



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

The Garcia Center for Polymers at Engineered Interfaces was founded in 1996 and is named after the late Queens College professor Narciso Garcia, who was a pioneer in the integration of education and research. The Center focuses on the integration of materials research with tissue engineering, biomaterials, drug delivery systems, sustainable energy, nanocomposites, and recently, additive manufacturing. The Center also supports innovation through entrepreneurship and has multiple collaborations with industry and national laboratories, both in the US and abroad.

The research scholar program offers the opportunity for high school teachers, undergraduate, and high school students to perform research on the forefront of polymer science and technology together with the Garcia faculty and staff. Students work as part of focus research teams and are taught to make original contributions of interest to the scientific community. In addition to entering national competitions, the students are encouraged to publish in refereed scientific journals, present their results at national conferences, and develop patents to protect their intellectual property.

Our goal is to convey to the students the excitement we enjoy daily in research and provide for them a supportive network within the scientific community. Research is a lifelong experience and we hope to remain a resource to our students long after "graduation".



. Jonathan Sokolov



Miriam Rafailovich









Alagappan, Vimala

Balsam, Abraham

Bian, Carter





Cai, Frank



Cai, George



Chai, Esther



Chan, Christopher



Chen, Yijun



Cheng, Kimberley



Cheng, Richard



Choo, Dianne



Christianson, Finnur



Cong, Rhea





Cox, Jack



Cui, Audrey



Dhulipalla, Suraj



Duong, Teresa



Eisenberg, Ethan



Garg, Nyle



Gopal, Megha



Grajower, Meirav



Gu, Kevin



Gulzar, Saba



Guo, Ellen



Hamerman, Hannah



Han, Michael







Huq, Zahin



Kim, Eric





Kong, Christine

Korn, Elizabeth







Lederer, David





Lederer, Jonathon Lee, Clara (Dokyung)



Kwandou, Alexander

Leger, Luca



Lessler, Stella



Levy, Victoria







Li, Jeffrey



Li, Mingkang





Li, Songtao



Liu, Addison (Yeongsing)



Liu, Qinxi





Luo, Daniel

Ma, Carl (Zijian)









Meehan, Ryan

Mehta, Dipen

MALI

Mehta, Jalaj





Milan, Roberto

O'Keefe, Edward

Padwa, Shmuel



Pan, James (Bole)



Pan, Luisa



Pandey, Ikshu

Paramesh, Rithu



Pollner, Alina



Rai-Gersappe, Diya



Rajan, Surya





Ramrakhiana, Sahana

Raniwala, Rishabh











Salunke, Nikita

Sandhu, Bhawan



Shanmugam, Mukil



Shen, Hans





Silverstein, Emily

Stabile, Michael



Stabile, Nicholas



Steifel, Lauren



Tian, Katherine

Walsh, Emma



Wolberg, Jeffrey



Wu, Songze



Xiang, Eric

Xing, Kathy



Yang, Doris

Yang, Kerui

Yang, Kevin

York, Aidan



Zhang, Mark

Zhu, Aris

Zhu, Jocelyn

Research Experience for Undergraduates (REUs)



Akhter, Atif









Christie, Olias

Del Valle, Anthony

Research Experience for Undergraduates (REUs)



Essuman, Bernard



Etwaru, Karena



Franquiero, Angelina





Huq, Zahin



Jennings, Joseph



Lam, Bill



Linskens, Kelvin



Marcelin, Jonathan



Semel, Jessica



Meacham, Rachel



Su, Vivian



Paz, Rachell



Quinto, Lisa



Graduate Students



Chuang, Ya-Chen Feng, Kuan-Che





Hofflich, Jessica



Li, Juyi



Li, Kao



Lin, Yu-Chung



Raut, Aniket



Shmueli, Yuval



Wang, Likun



Zhou, Yuchen



Xue, Yuan



Zuo, Xianghao



Yang, Fan



Koosha, Farzad



Yin, Yifan



Faculty/Staff



Isseroff, Rebecca



Bertolotti, William





Recruit, Fresh :)



Bliznakov, Stoyan



Sadasivan, Chandramouli



Weiss, Herb

Cuiffo, Michael



Nitodas, Steve



Gersappe, Dilip



Jerome, John



Walker, Steven



Simon, Marcia



Friends

AMDI

56



Dunkin' and Softball







Canoeing!































Daily S Y TUESDAY	Schedule of Ad WEDNESDAY 6/26	ctivities THURSDAY	FRIDAY
Y TUESDAY		THURSDAY	FRIDAV
	6/26		TRIDAT
	0/20	6/27 10:00am -10:10	6/28 10:00am
		Introduction to Garcia	General meeting Statistics Lecture I
	4:00 PM Housing Check in	10: 10am-10:20 am Judith Berhannan	10:30-12:30
	Begins	Dean of Admissions Welcome to Stony Brook	Library/Data Mining/SBU ID problems DoIT, Maoro Nicoletto
		-	Clara Yuet , Jin Guo
		10:30 am-11:00 am Groups 1-4 ID Cards at SAC	Yuval Shmueli,
		Groups 5-8: Intro to theory and modeling, Dr. Dilip Gersappe	12:30 Working Lunch PIZZA (from Hunki's)
		11:00 am-11:30am Groups 4-8 ID Cards at SAC	12:30pm- 1:30pm Mariah Geritano SKYPE Tour or the Boston Children's
		Groups 4-8 ID Cards at SAC Groups 1-4: Intro to theory and modeling, Dr. Dilip Gersappe	Hospital 3-D Printing Simulation Laboratory
		11:30-12:30 Lunch at East Side Dining	1:30-2:00 Highlights of Science Research on Hydrogen Fuel Cells –former
		12:45 pm- 1:45 pm	Garcia students Audrey Shine, Plainview HS
		Dr. Srinivas Pentyala: The Why of Research	Danielle Kelly, Friends Academy HS
		1:45 pm -2:40 pm Dr. Tim Benseman CUNY-Queens College Teraherz radiation imaging	2:00 Dismissal to LIRR Have a good weekend!!
		2:40 pm- 3:30 pm	
		Dr. Sunil Sharma	
		Cellulose Chemistry	
		3:30 pm-4:00 pm Yuval Shmueli	
			modeling, Dr. Dilip Gersappe11:30-12:30 Lunch at East Side Dining12:45 pm- 1:45 pm Dr. Srinivas Pentyala: The Why of Research1:45 pm -2:40 pm Dr. Tim Benseman CUNY-Queens College Teraherz radiation imaging2:40 pm - 3:30 pm Dr. Sunil Sharma Dr. Priyanka Sharma Cellulose Chemistry3:30 pm-4:00 pm

	Stony Brook Univers		olymers at Engineered I	A design of the second s	
	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
I. This week we begin lab work. Starting Tuesday morning, please wear proper laboratory attire: (1) Closed toe shoes. (2) NO shorts (3) NO tank tops. You will get your own lab coat and goggles which must be work in the labs at all times. II. Written individual lab reports are due on Monday, July 8 th —uploaded under your name in the spin casting folder for your group. III. Quiz on Monday morning covers lab safety and facilities. IV. Please prepare Group presentations for Monday morning.	7/1 10:00am -10:05 General Meeting 10: 15-11:00 Dr. Chang Yong Nam, BNL Atomic Layer Deposition Journal Club 11:00 am-12:50 pm Divide into 8 groups and report to designated rooms for presentations with your REUs and grads. 12:50-1:30 pm LUNCH At East Side Dining with your group 1:30-2:15 pm Dr. Steve Schwarz, Queens College, CUNY Rheology of Entangled Polymers 2:15 -3:00 pm Dr. Stovan Bliznakov				FRIDAY7/510:00amGeneral meetingWriting the lab reports10:05-10:45 AMDr. Marcia Simon, SDM"Printing Skin"10:45-2:00 PMFacilities tourAFM - Ya-Cen ChuangLB trough – Aniket RautZeta potential/UV/VIS- Fan YangCell Lab/ Kuan-Che FengRheology/Bioprinter- Juyi LiElectrospinning - Kao LI, Fuel cells/TGA - Likun WangTensile/ Impact/Extrusion Xianghao ZuoConfocal microscope – Yuchen ZhuoUV vis and DLS - Fan Yang12:15 PIZZA working lunch (Hunkis)

lotes:	<u>MONDAY</u> 7/8	TUESDAY			
		7/0	WEDNESDAY	THURSDAY	FRIDAY
afety Quiz moved to		7/9	7/10	7/11	7/12
afety Quiz moved to	10:00am -10:05 General Meeting	10:00am	10:00am	10:00am	10:00am
	General Wreeting	General meeting/science	10.00am	General meeting/science	General meeting/science
ues.	10:05-10:15 AM Group	moment	General meeting/science	moment	moment
tudy materials will be	Picture in Lobby		moment		
rovided.		10:15-11:00AM		10:15-10:45	10:10 5 minute project
	10:15-11:00 AM	Dr. Ying Liu-EH&S	10:15-11:00 Dr. Robert	Dr. Sima Mofakham	updates
ab reports must be	Dr. Peter Brink, HSC	Writing the SOP	Harrison	Neuroscience	1.Polymer Blends—
ploaded by 11:59	Swimming with Sharks While curing cancer	11:00-11:30 Safety Quiz	Institute for Advanced Computational	Finalize SOP and upload to your project	Xianghao's groups
M Monday 7/8.	while curing cancer	11:00-11:50 Safety Quiz	Science	folder.	2. Gels for fire
	11:00-11:45 AM	11:30-12:00 10 minute	11:00SELECTION OF		retardance—Yuan's
efore starting lab	Dr. Jonathan Sokolov	research talks III	PROJECTS/WRITING		groups
ork:	DNA Science		SOP		
on.		1. Yuan Xue		Lab work	3. 3-D Skin printing—
a) Pass Safety Quiz	11:45 -12:10 PM 10	2. Ya-Chen Chuang	Lunch as coordinated with	PROPER LAB ATTIRE	Juyi/VIP/Dr. Simon
o) Write SOP with	minutes Research Talks part I	12:00PM-12:45	your projects	FROPER LAD ATTIRE	groups
our graduate student	parti	12.001 11-12.4.	your projects		Hunkies Pizza Lunch in
upervisor	1. Juyi Li—Hydrogels and	Take Your			Lecture Hall 145
uesday : Last day of Research Bootcamp.	bioprinting		Lab work		
ast day of Lunch with		3 REU Out	PROPER LAB ATTIRE		
GroupsTake an	2. Likun Wang—Fuel Cells	for Lunch			Lab work
REU out for Lunch to	12:00-12:45 Lunch				PROPER LAB ATTIRE
ay thank you!	12:00-12:43 Lunch	Day /			
nce you select a	12:45-2:30PM				REUs Please have pics o
esearch project— oordinate your time	Presentations of Groups I-				your groups
ith other members of	VIII	12:45-1:30PM			completed.
ne team.		Research Talks Part IV			
Research	2:30-3:00 Dr. Stephen	1 Ean Vang			Save the date next week
	Walker, Microbiology	1. Fan Yang 2. Kao Li			July 17 @10:AM Dr. Mary Truhlar, Dean of
Rules	3:00-4:00 10 minute	3. Kuan-Che Feng			School of Dental
. All Groups remain	Research Talks Part II	contrain end tong			Medicine –
n lecture hall 145 till ney are called out by					Preparing for a Career
heir Grad/Staff	1. Yuan Xue	1:30 -4:00 PM			Dentistry
eader.	2. Ya-Chen Chuang	SELECTION OF			. .
. NO One works	 Fan Yang Xainghao Zuo 	PROJECTS			Upcoming events next
lone in the labs	5. Kuan-Che Feng				week: Evening Baseball Game
vithout a					Bring Instruments—Dr
upervisor (21+)					Jerome is beginning his
the room.					musical ensemble

meeting

	MONDAY	TUESDAY	for all: daily at 10:00 AN WEDNESDAY	THURSDAY	FRIDAY
^{Notes:} Research	7/15 10:00am -10:05 General Meeting	7/16 10:00am	7/17 10:00 am	7/18 10:00am	7/19 10:00am
Rules . All Groups remain n lecture hall 145 till	**10:10-10:50 AM Prof. Brooke Ellison Engineering Ethics/Science	General meeting/science moment: Young's Contact Angle	General Meeting 10:05-10:20 am Dr. Mary Truhlar Dean, School of Dental	General meeting/science moment 10:05-10:20 Grace	General meeting/scienc moment 10:00-11:00AM Dr. Le
hey are called out by heir Grad/Staff eader. 2. NO One works alone in the labs vithout a	with Social Responsibility 11:00 Dr. Marcia Simon will speak to the neural group on protocols for differentiation of DPSC	Lab work proper lab Attire	Medicine Exploring careers in dentistry Lunch as coordinated with	Agnetti, Assistant Dean for Admissions Renaissance School of Medicine Exploring careers in medicine	Neymotin- <i>BNL emeritu</i> Effects of Nuclear Radiation Nuclear Dilemma: Energy vs. Weapons. Neither?
supervisor (21+) n the room. 3. Everyone must attend 10 o'clock meeting. 4. Every group will	along neurogenic lineage.	e de la constantina de la cons	your projects schedule Lab work	Lunch as coordinated with your projects schedule	11:00-11:50AM 1. Supercapacitor grou 2. Xianghao's thin film crystallization group 3. CASA Group 4. Yuan's flame
oresent a status eport before the end of the program. 5. Garcia values continual learning. We vill continue to have	Lab work	6:30PM-8:30PM	PROPER LAB ATTIRE	Lab work proper lab Attire	retardant group Hunkies Pizza Lunch in Lecture Hall 145
ectures, which you have the option of httending if you are not scheduled for work with your nentor.		Night Fishing and Bagel Sunset Dinner on the Celtic Quest. Meet in Lecture			Lab work proper lab Attire
. Some lectures are till MANDATORY for veryone. They will be narked in red and tarred; * Mandatory lecture		Hall 145 at 5:30. Buses leave SAC loop at 5:45.			
EUs: Please omplete uploading ne head shots of ogroups and upload ead shots of ourselves and your					

			for all: daily at 10:00 AM		
	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
Jpcoming Events:	7/22 10:00am -10:15	7/23	7/24	7/25	7/26
BNL Summer Sundays Trip: July 28 th –visit to	General Meeting Atomic Force Microscopy	10:00am General Meeting 10:05-10:20AM	10:00 am General Meeting	10:00am General meeting/science moment	10:00am **Donna Tuminello Intellectual Property
he Center for ⁻ unctional Nanomaterials. With Drs Chang-	Lunch as coordinated with your projects schedule	12:00 PM Dr. Jerry Cymerman: Dental shadowing opportunities	Lunch as coordinated with your projects schedule	**Dr, Rina Tannenbaum FTIR and RAMAN spectroscopy	General meeting/science moment
Yong Nam and Mircea Cotlet Sign up sheet on	T . Is succedure	at the Stony Brook Dental Clinic	5:00 PM Softball Game Cells vs Cells	Lunch as coordinated with your projects schedule	10:00-11:30 AM 1. DNA group 2. The group
Google Drive. Buses leave Stony Brook at 10:00 and eturn at 3:00 PM	Lab work Proper lab Attire	Lunch as coordinated with your projects schedule	(2. Theory group 3. Kao Li's cell groups 4. Yuchen's group
July 28 Exploring the Ultra Small Tour the Center for Functional Nanomaterials.		Lab work proper lab Attire	Meet in Lobby in front of	Lab work proper lab Attire	Outdoor BBQ
Canoe Trip 7/31 or 7/30, weather permitting. Stay tuned			Lecture Hall 145		
or details. Research Rules I. All Groups remain n lecture hall 145 till hey are called out by heir Grad/Staff			Lab Work PROPER LAB ATTIRE		Lab work proper lab Attire
eader. 2. NO One works alone in the labs vithout a supervisor 21+) in the room. 3. Everyone must attend 10 o'clock					

Stony Brook University | Garcia Center for Polymers at Engineered Interfaces



Mandatory meeting for all: daily at 10:00 AM
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	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
Upcoming Events:		7/30	7/31	8/1	8/2
Please be prompt on days of scheduled trips. Buses will leave promptly. Labs are closed till 4 PM on Wednesday to allow for maintenance. INVITATIONS for symposium will be uploaded: Please send to parents, teachers, friends, and family. We need to have RSVP for the end of summer symposium on 8/8/19	10:00am -10:15 General Meeting Electron Microscopy— TEM vs SEM Yuan XueAERTC	 10:00am General Meeting Canoe Trip Today Bob's canoe rental Buses leave at 10:00 AM. We are aiming to return at 2:00PM to Stony Brook Do NOT bring computers, electronics, backpacks, etc on boats. Bring water bottles, sunscreen,we will also have water bottles, snacks, Hunki's bagel lunch 	//31 10:00 am General Meeting Garcia Educational Enrichment trip: Cradle of Aviation Museum Special tour of Grumman Lunar Lander and IMAX Theater. Bagel Lunch from Hunkis Museum security does not allow Backpacks	8/1 10:00am General meeting/science moment Special Seminar: Anion-Exchange Membrane Fuel Cells Dario R. Dekel Technion – Israel University of the second s	8/2 10:00am General meeting/science moment 10:00-11:30 AM 1. Aneurism group 2. Nanotoxicology group(Fan Yang's group) 3. Kao Li's cell groups 4. Fan Yang's DISC movie group 5. Hydrogen cellulose fuel cell Hunki's Pizza Lunch
Research Rules 1. All Groups remain in lecture hall 145 till they are called out by their Grad/Staff leader. 2. NO One works alone in the labs without a supervisor (21+) in the room. 3. Everyone must attend 10 o'clock meeting. 4. Only ** red lectures are mandatory	Lab work proper lab attire	Lab work Proper Lab Attire	REMEMBER the Materials Challenge!! PPT viewgraph: Science in the Service of Society Describe A Material or Technology Developed for the Manned Space Program which is now in civilian use. (a)Describe the technology, (b) what was its function in the space program, and (c) what is it used for today. Evidence basedwith references. Prizes for the best entries. Laby Closed for Clean Up till we return at 4 PMI	with your projects schedule	Lab work proper lab Attire

	MONDAY	TUESDAY	for all: daily at 10:00 AM WEDNESDAY	THURSDAY	FRIDAY
Jpcoming Events:	8/5	8/6	8/7	8/8	8/9
Abstracts due Monday at 5 PM. REMEMBER: One per project Title, authors, Iddress page -MAX one page with DNE inch margins, Minimum 10pt font. Must have one or nore of following; a)figures with figure aptions, mentioned in text. b) peer reviewed eference, MLA ormat. Symposium 10AM- PM, Formal music and science oresentations. SVP: 8/7/ 4 PM Bring Family, riends, teachers. SARCIA continues ofter 8/9 BUT- 1) dorms close after More for a supervisor 21. NO One works alone in the labs without a supervisor 21+) in the room.	10:00am General Meeting Science Moments by students: (a) Ya-Chen's groups (b) DNA project 12:00 in Lecture Hall 145 Dr. Marcia Simon will review principals of RT- PCR. Lunch as coordinated with your projects schedule	10:00am General Meeting Science Moment (a) Likun's groups (b) Aerogel group (c) Stoyan's group Lunch as coordinated with your projects schedule Lab work PROPER LAB ATTIRE	10:00 am General Meeting (LAST ONE) Announcement of Best REU and Grad Mentor Awards. Science moments: Kuan-Che's students—2 groups: PLA ALD and PLA gels Jonathan Lederer and Avi Balsam—RGO/Enzymatic acitivity Biosensor project SYMPOSIUM ppt due 2PM to projectionist Lunch as coordinated with your projects schedule Have any non-perishable food left? Don't throw it out—We are collecting donations for Island Harvest in room 145.	I0:00am-2:00 pm Garcia Symposium: Science and Music CONTROL CO	10:00am General meeting Trip to ICL-Ardsley, NY WALL Lunch sponsored by ICI Presentations: Yuan's Flame retardant groups Likun's Hydrogen/cellulose groups Return to SBU at 3PM



Annual Summer Scholar Research Symposium & Musicale Thursday, August 8th, 2019 10:00am — 2:00pm Student Activity Center, Ballroom A Buffet Luncheon: Wing Wan of West Hempstead Guest Speaker Steven C. Vaccarelli Vice President | Trust Officer BROWN BROTHERS HARRIMAN TRUST COMPANY, N.A.

