the silicon wafers horizontally into the trough, a film did attach to the silicon wafers. To compare the results to some sort of control, a silicon wafer was horizontally dipped into the LB trough with the PSS solution but not the fibronectin. Then this was compared to a wafer with the PSS and fibronectin. So far there seems to be some protein on the wafer, however, for further testing, we plan on letting the solution sit for a longer period of time, and using a higher percentage of sulfonated polystyrene than 24.4% (the percentage used for the experiment thus far).

(1)<u>http://www.science.fau.edu/chemistry/fieldslab/publications/Gregg/Ligand%20Access</u> <u>ibility.pdf</u>-pg. 76-77

(2) <u>http://colloids2001.cheme.cmu.edu/meetabs/abs101to150.html</u> -"Polymer-Surfactant Mixtures at the Air-Water Interface"

Sonochemical and Thermal Synthesis and Characterization of Polymer Supported Iron Nanoparticles for Selective Catalytic Reactions Amruta Desai, Ward Melville High School Dr. Miriam Rafailovich, Dr. Devinder Mahajan, and Henna Khalil

Dept. Material Sciences and Engineering, SUNY Stony Brook

Newly discovered and developed nanoparticle related catalysts, has been thought of to help remove harmful gases from the earth's environment and other remarkable procedures. Not only are these catalysts able to perform these procedures, but they also are able to complete them a lot faster. I have been working to find if certain polymers could be used to support iron nanoparticles, thermally and sonochemically, for use in selective catalytic reactions.

Iron nanoparticles were synthesized by sonochemical decomposition of $Fe(CO)_5$, in a hydrocarbon solvent, hexadecane. The synthetic technique of Sonolysis, which uses sound waves to generate acoustic cavitation, which caused the chemical decomposition of $Fe(CO)_5$. I am employing three routes; a mixing dispersion, a sonochemical dispersion, and a thermal dispersion, to synthesize very air sensitive, sonochemically synthesized particles.

The mixing dispersion procedure consisted of the solution being created by manual mixing. The solution consisted of a polymer, polybutadiene, which was dissolved in an organic solvent, toluene, in order to support the iron nanoparticles. After creating a thin film of the solution, the Atomic Force Microscope (AFM), results indicates small aggregations. The magnetic properties of this solution were characterized by a Magnetometer, which indicates a remarkable hysterisis, which are presently being studied.

The other remaining procedures, sonochemical dispersion and thermal dispersion, are still being conducted. After undergoing characterization with devices such as the Transmission Electron Microscope (TEM), etc., the results of these three procedures will be tested for use in catalytic activity.





AFM of spin casted, Polybutadiene supported Iron Nanoparticles dissolved in Toluene.



Magnetometer graph of Polybutadiene and Toluene and Iron Nanoparticle solution.

Synthesis and Characterization of 1-Decanethiol Functionalized Gold Nanoparticles

 Nina Bai, Plainview – Old Bethpage John F. Kennedy High School, Neil Chheda, Great Neck South High School,
Jessica Jiang, and Nik Ray-Mazumder, Ward Melville High School, Rebecca Isseroff, Stella K. Abraham High School for Girls, C.V. Krishnan, Henry White, Yuan Sun, and Miriam Rafailovich,
Department of Materials Science and Engineering, SUNY Stony Brook

Nanoparticles have many potential uses in quantum physics, information storage, electronics and catalysis. The application of these nanoparticles depends greatly upon their size and other physical properties. The purpose of this research is to determine the most effective method of synthesizing nanoparticles of uniform size and morphology.

Two methods were used to synthesize 1-decanethiol ($C_{10}H_{21}SH$) functionalized gold nanoparticles. The one phase method was accomplished through the reduction of hydrogentetrachloroaurate (III) trihydrate (HAuCl₄•3H₂O) by lithium triethyl borohydride (Li(C_2H_5)₃BH) in terahydrofuran ((CH₂)₄O) solvent (1). In the two phase method, aqueous sodium borohydride (NaBH₄) was used as the reducing agent in a toluene-aqueous system (2). A 1:2 ratio of gold to thiol was used for both methods. Using a Langmuir-Blodgett (LB) trough, thin monolayer films of the nanoparticles were prepared on silicon wafers for analysis.

Both procedures produced nanoparticles with thiol covered gold cores as determined by composition analysis using X-Ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Reflectroscopy (FTIR). Images taken by Transmission Electron Microscopy (TEM) revealed particle sizes generally within a range of 2 to 4 nanometers with the two phase method yielding slightly smaller sizes. Two phase nanoparticles produced significantly higher LB pressure isotherms. This and differences in coloration and settling properties hint to a difference in chemical makeup of the two kinds of nanoparticles. High resolution TEM will be used to study the atomic structure of the nanoparticles. X-Ray Reflectivity studies will be performed to give further evidence of the shape and dimensions of the particles. It is also hoped that by altering the gold to thiol ratio and rate of reduction, control of particle size and uniformity will be achieved.





Figure 1. TEM image of single phase gold nanoparticles at 340,000X.

Figure 2. Frequency of size of single-phase gold nanoparticles

1. Yee, Chanel K.; Jordan, Rainer; Ulman, Abraham; White, Henry; King, Alexander; Rafailovich, Miriam; Sokolov, Jonathan. "Novel One-Phase Synthesis of Thiol-Functionalized Gold, Palladium and Iridium Nanoparticles Using Superhydride." *Langmuir*, 15 (10): 3486-3491 May 11 1999.

2. Brust, Mathias; Walker, Merryl; Bethell, Donald; Schiffrin, David J.; Whyman, Robin. "Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid-Liquid System." *J. Chem. Soc., Chem. Commun.*, 1994.

DNA Morphology in an Evaporating Droplet

Joseph Barone, West Islip High School Xiao-Hua Fang, Dr. Miriam Rafailovich, Dr. Jonathan Sokolov Dept. Material Sciences and Engineering, SUNY Stony Brook

With the onset of the Human Genome Project, which has a goal of deciphering the coding of human DNA, research has been performed concerning the physical characteristics of DNA and how it moves. In order for DNA to be studied properly, it must first be able to be manipulated to allow study. The purpose of this experiment is to understand how DNA moves within an evaporating drop on silicon substrates. By understanding the mechanics by which different types and concentrations of DNA behave on various surfaces, new techniques for manipulating DNA can be developed. (1)

By using confocal microscopy and a contact angle-measuring camera, DNA droplets can be observed as they evaporate. Three different lengths of DNA are used within this experiment. DNA length is determined by the number of base pairs (A, T, C, and G) within the molecule. The three types of DNA used are T5 (121,000 base pairs), Lambda (48,502 base pairs) and Phi-X174 (5,386 base pairs). DNA solutions are made by dissolving the DNA into a solvent. Five different concentrations were made for use in this experiment: 500 ig/mL (100%), 400 ig/ml (80%), 250 ig/mL (50%), 100 ig/mL (20%) and 25 ig/mL (5%). 2 iL drops of solvent are placed upon silicon wafers and then observed, over time, under the instrumentation.

Thus far, there have been some very good observations. As expected, confocal imaging has showed that DNA migrating towards the edge of a drop forms a ring of DNA adhered to the silicon/air/solvent interface. Also as expected, this ring intensity increases over time. (2) New discoveries are also being made as this experiment progresses. Distinct trends exist for different concentrations of DNA. It seems that very low concentrations of DNA (25 \grac{1}{g}/mL) behave differently then higher concentrations. These samples have extended drying times, many times longer then lower concentrations. There also seems to be a trend with DNA length in relation to drying time, as Phi-X174 DNA with only 5,386 base pairs has longer drying times then other DNA groups. Secondly, a distinct correlation between intensity of the DNA ring and the contact angle has been discovered. They seem to have an inverse relationship. A model depicting these trends will be made in order to further study other effects upon DNA droplet morphology as the experiment progresses.