Please RSVP before Tues August 6, 2019 Via email to : Michael.Cuiffo@stonybrook.edu



Anthony Ginez, Nassau Community College, Garden City, NY



10:25 AM -	Medical Hydrogels and Bioprinting					
10:35 AM	Chair: Adeel Azim and Zahin Huq, Stony Brook University					
	Development of Novel Cerebral Aneurysm Embolization Method via Injection of Pluronic® F-127 Multiblock Copolymer Hydrogel					
	Finnur Christianson, Ponte Vedra High School, Ponte Vedra, FL Kevin Yang, Fairview High School, Boulder, CO Rithu Paramesh, Presentation High School, San Jose, CA Diya Rai-Gersappe, Huntington High School, Huntington, NY					
	Ikshu Pandey East Meadow High School, East Meadow, NY					
	Measuring Collagen Contraction and Keratinocyte Colony Efficiency for the Viability of Bioprinting Skin Using Extrusion-Based Printing vs. Traditional Skin Grafting Methods					
	Christopher Chan, Hicksville High School, Hicksville, NY Teresa Duong St. Anthony's High School, Melville, NY					
	Saba Gulzar, New Hyde Park Memorial High School, New Hyde Park, NY Katherine Tian, Ward Melville High School, East Setauket, NY					
	Analyzing and Comparing 3D Bioprinted Organotypic Dermis and Epidermis to Native Skin Dokyung Lee, Daegu International School, Daegu, South Korea Stella Lessler, Yeshivah of Flatbush Joel Braverman High School, Brooklyn, NY Somya Mehta, Hicksville High School, Hicksville, NY					
10:35 AM -	Hydrogels for Flame Retardant Applications					
10:45 AM	Chairs: Pik Hoi Lam , Caltech and Lisa Quinto , Stony Brook University					
	Enhancing the Flame Retardancy of Biodegradable Poly(vinyl alcohol) Hydrogels with Resorcinol Bis(diphenyl phosphate) Coated Starch Jalaj Mehta, Hauppauge High School, Hauppauge, New York Lauren Stiefel, Samuel H. Wang Yeshiva University High School for Girls,					
	Holliswood, NY					
	Synthesis of A Novel Flame-retardant Hydrogel for Skin Protection Using Xanthan Gum and Resorcinol Bis(diphenyl phosphate)-coated Starch Mingkang Li, Shanghai Star-river Bilingual School, Shanghai, China Bole Pan, Guangzhou Tianhe Foreign Language School, Guangzhou, China					
	Development of a Hydrogel-based Intumescent Flame Retardant System for Limiting Wildfire Propagation Audrey Cui, Monta Vista High School, Cupertino, CA Kimberley Cheng, Princeton High School, Princeton, NJ Frank Jin Rui Cai, Arcadia High School, Arcadia, CA					



	ENGINEERED INTERFACES
10:45 AM -	DNA Chip Technologies
10:55 AM	Chairs: Anthony Del Valle, Stony Brook University, Joseph Jennings,
	Nassau Community College
	Hussud Johnnunky Johnege
	A Novel Method to Apply Restriction Enzymes Through Low Volume Chambers for
	DNA Fragmentation in Next Generation Sequencing Library Preparation
	Kerui Yang, Edina High School, Edina, MN
	Qinxi Liu, Shenzhen Middle School, Shenzhen, Guangdong
	Jocelyn Zhu, Amador Valley High School, Pleasanton, CA
	jocely in Zindy Finitador Vancy Fingh School, Fredsancon, or
	Temperature- and Solubility-Dependent Desorption of Linearly Combed DNA from
	Polymer Substrates for Ordered Fragmentation and Sequencing
	Ellen Guo, The Harker School, San Jose, CA
	Luisa Pan, The Harker School, San Jose, CA
	Kathy Xing, Leland High School, San Jose, CA
	inder y ining, Boland ingh bollool, ban jobo, on
	Gel and Electric Field-Based Desorption of DNA from PMMA-Coated Silicon Surfaces
	to Optimize Sequencing Accuracy
	Elizabeth Korn, Plainview-Old Bethpage John F. Kennedy High School, Plainview, NY
10:55 AM –	Theory and Modeling
11:05 AM	Chairs: Kelvin Linskens, Stony Brook University
	Chan's. Kervin Emskens, stony brook oniversity
	Molecular Dynamics Simulation of Biopolymer-based Pore Fluids
	Jeffrey Li, Gilman School, Baltimore, MD
	jem cy E, diman school, Baltimore, MB
	<i>Optimizing Graphite Electrode of Lithium-ion Batteries with Lattice Boltzmann</i>
	Modeling
	Yijun Chen, Shenzhen Middle School, Shenzhen, China
	njun enen, enen indule beneen, eneninen, ennid
	Lattice Boltzmann Modeling of Hydrogen Ion Transport in a Proton Exchange
	Membrane Fuel Cell
	Alexander Kwandou, Bellarmine College Preparatory, San Jose, CA
11:05 AM -	Nanocomposites and FDM printing
11:15AM	Chair: Bernard Essuman and Steve Nitodas, Stony Brook University
	Shan - 2011ar a Lobanian and Stove Micouus, Stony Brook Oniversity
	Optimizing Thermal and Mechanical Properties of Poly(Lactic Acid) / Polypropylene
	/ Graphene Nanocomposite Polymer Blends in Fused Deposition Modeling (FDM)
	Systems
	Larry Huang, Wilton High School, Wilton, CT
	Richard Li , Conestoga High School, Berwyn, PA
	Addison Liu, Unionville High School, Kennett Square, PA
	Nikita Salunke, Evergreen Valley High School, San Jose, CA

	GARCIA Summer Symposium
	CENTER FOR POLYMERS AT ENGINEERED INTERFACES
	Mechanical and conductivity study of the 3D printed PBAT/PLA/graphene nanocomposites
	Da Hyun (Dianne) Choo , Kent School, Kent, CT Zhehua (Eric) Xiang , Lawrence Woodmere Academy, Woodmere, NY
	Studying the Crystal Formation and Interdiffusion Mechanisms of PLA Thin Films Suraj Dhulipalla , Eastlake High School, Sammamish, WA Mukil Shanmugam , Redmond High School, Redmond, VA Doris Yang , Lake Oswego High School, Lake Oswego, OR
11:15 AM – 11:30 AM	Dental Pulp Stem Cells: Mechanical and Chemical Sensing Chairs: Jessica Hofflich, Stony Brook University, Atif Akhter , Cornell University, and Rachel Meacham , Nassau Community College
	Elucidating the Effects of Direct Contact of Dental Pulp Stem Cells Cultivated Under Various Physical Parameters on Lineage Specification Pathways Yihan Shen, St. Andrew's School, Middletown, DE Zijian Ma, Tianjin Nankai High School, Tianjin, China
	Determining DPSC Differentiation Pathways and Biomineralization on ALD TiO2 PB Thick and Thin Films Megha Gopal , New Hyde Park Memorial High School, New Hyde Park, NY
	Investigating the Mechanics and Differentiation of Dental Pulp Stem Cells on Polybutadiene-Polystyrene Substrate Nanopatterns Meirav Grajower , Yeshiva University High School for Girls, Queens, NY Ilana Sacolick , Hebrew Academy of the Five Towns and Rockaway, Cedarhurst, NY
	The Effect of Fibrin on the Differentiation of Human Dental Pulp Stem Cells Victoria Levy, Saint Anthony's High School, South Huntington, NY Vimala Alagappan, Friends Academy, Locust Valley, NY
11:30 AM – 11:50 AM	Differentiating Dental Pulp Stem Cells on Scaffolds Chair: Jonathan Marcelin and Jessica Semel , Stony Brook University
	Optimization of 3D-Printed Scaffolds for Dental Pulp Stem Cell Differentiation via Surface Coating of Proteins and Titanium Dioxide Esther Chai, Townsend Harris High School, Flushing, NY Richard Cheng, Clayton High School, St. Louis, MO Rhea Cong, Huron High School, Ann Arbor, MI
	Effect of PLA Scaffold Roughness on Dental Pulp Stem Cell (DPSC) Differentiation and Growth in an In Vitro Setting Roberto Milan , South Side High School, Rockville Centre, NY Todor Bliznakov , Ward Melville High School, East Setauket, NY

	Determining Discrepancies in the Migrational Behavior of Osteosarcoma and Dental Pulp Stem Cells by Comparing Their Movement Hannah Hamerman, Yeshiva University High School for Girls, Holliswood, NY Sahana Ramrakhiani, Sachem North High School, Lake Ronkonkoma, NY Emily Silverstein, Hebrew Academy of the Five Towns and Rockaway, Cedarhurst, NY
	Investigating Neurogenic Differentiation of Dental Pulp Stem Cells using Novel PLA and Graphene Thin-Film and Electrospun Fiber Scaffolds in Vitro Dipen Mehta , George Walton Comprehensive High School, Marietta, GA Michael Stabile , Plainedge High School, N. Massapequa, NY Nicholas Stabile , Plainedge High School, N. Massapequa, NY Daniel Luo , Monroe-Woodbury High School, Central Valley
	Utilization of Patch Clamping to Investigate the Influence of Graphene on Transmembrane Ion Current in HeLa Cells and the Efficacy of Novel Fluorescent Dye Daniel Luo, Monroe-Woodbury High School, Central Valley, NY Dipen Mehta, George Walton Comprehensive High School, Marietta, GA Michael Stabile, Plainedge High School, N. Massapequa, NY Nicholas Stabile, Plainedge High School, N. Massapequa, NY
11:50 AM – 12:00 PM	Perovskites and Graphene: Photovoltaics and Energy Storage Chair: William Bertolloti, Plainedge High School Science Research Coordinator
	Optimization of EDLC Supercapacitors via a Novel Comparison of Acetonitrile Versus Diethyl Carbonate - Ethyl Carbonate - Tetraethylammonium Tetrafluoroborate Electrolytes along with the effects of Graphite-Active Carbon versus Carbon Nanotube-Active Carbon versus Carbon Nanotube-Graphene Nanoplatelet in Supermaterial Electrodes Shmuel Padwa, Bronx High School of Science, Bronx, NY Rishabh Raniwala, Wilton High School, Wilton, CT Nyle Garg, Greenwich High School, Greenwich, CT
	Preparation of MAPbI3 Perovskite via Hot-Casting Technique for Photovoltaic Application Jasmine Li, Fairview High School, Boulder, CO Aidan York, Kellenberg Memorial High School, Uniondale, NY
	Stability Enhancement of Perovskite Solar Cells Using Mixed Cation/Halide Perovskite Ethan Eisenberg, George W. Hewlett High School, Hewlett, NY Jack Cox, South Side High School, Rockville Centre, NY

CENTER FOR POLYMERS AT LE Story Brook

	ENGINEERED INTERFACES
12:00 PM-	Fuel Cell Technologies
12:30 PM	Chair: Aniket Raut and Priyanka Sharma, Stony Brook University
	Enhancement of Quaternized Ammonium Polyaromatic Anion Membrane Performance in Alkaline Fuel Cells by Deposition of Graphene Oxide and Catalyst Ink Optimization Avinash Rao , Dougherty Valley High School, San Ramon, CA Michael Han , Dougherty Valley High School, San Ramon, CA Carter Bian , Cupertino High School, Cupertino, CA
	Facile Synthesis of Carbon Aerogel and Application as Catalyst Support to Increase Performance of Proton Exchange Membrane Fuel Cells Kevin Gu , Deerfield Academy, Deerfield, MA Eric Kim , Stuyvesant High School, New York, NY
	Citric Acid Crosslinking of Carboxycellulose Nanofiber Membranes to Enhance Proton Exchange Membrane Fuel Cell Performance George Cai , Wayzata High School, Plymouth, MN Songze Wu , High School Affiliated to Renmin University of China, Beijing, China Songtao Li , Princeton International School of Science and Mathematics, Princeton, NJ
	Enhancing the Performance of Novel Cellulose Membranes for the Proton Exchange Membrane Fuel Cell Christine Kong, Commack High School, Commack, NY Bhawan Sandhu, Lawrence High School, Cedarhurst, NY
	Optimization of Pt/C Catalyst Nanofibers Electrospun on Nafion 117 Membranes in Polyelectrolyte Membrane Fuel Cells Surya Rajan, California High School, San Ramon, CA Edward O'Keefe, Ridgewood High School, Ridgewood, NJ David Lederer, Hebrew Academy of the Five Towns and Rockaway, Cedarhurst, NY
	Reduction of Carbon Monoxide Poisoning in Proton Exchange Membrane Fuel Cells via Application of Gold/Ruthenium Nanoparticle Monolayer Luca Leger, Medfield High School, Medfield, MA Ryan Meehan, Sachem High School East, Farmingville, NY Mark Zhang, Green Valley High School, Henderson, NV
12:30 PM	Buffet Luncheon Catered by WingWan of West Hempstead

We gratefully acknowledge the Louis Morin Charitable Trust



Session 1: Materials Research for Biomedical Applications

Chairs: Fan Yang, Farzad Koosha



Characterization of Salicylic Acid and Calcium Hydroxide Paste (CASA) as a Novel **Antimicrobial Medicament for Endodontic Applications**

Aris Zhu¹, Jeffrey Wolberg², Karena Etwaru³ Fan Yang⁴, Farzad Koosha⁵, Stephen Walker⁶, Miriam Rafailovich⁴, Marcia Simon⁶

¹Hamilton High School, Chandler, AZ 85248, ²HAFTR High School, Cedarhurst, NY, 11516, ³Cornell University, Ithaca, NY 14850, ⁴Department of Materials Science and Chemical Engineering, Stony Brook University, NY 11794, ⁵Department of Endodontics, Stony Brook University, NY 11794 ⁶Department of Oral Biology and Pathology, Stony Brook University, NY 11794

Endodontic infections are primarily caused by persistent bacterium Enterococcus faecalis and fungus Candida albicans. Currently, calcium hydroxide is routinely used as a disinfectant in endodontic procedures despite its inefficacy against both microbes.^[1] Additionally, its high pH contributes to dental pulp necrosis. To improve antimicrobial properties and neutralize the pH, salicylic acid was added to calcium hydroxide in a 3.7: 1 mass ratio to formulate CASA. This study characterizes the antimicrobial properties and cytotoxicity of CASA.

To assess the effectiveness of CASA against common endodontic pathogens, agar plates containing CASA or calcium hydroxide were incubated for 24 hours with Enterococcus faecalis, Candida albicans, Staphylococcus aureus, Escherichia coli, Streptococcus gordonii, Lactobacillus salivarius, and Actinomyces viscosus.^[2] Zones of inhibition were subsequently measured to quantify antimicrobial properties. For all the tested microbes, CASA consistently vielded larger zones of inhibition compared to calcium hydroxide (Fig. 1), suggesting CASA is the more effective antimicrobial agent.

However, further analysis was needed to determine whether the supernatant or precipitate of CASA contributes to its antimicrobial nature (Fig. 2). To determine the antibacterial properties of each CASA component, different concentrations of supernatant and precipitate were suspended in liquid growth media containing E. faecalis or C. albicans with 0.2 OD at 600 nm. After 24 hours, live and dead E. faecalis and C. albicans were stained using green and red fluorescent proteins, respectively. The precipitate had a greater ratio of dead to live microbes than the supernatant for both *E. faecalis* and *C. albicans* (Fig. 3), indicating the precipitate contributes most to the antimicrobial properties of CASA.



Figure 1: Graph of zones of inhibition of CASA and Ca(OH)2 incubated with various microbes.

In order to be considered for clinical use, CASA must not only be antimicrobial but also non-cytotoxic to dental pulp stem cells (DPSC). Cytotoxicity was measured over a four-day period by counting DPSC with 0.25 mg/mL of CASA in media. The results show doubling times of control DPSC and DPSC with CASA are both approximately 27 hours, suggesting CASA is not cytotoxic and will not cause dental pulp necrosis if used for endodontic procedures.

Further investigations may use x-ray diffraction and ¹H NMR spectroscopy to elucidate the chemical structure and composition of the CASA supernatant and precipitate. Additional studies may determine the effect of CASA on DPSC differentiation for clinical knowledge.





[1] Mohammadi, Z., & Dummer, P. M. H. (2011). Properties and applications of calcium hydroxide in endodontics and dental traumatology. International Endodontic Journal, 44(8), 697-730. doi:10.1111/j.1365-2591.2011.01886.x

[2] Narayanan, L. L., & Vaishnavi, C. (2010). Endodontic microbiology. Journal of conservative dentistry: JCD, 13(4), 233-239. doi:10.4103/0972-0707.73386

Titanium Dioxide Nanoparticles Increase Risk of Bacterial Infection in Human Cells By Alina Pollner¹, Angelina Franqueiro², Fan Yang³, Miriam Rafailovich³ ¹Canyon Crest Academy, San Diego, California ²Cornell University, Ithaca, New York ³Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY

Titanium dioxide (TiO₂) nanoparticles are widely used in many cosmetic products, most notably sunscreen and toothpaste, for their white pigment and UV radiation blockage capabilities. As roughly four million tons of titanium dioxide particles are produced worldwide annually, a comprehensive review of their potential cytotoxic effects is needed. Previously, exposure to TiO₂ nanoparticles (NP) increased HeLa (cervical cancer) cells' susceptibility to *Staphylococcus aureus* infection[1]. *Staphylococcus aureus* and *Enterococcus faecalis* (*E. faecalis*) are some of the most successful human pathogens, and are present in millions of humans. Here, we evaluated the effect of TiO₂ nanoparticles (NP) on the proliferation of dental pulp stem cells (DPSC), fibroblasts, and human umbilical vein endothelial cells (HUVEC) and susceptibility to infection by *S. aureus* and *E. faecalis*.



Figure 1: Average cell counts for DPSC as measured by Alamar Blue Assay and hemocytometer. Nanoparticle exposure did not affect proliferation.

Cells were exposed to *S. aureus* and *E. faecalis* (at a ratio of 1:1,000 cells to bacteria) for 90 minutes and then analyzed by a confocal microscope. For *S. aureus*, dental pulp stem cells exposed to TiO₂ NP had on average 545% more bacteria attached to their surface (p<0.0001) as seen in Figure 2. Fibroblasts exposed to TiO₂ NP similarly had 286% more bacteria (p=0.0001) than unexposed fibroblasts (Figure 2). Unlike DPSC and fibroblasts, HUVEC cells exposed to NP did not have a statistically significant difference in bacterial attachment with *S. aureus* as compared to HUVEC cells without exposure to NP. For *E. faecalis*, there was not a statistically

Cell proliferation was measured using the Alamar Blue assay, which measures the viability of cells through the reduction of resazurin to resorufin, and a hemocytometer over a five-day period. Using a concentration of 0.4 mg/ml rutile $TiO_2 NP$, cell counts were measured and compared to standard samples. As shown in Figure 1, the addition of $TiO_2 NP$ did not affect cell proliferation of dental pulp stem cells, grown on either collagen or tissue culture plastic (TCP).



Figure 2: Average *Staphylococcus aureus* bacteria per cell, as measured by confocal microscopy.

significant difference in bacterial attachment for cells that were exposed to NP.

These results suggest that exposure to TiO2 nanoparticles may increase the cells' risk of bacterial infection. Further data, such as the measurement of colony forming units (CFU), are needed to support these findings. Future research involves investigating mechanisms that cause cells to be more susceptible to the bacteria (such as Lactate Dehydrogenase assays), NP skin permeability studies, and engineering solutions for prevention.

[1]: Xu, Yan, et al. "Exposure to TiO₂ Nanoparticles Increases Staphylococcus Aureus Infection of HeLa Cells." *Journal of Nanobiotechnology*, vol. 14, no. 1, 22 Apr. 2016, doi:10.1186/s12951-016-0184-y.

Modification of Thrombin Enzymatic Activity Using Graphene Oxide and Partially Reduced Graphene Oxide Nanoparticles

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Graphene and its water-soluble derivative, graphene oxide (GO), have unique physical and chemical properties. GO, in particular, possesses a single-layered, two-dimensional (2-D), sp2 hybrid structure studded with charged functional groups, offering a unique double-sided, easily accessible substrate for multivalent functionalization and efficient loading of molecules from small organic materials to biomacromolecules. Many of its effects on biological material remain unknown, so we researched how GO and prGO (partially reduced Graphene Oxide) affect enzymatic activity. We chose to test was thrombin, the enzyme responsible for catalyzing hemostasis which prevents one from losing an excessive amount of blood. In severe circumstances, such as in car accidents or post surgery, hemostasis could be too slow to fully repair the vessel in time, and it would be helpful to introduce an external substance that would hasten blood coagulation. Additionally, in cases of thrombosis, when blood unnecessarily clots and the circulatory system is disrupted, introducing a substance that would inhibit blood coagulation would allow for a non-invasive treatment. We tested to see if GO and prGO would be capable of exhibiting either of these characteristics when interacting with thrombin.¹

Thrombin activates hemostasis by transforming fibrinogen into a fibrin network. We utilized rheology in order to test the onset of the formation of the fibrin clot. {2} We determined that 30 u/ml of thrombin was an appropriate concentration as it began to produce a clot about 6 min after thrombin was dispensed into the fibrinogen solution. Our control consisted of 3 ml of 10mg/ml bovine fibrinogen dissolved in pure PBS. The experimental groups were: 1) 3 ml of 10 mg/ml bovine fibrinogen dissolved in a solution containing 1mg/ml GO in PBS 2) 3 ml of 10 mg/ml bovine fibrinogen dissolved in a solution containing 1mg/ml prGO, reduced by 12 millimolar NaBH4, in PBS.

We observed 2 parameters from the rheology graphs which resulted²: 1) The time the sample took to begin to clot, determined by the time at which a spike, or a sharp increase in slope, was discerned on the logarithmic graph of the modulus of the sample. 2) The modulus of the sample after clotting.

Figure 1 shows the discrepancy between the gelation time of the control and GO. It indicates that GO delayed the onset of gelation by 35.7% when compared to the control. The fibrinogen solution without GO began to clot at 350 seconds and the solution with GO began to clot at 475 seconds. This can be beneficial for counteracting thrombosis. We predict that prGO will enhance thrombin's activity and this would assist the onset of hemostasis. We continue to search for optimal parameters which will allow pRGO to enhance the activity of thrombin. In the future



Fig 1B. This graph shows the rheology of GO in PBS mixed with a fibrinogen solution. Elastic modulus (Y-axis) indicates the strength of the clot over time (X-axis)

we hope to characterize GO and prGO with XPS, SEM, and AFM in order to determine the properties responsible for causing its effects on thrombin.

¹ Yang, Xinjian, et al. "Contrasting Modulation of Enzyme Activity Exhibited by Graphene Oxide and Reduced Graphene." *Chemical Communications*, vol. 49, no. 77, 2013, p. 8611., doi:10.1039/c3cc44632h.

² Kaibara, M. "Rheology of Blood Coagulation." *Biorheology*, vol. 33, no. 2, 1996, pp. 101–117., doi:10.1016/0006-355x(96)00010-8.

Using Digital Imaging Skin Correlation to Predict Comatose Recovery Anthony Ginez¹, Rachell Paz², Fan Yang³, Miriam Rafailovich³

¹Nassau Community College, 1 Education Dr, Garden City, NY 11530; ²Suffolk County Community College, 533 College Rd, Selden, NY 11784; ³Department of Material Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794

Digital Imaging Speckle Correlation (DISC) is a well-known method of measuring and graphing displacements and facial strains by analyzing a set of still images, especially in mechanical testing. Other applications include studying the recovery of skin after use of Botox or skin tightening cream, facial recognition software, and clinical diagnostics. The project focuses on honing a new application, the tracking of micro expressions in comatose patients to better predict their rate of recovery. This is possible because facial skin is directly attached to underlying muscles. Using the subject's pores as "speckles," we are able to graph and map the micro movements that may be undetectable by the human eye. It is known that recovery rates can vary between patients, at times with no obvious correlation. By imaging and recording the trends in healthy volunteers as a control, we hope to develop the code and procedure used

to record signs of consciousness in affected patients.

Our recording is done by a Nikon D300 as an unedited video. In order to calculate displacement, we needed to cut the file into individual photos. These are then sorted by the timestamp of the associated presentation, which in turn is connected to the slide shown; good, bad, and neutral. The now sorted photos are averaged as a unit and compared to a predetermined 'neutral photo', seen in Figure 1. The average is plotted and graphed as a heat map as shown here.

The displacement is measured and graphed with the intensity of color reflecting the degree of displacement. Warmer tones represent more distortion from the original neutral photo.



Figure one: Neutral slide shown (left) Good image (middle) Bad image (right)

During testing, it was seen that the head needed to be in a still position for the entire duration of the recording session. In order to keep the head as still as possible, we created a special chin rest that attached to the camera facing the subject. Talking, head tilting or an over enthusiastic smirk would move the entire face a millimeter or more. To our eyes these slights make for good communication in a natural setting, but with the project focus in mind the shifts become detrimental to an accurate response, attributable to a wide error margin in our final project. Something else we noticed in the above pictures was the concentration of distortion in the cheeks and forehead, seen by the intensity of the heat map. When analyzing the "bad" photos, the forehead is noted as a major area of interest. Conversely, when looking at the "good" slides, the cheeks show more displacement as compared to the neutral slide.

In order to predict the recovery rate of comatose patients, more data is needed from our control group. This data can then be compared to the recorded response of affected in-patients and record if there are results correlative to healthy, wake patients. Similarly to how we predicted the recovery rates of botox patients, we can attempt to graph the recovery of comatose patients. By imaging them daily and comparing their results, we can measure whether their reaction, if there is one, strengthens over time. As with all studies, a larger sample size is ideal to better generalize for the public. More work will have to be done, but these are only the instrumental first steps.

- 1. Divya Bhatnagar, et al. "An in vivo analysis of the effect and duration of treatment with botulinum toxin type A using digital image speckle correlation" 8, Apr. 2013 <u>https://www.ncbi.nlm.nih.gov/pubmed/23565582</u>
- Satprem Pamudurthy, et al. "Dynamic Approach for Face Recognition using Digital Image Skin Correlation" AVBPA 2005 https://link.springer.com/chapter/10.1007/11527923 105
- 3. E. Guan, et al. "Determining the Mechanical Properties of Rat Skin with Digital Image Speckle Correlation" 10 Oct. 2003 https://www.ncbi.nlm.nih.gov/pubmed/15056999
- 4. Divya Bhatnagar, et al. "An Analysis of Facial Nerve Function in Patients with Vestibular Schwannomas Using Digital Image Speckle Correlation" Feb. 20
- Isabelle Afriat Staloff, et al. "An in vivo study of the mechanical properties of facial skin and influence of aging using digital image speckle correlation" May 2008. <u>https://www.ncbi.nlm.nih.gov/pubmed/18412553</u>
Session 2: Medical Hydrogels and Bioprinting

Chair: Juyi Li



Development of Novel Cerebral Aneurysm Embolization Method via Injection of Pluronic® F-127 Multiblock Copolymer Hydrogel

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 ⁴Huntington High School, Huntington, NY 11743, ⁵East Meadow High School, East Meadow, NY 11554, ⁶Department of Mat. Sci. & Chem. Eng., Stony Brook University, Stony Brook, NY 11790, ⁷Department of Neurological Surgery, Stony Brook University, Stony Brook, NY 11790

Endovascular embolization is a recently developed minimally invasive technique used for treatment of cerebral aneurysms¹. The technique involves embolization of the injured artery with metallic or hydrogel coils to occlude the vessel and induce thrombosis. However, this technique is limited by the packing density achieved by the coils, and currently results in a high recurrence rate of 17%². Hydrogels are networks of polymer chains that are



Figure 1. Temperature dependent rheological tests conducted on Pluronic hydrogels with and without multiblock copolymer PF127

nce rate of 17%². Hydrogels are networks of polymer chains that are biocompatible and highly absorbent, and therefore can be injected directly into aneurysms to occlude the vessel. In this study, we therefore developed a novel aneurysm occlusion technique through injection of a shear thinning hydrophilic triblock copolymer, Pluronic® F-127³.

Pluronic® F-127 hydrogels were synthesized at concentrations of 20%, 25% and 30% w/v, and contrast agent iopromide was added at concentrations of 20% and 30% v/v to 20% F-127 for angiography. To increase rigidity, 1% and 5% w/v PF-127 multiblock copolymer was added to F-127 to achieve final hydrogel concentration of 25%⁴. Various rheological techniques, including amplitude sweep, single frequency, and temperature dependent tests were conducted to determine the viscoelastic range and elastic modulus as a function of temperature of each gel. After the sol-gel transition temperature was reached, the elastic modulus of the 25% F-127 hydrogel changed from <10 Pa to a maximum

of 43 kPa, while the 20%

F-127 5% PF multiblock copolymer solution reached a maximum of 51 kPa after the sol-gel transition at 25 °C (Fig 1).

Deionized water at 37 °C was circulated by a peristaltic pump with a mean flow rate of 4.06 cc/sec through a silicone model of a saccular cerebral aneurysm in order to simulate blood flow in a carotid artery. A catheter was then threaded into the model aneurysm through silicone tubing simulating the vasculature of a human body. Incorporating a red dye additive into the hydrogels and recording the color density in the aneurysm over time indicated that greater concentrations of F-127 hydrogel successfully occluded the aneurysm for longer time spans and were injectable for concentrations up to 30% w/v. The addition of multiblock copolymer PF-127 at concentrations of 1% and 5% resulted in occlusion times of 31 minutes and 61 minutes. respectively (Fig 2a). The 5% multiblock copolymer showed a nearly fivefold improvement over the occlusion time of 25% w/v F-127 without multiblock copolymer (occlusion time of 13 minutes) (Fig 2b). However, excessive concentrations of multiblock copolymer at 25% w/v were too stiff for injection through a catheter.

Due to their biocompatibility and absorbent properties, coupled with high elastic moduli and shear thinning properties, hydrogel injection for aneurysm embolization has great potential for intracranial aneurysm treatment. This study shows the effectiveness of a novel temporary embolization method, with promise for future improvement through addition of fibrinogen with thrombin coagulant or other crosslinking polymers to ensure effective permanent embolization.



Figure 2. Effect of concentration of (a) Pluronic F127 and (b) multiblock copolymer on aneurysm occlusion time.

 ¹ Molyneux, A., Kerr, R., & Yu, L. (2005). International Subarachnoid Aneurysm Trial (ISAT) of Neurosurgical Clipping Versus Endovascular Coiling in 2143 Patients With Ruptured Intracranial Aneurysms: A Randomised Comparison of Effects on Survival, Dependency, Seizures, Rebleeding, Subgroups, and Aneurysm Occlusion. *ACC Current Journal Review*, *14*(12), 52. doi:10.1016/j.accreview.2005.11.083
 ² Knap, D., Gruszka, W., Sieroń, D., Gruszczyńska, K., Zawadzki, M., Zbroszczyk, M., & Baron, J. (2017). Evaluation of Endovascular

 ³ Shirwaiker, R., Purser, M., & Wysk, R. (2014). Scaffolding hydrogels for rapid prototyping based tissue engineering. *Rapid Prototyping of Biomaterials*, 176-200. doi:10.1533/9780857097217.176

⁴ Jun Jiang, Miriam H. Rafailovich, Ram Malal, Chunhua Li, Min Y. Lin, Ralph H. Colby, ... Daniel Cohn. (2008). Rheology of Thermoreversible Hydrogels from Multiblock Associating Copolymers. *Macromolecules*, *41*(10), 3646–3652. https://doi.org/10.1021/ma800192m

Measuring Collagen Contraction and Keratinocyte Colony Efficiency for the Viability of Bioprinting Skin Using Extrusion-Based Printing vs Traditional Skin Grafting Methods

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Multiple methods through tissue engineering have been applied to construct skin grafts for treatment. However, several disadvantages accompany these methods, such as immune reactions, transmission of diseases, and shortages of donor skin. A novel technique - bioprinting - would alleviate the majority of these complications.¹ Bioprinting skin holds great potential for application in treatments as it would not only eliminate the need for donors, but it would also prevent homogeneity issues accompanied by current methods. Bioprinting allows for faster integration with the host tissue, lower risk of rejection and uniform tissue growth in vivo.² Currently, extrusion-based printing is found to be the most feasible bioprinting technique in terms of vertical configuration and allowing a larger variety of bioink, including more cell-dense bioinks; however, present limitations include lower cell survivability due to the shear stress that occurs during printing.² We aimed to evaluate the cell survivability rates, comparing poured and printed samples. *Table 1:* Volumes for collagen

Two essential components in artificial skin constructs include the extracellular matrix (collagen and fibroblasts) and keratinocytes. In order to test the viability of each of these components once passed through the bioprinter nozzle, the collagen contraction, as well as the damage to the keratinocyte cell membranes, was observed. The collagen gels were first prepared to have a final concentration of 1.2 mg/mL and a concentration of 7.5 x 10^4 cells/well for three plated and three poured samples. The associated volumes of each of the materials, shown in *Table 1*, were combined along with cells to create a collagen gel solution. Three samples were printed at a pressure of 10 kPa and three samples were plated to observe the effect of shear force on cell survivability. This gel solution was then placed in the incubator at 37 °C to set and the contraction rate of the collagen gel was measured and compared using EVOS imaging. Damage to the keratinocytes, on the other hand, was observed using trypan blue dye. This method allows us to count the intact and damaged cells and compare the printed (1 kPa) and poured samples. After letting these keratinocytes grow in a KC+ Medium for two weeks, a colony efficiency test was conducted to determine the effect of bioprinting on the functionality of the cells.

gel components		
Material	Amount/	
	20 mL	
10x	2.0 mL	
EMEM		
L-	166µL	
glutamine		
(.2M)		
FBS	2.0 mL	
Na ₂ CO ₃	568 µL	
Collagen	4.4 mL	
(5.44		
mg/mL)		
PBS	10.0 mL	
NaOH	Until pH	
	= 7	

The results of the collagen contraction experiment showed that the contraction rates look fairly similar, as seen in *Figure 1*. However, after doing two-sample t-tests assuming unequal variances for each day, *Figure 2* shows that most of the samples actually contracted quite differently. We believe these differences most likely occurred due to errors which took place during the pouring or printing of the samples and calculation errors in finding the area.



Future research would include repeating this experiment to discern if these differences occurred due to experimental errors, or if poured and printed samples truly have a statistically significant difference in collagen contraction rates. We would also like to test multiple trials involving varying pressures through the bioprinter nozzle as varying pressures would affect cell survivability.

¹Augustine, Robin. "Skin bioprinting: a novel approach for creating artificial skin from synthetic and natural building blocks." *Progress in biomaterials* vol. 7,2 (2018): 77-92. doi:10.1007/s40204-018-0087-0

²Kačarević, Željka P et al. "An Introduction to 3D Bioprinting: Possibilities, Challenges and Future Aspects." Materials (Basel, Switzerland) vol. 11,11 2199. 6 Nov. 2018, doi:10.3390/ma1112199

Analyzing and Comparing 3D Bioprinted Organotypic Dermis and Epidermis to Native Skin

Christopher Chan¹, Teresa Duong², Saba Gulzar³, Dokyung Lee⁴, Stella Lessler⁵, Somya Mehta¹, Katherine Tian⁶, Adeel Azim⁷, Olias Christie⁷, Michael Cottone⁷, Philip Cottone⁷, Michael Gozelsk⁷, Zahin Huq⁷, Vivian Su⁷, Juyi Li⁷, Marcia Simon⁷, and Miriam Rafailovich⁷

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3D bioprinting has exhibited promise for creating a functional skin equivalent, potentially helping treat patients with major burns and severe surgical wounds via a skin graft. However, the use of bioprinting to create skin organotypic holds many engineering and biological challenges, such as the body's potential allergenic reaction to printed skin¹. In order to attempt to accurately replicate human skin, we must print a skin organotypic that contains both a dermal and epidermal layer². Therefore, the purpose of this experiment is to compare different combinations of printed and plated skin in order to assess the possibility of bioprinting skin.

Four varying combinations of three different samples of dermal and epidermal organotypic were created in 6well plates with 24mm diameter wells: first layer of collagen printed and second layer collagen plated, both first and second layer collagen printed, both first and second layer of collage plated, and first layer of collagen plated with the second layer of collagen printed. For the first layer of the dermis, we printed (at 10 kPa) and plated 1 mL of 2mg/mL concentration of rat tail collagen solution in each well (*Table 1*).

After allowing the collagen to gel, we created a solution for the second layer of our samples (*Table 2*). The second layer of collagen consisted of 1.2mg/mL concentration of the same collagen and different chemical compounds mentioned above. Additionally, cells at a concentration of 2.5×10^4 cells/mL were added to the solutions. We then printed (at 10 kPa) or plated 3 mL of the solution into each sample based on the different combinations. For one week after, we changed the media every other day: 2mL on top of the insert and 3mL on the bottom of the insert.

Materials	Per 13ml	Materials	Per 28ml
10X EMEM	1.3ml	10X EMEM	2.8ml
Glutamine (.2M)	108.29µl	Glutamine (.2M)	232.4µl
FBS	1.3ml	FBS	2.8ml
Na ₂ CO ₃	367.9µl	Na2CO3	792.4µl
Collagen(4.82mg/ml)	5.4ml	Collagen(4.82mg/ml)	7ml
PBS	4.5ml to 13ml	PBS	14ml to 27ml
NaOH	Until Ph = 7	NaOH	Until Ph = 7

Three days into the week, a metal ring was added to each insert. Following the seven days, we then printed (at 0-1 kPa) 50μ l of keratinocyte cells at a concentration of $600x10^4$ cells per mL in the metal ring, serving as the epidermis. After two weeks of changing the media and allowing the keratinocyte cells to properly develop, the artificial skin was then extracted from the inserts and sent to a lab for H&E staining.

In January 2019, Stony Brook University students conducted a similar experiment in which three samples of entirely printed skin and three samples of entirely plated organotypic were grown. From the results of their experiment (*Figure 1*), we expect the layers that were placed through the printer nozzle to be generally thinner than the layers plated without being placed through a pressurized environment. However, due to the recent data acquired via a collagen contraction experiment, we do expect the cells to react normally in every other way aside from the thickness of the dermis.

DERMAL EQUIVALENT FOR PRINTED COMPARED TO CONTROL (POURED)





[1] van der Veen, Vincent C., et al. "Biological Background of Dermal Substitutes." Burns, vol. 36, no. 3, Jan. 2010, pp. 305–321. EBSCOhost, doi:10.1016/j.burns.2009.07.012.

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Session 3: Hydrogels for Flame Retardant Applications

Chair: Yuan Xue



Enhancing the Flame Retardancy of Biodegradable Poly(vinyl alcohol) Hydrogels with Resorcinol Bis(diphenyl phosphate) Coated Starch

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Flame retardant components are necessities to a firefighter's protective gear, such that more eco-friendly advancements in this technology have become more pertinent in an effort to better ensure the safety of both firefighters

and victims in fire. Conventionally, flame retardants have been created from only slightly biodegradable superabsorbent polymers with extremely high water content[1]. Generally these superabsorbent polymers are derived from acrylic acid and acrylamide and unless these are oligomers it is likely that they are not biodegradable[2,3]. In lou of these facts the primary goal of this research was to synthesize a biodegradable hydrogel flame retardant that is as efficient as its less environmentally friendly equivalents.

To create the hydrogel samples we used a cyclic freezing and defrosting procedure consisting of 24 hours in a -20 degree Celsius freezer and then 1 hour of defrosting at room temperature 3 times for each set of samples. Our samples consisted of various concentrations of starch, resorcinol bis(diphenyl phosphate) (RDP), and RDP-coated starch

	Controls	5% RDP	16.7% RDP-starch
1% PVA	A	в	с
1% RDP-PVA	D	Е	F
2% PVA	G	н	I
2% RDP-PVA	J	К	L
4% PVA	М	Ν	0
4% RDP-PVA	Р	Q	R

Fig. 1: Hydrogel sample make-ups and concentration

suspended/dissolved in multiple bases that were created through the addition of poly(vinyl alcohol) (PVA) and RDP-coated PVA in deionized water. The samples created can be seen in Figure 1.

Starch and RDP were chosen as a result of their performance as flame retardants and chemicals with excellent charring both in our preliminary testing with gelatin based hydrogels and in previous literature. We also suspected that the free hydroxyl groups on starch and the double bonded, outstretched oxygen on RDP would interact well, likely through hydrogen bonds, with the surface of the PVA molecules in the PVA based hydrogel. The PVA was also chosen as a result of its positive performance and flame retardant properties along with strong mechanical properties



and flexibility in literature[4,5,6].

All the samples were 5 grams and we created 3 identical versions of each solution for testing with Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), burn tests and Rheometry. FTIR revealed the interactions between the gel and the particles in each sample, TGA identified the degradation of the samples in relation to temperature, the burn tests helped us compare the effectiveness of each sample in terms of charring, temperature, and amount of gel/skin remaining. Rheometer tests gave us in depth information on the mechanical properties of our gels, the most important being whether they were shear thinning or thickening.

We derived from the FTIR results in Figure 2 that hydrogen bonds were present in the PVA and RDP-PVA, and learned that the gels were mainly shear-thinning through the rheological studies. Overall samples *R* and *O* performed the best in terms of the completeness of the

char layer formed, the lowest max temperatures, both being below $65^{\circ}C$ (the temperature for a burn to almost instantaneously be second degree), the amount of gel remaining with *R* having .60 grams of gel remaining and *O* having .51 grams remaining. Additionally these two samples displayed clear shear-thinning which is useful for flame retardants. Compared to previous results, our gels are better while still retaining their biodegradable nature, as they keep the temperature under 65 degrees celsius for longer then 200 seconds[7]. With the knowledge that the hydrogels synthesized in this experiment behave in the ways described and that 4% RDP-PVA with RDP-Starch hydrogels perform the best, in future studies we aim to test additional concentrations of RDP-PVA, starch, RDP-starch, and PVA to determine the optimal combination for a flame retardant.

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Synthesis of A Novel Flame-retardant Hydrogel for Skin Protection Using Xanthan Gum and **Resorcinol Bis(diphenyl phosphate)-coated Starch**

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Firefighters continually endanger their lives in order to rescue others. This can leave them with severe burns; in 2017 alone, 2,835 U.S. firefighters suffered from burn-related injuries [1]. Developing a flame-retardant hydrogel for skin protection would greatly reduce these risks. This research presents the synthesis of said hydrogel using biodegradable, nontoxic materials: xanthan gum (XG) and resorcinol bis(diphenyl phosphate) (RDP)-coated starch [2].