Fig. 1: Confocal Microscopy Image of Phi-X174 (25 ìg/mL) DNA Ring

⁽¹⁾ N. Pernodet, V. Samuilov, K. Shin, J. Sokolov, M. Rafailovich, D. Gersape, B. Chu, (December, 2000) *DNA Electrophoresis on a Flat Surface* <u>Physical Review</u> Volume 85, Number 26
⁽²⁾ Robert Deegan, Olgica Bakajin, Todd Dupont, Greg Huber, Sidney Nagel, Thomas Witten, (February 3, 2001) *Contact Line Deposits in an Evaporating Drop* <u>Physical</u> Review Volume 62, Number 756

Protein Adsorption on Polypropylene Scaffolds and Flat Surfaces

Jacqueline Brazin, HAFTR High School L. Collazo, M.S., M. Rafailovich, Ph.D. Dept. Materials Science and Engineering, SUNY Stony Brook R. Occhiogrosso, Ph.D., Locust Valley High School

Finding a way to grow cells on artificial substrates is a new frontier in biomedical engineering. The use of biomaterials is one of the newest methods for treating tissue loss or organ failure with an engineered biological substitute (1). The current techniques for tissue repair or replacement include transplantation, mechanical devices, and artificial prostheses. These, however, each have its own setback such as induced inflammation and a limited supply of compatible donors (1). Therefore, new development focuses on an in vitro approach where a matrix is set to reattach damaged tissue. Using polypropylene fibers and molded plastic samples, studies were carried out to determine whether it is a viable synthetic polymer for cells to proliferate and grow onto.

Initially, polypropylene fiber and plastic (surface) samples were placed in 35mm petri dishes and 2 $\frac{1}{2}$ mL of either bovine calf serum (BCS)100% or fetal bovine serum (FBS) 100% was added. The samples were then incubated for 24 and 48 hour periods at 37°C. After which, protein adsorption was measured by Bicinchoninic Acid (BCA) assay and read by spectrophotometry. Additional research compared polypropylene samples to those treated with supercritical CO₂ at a pressure of 1100 psi and at a temperature of 37°C.

Future work will involve improving cell adhesion to polypropylene and growing osteoblast cells on these surfaces as a preliminary step of bone growth. These novel approaches show great promise and enhanced applicability in bone repair (2).



(1) Tissue Engineering, National Institute of Standards and Technology. 2000.

(2) Service, Robert F., "Tissue Engineers Build New Bone." Science. 289 (5484) 2000.

Quantifying the Surface Structure and Properties of Hyaluronic Acid Thin Films

Felicia Chiu & Arvin Thachara, The Wheatley School Miriam Rafailovich, Yang Yun (Ph.D), Jeffery Javidfar Dept. Material Sciences and Engineering, Center for Biotechnology, SUNY Stony Brook

Heart attacks are the most common health problems for Americans in the United States. These heart attacks are caused by the blockage of blood vessels within the body. To try to prevent the blockage of blood in these vessels, vascular stents will be placed in the vessels. A vascular stent is not completely successful because certain cells will attach to the stent, causing clumps. Therefore, a chemical coating is necessary to eliminate the clumping on the stent.

The main substance used as the film to test the coatings is called Hyaluronic Acid (HA). Hyaluronan (HA) is a linear polysaccharide composed of repeating disaccharide units of N-acetyl-glucosamine and D-glucuronic acid. The uronic acid and the amino sugar are linked together by alternating beta-1,4 and beta-1,3 glycosidic bonds (Figure 1). To find the best combination for the stent coating, HA, HA mixed with DNA, and HA mixed with DNA and Protamine were used. All three were cross-linked with ADH and EDCI for both 24 and 72 hours in an acidic environment. Once the films were made, two different cells, A-10 and fibroblast, were tested on the films fro analysis.

As of now, the research is currently being completed; therefore, our results have not been completely recorded. We plan to use the Atomic Force Microscope (AFM), the Confocal Microscope, and the Scanning Electron Microscope (SEM) to measure the adhesion of the different cells on the varying surfaces, to determine the force at which the cells are driven off the surfaces, and to view the topography of the surfaces as well. However, we have learned that the process of creating HA films is a tedious and twoweek long process.

Figure 1 (Vascular Stent)



Figure 2 (Hyaluronic Acid)



Effects of Supercritical Fluid Exposure On Compatibility of Polymer Thin Films

Hyeyeon Choi, Half Hollow Hills High School East Aaron Long, Locust Valley High School Miriam Rafailovich, Young-Soo Seo, Dept. Material Sciences and Engineering, SUNY Stony Brook Edmund Palermo, Cornell University

The purpose of this study was to improve the compatibility of various polymer blends and bi-layers using supercritical fluids, specifically carbon dioxide and ethane. The compatibility of the polymers was determined by measuring the contact angle of blends and interfacial width of bi-layers. The polymers studied were 50/50 blends of polystyrene (PS) with poly-methyl-methacrylate (PMMA), poly-brominated-styrene (PBrS) with PS, ethylene vinyl acetate (EVA) with PS, poly-butadiene (PB) with PS, EVA with PMMA, POSS-PMMA with PS. The polymers studied as bi-layers were a lower layer of PBrS with a top layer of PS and a lower layer of PMMA with a top layer of PS. The atomic force microscope was used to measure the contact angle of the 50/50 polymer blends and x-ray scattering was used to determine interfacial width. The 50/50 blends were exposed to supercritical fluids at variety of isothermal and isobaric points. It was hypothesized that the exposure to supercritical fluids would improve the compatibility between polymers and preliminary results prove that the polymers become more compatible after exposure to supercritical fluids as shown below.



PS/PBrS before exposure to supercritical CO₂

PS/PBrS after exposure to supercritical CO₂

DNA Electrophoresis on Modified Silicon Surfaces in the Presence of Electroosmotic Flow Dina Gewaily, Brown University; Vinitha Jacob, Princeton University; Maanasa Indaram and Joan Rho, The Wheatley School, Xiaohua Fang, Binquan Li and Miriam

Rafailovich, SUNY Stony Brook.

The separation of DNA based on electrophoretic methods is an essential part of the Human Genome Project, a worldwide effort to sequence and understand the entire Human Genome. Current electrophoretic methods, such as gel and capillary electrophoresis, are the primary means of separating DNA. However, there are drawbacks to each of these methods. Performing electrophoresis on a flat silicon chip [1] promises to alleviate these drawbacks, allowing for fast, efficient, automated results of high resolution quality [2].

In order to make this new type of electrophoresis a viable technique, the presence of electroosmotic flow (EOF), a current causing DNA to flow in the opposite (negative) direction, must be reduced significantly [3]. This project studies the effects of different modified silicon surfaces and buffer concentrations in order to decrease EOF and optimize electrophoretic separation. Using confocal/ fluorescent microscopy, the flow of DNA in varying ionic TBE buffer concentrations (0.0001 X TBE, 0.001 X TBE, 0.01 X TBE, 0.1 X TBE, 1 X TBE) in the presence of an electric field will be observed. Electrophoresis runs will be performed several times on surfaces PVP, PS, OTS, UTS and hydrophilic silicon that will serve as separation media. Atomic Force Microscopy (AFM) scans of the different surfaces will be taken before and after each electrophoresis run in order to detect any erosion or changes of the surface. This aspect of the research has important implications for capillary electrophoresis as well.



Schematic diagram of the electrophoretic cell with the substrate. DNA sample loaded on the surface of Si chip. The cell is filled with buffer solution (yellow color).

[1] DNA Electrophoresis on a Flat Surface, Pernodet, N., Samuilov, V., Shin, K., Sokolov, J., Rafailovich, M., Gersappe, D. and Chu, B., Phys Rev Lett, 85: (26), 5651-5654, Part 5651, (2000).

[2] Study of Droplet Morphology and Its Application for DNA Electrophoresis on a Chip, Gewaily, D., Seo, Y., Samuilov, V., Rafailovich, M. Unpublished.

[3] DNA Electrophoresis Without Topological Constraints, Jacob, V., Fang, X., Li, B., Seo, Y., Samuilov, V., Rafailovich, M. Unpublished.

Universality of the Supercritical Fluid Phenomena

Simon Ebrani, Dr. Ronald Occhiogrosso, HAFTR High School. Dr. Miriam Rafailovich, John Jerome, Dept. of Material Sciences and Engineering, SUNY, Stony Brook. Edmund F.Palermo, Cornell University. Dr.Steven A. Schwarz, Queens College.

This study investigates the effects of supercritical fluids on various thin films of polymers, in order to gain insight into the universality of supercritical fluid (scf) solubility and effectiveness as a foaming agent. The applications of SCFs are many, ranging from extraction of caffeine from coffee beans to fractionation of polymers to decrease their polydispersity. [1-2] Another potential application involves the insertion of certain drugs into a consumable polymer matrix, with subsequent time-released delivery to humans. The present research represents investigating how the SCF solvents, carbon dioxide and ethane, will change the morphology of thin-film polymers. We expect the films to swell, thus creating voids for insertion of the medicinal drugs.

PS (polystyrene), EVA (ethylene vinyl acetate), PBrS (poly-brominated styrene), PMMA (poly methyl methacrylate), and PB (poly butadiene) were exposed to sc-CO₂ at 1100 and 2200 psig, and at a temperature of 36.66 degrees Celsius. The samples were also exposed to sc-C₂H₆, near its critical point (705 psig and 37.1 degrees Celsius). Thicknesses of samples were measured via ellipsometry. It was seen that the thicknesses of the samples mostly increased after being exposed to both carbon dioxide and ethane, a result that favors use of the technology to creating drug-delivery agents. A sampling of the data is presented below.

	Original	* Thickness after CO ₂ exposure	
Polymer	Thickness (A)	at 1100 psig (A)	
PB	1536	1433	
	1514	1800	
PBrS	758	1389	
PMMA	587	1194	
	595	1336	
PS	784	1121	
EVA	855	1114	
All thicknesses	represents an average	of 3 values.	

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Extra Cellular Matrix Protein Adsorption on Sulfonated Polystyrene Surfaces Rikki Frenkel, Michelle Simpser

Stella K. Abraham High School

Dr. Rafailovich, Lourdes Collazo, Nadine Pernodet, Stephanie Kaszuba, Mr. Romanetti Dept. of Material Sciences and Engineering, SUNY Stony Brook.

Studies of cellular adhesion to sulfonated and protein surfaces are imperative in the field of biotechnology and the reparation of tissues. It is believed that the sulfonated surfaces give the necessary charge for cells to grow on. Proteins have also been found to be important instruments for cell adhesion, spreading, and growth. They provide the linkage between the surface and the cells bonding sites¹. Research has shown that Fibronectin, as part of the extracellular matrix, (ECM) is one of the basic proteins needed for cell adhesion. It is a "large multidomain glycoprotein found in connective tissue, on cell surfaces, and in plasma."²

Studies have been conducted to demonstrate that cells need a protein coated surface to grow, however, we have proved that given the right media cardiac fibroblasts will secrete their own protein extracellular matrix. Silicon wafers coated with a sulfonated polystyrene film provided the media to promote cell growth. Plain polystyrene was used as a control to demonstrate that the sulfonated properties of the polymer enabled the cells to adhere. The cells were placed in minimal essential media (MEM) to ensure that the cells themselves secreted these proteins. Using Atomic Force Microscopy (AFM) we imaged the cell samples to view the lattices that were formed.

In connection to these results, we have also conducted an experiment on the properties of the interactions between two proteins, fibronectin and elastin. When these proteins were grown on sulfonated polystyrene surfaces, they both formed lattices within 2 days of incubation at 37 degrees Celsius and 5% carbon dioxide. When compared with the lattices formed by the cells, fibronectin was found to be the protein most similar in structure. However, elastin had the tendency to adsorb onto the surface at a faster rate than fibronectin. These two proteins were then combined to view what effect, if any, a mixture of the two would have on the resulting structure. In addition, a trivalent ion, Fe(III) was added to determine if this common pollutant would disrupt the matrices of these substances. As a summation of this data we plated cells onto these protein surfaces to observe the differing orientation of the cells due to varying conditions.



¹ McFarland, C. Thomas, C. DeFilippis, C. Steele, J. Healy, K. Protein Adsorption and Cell Attachment to Patterned Surfaces (1999).

² www.gwumc.edu/biochem/ingham/fnreview.htm

The Effects of Nanofillers on Polymer Thin Films

Lauren Goldstein, Abigail Maller. Stella K. Abraham High School Rebecca Klein, Dora Sosnowick, Research Undergraduates

Song Li, Sarika Sharma, Miriam Rafailovich, Dept. of Material Sciences and Engineering, SUNY Stony Brook

Polymer films are used as coatings in various types of machinery. Recent studies of Microelectromechanical Systems (MEMS) showed that, due to the small size of the system's components, the lubricant evaporates and causes stiction (a sticking of the machine's surfaces) causing the gears to freeze. We worked on modifying lubricants with nanoparticle fillers to prevent stiction in MEMS devices.

We created two types of bi-layer samples on hydrophobic Silicon wafers. One was poly(methyl methacrylate) (PMMA) on top of 123K Polystyrene (PS), and the other was PS:dPS solution over 123K PS. We tested two characteristics of nanofillers: the effect of the size of Gold (Au) and Palladium (Pd) nanoparticles on polymer behavior, and interaction of C-POSS when added to PS solution. Three concentrations of Au and Pd nanoparticles (1%, 2%, and 4% by mass) were dissolved in 123K PS and then spun to form the bottom of a bi-layer. To study interaction of C-POSS with 123K PS, we made 3 concentrations of C-POSS in PS solutions (.25%, .75%, and 1% by mass). These were also used as a lower layer.

We then floated a film of 105K PMMA as a top layer for each of the bi-layers. Each of our samples was then annealed in a high vacuum turbo oven at 150 C to let the polymers relax and interact. Dewetting of the polymers occurs due to the high interfacial energy between PS and PMMA, forming holes in the bi-layer.(1) The radii of the holes were then measured by Optical Microscopy and by Atomic Force Microscopy to measure their dewetting velocity. Based on the Brochard-Wyart Theory we were then able to calculate their viscosity.(2)

Using the same bottom layers we studied above, we now used a PS:dPS solution (80:20 ratio) with a matching concentration of C-POSS, Au, or Pd nanoparticles in the lower as in the top layer. The diffusion coefficients were calculated using data taken by Secondary Ion Mass Spectroscopy (SIMS). We then calculated their viscosities based on their diffusion coefficients.

It is our hope that the use of nanoparticle-polymer lubricants in MEMS devices will solve the current problems facing the industry. We will determine if their use will prevent stiction and be able to withstand the friction that occurs due to the small size of the MEMS' components.