To synthesize the flame-retardant hydrogel for skin, RDP and starch (weight ratio of 3:7) were mixed, stirred, centrifuged, and dried to obtain RDP-coated starch. RDPcoated XG was also prepared in a weight ratio of 1:3. The powders were combined with deionized water and put into an incubating waver at 45 °C for 10 hours to form the hydrogel samples. Different gel formulations varied in 2 aspects: 1) the concentration of XG or RDP-XG (at 1 wt.%, 2 wt.%, and 2.5 wt.%) and 2) with or without 10 wt.% RDP-coated starch. All samples were characterized with burn tests, Thermal Gravimetric Analysis (TGA), Fourier-transform Infrared Spectroscopy (FTIR), viscometry, and goniometry.

The set-up of the flammability assessment is demonstrated in Figure 1. Sheepskin was embedded in aluminum pans, covered with hydrogel, and burned continuously for 150s. Results from the test showed



Fig.2. Increase in temperature over time for 2.5 wt.% hydrogel samples in burn test for sheepskin

between approximately 90 °C and 110 °C, which was mainly attributed to the loss of water in the hydrogels [3]. The starch-containing gels, on the other hand, underwent two-stage thermal degradation, one at around 110 °C, and another between 250 °C and 360 °C, before losing most of its weight. The addition of RDPstarch significantly increased the thermal stability of our hydrogel, by reducing weight loss at both stages of decomposition.

without

RDP-starch



Fig.1. Illustration of the set-up for burn tests

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37.6 C

that the 2.5 wt.% RDP-XG+10 wt.% RDP-coated starch had the best performance, forming a uniform char layer which protect the underlying gel layers and skin. The sample outperformed its pure XG gel counterpart by 29% in terms of the final temperature. The best-performing hydrogel remained below 45 °C for over 50 seconds and below 55 °C for

completely

300 350 400 450 500 Temperature (°C)

FTIR spectra identified the presence of hydrogen bond between RDP/starch and Fig.3. TGA curves for the 2.5 wt.% hydrogels RDP/XG. Data from the viscosity tests revealed that all samples displayed shear-thinning behavior. From viscometry, gel viscosity increases as the concentration of XG increases, whereas the presence of RDP reduces the gel's viscosity; the addition of starch increases the viscosity overall. Moreover, through goniometry we determined the contact angle of gels on sheepskin surface, which demonstrated the hydrophilicity of the XG gels. The feasibility of the gel's application is supported by its thermal stability, flame retardancy, shear-thinning and hydrophilic properties, which indicated that the flame retardant RDP-XG/RDP-starch gel was easily spreadable and safe to use as a protective measure for not just firefighters but also for commercial use. Further studies could examine skin irritation and toxicity of the hydrogels, compare their limiting oxygen indices through cone calorimetry, and establish a heat transfer model to further evaluate their thermal protective performance.

and RDP-XG gel with RDP-starch were investigated through TGA. As depicted in Figure 3, the gel samples

were

decomposed after a single-stage thermal decomposition

almost

^a. These authors contributed equally to this work

^[1]Fahy, R. F., LeBlanc, P. R., & Molis, J. L. (2017). Firefighter fatalities in the United States. Quincy, MA: NFPA.

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Development of a Hydrogel-based Intumescent Flame Retardant System for Limiting Wildfire Propagation

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Figure 1 Top: fresh gel Middle: charring while burning Bottom: char after 3 min of burning

Due to global warming, wildfires are becoming increasingly prevalent and destructive — \$5.1 billion lost in the past decade¹. To limit the spread of wildfires, we developed an ecofriendly, hydrogel-based fire retardant solution that can be sprayed upon vegetation. Our testing focused on dried grass, as dry grass is a major fuel source that sustains and propagates wildfires².

The addition of water to Xanthan Gum (XG) forms a hydrogel, whose ~90% water content makes it naturally fire resistant. However, the pure XG gel won't be effective after the water being evaporated. In order to increase the flame retardancy of XG gel for both wet and dry application conditions, an intumescent fire retardant (IFR) system with resorcinol diphenyl

phosphate (RDP) as acid source and starch as charring agent was suspended in the XG gel matrix³. Due to RDP's high mobility, it was first coated onto XG and starch surface with a 1:3 and 3:7 weight ratio, respectively. The intensity increase in the hydrogen bonding region on the FTIR spectrum, shown in fig. 3,

confirmed the successful coating of RDP onto the starch and XG surface. The fire retardancy of candidate gels was assessed by measuring the percent mass loss after 1, 2, and 3 minutes of using a propane torch to burn samples of grass coated in a thin layer of gel; test setup is shown in fig. 1. Burn test results showed that the gel formulation of 1g/100ml RDP-XG gel with 10 wt.% RDP-starch yielded the highest percent of weight remaining in both wet and dry conditions, shown in fig. 2. Rheology results also proved that this formulation is shear thinning and has one of the lowest viscosities, which is promising for spray application. Thus, we identified the 1g/100ml RDP-XG with 10 wt.% RDP-starch as the most effective flame retardant gel formulation, whose FR property was not compromised even following the complete evaporation of its water content.



TGA supported the addition of starch as a charring agent, as shown by the elevated char residue between 150-350°C in fig. 4. Through the successful bonding of RDP onto the XG and starch surface, RDP is immobilized inside the gel matrix, which increased its stability. The plasticizing effect of RDP also effectively decreased the gel viscosity.





In the future, in order to better quantify the effectiveness of our solutions,

we plan to run cone calorimetry of our solutions on compression molded grass, which would characterize the heat release process of gel on grass during combustion. Limited oxygen index, which is level of oxygen necessary for a fire to persist, will also be measured.

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³ Chen, Xingyou, and Chen, Yinghong. "Synthesis of a Hydrogen-Bonded Complex Intumescent Flame Retardant through Supramolecular Complexation and Its Application in LDPE Foam." *RSC Advances*, Royal Society of Chemistry, 19 June 2017.

Session 4: DNA Chip Technologies



A Novel Method to Apply Restriction Enzymes Through Low Volume Chambers for DNA Fragmentation in Next Generation Sequencing Library Preparation Kerui Yang¹, Qinxi Liu², Jocelyn Zhu³, Joseph Jennings⁴, Dr. Jonathan Sokolov⁵, Anthony Del Valle⁵

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Significant progress has been made in the past few decades in genome sequencing technologies. Next Generation Sequencing (NGS) Technology is highly valued for DNA sequencing as it provides a platform to tackle greater and more diverse genomic sequencing¹. A common method for sequencing, NexteraTM technology utilizes TransposomeTM complexes to randomly cut and tag DNA². However, an ordered method of fragmenting DNA would offer significant advantages in simplifying the assembly problem of sequencing. Microfluidic channels have been used to diffuse an enzyme solution via capillary force in a vacuum, but due to the attraction of enzymes to the channel walls, the distance of enzyme diffusion is limited. An alternate method in which restriction enzymes are stamped onto microfabricated surfaces has a low success rate since a liquid environment must be maintained during the fragmentation process.

In this project, we aim to develop a novel method to effectively apply cutting enzymes onto PMMA surfaces combed with *JDNA*. Using 1mm long low- volumechambers in PDMS (Polydimethylsiloxane), in theory, the restriction enzyme solution should be able to diffuse more efficiently in comparison to it diffusing through the longer microfluidic channels. The first step was to produce uniform rows of microchambers in PDMS for enzyme delivery. Initially, chambers were created via a micro-needle (d=250µm) penetrating three layers of PDMS. It was observed that uniformly spaced cracks were created instead of circular chambers (Fig. 1). In order to produce regular micropatterns, a molding device was engineered so the PDMS would cure around prelocated, upright needles. Through observation with an optical microscope, circular Figure 1. On the bottom: cracking chambers with diameters conforming to those of the needles were successfully observed in (Fig. 1).



PDMS caused by the mechanical needle machine. On



Figures 2a, 2c, 2d showcases the enzyme cutting areas for the test with molded PDMS holes. Figures 2b, 2d showcases the enzyme cutting areas for the test with the needle machine PDMS holes.

A PDMS peel test was subsequently the top: uniform circular holds conducted to confirm that the enzyme was created by molding technique. digesting the DNA instead of the PDMS ripping

the DNA off of the surface of PMMA. There was a difference in the amount of observable DNA on the PMMA surface before and after the test under the same exposure time (\approx 805ms). However, after increasing the exposure time (\geq 1.4s), more visible λ DNA molecules were observed, suggesting that the SybrGold dye for λ DNA labelling might be weakened after being in contact with PDMS.

Enzyme digestion tests were run utilizing a vacuum filling method to transfer DNase I (RNase-free) solution through PDMS chambers and a heating plate for enzyme activation and inactivation. Fabricated PDMS micro-channels produced by both mechanical needle poking and molding devices were tested. For the PDMS treated with mechanical poking, two types of enzymes digestion traces were observed: circular and linearly fragmented dots (Fig. 2). The intermittent linear pattern was possibly caused by the potentially high viscosity of DNase I solution and varying spaces within the PDMS cracks. Successfully digestion of DNA was observed using the molding-device fabricated holes (Fig.

2). The bright spots visible at the center of holes in Figure 2(c) and 2(d) are believed to be cut DNA fragments concentrated by the flow pattern of evaporating solutions (during the enzyme deactivation step).

Potential future research includes DNA fragmentation and desorption on PAA (Polyacrylic Acid) substrate using low-volume chambers and microfabrication of PDMS hole patterns using a femtosecond fiber laser.

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Temperature- and Solubility-Dependent Desorption of Linearly Combed DNA from Polymer Substrates for Ordered Fragmentation and Sequencing

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Accurate DNA sequencing proves invaluable to fields ranging from archaeology to biotechnology.¹ Despite the successes of fast and cost-effective short-read technologies, current methods require chemical or physical fragmentation in solution that loses information about spatial organization, necessitating costly computational reassembly or simply overlooking structural rearrangements, duplications, inversions, and mobile elements.^{2,3,4} To combat this issue, Cho and colleagues immobilized DNA on polymethylmethacrylate (PMMA) surfaces by molecular combing and cutting the strands with a soft lithography stamp.³

However, removal of the DNA from the PMMA surface involves extremely complex downstream methods and reagents like chloroform that need further purification.³ Thus, this study aims to first, simplify PMMA desorption and second, explore the potential of a second substrate: polyacrylic acid (PAA), a polymer with a solubility switch.⁵

PMMA and PAA solutions were spuncast onto silicon wafers at varying speeds, annealed in a vacuum oven at different temperatures and lengths of time, and dipped in various concentrations of λ DNA solution to comb the molecules; PAA wafers were rendered insoluble by immersion in CaCl₂ prior to dipping. We employed fluorescent microscopy and imaging to analyze the linearity, uniformity, and overall success of combing. Then the samples were desorbed. PMMA wafers were submerged in various buffer solutions and heated at different temperatures for times ranging from 30 minutes to overnight. PAA samples were soaked in NaCl to initiate ion exchange and dissolve the polymer, thus removing the DNA. Samples were again analyzed with fluorescence microscopy at the same locations as prior to desorption. Quantitative image analysis was achieved with ImageJ.

 $Qualitative \ observation \ of the \ PMMA \ samples \ reveals \ successful \ combing \ at \ an \ optimal \ DNA \ concentration \ of 0.5 \ \mu g/mL \ for \ desorption \ tests. \ On \ the \ other \ hand, \ the \ DNA \ immobilized \ on \ PAA \ was \ often \ inconsistent \ in \ density$

and direction, even at the optimal conditions of 180nm thick PAA layers, overnight vacuum anneal at 130°C, and 10 mm/s velocity of combing. However, DNA desorption from PMMA proved more difficult than from PAA. Despite the desorption of PMMA at various temperatures, times, and pH resulting in an overall decrease in average amount of adsorbed DNA of up to 91.52% at 60°C and three hours soaking in NEB 3-1 buffer (pH ~7.9), we observed a reduction in the linearity of desorbed DNA, indicating unideal breakages. Conversely, all DNA was successfully removed by complete dissolution of the PAA substrate within seconds. See Figure 1 for details.

In conclusion, both the improved PMMA and the new PAA methodologies present promising strategies for ordered fragmentation in DNA sequencing, though future research should be done to improve the desorption of DNA from PMMA and molecular combing onto PAA. Furthermore, other polymers with solubility switches, such as chitosan or polyethyleneimine (PEI), may provide viable options as well.



Figure 1. Top left: PMMA dipped in DNA, before desorbing. Top right: PMMA dipped in DNA after desorbing at 60°C for 3 hours in NEB 3-1. Bottom left: PAA dipped in DNA, before desorbing. Bottom right: PAA dipped in DNA after desorbing for 10 seconds in 24 mM NaCl.

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² Chin, Chen-Shan, et al. "Nonhybrid, finished microbial genome assemblies from long-read SMRT sequencing data." *Nature methods* 10.6 (2013): 563.

³ Cho, N., et al. "Fragmentation of Surface Adsorbed and Aligned DNA Molecules using Soft Lithography for Next-Generation Sequencing." J. Biosens. & Bioelectro 8 (2017).

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Gel and Electric Field-Based Desorption of DNA from PMMA-Coated Silicon Surfaces to Optimize Sequencing Accuracy

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Following the success of the Human Genome Project in 2003, DNA sequencing has been applied successfully to whole genome genotyping, mutation detection, carrier screening, detection of inherited disorders, and DNA library preparation.¹ Unfortunately, current sequencing methods are limited to DNA fragments at most a few kilobases long and result in many inaccuracies due to random cutting and the repetitive nature of DNA.² In one practice called molecular combing, a substrate is slowly pulled out of a DNA solution, depositing DNA molecules linearly on its surface. This offers the advantage of controlled cutting of DNA to then be sequenced in an orderly fashion.³ PMMA-coated silicon wafers have been effectively used for both DNA combing and cutting; however, they have presented issues in the removal of DNA fragments for subsequent replication and sequencing.

In order to address this issue of desorbing the DNA from the polymer coated silicon wafer, we decided to use agarose gels and create an electric field to draw the DNA off the surface. This setup relies on the same electromotive force that is employed in gel electrophoresis to move the DNA molecules through the gel matrix due to the negative charge of DNA. We cleaved 0.5 in x 0.5 in silicon wafers and spun cast them with varying concentrations of PMMA and PAA. PAA samples resulted in nonlinear DNA deposition and were not selected to be

used in this experiment. Through testing several combinations of PMMA and DNA concentrations, it was determined that the 1 μ g/mL λ DNA solution on 80-100 nm PMMA-coated silicon produced the best samples. Successful samples were dipped in the DNA solution, which was first heated at 60°C for 30 minutes to eliminate formation of DNA dimers. DNA-dipped samples were assigned to four different treatments. Some were placed in wells and covered with 4 mm thick 3% agarose gels made with NEBuffer 3.1 and incubated in a 60°C oven overnight. Others were placed in a well with an electric field parallel to the sample at field strengths for different lengths of time, with and without a gel. All samples were then re-dved in diluted SYBR gold solutions, washed with DNase reaction buffer, and blown dry with nitrogen gas. A Leica TCS SP2 confocal microscope was used to photograph 8 areas on each sample before and after DNA was desorbed and ImageJ was used to quantify the percent change in DNA on the samples.

As shown in Figure 1, the samples that were placed in an electric field desorbed significantly better than those that did not, regardless of the voltage, running time, or presence of a gel. Compared to the 79.1% DNA desorbed on the sample that sat with a gel in the oven overnight, the other samples which electrophoresed at .55 V/mm for 10 minutes, .39 V/mm for 15 minutes, and .55 V/mm for 10 minutes with a gel experienced a greater percent DNA desorption at 92.0%, 96.5%, and 97.8%, respectively. Among those three, the lower voltage for a longer time resulted in less remaining DNA, and the sample that was in contact with a gel had the least remaining DNA. This suggests that electrophoresis is a viable method of removing cut DNA from PMMA for replication and sequencing of systematically cut fragments, resulting in a more accurate technique for sequencing long DNA molecules.



Figure 1- Confocal microscope images (63x) of samples before (left) and after (right) desorption with only a gel (a), 7 volts for 10 minutes (b), 5 volts for 15 minutes (c), and 7 volts for 10 minutes with a gel (d).

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Session 5: Theory and Modeling

Chairs: Hongyu Li Shoumik Saha Zhuolin Xia



Molecular Dynamics Simulation of Biopolymer-based Pore Fluids

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Given the ubiquity of soil as a structural material in both civil and geotechnical engineering, it is imperative to have a comprehensive understanding of its mechanical properties under a range of conditions. Soil by itself possesses little merit as a foundational material and thus often has its mechanical strength augmented through the addition of various fillers, the most common of which is cement. Cement-based fillers significantly improve soil's mechanical performance, but this comes at the cost of a large environmental impact¹. As such, efforts are being made to develop more sustainable methods of soil reinforcement. One fast-emerging technique is the addition of biopolymer pore fluids that modify the internal structure of the soil and thus supplement its mechanical strength. Although the efficacy of such methods has been experimentally demonstrated², the mechanisms by which reinforcement is achieved are not well understood. In this study, we help to answer such questions by using coarse-grain molecular dynamics techniques as implemented in the LAMMPS code package³ to simulate the behavior of a pore fluid composite consisting of various concentrations of nanoplatelet clay fillers, biological polymers, and water under different levels of mechanical strain. Scripts were developed to randomly

generate the positions of the contents of the pore fluid. Any remaining space inside the simulation domain was filled using either a simple cubic, psuedo-BCC, or psuedo-HCP packing method (see Fig. 1) to achieve any solent concentration up to the theoretical maximum allowed by the system - thus replicating a variety of real-world conditions. These generated samples were then equilibrated in both a canonical ensemble and a piston model, after which they were sheared at different speeds to simulate realistic weight-bearing scenarios.



Figure 2 | Rheological properties of soil sample with twenty (20) nanoplatelets and fifty percent (50%) by volume biopolymer concentration. Left | Density profile across height of soil sample - no that the density at the center of the sample is around 0.8 and thus in agreement with QFT prediction Right | Average particle velocity across height of soil sample - note the close fit to the LSRL model and occurrence of zero (0) velocity at half of the height of the sample.



Figure 1 | Effect of explicit solvent generator script. Left | Original pore fluid with solvent in green, clay nanoparticles in blue, and biopolymers in purple. Right | Pore fluid with 696 additional solvent particles generated by a psuedo-BCC packing method. This increases the density at the center of the system to 0.8, which aligns with both QFT predictions and the established experimental literature.

In order to better understand the rheological properties of the pore fluid, we calculated the internal system density, pressure, viscosity, and velocity profiles (see Fig. 2) and kept track of possible microstructure formation for each simulation. Our findings provide valuable insight on how to improve the mechanical properties of soil - a practice which has, until now, had little to no theoretical basis for its selection of treatments. Knowledge of this nature will

help scientists better understand soil phenomena and thus allow them to engineer informed solutions better tailored to individual situations.

² Latifi, Nima & Horpibulsuk, Suksun & L. Meehan, Christopher & Abd Majid, Muhd.Zaimi & Tahir, Mahmood & Tonnizam Mohamad, Edy. (2016). Improvement of Problematic Soils with Biopolymer-An Environmentally Friendly Soil Stabilizer. Journal of Materials in Civil Engineering. 29. 10.1061/(ASCE)MT.1943-5533.0001706. ³ S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, J Comp Phys, 117, 1-19 (1995).

¹ Naeimi, Maryam & Haddad, Abdolhosein. (2018). Investigation on the Environmental Impact of Soil Improvement Techniques: Comparison of Cement Grouting and Biocement. 10.1007/978-981-13-0128-5 53.

Optimizing Graphite Electrode of Lithium-ion Batteries with Lattice Boltzmann Modeling

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Graphite is a widely used material for the anode of Li-ion batteries. There have been various attempts to optimize the electrode performance, and one of the goals is to achieve a higher final charge density, which is mainly concerned with suppressing the plating of Li metal, or the formation of dendritic structure [1]. Instead of focusing on the performance of electrode-electrolyte interface of the Li-ion batteries, this study aims to optimize the morphology of electrode under multiple conditions by simulating its influence on intercalation reactions in the graphite electrode with Lattice Boltzmann Method.

The 3D printing technology offers people more control on the structure of electrodes, and previous work tests two types of morphologies, which are random and sorted; in this study, we adopt the general reaction model developed by Ning Sun [1], and add a cluster counting algorithm to check if the generated morphology is appropriate. Besides, we create a parameter called density distribution factor to describe the general structure of the graphite electrode (Figure 1). The according morphology can be easily manufactured with current technologies. The diffusivity of Li atoms in graphite is set at 1e-6 mm²/s [2]. Other material parameters such as electrode density are altered to see the performance of electrodes under different charging conditions. In



Figure 2: The final charge density when plating at different density distribution factors and electrode densities of 50%, 60% and 70% in simulation with 1C-rate current



Figure 1: 2D slices of graphite morphologies at different density distribution factor with electrode density of 50% and 1C-rate current. From left to right, the factors are -4, 4 and 0. The factor determines whether the graphite density is higher near the current collector (left) or the electrolyte (right).

the end, we analyze the results in terms of final charge density, charging time, and actual current.