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AFM images. Left: 123K PS with 105K PMMA upper layer. Right: 4% Au in 123K PS with 105K PMMA upper layer. Both samples annealed 450 min

Gold Nanopatterning and Protein Adsorption on Sulfonated Polystyrene 28%

Madelyn Ho, William P. Clements High School Pamela Li, Massachusetts Institute of Technology John Jerome, Nadine Pernodet, Miriam Rafailovich, Dept. Material Sciences and Engineering, SUNY Stony Brook

We are investigating the effects of gold nanopatterns on fibronectin (Fn) adsorption. It has been shown that Fn matrix formation can be reproduced onto sulfonated polystyrene (SPS) 28% on silicon but does not self-organize onto SPS on gold [1], thus Fn matrix formation in the presence of gold patterns will give insight into its adsorption properties. Surfaces were prepared through vapor deposition of chromium onto silicon, followed by deposition of gold onto the chromium. Two kinds of polymer blends, polystrene/poly(methyl methacrylate) (PS/PMMA) and polystyrene/poly(bromo-styrene) (PS/PBrS), were spun cast onto the gold surfaces because of their ability to phase separate and form distinct three dimensional patterns [2]. Polymer solutions were made in 1:1 ratios. After annealing, the patterns were confirmed with atomic force microscopy (AFM) [figures 1,2]. Using the data collected on the sputtering rates of PS and PMMA, nanopatterns were etched into the surface using the ion mill. The polymers were removed, leaving behind a nanopattern of gold and silicon, which was confirmed by scanning electron microscopy (SEM). Sulfonated polystyrene (SPS) 28% was spun cast onto the samples to create the surface charge necessary for Fn adsorption [3]. These surfaces were then incubated C in a solution of Fn (100 ig/mL). After five days, AFM images revealed that Fn selfat 37 organized only onto SPS on silicon, avoiding the SPS spun cast on the gold.



Figure 1: 2-D AFM image PS:PMMA PS:PMMA

after annealing

Figure 2: 3-D AFM image

after annealing

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Characterization of Rat Ventricular Fibroblasts and Cardio Myocytes on Polybutadiene and Polydimethylsiloxane Polymer Surfaces

Josh Levine, Ramaz, Tedi Setton, POB JFK High School L. Collazo, M.S., E. Guan, PhD, N. Pernodet, PhD, Emelia Entcheva, PhD, S. Ge, PhD, M. Rafailovich, PhDDept. Material Sciences and Engineering, SUNY Stony Brook

Dr. Donald E. Ingber suggests that cytoskeletal actin microfilament (MF) lattices are tensegrity structures that constantly remodel cell shape in response to force stimuli that may originate within or outside the cell³. The focus of this project is an analysis of this hypothesis through an evaluation of the effect of various polymers and polymer thicknesses upon the cell patterning of ventricular fibroblasts and myocytes cultured from neonatal rats. Because different polymers display different mechanical properties at varying thicknesses, we propose that if Ingber's hypothesis is indeed correct, different cell patterns will emerge as a result of varying forces required to sustain cellular adhesion to the polymer surfaces.

Though this project has grown to encompass a growth curve comparing fibroblast morbidity upon Polybutadiene (PB) and Polydimethylsiloxane (PDMS), the central hypothesis has been and continues to be assessed by spinning thin film samples of PB and PDMS of approximate thicknesses 400, 1200, and 2800 Å onto cleaned Silicon (Si) surfaces. Samples undergo ellipsometry to measure exact polymer thickness and are then annealed to ensure sterility and polymer adhesion to the Si substrate. PB samples are however annealed at 170° C for one hour while PDMS samples are annealed overnight at 70° C. All samples are then incubated with Fibronectin (Fn), a cell adhesive for 90 minutes at room temperature before being plated with ventricular fibroblasts at a density of 2000 cells/cm² or cardiac myocytes at high density. Cell samples are incubated at 37° C and 5% CO₂ concentration for two days before undergoing mechanical analysis. Atomic Force Microscopy (AFM) measures cell patterning under topography mode and the mechanical properties of cells and polymer films using lateral force modulation. Following AFM analysis, cells may be stained and observed under a confocal microscope.

Because this is an ongoing project, comparative data for PB and PDMS is still pending for both fibroblast and cardiac myocyte experiments. Initial data collection however, reveals a consistent concentric ring patterning of cardio fibroblasts upon the PB polymer (Figure 1). Moreover, the cells exhibited different levels of rigidity due to the different type and size of the polymer film (Figure 2). Though also incomplete, growth curve comparison has thus far shown that cell growth is better sustained upon the Polybutadiene.



³ Ingber, DE. *Cellular Tensegrity: Defining New Rules of Biological Design That Govern the Cytoskeleton.* J Cell Sci. 1993 Mar;104 (Pt 3):613-27.

Fibronectin Fibrillogenesis on Sulfonated Polystyrene Surfaces

Stephanie Kaszuba, Smithtown High School Miriam Rafailovich, Nadine Pernodet, Dept. Material Sciences and Engineering, SUNY Stony Brook

Tissue that keeps joints and bones stable dies naturally all the time in the process of movement and friction. Normally, this tissue can regenerate itself and replace lost tissue through a process known as fibrillogenesis. A protein known as fibronectin recognizes the normal bone or joint recognition sequences and grows a matrix on which tissue cells can grow. If this matrix is not present, tissue will not grow and the bone or joint will not be stable. When one receives a bone or joint implant, these recognition sequences are not present, and the fibronectin cannot produce its matrix on which cells can grow. I have worked to find the optimal surface on which these recognition sequences will be present and will cause fibronectin to grow a matrix for cell growth.

The surface had to be charged and organic so the protein wouldn't reject it, so sulfonated polystyrene was an optimal choice. This was spun on pure, clean silicon. Then the problem developed of what percentage of sulfonation was optimal for the fibronectin. It was determined that 24% sulfonation produced a lattice that was viewable under an atomic force microscope. From previous studies on this topic, I found that if the surface was incubated, at 37°C, for four days, in a solution of fibronectin, a lattice would form. This could be viewed under an atomic force microscope. However, because of this long waste of time I sought to find an amount of time that would be sufficient for incubation. Creating a time dependence experiment and testing the effects of incubation time on lattice size did this.

I also worked with the surface area of the samples. Gratings, which have more surface area, seemed to produce better results than flat silicon. Other surfaces, such as gold and nickel were tested for their ability to produce lattices when sulfonated polystyrene was spun on them, but the results were disappointing. Fibronectin doesn't seem to like metals and wouldn't form a lattice on them. This shows that implants should not be made of these metals due, not only, to their price, but also due to their ineffectiveness. Even gratings of combinations of silicon and metals showed that the lattice only formed on the silicon, leaving holes on the metal parts of the surfaces.

As of right now, implants are not being coated with sulfonated polystyrene, and therefore have a lifespan of about 10 years. One must go for a long and costly operation every ten years to replace their implant or infection will develop. Coating the surfaces with sulfonated polystyrene could greatly increase the lifespan of the implants, reducing overall cost and increasing the benefits of implants.

Fig. 1: Heparin binding cradle



Fig. 2: Structure of fibrinogen

Studying the Mechanical and Adhesive Properties of Hyaluronic Acid for Their Use on Vascular Stents

Rachel Lavon, John L. Miller Great Neck North High School Miriam Rafailovich, Jeffery Javidfar, Dr. Yang Yun, Dr. Weiliam Chen, Nadine Pernodet

Each year many people are afflicted with coronary artery disease, an ailment which is comprised of the clogging of blood vessels by cholesterol build up until blood flow is completely cut off. To treat this condition, a surgical technique known as balloon angioplasty opens the vessel and clears it, permitting blood to flow once again. Along with this procedure, a stent (see figure 1), a small wire mesh tube, is inserted into the vessel to provide support and allow for blood flow to occur regularly (1). This technique however is not perfect, as stented vessels can reclose in a phenomenon referred to as restenosis (2).

A Study was conducted by the Society for Biomaterials which demonstrated that Hyaluronic Acid (see figure 2), a naturally occurring substance, as been used to coat stents and allows drugs to penetrate its matrices to aid in healing (3). Although Hyaluronic Acid (HA) is mainly found in rooster combs, it also exists in the human body thus causing no inflammatory response when used to coat a stent (4). The purpose of this experiment is to create varying mixtures of HA and test their mechanical and adhesive properties to determine which blend will demonstrate the ideal characteristics needed to coat a stent.

The methods of this experiment were as follows: Three mixtures were created: HA by itself, HA with Beta-Gal DNA, and HA with Beta-Gal DNA and Protamine Sulfate. The samples were poured onto various surfaces, desiccated, and became films. These new HA films were then placed into cell culture dishes and prepared for crosslinking. Crosslinking is a technique which involves the addition of different substances to the HA mixtures that over a week will cause the HA to become stronger and more resistant to heat (5). The films were split up into two groups to demonstrate a variable of time: 24-24 hour crosslinking and 24-72 hour crosslinking.

In order to determine the effects of the different mixtures and their various crosslinking times on HA films, two tests need to be administered. The first, adhesion, will be calculated by an Atomic Force Microscope (AFM). Its cantilever can measure adhesion by calculating the force it takes to knock a material off a surface. The material that will be used is monocytes (white blood cells) which were obtained from a pig. The second, tensile strength, will be calculated using a tensile tester which will pull apart the film and based on how long it takes to snap, each film's strength will be determined. Statistical analyses of this data will be collected as soon as results are obtained.



Optimizing the Properties of a PB-EVA Blend

Steven Lubin, West Islip High School Edmund Palermo, Cornell University Ronald Occhiogrosso, Ph.D., Locust Valley High School Miriam Rafailovich, Ph.D., Dept. Material Sciences and Engineering, SUNY Stony Brook

Polybutadiene (PB) is a type of synthetic elastomer. Because of its low glass transition temperature, it is good for uses which require exposure to low temperatures. Polybutadiene can be found in hoses, gaskets, and many automotive parts. (http://www.psrc.usm.edu) Ethylene vinyl acetate (EVA) is a copolymer which provides outstanding toughness and resilience and maintains flexibility over a broad temperature range. (http:// www.dupont.com) It is hypothesized that when a blend of PB and EVA is exposed to supercritical carbon dioxide, the properties of the substance will be enhanced. Also, it is hypothesized that the pressure at which the blend is exposed to will have an effect on the properties of the material.

In order to create a polymer blend, 25 grams of polybutadiene and ethylene vinyl acetate were mixed in a Brabender for ten minutes at 190°C and at 100 rpm. I then placed the blended material into two different types of templates in order to mold them into shapes appropriate for ASTM tensile testing. I placed them into a heat press for ten minutes at a temperature of 315°F and with an applied load of six metric tons.

The samples were then placed into a supercritical chamber and exposed to carbon dioxide around its critical point. All of the samples were exposed at 90°F, which is just above the critical temperature for carbon dioxide. The various pressures being investigated are 800 psi, which is sub-critical; 1100 psi, which is just about the critical pressure; 2000 psi; and 3000 psi.

The physical properties of the samples will be tested. The Instron Machine records the stress vs. strain of the different samples. This type of testing requires the dogbone shape. The rectangles will be used for Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC). The DMA will determine the modulus of elasticity which is the measure of the elastic force of the substance. The DSC will determine the glass transition temperature, which is the temperature that a material changes from a crystalline, brittle substance to an amorphous, rubbery one. The DSC will also determine the specific heat of all of the blends.

$$\xrightarrow{\mathrm{CH}_2} \operatorname{CH}_2 \xrightarrow{\mathrm{CH}_2} \operatorname{H}_n$$

The chemical structure of PB

$$- \left[\begin{array}{c} \operatorname{CH}_2 - \operatorname{CH}_2 \end{array} \right]_n \left[\begin{array}{c} \operatorname{CH}_2 - \operatorname{CH} \end{array} \right]_m \\ c = 0 \\ c \\ c \\ c \\ H_3 \end{array} \right]$$

The chemical structure of EVA



A "dogbone" template

Joan Rho and Maanasa Indaram, The Wheatley School; Dina Gewaily, Brown University; Vinitha Jacob, Princeton University; Xiaohua Fang, Binquan Li and Miriam Rafailovich, SUNY Stony Brook.

The separation of DNA based on electrophoretic methods is an essential part of the Human Genome Project, a worldwide effort to sequence and understand the entire Human Genome. Current electrophoretic methods, such as gel and capillary electrophoresis, are the primary means of separating DNA. However, there are drawbacks to each of these methods. Performing electrophoresis on a flat silicon chip [1] promises to alleviate these drawbacks, allowing for fast, efficient, automated results of high resolution quality [2].

In order to make this new type of electrophoresis a viable technique, the presence of electroosmotic flow (EOF), a current causing DNA to flow in the opposite (negative) direction, must be reduced significantly [3]. This project studies the effects of different modified silicon surfaces and buffer concentrations in order to decrease EOF and optimize electrophoretic separation. Using confocal/ fluorescent microscopy, the flow of DNA in an ionic TBE buffer concentration of 0.001 X TBE on all surfaces, and ionic buffer concentrations of 0.0001 X TBE, 0.01 X TBE, 0.1 X TBE, 1 X TBE in the presence of an electric field will be observed. Electrophoresis runs will be performed several times on surfaces PVP, PS, OTS, UTS and hydrophilic silicon that will serve as separation media. Atomic Force Microscopy (AFM) scans of the different surfaces will be taken before and after each electrophoresis run in order to detect any erosion or changes of the surface. This aspect of the research has important implications for capillary electrophoresis as well.



Schematic of a DNA chain moving on a flat surface.

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The Effects of Supercritical Carbon Dioxide and Ethane on PS-PMMA, PMMA-EVA, and PMMA-PB Blends

Mitchell Fourman, Ward Melville High School Edmund Palermo, Cornell University Ronald Occhiogrosso Ph.D., Locus Valley High School Miriam Rafailovich Ph.D., Dept. Material Sciences and Engineering, SUNY Stony Brook

Supercritical Fluid exposure is a method which enhances the physical properties of various polymer blends. A polymer blend is usually two polymers with distinct physical properties mixed together. The goal of supercritical exposure is to create a blend that has the physical properties of both polymer components.

The polymers analyzed in this research include Polystyrene (PS), Poly(methyl methacrylate) (PMMA), Ethylene co-vinyl-acetate (EVA), and Polybutadiene (PB). These polymers were combined to produce PS-PMMA, PMMA-EVA, and PMMA-PB blends. In order to create these blends, equal proportions of the polymers were combined using a Brabender machine at ~170°C. Molds of "dogbone" and "rectangle" shaped templates were used to shape the resulting blends, which were then exposed to supercritical carbon dioxide, or supercritical ethane. The exposure lasts for about 45 minutes, and usually ranges from about 96 °F, and about 1200 psi.

The results of these exposures were analyzed using the SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscopes), in order to gain data from surface scans and cross-sections at high magnifications. Other methods of analysis include DMA (Dynamic Mechanical Analysis) test, and Instron (tensile strength) tests were performed. The SEM results showed that significant foaming took place, which justifies that the exposure had major affects on the blend. The Instron, however, proved that all three blends cannot be pulled, as they will break very quickly, though always displaying an extremely large peak load (~150 N).