We show that the capacity of the Li-ion batteries has a functional relationship with the density distribution factor. By simulating electrode densities of 50%, 60% and 70%, we show a quadratic relationship between the final charge and the density distribution factor, and the fitted curve changes from concave down to concave up at 70% (Figure 2). Besides, we see a linear relationship between the charging time and the total charge, which is not a strong function of the electrode density, while the actual current is higher when the electrode density is higher, because of the higher mass density. These results can be used to better design the morphology of graphite anodes for superior performance.

[1] Sun, Ning. Application of Lattice Boltzmann Methods in Complex Mass Transfer Systems. 2016. State University of New York at Stony Brook, PhD dissertation.

^[2] Yu, P., et al. "Determination of the lithium ion diffusion coefficient in graphite." *Journal of the Electrochemical Society*, vol. 146, no. 1, 1999, pp. 8-14.

Lattice Boltzmann Modeling of Hydrogen Ion Transport in a Proton Exchange Membrane Fuel Cell

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Proton exchange membrane fuel cells (PEMFC), better known as hydrogen fuel cells, are energy sources powered by hydrogen gas that can supply the world with clean, sustainable electrical power. First invented by Sir William Grove in 1839, fuel cells have become the center of modern research due to their high efficiency and power density. In order for hydrogen fuel cells to achieve their full potential, a critical improvement needed is to develop new materials for the membrane that controls the transport of ions.

In this project, we investigate the transport properties of the proton exchange membrane, specifically two different membrane structures to find the most efficient one. The underlying principle of this project is the polaron theory which states that waves of movement in a crystal lattice, called polarons, spread particles through deflection and reflection. In our case, protons "hop" from one position to the next by "worming" their way along the backbone of polymer chains¹. The first structure consists of nanometer-sized channels where the chains are all aligned and provide an excellent conduit for transporting protons². The second structure consists of nanocellulose which functions similarly to the first structure, but transports the protons with randomized motion³.

The modeling approach we use in this project is the Lattice Boltzmann Method (LBM), which makes it much simpler to simulate single and multiphase fluids by offering a numerical solution to difficult Navier-Stokes equations. LBM especially excels at simulating complex physical phenomena while proving to be efficient and convenient compared to other methods of modeling. To apply the LBM, we used the program, Palabos, wrote C++ scripts in XCode, and executed those scripts with Unix. After running our simulations on a server, we used Paraview to create 3D models of our system and Matlab to plot the data. Regarding the simulation, we created a lattice of 60x10x60 lattice units and ran the simulation for 30 timesteps, recording the density every timestep. The simulation was created by initializing a higher region of density in the left and by using advection-diffusion and Guo external force fluid dynamics. We then changed the diffusion properties, either patterned or randomized, to simulate the two different structures by having the particles diffuse through the structures.

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Diffusion gradient vs Time for different structures

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The diffusion gradient for the two structures can be seen in figure 1 and a 3D model of the nanocellulose structure in action can be seen in figures 2-4. In figure 1, the diffusion gradient for the nanometer-sized channels is greater than that of nanocellulose, and since the gradient is inversely proportional to the diffusion coefficient, the first structure diffuses faster than the second structure, which is to be expected as uniform motion should diffuse more quickly than randomized motion.



^[1] How protons move through a fuel cell. (2017, June 21). Retrieved from https://www.nanowerk.com/nanotechnology-news/newsid=47150.php [2] Braun, A. (2017). Swiss team discovers how protons move through fuel cell. *Fuel Cells Bulletin*, (6). https://doi.org/10.1016/S1464-2859(17)30237-7

^[3] Bayer, T., Cunning, B. V., Selyanchyn, R., Nishihara, M., Fujikawa, S., Sasaki, K., & Lyth, S. M. (n.d.). High Temperature Proton Conduction in Nanocellulose Membranes: Paper Fuel Cells. *CHEMISTRY OF MATERIALS*, *28*(13), 4805–4814. https://doi.org/10.1021/acs.chemmater.6b01990

Session 6: Nanocomposites & FDM Printing

Chairs: Yu-Chung Lin Yuval Shmueli Xianghao Zuo



Optimizing Thermal and Mechanical Properties of Poly(Lactic Acid) / Polypropylene / Graphene Nanocomposite Polymer Blends in Fused Deposition Modeling (FDM) Systems

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Additive manufacturing, commonly known as 3D printing, has increased in popularity within the last decade¹ due to its versatility and accessibility. Coupled with the rise in polymer blend systems applications and graphene-based devices, this study aims to combine the three in the development of an optimized nanocomposite polymer blend for 3D printing applications.

Polymer composite systems have been especially popular in recent years because of their unique mechanical and thermal properties. This work explores a binary polymer blend of polylactic acid (PLA) and isotactic polypropylene (iPP) with added graphene nanoplatelets (GNPs). This nanocomposite utilizes PLA/iPP immiscibility² to aid in filament fusion and the compatibility of GNPs to enhance thermal conductivity of 3D-prints.

The focus of this study was two-fold: optimizing properties of (1) binary PLA and iPP blends at varying concentrations and (2) PLA/iPP blends with GNPs. Mechanical properties were studied using tensile testing, and thermal properties were studied using forward-looking infrared radar (FLIR) imaging. Raman spectroscopy, optical microscopy (OM) and scanning electron microscopy (SEM) were employed for structural characterization and morphology determination. Tensile testing revealed that in comparison to a control sample of pure PLA, the 99PLA/1iPP and 97.5PLA/2.5iPP concentrations exhibited an increase in Young's modulus, followed by a decrease in modulus with the addition of iPP beyond the 2.5% level. This aligns with the theorized interfacial fusion enhancements that result from iPP migrating to the surface of PLA, as low concentrations of iPP allow for migration due to uniform dispersion with minimal consequences to printability. OM offered insight into the interfilament fusion along the horizontal cleave of a 3D printed sample. Figure 1a. displays the poor interfilament fusion within the 100% PLA sample. As depicted in Figure 1b, the addition of iPP resulted in a total fusion at the interface at the cost of voids due to the poor miscibility of the polymer composite. Raman spectra of filament cross-sections confirm polypropylene filament rings observed during optical microscopy. These polypropylene channels hold promise in facilitating the organization of GNPs, likely boosting thermal conductivity and mechanical properties. Figure 2. shows relative PLA/iPP concentrations and clearly illustrates an iPP phase separation within the PLA matrix. PLA/iPP/GNP blends at multiple ratios were also prepared and 3D printed, using a minimum GNP concentration of 5% weight for weight. Mechanical testing showed a small reduction in the Young's modulus in the composites as compared with pure PLA and the binary blends.

Preliminary FLIR imaging indicated that the addition of graphene to PLA significantly enhances thermal conductivity and the addition of PP to this blend further improves thermal conductivity, supporting the theorized orientation of GNPs within the polymer matrix as a result of its incorporation with PP.

Future research should be conducted to investigate the effects of substituting iPP with polymers such as polybutadiene (PB) and polydimethylsiloxane (PDMS). Additionally, for enhanced FDM capabilities, it may be beneficial to add polybutylene adipate terephthalate (PBAT) as a compatibilizer during blending. To better understand additional properties of the blend, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis would also be advantageous.





FIG. 2: Raman Spectra of 90PLA/10iPP polymer blend demonstrating aggregation of iPP rings in filament

[1] Wohlers Assoc., "Additive manufacturing & 3D printing state of the industry," 2013, Morgan Stanley Research, September 2013; J.P. Morgan, January 2012.

[2] Choudhary, Priyanka, et al. "Poly(L-Lactide)/Polypropylene Blends: Evaluation of Mechanical, Thermal, and Morphological Characteristics." Journal of Applied Polymer Science, vol. 121, no. 6, 2011, pp. 3223–3237., doi:10.1002/app.33866.

Mechanical and conductivity study of the 3D printed PBAT/PLA/graphene nanocomposites

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In recent years, manufacturers are facing the requirements to enhance the thermal and electrical conductivity with reliable mechanical properties since the demand of electrical appliances is increasing. Polystyrene (PS) and its copolymers are among the most used materials of recent products. However, the concern of the environmental pollution caused by styrenic products has attracted more attention from the public and the government. Considering this, we chose a more environmentally friendly PBAT/PLA blend to mix with graphene (GNPs) H-5 to study the mechanical and conductivity performance. Previous study has shown that graphene prefers to stay in PBAT phase than PLA phase, and for the molded samples, they used PLA as a minor domain to confine the arrangement of GNPs H-5^[1]. Inspired by this, we are trying to further orientate the H-5 platelets under the shear force of the nozzle during 3D printing^[2].

The 3D printed samples present a relatively similar impact strength comparable to the molded ones, as shown in Figure 1(a). While in figure 1(b), we can see that the Young's modulus of 3D printed samples performed a higher tensile strength than the molded samples. These results suggest that the polymers made

through 3D printing can perform better mechanical properties. In addition, as the concentration of graphene H-5 increases, the impact strength decreases slower than the molded samples, and maintained at 65 J/m, which is much stronger than PS and the tensile strength, increases with the addition of H-5 content.





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For the thermal conductivity test, we tested the significance of the direction of graphene platelets can have on conductivity by making the testing direction vertical to the printing direction.

In figure 2(a), we can conclude that the thermal conductivity of the 3D-printed samples is lower than

that of molded samples, which can be explained as the printing direction is perpendicular to the testing direction, thus the orientated H-5 pathways is not applied at the direction of the heat diffusion. In the other hand, the electrical conductivity, which is measured in a closed loop and the electrons was transferred right on the printed direction, showed a significant increase, nearly 240 times higher for the 3D-printed 20% H-5 mixed PBAT/PLA blends than the molded sample, as shown in figure 2(b).

The high magnitude and low magnitude SEM image of 69PBAT/23PLA/8H-5 and 60PBAT/20PLA/20H-5 are shown in figure 3(a) - (d). From the low magnitude images, we can see that the printing of 69PBAT/23PLA/8H-5 is better than the 60PBAT/20PLA/20H-5 as the fusion and connections between each layer of the 8H-5 samples are significantly better than those of 20H-5 samples. From figure 3(a) we can hardly tell the boundaries of the layers. In figure 3(b) and 3(d), the orientation of the H-5 platelets was clearly displayed, shown as arrow directions, which is in agree with the enhancement of the mechanical and electrical conductivity.

[1] Weng, Y. X., Jin, Y. J., Meng, Q. Y., Wang, L., Zhang, M., & Wang, Y. Ž. (2013). Biodegradation behavior of poly (butylene adipate-co-terephthalate)(PBAT), poly (lactic acid)(PLA), and their blend under soil conditions. *Polymer Testing*, *32*(5), 918-926.

[2] Jia, Y., He, H., Geng, Y., Huang, B., & Peng, X. (2017). High through-plane thermal conductivity of polymer based product with vertical alignment of graphite flakes achieved via 3D printing. *Composites Science and Technology*, *145*, 55-61



Figure 3. SEM images: (a)Low magnitude of 69PBAT23PLA8H-5, (b) High magnitude of 69PBAT23PLA8H-5, (c) Low magnitude of 60PBAT20PLA20H-5 and (d) High magnitude of 60PBAT20PLA20H-5

Studying the Crystal Formation and Interdiffusion Mechanisms of Polylactic Acid Thin Films

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Polymer thin films are widely utilized as industrial coatings in fields ranging from photovoltaics to organic LEDs. Due to growing environmental concerns, however, petroleum-based plastics commonly used in thin films have come under scrutiny. The thermoplastic polylactic acid (PLA) has emerged as an inexpensive, eco-friendly replacement for nonbiodegradable plastics.^[1] Little is known, however, about the interfacial diffusion or crystal formation in PLA thin films, which are important to the surface performance of confined polymers.



Figure 1 (a) PLA (b) 99PLA/1PS (Mw 9.4k) (c) 99PLA/1PS (Mw 2mil) (d) 99PLA/1dSMMA on PS (e) PS on 99PLA/1dSMMA (f) PS on PLA on PS middle

Table 1: Roughness (10 mg/mL)

Sample Name	Roughness (nm)
PLA Control	14.0
Mwps 9,400	21.1
MwPs 2 million	14.9
PLA/dSMMA on PS	14.7
PS on PLA/dSMMA	10.0

further examine the effect of confinement on PLA crystal formation.

The control group was pure PLA. AFM showed that the surface roughness for the pure PLA was 14.0 nm and that the average crystal size was 4.09 nm. When PS with Mw=9,400 amu was added, the roughness grew 50.7% to 21.1 nm, and the average crystal size grew 66.5% to 6.810 nm. When the polystyrene with Mw 2 million was added, the roughness increased just 6.04% to 14.9 nm, while the crystal size increased 84.7% to 7.554 nm. These results show that the addition of PS consistently increased both the roughness and the crystal size within the thin films; the increase in roughness is due to the rigidity of polystyrene as compared to PLA (Table 1). In addition, they show that larger molecular weight PS additives increase crystal size by a greater amount. Next, the 99 % PLA/1% dSMMA top layer of the bilayer samples with PS on bottom that were analyzed using AFM and SIMS. AFM revealed that the roughness of the surface was 14.7 nm; when the top layer was PS the roughness decreased 31.97% to 10.0 nm (Table 1). In addition, SIMS data from samples with 1%, 2%, and 5% dSMMA annealed at 120°C and 170°C for 1 hour proved that samples with higher SMMA concentration and at higher annealing temperatures saw more interfacial diffusion (Figure 2; Table 2).

In this study, various PLA, polystyrene (PS) and deuterated styrene methyl methacrylate (dSMMA) blends were examined as confined thin films on different substrates. The first part of this study used atomic force microscopy (AFM) and ellipsometry to determine the impact of polymer chain length on crystal formation and was investigated by comparing PS of molecular weights (Mw) 9.4k and 2 million amu in 99% PLA/1% PS thin films on silicon wafers annealed for 24 hours at 170°C. The second part of this study involved testing different substrates by creating bilayer thin films through a floating procedure. Since PLA and PS are immiscible^[2], dSMMA was

added to the PLA layer to strengthen the PLA-PS interface. Secondary ion mass spectrometry (SIMS) was conducted to measure the diffusion of dSMMA to the interface. PS on PLA/dSMMA samples were also analyzed. The final part of this study involved triple layer films consisting of PS on PLA on PS in order to



Table 2: dSMMA Interfacial Thickness (nm)

	99/1	98/2	95/5
120°C	25.080	39.937	in progress
170°C	37.456	46.355	57.425

SIMS data for the samples with PS on top is currently being generated to confirm the interfacial diffusion phenomenon. AFM performed on the triple layers in a region covered only by the PLA on PS revealed that crystallization on the PLA layer was heavily suppressed even when the PLA was not completely covered by PS (Figure 1f). To continue this study, it is necessary to study the roughness when PLA/dSMMA is the bottom layer and its effects on the interfacial thickness of the bilayer after diffusion. Furthermore, to study the broader applications of the dSMMA compatibilizer, we can use dSMMA and monitor its diffusion when miscible with similar polymers such as PEO and PVDF.

Kikkawa, Yoshihiro, eta. "Crystallization, Stability, and Enzymatic Degradation of Poly(L-lactide) Thin Film," *Biomacromolecules*, 2002.
 Guo, Yichen, et al. "Enhancing Impact Resistance of Polymer Blends via Self-Assembled Nanoscale Interfacial Structures," *Macromolecules*, 14 April 2018.

Session 7: Dental Pulp Stem Cells: Mechanical & Chemical Sensing

Chair: Ya-Chen Chuang

Kao Li



Elucidating the Effects of Direct Contact of Dental Pulp Stem Cells Cultivated Under Various Physical Parameters on Lineage Specification Pathways

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Dental Pulp Stem Cells (DPSCs) have demonstrated immense potential for therapeutic purposes and might be used to treat a myriad of diseases such as neurological disorders and ischemic heart disease¹². Nonetheless, the means through which odontogenic signals transmit in between DPSCs remains enigmatic. As previously demonstrated by Chang, C., et al., besides well-studied chemical-initiating differentiation, differentiation of DPSCs can also be manipulated by polybutadiene(PB) substrate mechanics, as odontogenesis is inhibited by soft, thick PB films while promoted by hard, thin ones³. Therefore, this research was conducted to investigate how physical contact of stem cells cultured on substrates of various stiffness impacts differentiation pathways.

PB was dissolved in toluene at concentrations of 3mg/ml and 20mg/ml, which were then spun cast onto silicon wafers to produce thin (20nm) and thick (200nm) films for cell cultivation. The wafers were designated into 3 groups: contact group composed of one 1cm*2cm thin-film wafer adjoining one thick-film wafer of the same size, non-contact group with thin and thick films on two separate 1cm*2cm wafers in the same well, and 2cm*2cm control group with only thin or thick film. Strain 13 DPSCs were incubated at



Figure1. Relative Modulus of Various DPSC Samples

37.5 °C with 5% CO₂ and fed every other day with osteogenic medium solution comprised of 89% MEM Alpha medium, 10% Fetal Bovine Serum, 1% Penicillin, L-ascorbic acid, and β -glycerol phosphate. On days 3 and 7, moduli of cells were measured by Atomic Force Microscopy in contact mode. On days 3 and 7, cell samples were first fixed by applying formaldehyde, then stained with AF488 and DAPI, and finally examined by Confocal Microscopy.

One day 3 {Fig.1}, the relative moduli were high for cells on thin films and low for those on thick films. In addition, the moduli of cells in touching group and non-touching group did not vary notably before confluence. Interestingly, the moduli of cells on touching thin films demonstrate a gradual decrease, progressively approaching that of cells grown on thick films. This phenomenon may stem from the various degrees of cell contact according to their respective locations on the film. On day 7, all touching cells exhibited similar low moduli. In images of confocal microscopy on

day 3 {Fig.2}, cells on thin films outnumbered those on thick films and meanwhile were more attached and stretched, indicating cells' preference for hard substrates. On day 28 {Fig.3}, biomineralization images suggested that cell on the thin film lost the ability to produce minerals after cell contacts.

On days 3, 7, 14, and 28, RNA was isolated for RT-PCR using QIAzol Lysis Reagent. After purification and cDNA preparation, the expression of early markers, ALP, Runx, and late markers, DSPP, OCN will be measured by qRT-PCR. The latter will



Figure 2. Confocal Microscopy of DPSCs on day 3. Actin stained with AF 488(green) and Nucleus stained with DAPI(blue). A)Thin Control Group B) Thick Control Group C)Thin Touching Group D)Thick Touching Group



Figure 3. Biomineralization Image captured by Scanning Electron Microscopy on Day 28 of DPSCs from A)NT Thin Films B)NT Thick Films C)T Thin-Thick Films

serve as indicators of odontogenic and osteogenic differentiation. Additionally, a microarray will be conducted with microRNA kits to explore whether genetic expressions are affected by cell contacts.

¹ Potdar, Pravin D., and Yogita D. Jethmalani. "Human dental pulp stem cells: Applications in future regenerative medicine." *World journal of stem cells* 7.5 (2015): 839.

² Chalisserry, Elna Paul, et al. "Therapeutic potential of dental stem cells." Journal of tissue engineering 8 (2017): 2041731417702531.

³ Chang, C., et al. "Entangled polymer surface confinement, an alternative method to control stem cell differentiation in the absence of chemical mediators." *Ann J Materials Sci Eng* 1.3 (2014): 7.

Determining DPSC Differentiation Pathways and Biomineralization on ALD TiO₂ PB Thick and Thin Films Megha Gopal¹, Jessica Hofflich², Ya-Chen Chuang², and Miriam Rafailovich²

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Dental Pulp Stem Cells (DPSC) provide a valuable and enticing avenue for the field of regenerative medicine. In order to better control cell proliferation, studies have been conducted to determine the extent to which environmental factors influence differentiation. Titanium nanoparticles, for example, have synergistic effects on DPSC growth as well as high biocompatibility, so it is frequently used in dental implants [1]. Similarly, cell modulus has close ties to actin formation and density, as well as later stage collagen formation [2]. Hence, there is great need to elucidate a relationship between titanium nanoparticles, template biomineralization, and differentiation of DPSC.

Si wafers were cut and coated with thin (TN) or thick (TK) films of polybutadiene (PB), with PBTN having an average thickness of 24 nm and PBTK thickness 240 nm. Half of the Si wafers with PBTN and half with PBTK, along with untreated Si wafers, were further treated with 80 cycles of Atomic Layer Deposition of TiO₂ at



Figure 2 Day 28 SEM images (a) and (b) ALD PBTN, (c) PBTN, (d) ALD PBTK

Brookhaven National Laboratories. Afterwards, all wafers were cultured

with AV3 line human DPSC, held in a medium of 2% DPBS by mass. Culture medium was changed every 2 days through aspiration and pipetting procedures. Data samples were taken 2, 4, 7, 14, 28, and 35 days after culturing.

Confocal microscopy was used with an AF 488 dye for actin and DAPI stain for the nucleus for Day 2, 4, and 7 cells. PCR was used to find general differentiation markers (ALP, RUNX) in day 7 and 14 cells and more specialized markers (DSPP, OCN) in day 28 and 35 cells. Day 28 and 35 cells were also analyzed under Scanning Electron Microscopy (SEM) and RAMAN for biomineralization and collagen formation.

First, cell count and doubling time was analyzed. As per the interval between days 2 and 4 of cell growth, cell doubling time was

very similar between PBTK and PBTN groups, leading a conclusion that there was no significant effect of ALD on cell proliferation. Subsequently, confocal images of early-stage DPSC cell division, as referenced in Figure 1, demonstrate similar actin density and length between ALD PBTN and PBTN cells, while ALD PBTK and PBTK cells both exhibited significantly less actin development. Therefore, it may be stated that the titanium nanolayer has minimal effect on cell presentation in the initial period, while substrate thickness is more influential on this early-stage cytoskeleton.

However, when biomineralization data in Figure 2 is presented, it is apparent that the titanium does indeed affect collagen development in later-stage cells, especially in terms of creating templated structures. ALD samples exhibited substantially more collagen banding than the non-ALD samples did, providing reason that TiO_2 is a physiological impetuous for DPSCs for this favorable behavior. Thus, it is posited that an ALD coating of titanium nanoparticles on any polymeric substrate will allow for templated biomineralization.

Further research in this project will include extended data analysis and testing. Day 28 and 35 cells will be examined with RAMAN to determine mineral composition. Hydroxyapatite and collagen peak integral ratios will be calculated to have a preliminary sense of differentiation path (i.e. dentin, bone, etc.). This result will be bolstered by RT-PCR of all samples for aforementioned markers.

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 Titushkin, Igor, and Michael Cho. "Modulation of Cellular Mechanics during Osteogenic Differentiation of Human Mesenchymal Stem Cells." Biophysical Journal, vol. 93, Nov. 2007, pp. 3693–3702.



Figure 1 Day 4 Confocal Images of (a) ALD PBTN, (b) PBTN, (c) ALD PBTK, (d) PBTK

Investigating the Mechanics and Differentiation of Dental Pulp Stem Cells on Polybutadiene-Polystyrene Substrate Nanopatterns

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Understanding the causes of cell differentiation furthers the field of tissue engineering and contributes to

the goal of creating tissue for implantation and bioprinting. This study involves understanding and analyzing how dental pulp stem cells respond to different moduli. In the past, researchers have etched silicon wafers using SIMS in order to achieve a substrate to create differing moduli. In this study, a mixed solution of Polybutadiene(PB) and Polystyrene(PS) was created because there is a repulsion between them which causes them to form protruding structures with a variety of moduli.

The first step of the study was to create solutions of PS and PB with varying ratios and concentrations, spincast the solutions onto silicon wafers, and analyze the height to determine which solution is optimal.

Previous researchers measured the height using a concentration of 11mg/ml of PS with 8mg/ml of PB in the ratio of 1:3. They found that there was not enough contrast in moduli, so we used a higher concentration of PS in different

ratios, using concentrations of 15 mg/ml of PS and 8mg/ml of PB with concentrations of 3:1, 1:1, and 1:3. The three solutions were spuncast onto silicon wafers and analyzed by atomic force microscopy (AFM), which displayed that the solution with the greatest height and contrast in moduli was the 1:3 ratio at 182.6 nm, as referenced in Figure 1. The cells were cultured onto the 1:3 solution of PS and PB.

Multiple analyses included cell counts, confocal microscopy, and atomic force microscopy. Using ImageJ, cells were counted on days 2, 4, and 7 and it was found that they were growing slower than the control. It was hypothesized that this was because of the uneven topography, which most likely made it more difficult for cell growth.

From the confocal images, it was observed that on days 2, 4 and 7 many of the cells were stretched out, indicating that the substrate was compatible, as referenced in figure 2. A small portion of the cells were constricted, suggesting that those cells either found the position or the substrate unsatisfactory.

The moduli of the cells were then tested with AFM. The relative moduli were calculated based on past research¹. It was hypothesized that because PB is soft and PS is hard (PS moduli are 2.28 times greater than the PB moduli), the cells would react similarly, but the results did

Figure 1. AFM image of 1PS:3PB

182.6 nm



Figure 2. Confocal Microscopy of cells on PS-PB Substrate vs. Cells on Pure PB Substrate



Figure 3. Relative Moduli from AFM. Left Day 4. Right Day 6

not follow this pattern. There were three different moduli: soft, medium and hard, as referenced in Figure 3. AFM analysis determined that the average width of the spikes was 0.595 um. This was compared to the average length of the cell found from the confocal which was 61.43 um. Because the cell is large enough to cover multiple parts of the substrate, both soft and hard, this may be the reason the cell exhibits a medium modulus. Another possible explanation is that the interaction between the PS and PB produced a medium modulus, to which the cells are responding. On day 28, RT-PCR will be conducted on the mRNA to determine if differentiation occurred, using markers such as ALD, Runx, DSPP, and OCN. Scanning electron microscopy will also be done to visualize each individual cell in its specific place on the substrate.

¹ "Structure and Nanomechanical Characterization of Electrospun PS/Clay Nanocomposite Fibers." Langmuir. 06 Aug. 2019 <https://pubs.acs.org/doi/abs/10.1021/la0525022>.

The Effect of Fibrin on the Differentiation of Human Dental Pulp Stem Cells

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Due to their accessibility and multipotency, dental pulp stem cells (DPSCs) are of particular interest to researchers, having shown potential for use in regenerative medicine and treatment of various human diseases. A less invasive option compared to bone marrow stromal mesenchymal stem cells, following interaction with growth factors, extracellular matrix proteins, and transcriptional factors, DPSCs are capable of differentiating into various cell types, including odontoblasts, osteoblasts, chondrocytes, cardiomyocytes, and neuron cells. As the regenerative properties of the pulp-dentin complex are dependent on the formation of dentin, a proposed approach for the regeneration of the tissue includes the placement of a scaffold and odontoblast-like cells on open pulp, with the scaffold maintaining cell mobility and promoting differentiation while adhering the cells to its surface^[1]. In addition to having non-toxic degradation products, being cytocompatible, and causing the formation of an extracellular matrix, fibrin, the result of the fibrinogen polymerization under thrombin, has been found to be highly suitable in supporting dental tissue formation and improving cell-dentin interactions^[2]. As a result, this study sought to determine the effects of fibrin on the proliferation and differentiation of dental pulp stem cells, an investigation with,

as indicated above, potential applications in odontogenic and osteogenic regenerative medicine.

Prior to the collection of data indicating these effects of fibrin on human DPSCs, gelatin-fibrinogen hydrogels were created using 15% gelatin and 12 mg/mL bovine fibrinogen cross-linked by 10% mTG (microbial transglutaminase) and thrombin, respectively. Gelatin hydrogels were created as a control, fibrinogen being replaced by PBS (phosphate-buffered saline) and thrombin not being used. Those samples which did not undergo rheology were plated at $4x10^3$ cells/cm³ with cultured 13 y.o. DPSCs (*Figure 1*). The stem cells, plated on the hydrogels, were then provided with a-MEM (containing 10% FBS, Pen Strep, L-ascorbic acid, and β -glycerol phosphate) and were incubated at 37°C and 5% CO₂ until observation on Days 11 and 28.

In the meantime, rheology has been performed on the gelatin and gelatin-fibrinogen gels, to see if there is any significant difference between



Figure 1. 4x optical microscopy image of 13 y.o. h-DPSCs on gelatin-fibrinogen hydrogel – Day 3 after plating of cells.

the elastic and viscous moduli of the two gels. An amplitude sweep test of three samples of each of the two gels was carried out, and the viscous and elastic moduli measured by taking the average of these values before the breaking point at which the gel deteriorated. The recorded modulus for gelatin and gelatin-fibrinogen gels was the average modulus of the three gels of the respective composition. The viscous moduli of the gelatin and gelatin-fibrinogen gels was the average gels were 176.95 Pa and 92.70 Pa respectively, and the elastic moduli 6301.44 Pa and 6857.27 Pa. A t-test showed that there was no significant difference between the two gels for each modulus at an alpha level of 0.05. Due to the high price of collagen, gelatin was used in its place because the fibrinogen would have unfolded the collagen in the gels anyway. In future studies, collagen will be used, so to see the effect of switching gelatin for collagen, rheology will also be carried out on collagen gels and the values compared.

On Days 11 and 28, the methods of observation will be SEM, confocal microscopy, and RT-PCR. The proliferation of the cells will be measured by the microscopy, and the extent of differentiation will be determined by the presence of certain genetic markers of differentiated cells found with the RT-PCR. Further research will include the preparation of gelatin and gelatin-fibrinogen gels containing dexamethasone, a glucocorticoid known to promote osteogenic stem cell differentiation^[3]. The effect of fibrinogen on already prompted cell differentiation will thus be analyzed.

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^[2] Ducret, M., Montembault, A., Josse, J., Pasdeloup, M., Celle, A., Benchrih, R., . . . Farges, J. (2019). Design and characterization of a chitosan-enriched fibrin hydrogel for human dental pulp regeneration. *Dental Materials*, 35(4), 523-533. doi:10.1016/j.dental.2019.01.018
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Session 8: Differentiating Dental Pulp Stem Cells on Scaffolds

Chair: Kuan-Che Feng Kao Li



Optimization of 3D-Printed Scaffolds for Dental Pulp Stem Cell Differentiation via Surface Coating of Proteins and Titanium Dioxide

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Tissue engineering, despite substantial advancements in recent years¹, requires significant improvements in order to become a more pervasive methodology in regenerative medicine. One of the most important components that still requires further research is the artificial scaffolds that facilitate cell attachment and growth. In order to better guide and predict the differentiation of human dental pulp stem cells (hDPSCs), this study aimed to parse the relationship between coats of titanium dioxide and various proteins on the surface of these scaffolds and the adhesion, proliferation, and differentiation of hDPSCs.

The structure of this research fell into a three-fold process: creating the scaffolds, plating the cells, and monitoring the growth of the cells over a 35-day duration. In order to construct the scaffolds, we used a Ultimaker 2 Extended+TM 3D FDM Printer to produce standardized, biodegradable polylactic acid (PLA) discs², half of which were then coated with a thin (~5 nm) layer of titanium dioxide by way of Atomic Layer Deposition (ALD). After sterilization, three different proteins were added to the surface of the scaffolds: gelatin (G), collagen gel (CG), or fibronectin (FN). hDPSCs in passage 5 were cultured for four days in cell medium and then transferred to the scaffolds (Day 0).

Scanning Electron Microscopy (SEM) of Day 5 scaffolds allowed the surfaces of the substrates to be visualized, revealing the deposition of titanium dioxide and morphology of the attached cells (Figure 1). In addition, EVOS fluorescence



Figure 1. SEM images show (A) deposition of titanium dioxide on a non-coated scaffold and (B) cell adhesion to a FN coated scaffold with ALD. EVOS microscopy visualized cell nuclei and actin filaments on (C) a G coated scaffold with ALD. AFM provided a scan of the surface topography on (D) a non-coated scaffold with ALD.

microscopy of DAPI and AF488-stained scaffolds displayed cell nuclei and actin filaments, respectively. From these images, it was determined that hDPSCs typically orient along the 3D-printed filament.

On Days 1, 3, and 5, cells were counted using alamarBlue Cell Viability Reagent in order to calculate plating efficiency and doubling time. This data revealed that the scaffolds coated with fibronectin and ALD supported increased plating efficiency, similar to scaffolds with only ALD (Figure 2). Doubling time was not significantly



Figure 2. DPSCs plated on FN coated scaffolds with ALD showed a marked increase in plating efficiency in comparison to not coated (control) scaffolds.

different for any of the conditions, suggesting that neither the protein coats nor ALD greatly enhanced or reduced the proliferation capacity of the hDPSCs.

The differentiation of the hDPSCs will be closely monitored from Day 10 to 35. Reverse Transcriptase PCR (RT-PCR), the process of reverse transcribing RNA into complementary DNA and the use of DNA polymerase and primers to amplify a DNA sequence³, will divulge any gene expression of osteogenic or odontogenic differentiation markers. The Day 10 early differentiation biomarkers ALP and RUNX2 will be quantified using RT-PCR, and presence of later stage markers osteocalcin and DSPP on Day 28 and Day 35 will clarify osteogenic and odontogenic differentiation on each substrate. Postliminary examination of the scaffolds under the SEM will reveal possible biomineralization, confirming cell viability. Finally,

Raman spectroscopy will be performed on the fixed Day 35 hDPSCs to detect the presence of hydroxyapatite and its crystallinity. Osteogenic and odontogenic fates of the cells will manifest as different ratios of enamel to dentin and varying morphologies.

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^[2] Galler, K.m., et al. "Scaffolds for Dental Pulp Tissue Engineering." Advances in Dental Research, vol. 23, no. 3, 2011, pp. 333–339., doi:10.1177/0022034511405326.

^[3] Ohan, Heikkila. "Reverse transcription-polymerase chain reaction: An overview of the technique and its applications." Biotechnology Advances, vol. 11, Issue 1, 1993. doi:10.1016/0734-9750(93)90408-F.

Effect of PLA Scaffold Roughness on Dental Pulp Stem Cell (DPSC) Differentiation and Growth in an In Vitro Setting

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The field of regenerative sciences has been focusing on the use of mesenchymal stem cells due to their ability to differentiate into various cell types. DPSC are the most promising source of stem cells for reasons including their accessibility within the central pulp cavity, the noninvasive surgical process that is utilized to retrieve them, and their multilineage differentiation¹. Our research has to do with the physical mimicking of the extracellular matrix (ECM) by creating scaffolds with varying roughness to create a situation that maximizes cell attachment and promotes the biomineralization of developing cells.

The procedure began with the 3D-Printing polylactic acid (PLA) well plates of varying distances between each line filament in order to create scaffolds with distinct anisotropic surface roughness². We used distances of 0.7 mm, 0.3 mm, and a scaffold created using 150 flow rate making it extremely rough. We used atomic layer deposition, at the parameters of 80°C for 50 cycles, to coat TiO2onto a second batch of each roughness. Previous research has hinted that TiO₂has a positive effect on the adhesion of stem cells and their in vitro differentiation³. In order to view the topography of two of our sample scaffolds, we used Atomic Force Microscopy (AFM) as shown in figure one. AFM also allowed us to calculate each samples RMS value. Both samples had the same distance between filaments but one was coated with ALD of TiO₂while the other wasn't. In Image A, the scaffold was coated with TiO₂ and had an average RMS of 45.01 nm while in image B the scaffold, which was not coated with TiO₂had an average RMS of 60.92 nm. This difference in RMS confirmed that ALD of TiO₂ was successful and that ALD of TiO₂ has minimal effect on surface roughness. For cell plating, we created a growth medium comprised of 10% Fetal Bovine Serum, 1% Penicillin-Streptomycin, and 89% alpha Minimum Essential Medium. We then added 500,000 DPSC into 4 flasks containing 25 ml of the growth medium each. After 4 days, we removed the media and added 3.5 mL of trypsin to each flask which dissolved the protein connecting the cells to the flask. We then created a stock solution containing 5x10^scells/mL and poured 1mL into each well that contained our scaffolds.

Plating efficiency and doubling times of the cells on each scaffold were measured with Alomar blue during the first 5-days post-plating; this was quantified using a microplate reader. For day 10 and 28 we will be isolating mRNA and using RT-PCR to quantify the expression of early and late-stage gene markers in osteogenic and odontogenic differentiation. On day 35 we will be using SEM imaging and Raman spectroscopy in order to confirm biomineralization and view the crystalline structure of the differentiated stem cells.

Figure 1:





Image B(.3 no ALD)

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Determining Discrepancies in the Migrational Behavior of Osteosarcoma and Dental Pulp Stem Cells by Comparing Their Movement

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Cell migration is primarily driven by the protein actin, which propels the cell membrane forward from inside of the cell. Healthy cells migrate along the fiber they are resting on, but cancerous cells tend to migrate from the fiber to other areas of the body. Metastasizing cancers are difficult to treat; pathogenic cells deviate from their primary site, blurring the target for traditional cancer treatments such as chemotherapy. Mapping cancer cell migration will aid in the determination of the cells' intended path, which can have applications in cancer research and treatment.

Our interest was to observe and analyze cancer cell migration by comparing the movement of osteosarcoma cells (cell line SAOS-2) to that of healthy dental pulp stem cells (DPSC, strains 13 and AV3). While doing so we were additionally interested in comparing the makeup of different types of cells to understand their patterns of migration; when comparing them we considered actin, the protein specific to cell movement in the two cells.

We grew three cell lines: osteosarcoma SAOS-2, 13- DPSC, and AV3- DPSC, in DMEM and alphaMEM, to evaluate which medium was most favorable for the cell growth of all three lines. Based on the rates of proliferation obtained by counting cells using a hemocytometer, we concluded that DMEM

was ideal. In no case were cells overcrowded so that cell movement was not impeded.

After determining conditions for optimal cell growth, we spin casted solutions of chloroform and PMMA onto glass coverslips to plate the cells on [1]. Tissues in the human body are comprised of uneven planes, so we electrospun PMMA fibers onto the glass films to mimic bodily tissues. Half of our samples were plated on films with fibers, while half were left on flat surfaces to compare the possible differences. Using an Evos FL microscope, we composed time lapse videos of each cell line using sets of seven images per hour. Four cell lines were examined: DPSC on fiber, DPSC on thin film, SAOS-2 on fiber and SAOS-2 on thin film. The Evos microscope took clear images, enabling the viewing of the microscopic movement of cells (figures 1 + 2.)



Figure 1: Evos image of Osteosarcoma cells. Image (a) was taken ten minutes prior to image (b) showing the movement of cancerous cells off their fibers.



Figure 2: Evos image of dental pulp stem cells. Image (a) was taken ten minutes prior to image (b) showing the movement of healthy cells along their fibers.

In the future, we plan to quantify the cells migration using a MetaMorph operated CoolSNAP HQ camera attached to a Nikon Diaphot-TMD inverted microscope fitted with a 37 °C stage incubator and a 10 x objective lens. This program will assess the movement of individual cells over one hour periods to further analyze their migration patterns.

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Investigating Neurogenic Differentiation of Dental Pulp Stem Cells using Novel PLA and Graphene

Thin-Film and Electrospun Fiber Scaffolds in Vitro

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The nervous system is vital to the survival of humans and animals. Any disturbance or damage done to this system can dramatically disturb essential functions of the body and can have severe and far-reaching consequences.¹ Dental pulp stem cells (DPSCs) are pluripotent cells derived from the cranial neural crest, giving them the ability to differentiate into functional neurons and making them a promising candidate for neuroregenerative therapies because of their ease of availability.² Polylactic acid (PLA) is known to be a biocompatible polymer, especially in relation to stem cells,³ and graphene has been shown to enhance neurogenic differentiation,⁴ most likely through facilitating cellular electrical impulses and synaptic communication through its excellent conductive properties. Previously, morphology⁵, as well as electrical conductivity, have been shown to affect cell differentiation. This experiment investigates the efficacy and mechanisms of PLA and graphene thin-film and fibrous scaffolds in the differentiation of DPSCs into neurons.

To create a proper substrate for the cells, a solution of 15 mg/mL PLA and chloroform was spun-cast onto glass slides using a spin-caster at 2000 rpm for 30 seconds. This was done both with and without graphene at a concentration of 1.5 mg/mL. The glass slides are used for their convenient transparency during analysis. For electrospinning, a 12.5% PLA (by mass) solution in a ratio of 1:2 acetone-chloroform was used, with 3% graphene being used for the PLA with graphene samples. After spinning, approximately 4-5 layers of fiber were produced for each glass slide. In Figure 1, the success of the electrospinning of fibers is seen with and without graphene. The fiber diameters will be analyzed with SEM imaging and the DiameterJ plugin. Following the protocol described in Arthur et al., wells were coated with poly-L-ornithine (10 µg/mL), incubated overnight at room temperature, washed twice with water and then coated with laminin (5 μ g/mL) and incubated overnight at 37 °C. Following this, the wells were washed with phosphate-buffered saline (PBS) and growth media before cells were plated. The glass coverslips were placed in 24 well plates and plated with 3×10^4 cells in 1 mL growth media. The DPSCs were cultured in growth medium for 1 week, after which the media was replaced with neurobasal media (Thermo-Fisher Scientific), replacing every 2-3 days for 21 days. They were plated in 4 groups, spuncast PLA and PLA+G film, and electrospun PLA and PLA+G fibers, as well as additional control groups of Tissue Cultured Plastic and No Coating. Neurobasal A media, consisting of 100 U/mL penicillin, 1 x B27 supplement, 100 µg/mL streptomycin, 20 ng/mL epidermal growth factor and 40 ng/mL basic fibroblast growth factor (FGF).⁶

To observe differentiation, the cells will be imaged using optical microscopy during each replacement of the media. After 21 days, cells will be harvested and counted using a hemocytometer. Then, most cells will be lysed. 600 μ L of Qiazol will be used to lyse cells and inhibit RNA degradation. RNA will be collected for centrifugation at 1000 rpm for 5 minutes and then used for RT-PCR. Gene expression will be monitored at day 21 and compared to day 0 using primers against the neurogenic markers TBP, Nestin, neurofilament-medium chain, neurofilament-heavy chain, and PSA. This experiment investigates the impact on neurogenesis of growth on PLA with and without graphene. To date, it as indicated by figure 2, it appears that the cells are adherent to the spun-cast samples, but not to the fibers. This will be examined, and its significance will be validated in further research.