PS-PMMA Pre-CO₂ Exposure

PS-PMMA Post CO₂ Exposure

Optimization of Physical Properties in a Polystyrene / Ethylene-co-vinyl acetate Blend Using Supercritical Carbon Dioxide

Palermo, E.F., Occhiogrosso, R.N.*, Rafailovich, M.

SUNY at Stony Brook, Department of Engineering & Applied Sciences, Stony Brook, NY

Polystyrene was blended with ethylene-co-vinyl acetate using supercritical carbon dioxide (scCO₂). Due to low entropy of mixing in a natural environment, these amorphous thermoplastics were observed immiscible prior scCO₂ exposure and exhibited poor mechanical properties. Significant compatibilization and foaming of these materials was seen on a macroscopic scale, which led to enhanced toughness and flexibility of the material. Tensile tests showed that PS/EVA blends exposed to 3000psig and 93°F scCO₂ exhibited ductility values of nearly 1200 MPa, whereas unexposed blends showed a mean of approximately 90 MPa. Likewise, the percent elongation values for PS/EVA samples under stress increased, on average, from 134 to 682 percent of their original length due to scCO₂ exposure. SEM and AFM data collected also showed evidence of increased mixing compatibility.



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Modeling of the Interactions of Polymers on Clay Surfaces

Sarvajit Patil, Half Hollow Hills High School West Wenhua Zhang, Dr. Miriam Rafailovich, Song Li SUNY Stony Brook Department of Materials Science

Though the mixtures of polymers and clays are vital to the future of materials science, there is currently no way to ensure that a specific polymer will mix with given clay. By calculating the interaction energy between polymers and clays however, the mixing of a polymer and clay can be predicted, saving time and resources. The goal of this research is to develop a model to map the interactions between a polymer and clay so that adsorption can be predicted.

Cloisite® 6A clay was mixed with toluene and the solution was placed in the Langmuir-Blodgett (LB) Trough. Silicon Wafers were then dipped into the trough to pick up a uniform clay surface. Polystyrene (PS) and Polymethylmethacrylate (PMMA) solutions were then mixed with each other. In each mixture a small amount of either PS or PMMA was deuterated. These samples were annealed in a vacuum oven and run through Secondary Ion Mass Spectrometry (SIMS). A depth profile was taken to detect where the deuterium was found. The deuterium traces showed that the PMMA tended to adsorb to the surface. Using the specific data from the SIMS depth profile, a computer model can be simulated to calculate the interaction energy between the polymers. This should effectively predict if a polymer would mix with a clay.



Diffusion of DNA Adsorbed on a Flat Surface During Electrophorsis Eric Petersen, Ward Melvile High School Bingquan Li, Xiaohua Fang, Jonathan Sokolov, Miriam Rafailovich

Electrophoresis is one of the most widely used analytical techniques in molecular biology. One of the most important applications of electrophoresis, is DNA fractionation. This process is a crucial part of DNA sequencing. Several methods, such as capillary and gel electrophoresis, have been used to perform DNA electrophoresis. Although these methods have been shown to successfully fractionate DNA to a resolution suitable for actual DNA sequencing (1bp); they are very time consuming. However, attempts to speed up DNA electrophoresis compromised the resolution.

Diffusion of DNA during electrophoresis may effect the resolution of the DNA fractionation.

In this study, I analyzed the diffusion of λ -phage DNA on a hydrophilic silicon surface. A drop of this DNA was loaded onto a silicon chip, dried, and placed in the electrophoresis cell. Then the cell was filled with 1x10-2TBE buffer stained with EtBr dye. After the original size of the droplet was measured, an electric field was applied and the motion of the DNA band was imaged via laser scanning confocal microscopy during electrophoresis. The images were quantified by creating a time vs. fluorescence intensity plot (fig.1). The peaks correspond to the arrival of the DNA band at positions increasingly closer to the positive electrode. The diameter of these peaks reflects the diameter of the DNA band; thus the change in the diameter is a function of the diffusion constant and time. Future work will involve measuring diffusion of DNA in different buffer concentrations and under different electric field strengths with the goal of optimizing the resolution of DNA electrophoresis on a flat surface.

Flouresence Intensit	June(a) 2 3 3 3 3 3 3 3 3 3 3
	Fig.1-Peaks obtained at 2 and 4mm away from initial

point

of

 λ -DNA

loading



CCD camera image of DNA chains adsorbed on a flat surface, under 100xoil immersion.

Using Organoclays to Create Polymer Nanocomposites

Robert Fisher, Hebrew Academy of Nassau County Michael Goldman, Harvard University Miriam Rafailovich, Dept. Material Sciences and Engineering, SUNY Stony Brook

Polymers are rapidly replacing natural materials in everyday applications. For example, polymers are used to replace metal in automobile bumpers, and lightweight polymers are rapidly replacing heavier glass for beverage containers. However, these polymers are not biodegradable and are often only used once before they are discarded. This is because most polymers are naturally immiscible. When mixed together they phase separate and are not homogeneously mixed. When a material is phase separated it is generally opaque, and has poor mechanical properties.

A new class of materials has been developed using clay and polymers. These materials, called polymer nanocomposites (PNC's), have improved mechanical properties when compared to unmodified homopolymers. It has been reported that PNC's can have a higher glass transition temperature (T_g) than the original polymer. (Hsieh et al,1999) It has been hypothesized that polymer nanocomposites can be made out of more than one polymer and that even if these polymers are naturally immiscible, the clay platelets will exfoliate and hold the polymers together. This would allow for the creation of Nanocomposites that have the properties of more than one polymer. Additionally, this would be extremely beneficial to the plastic recycling industry, because it would allow for the mixture of many polymers without reduction of product quality.

I have worked to create nanocomposites of multiple polymers and clay. I mixed different polymers with clay in a C.W. Brabender twin-screw extruder (model#074, type# EPL-V501). The properties of these mixtures were analyzed using the TEM (Transmission Electron Microscope), DMA (Dynamic Mechanical Analysis), and DSC (Differential Scanning Calorimeter). It was found that the addition of clay successfully improves the mechanical properties of polymer composites.



Plastic Before and After it Has Been Ground in an Industrial Extruder

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Micropatterning and Fibronectin Adsorption on Sulfonated Polystyrene 28%.

Lenny Slutsky, Ward Melville High School N. Pernodet, Ph.D., L. Collazo, M.S., J. Jerome, M. Rafailovich, Ph. D. Dept. Materials Science and Engineering, SUNY Stony Brook

The importance of the physical environment of cells has long been appreciated. The organization and composition of the extracellular matrix (ECM) have been shown to have a drastic effect on cell behavior. Fibronectin (Fn) is a prominent constituent of the ECM, forming a complex fibrillar structure around and beneath many cells. Fibronectin-rich matrices provide substrates for cell adhesion and migration during development and wound healing, etc...(1). It has been shown that a Fn matrix formation can be spontaneously induced on sulfonated polystyrene (SPS) 28% that has been spun cast onto silicon (Si) wafers. This phenomenon, however, does not occur when SPS 28% is spun cast onto gold (Au), since Au as most metals has trouble holding a charge (2). We aim to utilize the latter property to control Fn self-organization through Au/Si micropatterning. These micropatterns are parallel ridges of Au with valleys of Si in between. The bands of Au and Si vary from 5 to 35 μ m in width. Spin casting SPS 28% onto the surface of the rigid gratings allows for a flat surface for fibronectin adsorption (3). By controlling where the Fn adsorbs, we want to see the influence of different Fn matrix organizations on cell behavior. And so, the gratings will be able with the ECM to control the cell organization.