Figure 1 (Left): Fibers with (left) and without (right) graphene

Figure 2 (Middle): Cell growth on electrospun fibers with (left) and without (right) graphene

Figure 3 (Right): Cell growth on thin-film with (left) and without (right) graphene

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Utilization of Patch Clamping to Investigate the Influence of Graphene on Transmembrane Ion Current in HeLa Cells and the Efficacy of Novel Fluorescent Dye

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Electrophysiology is a vital field of study in relation to cell growth and intracellular interaction, particularly in relation to body systems such as the nervous and cardiovascular systems. The study of ion channel currents and action potentials within stem cells is especially important because of the presence of special electrophysiological properties and markers on differentiated cells.¹ Differentiation of stem cells into tissues such as cardiac and neural tissue is also particularly sensitive to the conductive and electrical properties of the substrates on which they are grown (such as graphene, which is shown to enhance neural differentiation),² making the study of transmembrane currents and electrical activity within cells paramount. Patch clamping is one of the most commonly used techniques to study electrophysiology in a cellular level.³ However, conventional electrophysiology methods such as patch clamping are tedious and difficult procedures to apply to cells such as neurons or dental pulp stem cells, among other limitations.³ This experiment attempts to study the effects of graphene on cell membrane ion currents using patch clamping and test a novel fluorescent dye that fluoresces in response to high ion channel activity and current by comparing its activity with the patch clamping results.

The ion current activity of the cells was measured through patch clamping, which uses current and voltage to measure membrane potential. This was done with HeLa cells (parental and CX43) cultured in standard growth media (10% FBS, 1% Pen Strep). After the HeLa cells were grown in standard growth media, solutions of 7 mg/ml P4VP and 7/mg/ml P4VP + 3% graphene were spuncast on glass wafers. After plating those cells, we analyzed their concentrations. Our preliminary results of patch clamping HeLa cells (each group having sample size ranging from n=1 to n=3), as shown in **Figure 1**, may indicate that graphene is in fact successful in promoting growth via increased conductivity and cellular communication. **Figure 2** shows that cells grown on P4VP+graphene have a significantly more positive current density when compared to cells grown on just P4VP. These results will be further investigated with more patch clamping in the near future. These cells will then be tested with a fluorescent dye which can then be used comparatively to patch clamping on neural cells to demonstrate the ion current activity of the neural cells. Previous research done with the dye has indicated that it would fluorescently label any areas that had high concentrations of ion channels and current, meaning that dye fluorescence should correlate to patch clamping. Patch clamping utilizes electrodes to measure the amount of current passed through cells, so if the dye works, it would achieve similar results to the data that patch-clamping yields.

If the dye successfully functions on the HeLa cells when utilized under the same conditions that the patchclamping was done at, then it is safe to assume that the dye would also be applicable to a broad range of other cells, such as dental pulp stem cells and neurons, breaking the limitations posed by conventional electrophysiological methods.



Figure 1: The following graph shows the preliminary results of patch clamping a few cells from each experimental group. The slope of the lines, plotted with current density against voltage, indicate the transmembrane capacitor leakage current rate.



Figure 2: The following graph is the comparison of the current densities of parental HeLa cells grown on P4VP with and without graphene. The cells grown on P4VP with graphene have a more positive current density, which possibly indicates that graphene greatly increases the amount of transmembrane ion activity in cell membranes.

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Session 9: Perovskites & Graphene: Photovoltaics & Energy Storage

Chairs: Yuchen Zhou Yifan Yin



Optimization of EDLC Supercapacitors via a Comparison of Acetonitrile and Diethyl Carbonate - Ethyl Carbonate - Tetraethylammonium Tetrafluoroborate Electrolytes with the effects of Graphite-AC, CNT-AC, and CNT-GNP in Supermaterial Electrodes Samuel Padwa¹, Rishabh Raniwala², Nyle Garg³, Shi Fu⁴, Vladimir Samuilov⁴, Miriam Rafailovich⁴

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In the following work, various combinations of electrolytes and carbonbased electrodes were tested to find optimal performance for a supercapacitor. Three different electrodes were tested: a mixed adhesive and active layer consisting of Carbon Nanotubes (CNT) and Graphene Nanoplatletes (GNP), a adhesive layer of CNT and an active layer of Active Carbon (AC), and an adhesive layer of Graphite and an active layer of AC¹. All three of these electrodes were tested with two different electrolytes, one consisting of Diethyl Carbonate, Ethyl Carbonate, and Tetraethylammonium Tetrafluoroborate (DECEC), and the other consisting of Acetonitrile (AN)². The structure of each electrode was characterized via a scanning electron microscope (SEM) in order to predict the capacitance behavior of each type of electrode through observation of pore size and specific area.

Each supercapacitor cell underwent three electrochemical tests for characterization. The Electronic Impedance Spectroscopy (EIS) found both the parallel resistance and equivalent series resistance (ESR) of the supercapacitor, as well as the phase angle of the impedance at frequencies ranging from 100000 Hz to 0.01 Hz. The Cyclic Voltammetry (CV) found the supercapacitor's capacitance, the current flowing for five different voltage per second scan rates, and whether or not the cell remained stable up to 2.5 volts. The Cyclic Charge and Discharge (CCD) once again showed the capacitance, the time the supercapacitor took to charge and discharge, and the voltage dropped in each cycle. These measures allowed each variant supercapacitor to be compared to each other quantifiably in order to find the most optimal from the tested materials.

The most successful cell contained the AN electrolyte and the CNT-AC electrodes. It showed the highest specific capacitance of any cell at 3.32837 F/g as measured through CCD at a current of 10mA (Figure 2) and 3.47105 F/g as measured through CV at a scan rate of 50 mV/s (Figure 3). It also showed the lowest self-discharge at 0.047 V with a 10mA current (Figure 2), thus retaining more of its charge than any other cell tested. Moreover, this cell demonstrated a very low ESR of (Figure 1), which prevents a large voltage drop and allows the supercapacitor to have a higher power density and capacitance. Generally, the best electrodes for ensuring high capacitance, low self-discharge, and a low ESR were the CNT-AC electrodes, followed by the Graphite-AC, followed by the CNT-GNP. The highest measured specific capacitance from either CNT-GNP cell was 1.68724 F/g, far less than 3.47105 F/g from the AN CNT-AC cell or the 2.6338 F/g from the DECEC Graphite-AC cell. Other than the DECEC Graphite



Figure 1 − EIS Graph for an AN CNT/AC cell from 10⁵ Hz to 10⁻² Hz



Figure 2 - CCD Chart for an AN CNT/AC cell at 10mA



Figure 3 - CV Chart for an AN CNT/AC cell at 50mV/s

AC, cells with AN as the electrolyte consistently outperformed their DECEC counterparts, demonstrating an average specific capacitance 2.97% higher as measured by CCD, and 10.37% higher as measured by CV.

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² Zhong, Cheng, et al. "A Review of Electrolyte Materials and Compositions for Electrochemical Supercapacitors." *Chemical Society Reviews*, vol. 44, no. 21, 8 June 2015, pp. 7484–7539., doi:10.1039/C5CS00303B.

Preparation of MAPbI₃ Perovskite via Hot-Casting Technique for Photovoltaic Application

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Solar energy offers a solution to the growing problem of global warming and greenhouse gases. Conventional silicon solar cells display remarkable efficiencies; however, since silicon solar cells are too costly to be considered a legitimate alternative to fossil fuels in larger markets, there has been a demand for alternatives. Perovskite, a family of materials with crystal structure ABX₃, has shown great promise in maximizing efficiency and minimizing cost ever since its introduction in 2009.¹ Nonetheless, one of the greatest problems facing perovskite is the instability of the perovskite crystal quality during the fabrication process. To address this issue, previous research has shown that hot-casting the perovskite layer is a viable technique to promote larger crystal growth and thus decrease grain boundaries and defects.² Thus, the purpose of this study was to investigate the effect of the hotcasting technique as opposed to the conventional post-annealing process on the performance of planar, methylammonium lead iodide (MAPbI₃) perovskite solar cells (PSCs).

To maximize the size of perovskite grains, hot-casting of the photoconductive perovskite layer was utilized because spin-casting and annealing occur simultaneously. The perovskite precursor was prepared at three different concentrations, 0.24 M, 0.4 M, and 1.2 M. PSCs were later on built using FTO glass, TiO₂, MAPbI₃, and spiro-OMeTAD as the conductive substrate, electron transfer layer, photoactive layer and hole transfer layer, respectively. Au was coated via physical vapor deposition to act as an electrode at the end. The devices were prepared to test surface morphology, optical properties, grain size, substrate coverage, and power conversion efficiency (PCE).

Compared to conventionally prepared samples, hot-casted samples featured larger average grain sizes in scanning electron microscopy (SEM) images (Fig. 1). Atomic force microscopy (AFM) gave conclusive evidence that higher concentration solutions formed a more uniform surface morphology. SEM and AFM images show formation of edges because of collisions between large grains that form a compact, fully covered, and highly crystalline surface. Peaks & indices seen in the x-ray powder diffraction (XRD) analysis indicated that the crystal structure of perovskite contained no impurities and degradation (Fig. 3). A more uniform morphology of the photoconductive MAPbI₃ gives potential to achieve a greater PCE due to much fewer grain boundaries, defects, and traps. J-V curves display the greater efficiency of hot-casted samples compared to those of conventionally post-annealed perovskite, achieving a PCE approaching 14% (Fig. 4). In conclusion, hot-casting, particularly at higher concentrations, has proven to be an effective method to maximize grain size and increase efficiencies of PSCs.



Fig. (1a) SEM of hot-casted MAPbI3 (1b) SEM of conventionally prepared MAPbI3 (2a) AFM of hotcasted 1.2 M MAPbI₃ (2b) AFM of MAPbI₃ prepared by post-annealing. (3) XRD analysis of pure MAPbI₃. (4) J-V curves of postannealed & hotcasted 1.2 M MAPbI₃.

¹ Kojima, A., et al. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, *131*(17), 6050-6051.

² Nie, W. et al. (2015). Solar cells: High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science*. 347, 522-525.

Stability Enhancement of Perovskite Solar Cells Using Mixed Cation/Halide Perovskite Ethan Eisenberg¹, Jack Cox², Yifan Yin³, Yuchen Zhou³, and Miriam Rafailovich³ ¹George W. Hewlett High School, Hewlett, NY USA ²South Side High School, Rockville Centre, NY USA ³Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY USA

Through the past several years, perovskite (PVSK) has emerged as a solar cell material rivalling those of silicon and quantum dots due to their increasing power conversion efficiency (PCE) [1]. They serve as the active layer within a planar PVSK solar cell and have the common hybrid organic inorganic halide structure ABX3, with A representing an organic cation, B representing a metal cation, and X indicating a halide anion. The increasing efficiency of these cells can be attributed to several optoelectronic characteristics such as a high absorption coefficient, tunable bandgap and ambipolar carrier transport [1]. However, PVSK are limited because one of the most classic structures, MAPbI3, is unstable. The organic cation of methylammonium (MA) is hygroscopic, causing the cell to degrade under conditions of moisture, heat, oxygen, and light [3]. With these limitations, research has shown the promising photovoltaic properties of mixed cation/halide PVSK. These studies investigate the mixed cation/halide structure CsFAMAPbIxBr1-x on the performance of thin film planar PVSK. MA and Cs were used because they stabilize the PVSK by limiting transformation into its yellow photo inactive phase and preventing facile degradation. Furthermore, FA has a smaller bandgap, and the use of bromine makes the PVSK more resistant to oxidation and allows for the tuning of the band gap [2].

One-step spin coating was used to prepare the PVSK film. PbI2, MAI, CsI, FAI, and PbBr2 at a molar ratio of 1:.7:0.15:0.15 were placed in a mixed solvent of DMF and DMSO (8:2). Titanium dioxide was spin coated onto FTO substrates and annealed to induce an electron transport layer (ETL). The precursor PVSK solution was then deposited via spin coating and chlorobenzene was dipped onto the surface acting as an anti-solvent for crystal generation. Spiro-OMeTAD was coated as a hole transport layer (HTL) and physical vapor deposition (PVD) was used to add the gold electrodes.

Results from UV-Visible Spectroscopy indicated that the changing of the cation/halide component will not influence the absorption of the photoactive layer. Scanning electron microscopy (SEM) morphology results showed increased grain size for the mixed PVSK [Fig.1, 2]. Additionally, atomic force microscopy showed correspondent morphologies to SEM results, but with an increase in roughness, which is in an acceptable range after increasing the grain size [Fig.3]. Moreover, XRD results implicated that the mixed PVSK had two possible crystal phases (α and δ phases) in comparison to the single peak of (110) of MAPbI3 PVSK while only the cubic α phase is photoactive [Fig.4]. Therefore, the mixed PVSK layer was annealed at various conditions to optimize the cubic alpha photoactive phase. This is because the partial phase segregation can lead to increased recombination at Iodine rich centers, and would therefore hinder PCE. [3] After the optimization, results revealed that a temperature and time of 120 Celsius and 10 minutes allowed for the preferable crystallization of the mixed PVSK with a strong alpha peak and negligible delta phase (if any). Furthermore, the PCE measurement indicated the mixed PVSK has higher PCE, probably due to increased grain size [Fig.5]. The moisture and heat stability tests (XRD) revealed enhanced



structural stability against excessive heat, supporting the idea that mixed structure can successfully generate better performance and enhance the durability as well.

[1] Correa-Baena, Juan-Pablo, et al. "The Rapid Evolution of Highly Efficient Perovskite Solar Cells." *Energy & Environmental Science*,

vol.10,no. 3, 2017, p. 714., doi:10.1039/c6ee03397k.

[2]Xiao, Jia-Wen, et al. "The Emergence of Mixed Perovskites and Their Applications as Solar Cells." Advanced Energy Materials, DOI:10.1002/aenm.201700491.Page 1

3.Accessed 22 July 2019

[3]Zhou, Yuanyuan, and Yixin Zhao. "Chemical Stability and Instability of Inorganic Halide Perovskites." Energy & Environmental Science, vol. 12, no. 5, 2019, p. 1498., doi:10.1039/c8ee03559h.

Session 10: Fuel Cell Technologies

Chairs: Aniket Raut Likun Wang



Enhancement of Quaternized Ammonium Polyaromatic Anion Membrane Performance in Alkaline Fuel Cells by Deposition of Graphene Oxide and Catalyst Ink Optimization

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Current AFC technologies are significantly hindered by various limitations in existing membranes such as increased activation energy for ion transport, substandard mechanical properties, high resistance, and chemical instability, particularly of cationic groups.^[1] Polyaromatic ionomers with quaternary ammonium cationic groups are a particularly well-studied group of ionomers with the potential to compose an efficient alternative to commercial alkaline membranes and eventually proton exchange membranes. However, the ether moieties in many of these ionomers are prone to cleavage, which can diminish the mechanical stability and electrical properties of the ionomer.^[2]



Figure 1: Biphenylene (BPN) ionomer with quaternary ammonium ions on side chains to facilitate anion conductance.

In an attempt to bolster the power density of polyaromatic ionomer

membranes in AFCs, two major modifications were made. First, catalyst ink composition was optimized to yield the maximum power performance for the low platinum loading (.6 mg/cm²). Previous work and density functional theory calculations have demonstrated that benzene and other aromatic molecules adsorb strongly to Pt and could potentially reduce its catalytic activity.^[2] Consequently, multiple catalyst inks, each containing differing ionomer: catalyst: isopropanol ratios, were prepared and tested on a set of biphenylene (BPN) membranes (Figure 1). It was determined from the tested compositions that an 80:20 (catalyst: ionomer) ratio produced the greatest results for quaternary ammonium biphenyl membranes, yielding an improved 66 mW/cm² power density despite reduced back-pressure (Figure 2), comparable to the power density of a commercial PEMFC tested under identical conditions at the same



Figure 2: Power density and voltage recorded for MEA prepared from identical anodes and cathodes with 0.6 mg_{Pt}/cm² and BPN membrane and ionomer. Reached open circuit voltage of 1.02 V and peak power density of 66 mW/cm².

current density (48.2%).

In addition to determining an optimal ink composition, partially reduced graphene oxide (PRGO) was deposited by airbrush onto catalyst-loaded electrodes as a means of improving membrane performance. PRGO has been a staple in PEMFC research, enhancing both current and power density. When applied to the AFC, the performance improved slightly, seeing an increase of peak power density by 1 mW/cm², which was measured at a higher current density.

From these modifications, it was determined that the polyaromatic ionomer membranes based AFCs could be a potential alternative to traditional Nafion based PEMFCs. The membrane electrode assembly reached a power density of 66 mW/cm² at a low back-pressure of 50 kPa; likewise, the current density of 400 mA/cm² was unprecedented for this particular polyaromatic

membrane in prior tests. In the future, modifications to membrane structure that increase mechanical stability would allow for thinner membranes to decrease resistance and voltage losses as well as improve durability so significant tests can be made at back-pressures greater than 50 kPa.

¹Gottesfeld, Shimshon, et al. "Anion Exchange Membrane Fuel Cells: Current Status and Remaining Challenges." *Journal of Power Sources*, vol. 375, 31 Jan. 2018, pp. 170–184., doi:10.1016/j.jpowsour.2017.08.010. ²Maurya, Sandip, et al. "Rational Design of Polyaromatic Ionomers for Alkaline Membrane Fuel Cells with >1 W Cm-2 Power Density." *Energy & Environmental Science*, vol. 11, no. 11, 2018, pp. 3283–3291., doi:10.1039/c8ee02192a.

³ Wang, Xin, et al. "N-Cyclic Quaternary Ammonium-Functionalized Anion Exchange Membrane with Improved Alkaline Stability Enabled by Aryl-Ether Free Polymer Backbones for Alkaline Fuel Cells." *Journal of Membrane Science*, vol. 587, 2019, p. 117135., doi:10.1016/j.memsci.2019.05.059.

Facile Synthesis of Carbon Aerogel and Application as Catalyst Support to Increase Performance of Proton Exchange Membrane Fuel Cells

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Proton exchange membrane fuel cells (PEMFC) offer a clean alternative to fossil fuels and nonrenewable energy. Traditional PEMFCs employ platinum on carbon (Pt/C) as the catalyst, although research has been done on non-platinum metals to increase cost efficiency. [1] Carbon black is used as the catalyst support due to its low cost and ease of production; however, it has drawbacks due to its abundance of micropores, hence limiting diffusion of reactants and products and low performance.



Carbon aerogels are a viable replacement because they have a high surface area, high electrical conductivity, and controllable pore structure which can be easily adapted to electrochemical applications such as supercapacitors and fuel cell electrodes. In this study, carbon aerogel was prepared and impregnated with palladium. The aerogel's catalytic activity was compared with palladium on commercial carbon black (Vulcan XC72R), measured by peak power and current density for a 30% wt Pd loading catalyst ink.

We report a novel method for synthesis of carbon aerogel

using the freeze-drying technique. A resorcinol-formaldehyde gel (1:2 ratio) is formed through sol-gel

polymerization using sodium carbonate as catalyst. After gelation, we perform solvent exchange on the gels with DI water and age for three days. Then, the gels are freeze dried in a vacuum at -30 °C for 24 h, -10 °C for 24 h, 0 °C for 24 h. Finally, the organic aerogel is carbonized in N₂ atmosphere at 800 °C for 2 hours at a heating rate of 10 °C/min. After carbonization, the furnace was allowed to cool to room temperature.

Figure 1 shows the catalytic activity of palladium on carbon aerogel compared to palladium on carbon black. The aerogel showed an increase in current and power density in comparison to



commercial carbon black at 43% and 106%, respectively. To test the aerogel's thermal stability, the carbon aerogel was put into the thermogravimetric analysis machine. As seen in figure 2, even at 900 °C, the carbon aerogel exhibited little to no mass loss, illustrating its thermal stability in high temperature environments.

Future work includes testing the mechanical durability of the carbon aerogel as catalyst support compared to commercial options. We also hope to synthesize a new batch of nitrogen-doped carbon aerogel or possibly post-dope the carbon aerogel and observe improvements of durability. Previous literature has also shown that aerogels possess excellent CO_2 adsorption as well as hydrophobic characteristics. [2] These features can be adapted to address the poisoning and electrolyte crossover issues present in alkaline anion exchange membrane fuel cells.

^[1] Antolini, Ermete. "Palladium in Fuel Cell Catalysis." *Energy & Environmental Science*, vol. 2, no. 9, 2009, pp. 915–931., doi:10.1039/b820837a.