Au grating #5; pre-chromium etching Days

Fn on Grating 5 on SPS 28% for 5

Shee

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Determining Mechanical Properties of Rat Skin Using Digital Speckle Image Correlation

Sarah Smilow, Smithtown High School E Guan, Miriam Rafailovich Dept. Materials Sciences and Engineering, SUNY Stony Brook, NY 11790

The investigation of the mechanical properties of skin allows both quantitative and qualitative assessment of dermal alterations. Studies evaluating the healing and wrinkle smoothing process after laser treatment have been reported, in which the mechanical properties of the skin were measured with commercially available instrument such as SEM474, Courage & Khazaka, Cologne) based on the principle of suction elongation. [1]

In this study, tensile testing was used in combination with digital speckle image correlation (DSIC) technique to determine the Young's modulus and Poisson's ratio of two-day-old rat skin. Due to the delicate nature of skin, any deformation sensors attached to the skin may strengthen or weaken the material. DSIC is a non-contact technique, which can provide fairly precise

displacement distribution. Small silicon carbide particles were applied to the surface of skin in order to 200generate a good speckle pattern (as shown in the insert in Fig. 2). Briefly, DISC technique follows the 400particles of the speckle pattern, and then the displacement of these particles; consequently, the skin, 600 is determined by correlation function. [2] Fig. 1a is a vector map of displacement and Fig. 1b is its projection 800 along the vertical direction. Strain can be obtained by digital differentiation from displacement field and 1000stress can be estimated by the force over cross-sectional area. A typical stress-strain curve obtained by DSIC is shown in Fig. 2. Our preliminary results show that the Young's modulus of rat skin is approximately 1.64 MPa. From the nonuniform pattern observed in Fig. 1b, one can see that DSIC may be used to study the fracture mechanism of skin, as well.





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Improving Adhesion At Polymer Interfaces Containing Filler Mixtures Michael Snow, Mordechai Bronner, Miriam Rafailovich, Department of Materials Science and Engineering

The purpose of this study was to determine the effects of fillers on the adhesion at polymeric interfaces and to improve this adhesion. One filler, cloisite 6A clay, is used in industry as a strengthening agent, because it improves the mechanical and thermodynamic properties of the material. The effect of clay cloiste 6A on bulk properties in polymers has been the subject of previous research; my experiments investigated the impact of cloisite 6A on the strength of adhesion in polymers. The second phase of this study consists of minimizing adhesion of "dirt" particles to a polymer-clay nanocomposite. This has many applications in the steel and automotive industry where no adhesion is desired in coating materials. First, PS (polystyrene) and PMMA (polymethyl-methacrylate) slabs were molded in a hot press at 150°C. Solutions were created containing varying concentrations of filler in toluene, along with PS or PMMA. The solutions were then spun-cast onto the polymer slabs at 2500 rpm for 20 seconds, leaving a thin film of polymer containing carbon black. Ellipsometry was used to confirm a constant film thickness of 3000Å. Each coated slab was then joined with another slab of the same type in the hot press, so adhesive bonds could form. The resulting sample could then be tested via the Asymmetric Double Cantilever Beam (ADCB) test. This method allows the adhesion to be measured by propagating a crack at the interface, and measuring the length of the crack. Crack measurement allows for the calculation of the fracture toughness, or Gc, a value that quantifies adhesion. In the second phase of our experimentation we spun solutions of PB (Poly-Butadiene), PMMA and PS on silicon wafers for 20 seconds at 2500 RPM. We then spraved N299 Carbon Black in amorphous and partially crystalline form, and glass pellets onto the wafers. We then annealed the samples for one hour at 150°C. The samples were analyzed using SEM (Scanning Electron Microscope) at 87° to determine the area of interaction for the different particles. The results showed that increasing concentrations of the clay filler increasingly diminished the fracture toughness of the PS/PS interface. This finding is significant, because it shows that clay fillers, while beneficial to various bulk properties of polymers, can lower the adhesion at polymer interfaces. Future work will utilize Atomic Force Microscopy (AFM) to examine interfaces that have undergone adhesive failure and characterize the adhesion. Secondary Ion Mass Spectroscopy (SIMS) will be used to measure the impact of the fillers on diffusion, a quantity that is directly related to adhesive strength. Further experimentation will also be done with other fillers, such as colloidal silica, to determine an effect on fracture toughness.





SEM analysis of glass pellets on PB

Clay Concentration Dependency

Improving Thermal Stability of PMMA Resins by Way of Melt Blending with Modified Organoclays

Andrew Song, Jericho High School Jonathon Hefter, Davis Renov Stahler High School Miriam Rafailovich, Michael Goldman, Mayu Si Dept. Material Sciences and Engineering, SUNY Stony Brook

Recently, the automotive adhesives industry has called for the need of a new adhesive with better thermal properties than the current adhesive. Current adhesives use Poly methyl (methacrylate) or PMMA. PMMA is a high modulus glassy polymer but has poor thermal properties. It burns extremely hot and converts to ash completely, making it dangerous to car passengers. A solution to this dilemma would be to increase the flame resistant properties of PMMA without changing its advantageous physical properties as an adhesive. It is possible to increases the thermal stability of the polymer by melt blending it with Cloisite 6A, a modified organoclay. The flammability of a polymer depends on the polymer resin (1). Previous work with the actual PMMA and C6A showed great promise in improving the thermal properties of PMMA. Research performed by Blumstein (1965) revealed that preparation of a polymer nanocomposite by free radical polymerization of MMA intercalated in clay would increase thermal properties of the polymer (2).

The alternate hypothesis states that PMMA resin mixed with C6A by way of direct melt intercalation will enhance the thermal properties of PMMA resin and have no effect on the physical properties, enabling the development of an acceptable new product with greater properties. Two different grades of the resin for the experiment, 2013 and 2016 were used. These substances were mixed together in a twin screw Brabender extruder. Afterwards, samples were pressed into rectangular shapes for testing. DMA and DSC tests were performed on the various samples. Future work includes making control samples, and mixtures of pure resin, to enable comparison. Further tests would be done by the UV-VIS and FT-IR. Also, the samples were taken to the National Institute of Standards and Technology where the samples were tested in the Cone Calorimeter. This machine tests the flame retardant behaviors of the samples. The results show that the peak heat release rate of the two grades combined with C6A is half of the pure resins. The mass loss rate of the two is also about half of the original resin. This is a significant improvement of the flammability properties of the PMMA resin.



Fig. 1-Sample of 2013 grade after test



Fig. 2- Sample of 2013 and 20% C6A after test

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Effect of Alkylammonium Ions on Drying of a DNA Droplet

Unaza Khan, East Islip High School, C.V. Krishnan and Miriam Rafailovich, Department of Materials Science and Engineering, SUNY Stony Brook

Last year, the influence of monovalent cations, Li^+ to Cs^+ , was investigated on the drying of a bacteriophage lambda DNA droplet using contact angle measurements and a confocal microscope. This provided great insight on the hydrophilic and hydrophobic interactions between these ions and DNA. In this continuing research, the effect of alkylammonium ions, RNH_3^+ , $R_2NH_2^+$, R_3NH^+ , and R_4N^+ , where R is methyl and ethyl groups as well as propyl, butyl, and isopentyl groups for the tetraalkyl ammonium ions (1) were investigated using Langmuir-Blodgett method as well as contact angle and confocal microscope measurements. From these data one hopes to understand the interference of hydrogen bonding effects as well as the hydrophobic effects of the tetraalkyl groups on the formation of DNA droplet (2). These ions offer the possibility of understanding the mutual interference of the alkyl groups and the possibility of the formation of multiple hydrogen bonds affecting the DNA droplet formation. The influence of the anions, fluoride, chloride, bromide, and iodide is also studied using tetrabutyl ammonium ion.

Langmuir-Blodgett measurements are usually carried out for two-phase systems. In the present study the interest was to see whether there is a significant accumulation of hydrophobic groups at the surface. The preliminary results using tetraalkylammonium ions indicate that there is a pressure build up when the area is reduced and the pressure build up is more for alkyl groups with higher number of carbons. The contact angle measurements shown in the graph given below indicate the influence of higher alkyl groups and anions on the drying of the droplet. The higher

the alkyl chain, the more hydrophobic it is, and the less the contact angle on the hydrophobic OTS surface. Confocal Microscope images indicate some special crystal structures for DNA in the presence of these salts that warrant more detailed studies.

Tetra butyl Ammonium Bromide with DNA



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A Polystyrene and EVA Polymer Blend Using Supercritical Carbon Dioxide Varun Mehta, Sachem High School North Edmund Palermo, Cornell University Miriam Rafailovich Dept. Material Sciences and Engineering, SUNY Stony Brook Ronald Occhiogrosso, Locust Valley High School

Polystyrene is a brittle, clear polymer, which is used in making Styrofoam plastic (1). Poly (Ethylene Vinyl Acetate), commonly known as ELVAX, is manufactured by Dupont, and it is a soft, elastic polymer that is quite weak (2). The goal of my research has been to compatibilize these two polymers into a new blend, and create a new material that can have the strength of Polystyrene but the flexibility of EVA. Normally these polymers are immiscible, but it is hypothesized that exposing polymers blends such as this one to carbon dioxide in the supercritical phase (temperatures greater than 89°F and pressures greater than 1073psi) can enhance the degree of compatibility and therefore the overall strength of the material (3). These blends each varied in polystyrene content (ranging from 25% to 75%) were prepared in the C.W. Brabender at 190°C, which were then molded into "dogbones" for Instron analysis and "rectangles" for DMA analysis. These samples were then exposed to supercritical carbon dioxide at temperatures from 91°F and 125°F and pressures from 1100psi to 3000psi. Materials were tested using Instron testing to find overall toughness, tensile strength and elastic/plastic stretch regions. They were also tested using Dynamic Mechanical Analysis to determine the modulus of elasticity. When exposed to supercritical CO_2 , the samples that contained 75% EVA and 25% polystyrene foamed considerably, increasing volume about twofold. This sample became remarkably lightweight and flexible, but still with noticeable strength. Instron data shows that blends with more EVA can be stretched farther, and samples with more PS required more force to be pulled to the same elongation. Further testing will include Differential Scanning Calorimetry to determine glass transition temperature and specific heat and impact testing. Possible applications for a 75% EVA 25% polystyrene blend are insulative, soft shock-absorbent materials, or a replacement for the rubbers currently used in shoes.





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The Crystalline Properties of Polyethylene Oxide Thin Films

Hatty Hong, Manhasset High School Vivek Kuncham, The Wheatley School Miriam Rafailovich, Yantian Wang,Dept. Material Sciences and Engineering, SUNY Stony Brook

Recently, the importance of crystalline polymers has emerged for their industrial applications in the areas of high strength fibers and optical reinforcement. By further understanding the chemical and physical properties of these polymers, the development of technology in these fields may be enhanced. Anomalous behavior of polymers in thin films which encompasses both structural and dynamical behavior, has attracted a great deal of interest. Measurements showing such anomalous behavior include density, film stability and dewetting, glass transition temperature, diffusion coefficient and chain conformation and relaxation (2). Polyethylene oxide (PEO) is a crystalline polymer whose bulk properties are well known. The crystallization process entails the formation of layers or "lamellae" of crystalline regions separated by amorphous polymers. The layers of crystalline materials have a well defined characteristic size, which depends on the crystallization conditions. Since the mechanical properties of the crystalline and amorphous nano-domains in a partially crystalline polymer sample have a large difference in the mechanical properties, Atomic Force Microscopy is a precise method of observing visual images of the samples.

The purpose of this study is to investigate the effects of nanopatterning, film thickness, addition of cloisite 6A (modified organoclay), and addition of amorphous polyethylene propylene on the crystalline properties of polyethylene oxide. Hydrophobic silicon wafers were used as the surface substrate in this study, upon which PEO was coated and then annealed. The annealing process involved placing the coated substrates in a vacuum oven, which was heated up to 80°C, past its melting point of 67°C, and then cooled slowly down to 40°C to enable crystallization. Observations of the topography and friction of the PEO surfaces were performed through AFM, which was also used to measure the precise melting points of each sample. Results revealed that as thickness decreased with and without nanopatterned surfaces, the crystallization patterns and lamellar height changed in a constant relationship. Rabolt (1, 1996) concluded that a critical thickness of 150 angstroms in necessary for crystalline morphology to exist in which the rate of crystallization is initially slow but increases rapidly as the film approaches 500 angstroms in thickness. However, results of this study refute Rabolt's findings, since crystalline morphology was observed at thicknesses less than 150 angstroms. Future research includes investigating the relationship between melting points of the PEO affected by the varying factors and crystalline properties.



Fig 1. PS-PBrS nanopatterned surface used to test effects on PEO crystallization

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Controlled Drug Release from Surface Micelles

Evan Rouge, Sachem High School. Miriam Rafailovich, Young-Soo Seo,Dept. Material Sciences and Engineering, SUNY Stony Brook James Lai, Dept. of Chemical Engineering, Polytechnic University Brooklyn

It has long been the desire of doctors to have a means of dispensing medication to their patients in a time released fashion, thus eliminating time and money spent on weekly appointments. The adhesion of water soluble drugs onto copolymer covered surfaces might provide just such an option. The development of a "patch" that a patient could wear during daily life that could release chemotherapy drugs in a controlled fashion is the goal of my research. Through the process of self assembly, block copolymers can be used to produce various morphologies on a angstrom size scale unachievable through conventional patterning techniques. These patterned surface micelles include the formation of peaks or cylinders of one polymer, which can be useful in the release of a water soluble substance. In my case, the chemotherapy drug Cisplatin. The goal of my research is to procure a patterned surface of the copolymer PS-PVP Poly(styrene-b-2-vinyl pyridine), which may dispel the drug at a controlled rate. An AFM and Ellipsometer were used to determine the nature and exact scaling of the surface micelles.

Work began by choosing a copolymer that would upon dissolving in a selective solvent, create a series of peaks. It was known that the PS-PVP was a optimal choice, since the solvent toluene is a good solvent for PS and a non-solvent for PVP. The substrates used were chemically cleaned Si wafers. Copolymer/toluene solution was added with pipette onto wafers and then spincasted. PVP (not dissolved in Toluene) forms into a series of evenly dispersed peaks while the PS is stretched into a layer of very small particles upon which the PVP peaks rest. (1) I then took Atomic Force Microscopy scans and Ellipsometry readings allowed for a better understanding of the micelles. I have yet to begin direct testing with the drug Cisplatin.

Further work involved researching the other practical applications of evenly nanopatterened surfaces, the most significant of which was Iron nanoparticles. Iron seemed to me to be the most practical for research due to possible multi-functionalized properties. I carried out most of my nanoparticle research at Polytechnic University where I sonochemically synthesized Iron nanoparticles in suspension.(2) Further testing with XPS, PL and UHV will have to be carried out before the project can be brought to full completion. If successful, the nanoparticle coated wafers will hopefully exhibit interesting qualties including, magnetic, semi-conducting, and most importantly, optical properties.

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