^[2] Alhwaige, Almahdi A., et al. "Carbon Aerogels with Excellent CO2 Adsorption Capacity." ACS Sustainable Chemistry & Engineering, vol. 4, pp 1286–1295., doi:10.1021/acssuschemeng.5b01323.

Citric Acid Crosslinking of Carboxycellulose Nanofiber Membranes to Enhance Proton Exchange Membrane Fuel Cell Performance

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Proton exchange membrane fuel cells (PEMFCs) are clean, efficient electrochemical energy storage devices based on the spontaneous reaction between hydrogen and oxygen. Hydrogen gas can be reliably generated by solar and wind power, while atmospheric oxygen is sufficient, so PEMFCs can store and provide stable power from intermittent sources. However, there are barriers to competitive pricing and efficiency for widespread use in vehicles and other applications¹. Carboxycellulose nanofibers (CNFs) promise to be a green, cheap alternative membrane material that conducts protons via carboxylic acid groups. CNF membranes have excellent mechanical and hydrogen gas barrier properties, but the performance (maximum power density of 0.79 mW/cm^2) is around 3 orders of magnitude lower than Nafion (maximum power density of $\sim 450 \text{ mW/cm}^2$)². Additionally, nanocellulose swells significantly with high relative humidity and temperature, compromising mechanical stability.

In this study, citric acid, a naturally occurring, biodegradable tricarboxylic acid, was used to crosslink CNF membranes to enhance both performance and Figure 2 Polarization curve for citric acid crosslinked CNF membrane mechanical stability in PEMFCs. CNF membranes



were prepared by solvent casting 70 mL CNF suspension with 0 or 0.3 mL 1M citric acid, and then hotpressed and cut into 3 cm x 3 cm PEMs. The PEMs were tested in a custom fuel cell test station at 80°C and 100% relative humidity with 5 cm² electrodes of 0.1 mg/cm² Pt/C on carbon paper. The resulting polarization curves showed a 3044% increase in maximum power density (27.7 mW/cm² vs 0.91 mW/cm²) and 2236% increase in maximum current density (111.8 mA/cm² vs 5.0 mA/cm²) of the crosslinked membrane compared to the uncrosslinked control. Thermogravimetric analysis showed that the onset temperature of thermal decomposition was 170 °C for the crosslinked membrane, which is well above the operating temperature range of PEMFCs. In Fourier-transform infrared spectroscopy, the C=O peak was significantly larger in the citric acid crosslinked membrane, providing further evidence of crosslinking.

Further data is being collected on *in situ* proton conductivity. Mechanical properties will be characterized with temperature scanning DMA and tensile strength testing. Morphological and chemical characterizations such as 3D focused ion beam SEM, AFM, TEM, BET surface area, C¹³ NMR, zeta potential, ion exchange capacity, and x-ray diffractometry are ongoing.

¹ Yee, R. S. L., Rozendal, R. A., Zhang, K., & Ladewig, B. P. (2012). Cost effective cation exchange membranes: A review. *Chemical* Engineering Research and Design, 90(7), 950-959. https://doi.org/https://doi.org/10.1016/j.cherd.2011.10.015

² Bayer, T., Cunning, B. V, Selyanchyn, R., Nishihara, M., Fujikawa, S., Sasaki, K., & Lyth, S. M. (2016). High temperature proton conduction in nanocellulose membranes: Paper fuel cells. Chemistry of Materials, 28(13), 4805-4814. https://doi.org/10.1021/acs.chemmater.6b01990

Enhancing the Performance of Novel Cellulose Membranes for the Proton Exchange Membrane Fuel Cell

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Fossil fuels, non-renewable energy sources, damage the environment by increasing carbon emissions. Hydrogen Proton Exchange Membrane Fuel Cells (PEMFCs) provide an alternative way of producing clean energy using the reduction-oxidation reaction of hydrogen and oxygen gas. These fuel cells are extremely desirable because the only byproduct is H₂O. This research project examines the creation of a fuel cell membrane using cellulose filter paper and Resorcinol bis(diphenylphosphate) (RDP). RDP has recently been shown to be a proton conductor.¹

Ahlstrom cellulose filter papers with a 1.5 micron pore size were functionalized using sulfuric acid (H_2SO_4), citric acid ($C_6H_8O_7$), and phosphoric acid (H_3PO_4), respectively, by submerging them in 100 ml of 1M concentration of each acid for 30 minutes. A different set of membranes was also created by submerging the membranes in acids heated to 80°C and then soaked for 24 hours at room temperature in their respective acid. All membranes were dried overnight at room temperature. Membranes were coated with RDP by dropping six drops of RDP on one side of the

Table 1. Highest power density value for each membrane tested at 30, 60, 80, and 90° C.

	30°C	60°C	80°C	90°C
SA+RDP 30 min	1.623	2.66	2.542	1.67
CA+RDP 30 min	4.190604	4.5471	4.53468	3.7452
PA+RDP 30 min	6.14394	10.68162	6.367116	3.671
Cellulose+RDP	5.7618	9.9852	8.112	1.732
PA+RDP 24 hr	11.87844	12.98674	13.26932	7.2468
Percent Increase	106.158%	30.060%	63.576%	318.406%

membrane and three drops of RDP on the other side using a plastic pipette. The pipette and tweezers were used to spread the liquid RDP. Membranes were then placed in an oven at 150°C for 20 minutes to uniformly disperse the RDP across the membrane.

Membranes were tested on the Fuel Cell Testing Station (FuelCellsEtc) under 100% humidity with oxygen introduced from the air. Membranes were tested under varying temperatures, 30°C, 60°C, 80°C,



Figure 1. Polarization curves for each membrane tested at 30°C and 90°C.

displayed a significant percent increase compared to the control.

In the future, we would like to measure the Ion Exchange Capacity (IEC) through titration and compare the 30 minute membranes with the 24 hour membranes. Further testing is also required for membranes soaked in 24 hours. Finally, we would like to test membranes with a higher molarity of acid (5M, 7M) and explore methods of enhancing RDP function.

¹Wang, Likun, et al. "Operation of Proton Exchange Membrane (PEM) Fuel Cells Using Natural Cellulose Fiber Membranes." *Sustainable Energy & Fuels*, The Royal Society of Chemistry, 30 July 2019, pubs.rsc.org/en/Content/ArticleLanding/2019/SE/C9SE00381A#!divAbstract.

and 90°C. Standard carbon electrodes with platinum catalysts cut to an area of 5 cm^2 were used.

Table 1 shows the highest power output of each of the membranes tested at various temperatures in milliwatts. The membrane soaked in phosphoric acid (H₃PO₄) for 24 hours and then treated with RDP had the highest power output at each temperature and

Optimization of Pt/C Catalyst Nanofibers Electrospun on Nafion 117 Membranes in Polyelectrolyte Membrane Fuel Cells

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Polyelectrolyte Membrane Fuel Cells (PEMFCs) have been of great interest as a potential source of alternative energy due to their high power output and zero-emission activity, yet their low cost efficiency relative to combustion engines has impeded commercial success.¹ Research concerning the improvement of PEMFC performance has largely focused on optimizing the catalysis of the oxidation and reduction reactions in the cell. While the Pt/C catalyst is traditionally deposited on the electrodes of the fuel cell, this



Fig. 1: SEM image of 30.0 Pt/C wt. % nanofibers

study explores electrospinning Pt/C onto the commerciallyused Nafion 117 membrane and finely tuning the deposition and composition of the nanofiber structures to increase electrochemically active surface area and proton conductivity in the fuel cell.²

Catalyst ink solutions were made from Nafion 117, poly(acrylic acid) (PAA), and Pt/C as solutes in an isopropanol-water solvent, with Pt/C catalyst wt. % varying from 20% to 40%. Solutions were then electrospun onto Nafion 117 membranes at a potential difference of 15.0 kV, maintaining a platinum loading of approximately 0.1 mg/cm². Flow rates of 0.5 mL/hr and 1.0 mL/hr were employed at each Pt/C wt. %.

SEM and 3D laser microscopy imaging revealed that flow rate and Pt/C wt. % were positively

correlated with platinum agglomeration and nanofiber diameter, respectively (Fig. 1). Optical microscopy confirmed that uniform coating and consistent fiber patterns were maintained throughout the nanofiber structures.

The Nafion 117 nanofiber-coated membranes were tested in an H-tech PEMFC kit in an open-air environment at the cathode and with pure hydrogen flowing at 80 ccm into the anode. The peak power density achieved by the 32.5% wt. Pt/C nanofibers indicated an optimal fiber diameter of approximately 1.25 μ m. At all Pt/C wt. %, the 0.5 mL/hr nanofiber-coated membranes performed better than or equal to the 1.0 mL/hr nanofiber-coated membranes in terms of power



Fig. 2: Power density and polarization curves of PEMFCs with 32.5% wt. Pt/C nanofibers electrospun onto membranes at varied flow rates

density, supporting the agglomeration reduction theory derived from SEM imaging. Overall, tests showed a 62% increase in maximum power density with 32.5% wt. Pt/C nanofibers extruded at 0.5 mL/hr onto Nafion 117 membranes when compared with commercially-used Nafion 117 membranes (Fig. 2). Further work will concern optimizing components of the (Nafion 117)-PAA-Pt/C solution and implementation of this work in Anion Exchange Membrane Fuel Cells (AEMFCs).

[1] Iain Staffell, et al. "The Role of Hydrogen and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy System." Energy & Comparison and Fuel Cells in the Global Energy & Comparison and Fuel Cells in the Global Energy & Comparison and Fuel Cells in the Global Energy & Comparison and Fuel Cells in the Global En

[2] Ramakrishna S., Fujihara K., Teo W., Yong T., Ma Z., & Ramaseshan R. "Electrospun Nanofibers: Solving Global Issues." *Materials Today*, Elsevier, 18 Feb. 2006, www.sciencedirect.com/science/article/pii/S136970210671389X.

Reduction of Carbon Monoxide Poisoning in Proton Exchange Membrane Fuel Cells via Application of Gold/Ruthenium Nanoparticle Monolayer Luca Leger', Ryan Meehan', Mark Zhang', Likun Wang', Miriam Rafailovich'

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Proton exchange membrane fuel cells (PEMFCs) are a promising alternative to traditional forms of energy, such as fossil fuels, due to their environmental friendliness. PEMFCs utilize the reduction-oxidation reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + energy$. However, one issue currently plaguing cell efficiency is that hydrogen fuel inevitably contains carbon monoxide (CO) contaminant¹. CO can further be formed within the PEMFC through the reaction $H_2(g) + CO_2(g) \rightarrow CO(g) + H_2O(g)$ that occurs at the cathode¹. Unfortunately, due to the fact that the bonding of CO to Pt is energetically preferable to that of H₂ to Pt¹, CO adsorbs to active sites on the platinum catalyst, blocking hydrogen fuel conversion and rapidly reducing cell efficiency.

Gold (Au) and Ruthenium (Ru) nanoparticles (NPs) have proven to be effective at oxidizing CO and reducing its detrimental effects on PEMFCs²; however, their joint effect is largely unstudied.



Fig. 1: Polarization and power curves of PEMFCS with membranes coated with AuRu NPs at various surface pressures (SPs)

Here, we synthesized gold ruthenium nanoparticles through the two-phase method developed by Brust et al². Monolayers of the AuRu nanoparticles were deposited on Nafion membranes at various surface pressures using the Langmuir-Blodgett method. Following this, each membrane was tested using a hydrogen fuel cell demonstration kit.

Examining membranes coated at surface pressures of 1 mN/m, 2 mN/m, and 5 mN/m, we find that every membrane coated with AuRu nanoparticles experienced an increased maximum power output. The membrane coated



Fig. 2: Top-view TEM micrograph of assembled AuRu NPs at surface pressure of 2 mN/m.

at a surface pressure of 2 mN/m achieved the highest maximum power density in all testing environments. Under atmospheric oxygen conditions, the surface pressure 2 mN/m membrane achieved a 47.3% increase over the control (see figure 1) and with pure oxygen intake, it achieved a 21.5% increase over the control. The AuRu coated membranes experienced less improvement in pure oxygen conditions due to the fact there was no CO₂ present to form CO, meaning the improvements due to oxidation of CO were less pronounced. The results come as some of the first direct proof of the viability of gold ruthenium nanoparticles as a method of mitigating CO poisoning in proton exchange membrane fuel cells.

[1] Wang, Likun, et al. "Suppression of Carbon Monoxide Poisoning in Proton Exchange Membrane Fuel Cells via Gold Nanoparticle/Titania

Ultrathin Film Heterogeneous Catalysts." *ACS Applied Energy Materials*, vol. 2, no. 5, 2019, pp. 3479–3487., doi:10.1021/acsaem.9b00264.

[2] Brust, Mathias, et al. "Synthesis of Thiol-Derivatised Gold Nanoparticles in a Two-Phase Liquid–Liquid System." J. Chem. Soc., Chem. Commun., no. 7, 1994, pp. 801–802., doi:10.1039/c39940000801.



In order to drill and take samples from the Moon's surface, Apollo astronauts needed devices that could run on an independent source of energy with minimal consumption.



The Black & Decker Manufacturing Company in Towson, Maryland created a battery-powered, magneticmotor system. The computer application they used to minimize consumption and maximize efficiency in design was used to create further power tools. [1]

The

to

Materials

Challenge:

In addition

Devices that came out of this technology were [2]:

- "Dustbuster"- a handheld vacuum used for small messes and access to hard-to-reach places
- Power drill- can be used on construction sites where there is no ready power source
 - Orthopedics- drill, driver/reamer, sagittal saw. Once charge could allow 20 min use in early models

Portable Cordless Devices have increased the scope of power-using machines, allowing them to increase productivity in construction, household, and medical spheres.



NOW: MODERN-DAY LIFE

The Water Security Corporation now applies MCV technology to eliminate bacteria

ing stations in Pakistan (e.g. for earthqu d in a survival bag designed as a first response device

Over I billion people lack access to safe drinking water and over 10 million die each year of water bourne diseases. Today, Microbial Check Yalve space technology is ing provide safe drinking water the people who need it most right here on

sters, refugee camps, civil emergencies and remote locations

or water is a major health con

ter purifiers in India

MCV was also used as basis for the DentaPure ogy - designed to clean and decontar

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d water on Earth, providing these systems to de

ing systems in remote areas of Mexico, Central, and South America

credit Poly

noto credit:NAS

[1] Black and Decker Mfg. Co. ntrs.nasa.gov/search.jsp?R=20030005114. [2] Black and Decker Mfg. Co. ntrs.nasa.gov/search.jsp?R=20030005001

ADVANCED WATER PURIFICATION VICTORIA LEVY

THEN: INVENTION FOR SPACE

1978

earch, NASA deve d the eck Valve or MCV s g both contact mi artation of residual iodine to astronauts with safe drinking wate





POLYBENZIMIDAZOLE(PBI)

-A NASA SPINOFF FLAME RETARDANT MATERIAL THAT AIDS IN HYDROGEN FUEL CELLS BOLE (JAMES) PAN PBI in the space program (NASA, 2008)

- First synthesized by Dr. Carl Marvel in the late 1950s for U.S Air Force
- Characteristics: no melting point, exceptional chemical and thermal stability (Herward and Marvel, 1961)
- Instrumental in the Apollo missions, the Skylab missions, and the space shuttle missions
- · Incorporated in astronauts' clothing and gears like webbing and tethers

PBI translated into consumer products

- 1978-introduced to the fire service in project FIRES(Firefighters Integrated Response Equipment System
- 1983-commercially available; production plant opened in Rock Hill, South Carolina, to meet demand
- 1986-now steady evolution, gaining reputation in flame retardants industry
- PBI's contribution to our daily lives
- Prominent in applications like firefighting and emergency response, motor sports, military, industry, and aerospace.
- Create clothing that does not shrink, become brittle, or break open under extreme heat and flame exposure
- Protect firefighters and reduces injury rates
- Also used in high temperature separation membranes that increase efficiency in ethanol production
- Separate carbon dioxide from natural gas for carbon dioxide sequestration
- Future usages in hydrogen fuel cells
- Replace asbestos
- (James) Bole Pan



Photo credit: Wikipedia

significant advances in space exploration, many new materials were developed for the space program. These students answered the challenge to identify these materials and report how they have benefited society within the last 50 years.

Michael Han

ABOUT WD-40

- Water Displacement, 40th formula Designed as a rust-prevention ÷
- Designed as a rust-prevention solvent and degreaser for use if the aerospace industry Developed in 1953 in Son Diego. CA, by the Rocker Chemical Company (renamed WD-40 Company inc. after its sole product) In 1993, it was found that 4 of every 5 households had at least one can aft WD-40.



one can of WD-40

rements Enabat, Bytan, "Mercury Manned Flights Stummury," *MASA*, NASA, 17 Mar, 2015, www.imsa.gov "Gerning: Didge to the Moon," *MASA*, (NASA, www.imsa.govgeciaki/geninia/jaillety-"SMASA (Mars" *Maskul: Throat*, night-allethaut, acia org:missil-alatiata; "WD-40 Multi-Use Froduct Aeronal Material Safety Data Shoet," WD-40 Company, 5 Mar. 2019, "WD-40 Multi-Use Froduct Aeronal Material Safety Data Shoet, "WD-40 Company, 5 Mar. 2019,

landing for the Apollo 11 mission

Officially Declassified Entrepreneurs pushed for

commercialization

Keep the astronauts from being smashed

Memory Foam/Temper Foam

Make customizable seats for astronauts to reduce the effects of high gravitational forces especially during takeoff and

Improve uncomfortable seats made from hard materials

Improve crash protection for airline pilots and passengers

Top-Secret NASA Space Program

OMPOSITION

ccording to the MSDS provided by the WD-40 Company. VD-40 Multi-Use Product Aerosol is composed of:

- 45-50% low vapor pressure aliphatic hydrocarbons (to decrease viscosity and increase penetration
- into cracks) <35% petroleum base oil
- <25% aliphatic hydrocarbons 2-3% carbon dioxide (propellant)

All percents indicate percent mass. The exact

composition of WD-40 is a trade secret.)

The Atlas missile had a range of 14,000 km with a CEP of 3.7 km and carried a 1.5 MT W49 thermonuclear warhead. Unfortunately, with advances in missile technology, the Atlas missiles became obsolete. However, from 1962, they were used m-40 molti-e aerosol, 12 oz. missies became obsolete. However, from 1962, inter were use extensively by NASA in their space programs. Of the six crewed flights conducted during the Mercury program, the last four, Mercury 6, 7, 8, and 9, used Atlas rockets. Natably, Friendship?, the crait that carried John Glenn, the first America in orbit, to space in 1962, was propelled by an Atlas rocket.

www.wallicom/history

The Gemini Program followed the Mercury Program. The Gemini Program pioneered a new copsule that held two astronauts, which gave the program its name. Although the Gemini program used the more powerful Titan rocket to lift the larger and heavier capsule. Atlas rockets still saw use as cargo rockets during the program.

NASA

uned flights.html MATERIALS CHALLENGE

BY MICHAEL HAN

SM-65 ATLAS AND USE IN THE SPACE PROGRAM

WD-40 was first used in the aerospace industry by Convair, an aerospace contractor, to protect the outer surface of the Atlas missile. It was designed to deliver

nuclear warheads from long distances, which had been difficult to achieve due to the weight of the warhead as well as the distance



CMC

of SiC/Sit



launch vehicle

with the supratus

Material

SiC

The Prize Winners: Victoria Levy Megha Gopal **Ethan Eisenberg** Bole (James) Pan Jasmin Li Frank Gold

Now applied to things all around us Emergency blankets for refugee camps as well as long distance runners Incorporated into heat retaining jackets and clothing Has also become a hot

topic for fashion designers Allowed for a thin yet insulating laver







old or aluminium mylar (Polyethylene erephthalate) originally used by NASA as nsulation material that protects equipment rom Infrared as well as UV radiation while eing extremely lightweight Jsed to protect against the intense heat of he sun on oneside of space craft while

s seen above in the Apollo 11 !





he sun on oneside of space craft the frigidev ass povyion earth vector insulation html. etaining heat to protect against the frigidev ass povyion earth vector loader silver insulation html. Byza, William "Emergency Blankets." NASA, 1 Feb 2016, www.mass.gov/offices.oct/40-years-of-assa-spinoffemergency-blankets.

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Antheny Del Valle Uk.1 Sokolo Geoge Ca Ionathan 李松 涛 AUDREY CUI Ethan Eisenber KlvinGu ENC # Finny Vimala S alay Chri yerr KEVIN 2 2m YANG lide an Wheel Italik Millin 防灾毁 as Roberto Uilan Alina Pollner Lauren Stiefel Jonathern Ledlinen feffry hiller Ledere David Reui Sahana Ramrakhiani Cheverman Hai Shmuel Z Padwa Emily Silverstein Diga Rai - Chersoppe IKShu Fande Carler B: Jessica Some lana haca Flans She 5nallarin aley Car Songa Mette Jodor Blinstor LUISA PAN