

Digital Discovery of Polymers

Modeling the (De)polymerization of Polyurethane-like Polymers

Matthew Coile

Session 1, 10:00 - 10:15 AM, Anderson ABC

Polyurethane (PU) is the sixth most produced class of plastics in the world, with an annual production of some 17 million tonnes. Unfortunately, PU is not currently recycled, except for mechanical shredding for carpet underlay and a pilot-scale project in Europe. PU is a copolymer defined by its linkage, which results in considerable diversity in the sequence and topology of the final polymers. The urethane linkage is typically synthesized from the reaction of an isocyanate and alcohol, but alternative methods, such as the reaction of a cyclic carbonate and an amine group to form a hydroxyurethane linkage, have drawn attention for being a potentially less toxic route to PU synthesis. Two promising approaches have been studied for the recycling of PU materials: solvolysis to recover monomers and small oligomers, and shredding and pressing with carefully selected conditions to remold them as covalent adaptable networks into new materials. Both of these approaches require elevated temperatures, at which side reactions can become important. Kinetic Monte Carlo (kMC) is a modeling method in which the event-by-event formulation enables potential tracking of detail such as chain lengths, sequences, topologies, and even spatial locations within a control volume. We have developed a kMC model of the depolymerization process, including side reactions common to PU materials. We have employed this model to investigate the molecular weight distributions that result from heating linear PU materials synthesized from a three-component mixture of monomers that have different enthalpies of reaction, and found an odd-even effect where odd length chains are more likely than even length chains at some temperatures. We are currently using this approach to study the solvolysis of a model polyhydroxyurethane.

Molecular dynamics simulations of shockwave propagation in amorphous polyisobutylene (PIB) system.

Samantha Daymon

Session 1, 10:45-11:00, Anderson ABC

Development of polymer structures with improved shock wave resistance is an area of growing fundamental and practical interest. Experimental measurements of the shock wave characteristics are possible, but difficult to perform in the material due to the extreme pressures, temperatures, and the short timescale of the shock wave response. However, molecular dynamics (MD) simulations are easily able to track molecular movements within polymer systems at the picosecond timescales, allowing for a fundamental study of the shock wave behavior. This work specifically has focused on an investigation of the shock wave behavior in polyisobutylene (PIB), a rubbery polymer renowned for its high damping capacity. Here we demonstrate a computational model for simulating the shock wave in PIB using two shock methods, non-equilibrium molecular dynamics (NEMD), and multi-scale shock technique (MSST). Using this model, we tracked the evolution of kinetic parameters, as well as bulk quantities such as average speed, density, and pressure. Also, the MD calculations allowed generating the classic Rankine-Hugoniot relations between the states on both sides of a shock wave and predicting the speed of sound in PIB.

Energy and Separations

Developing ion exchange membranes with ultrahigh charge density

David Kitto

Session 1, 10:15-10:30, Anderson ABC

Ion exchange membranes (IEMs) are dense polymer films with covalently attached ionized moieties. IEMs are used extensively in electrochemical water and energy applications such as electrodialysis, fuel cells, flow batteries, and electrolysis. These technologies broadly require exclusive and expedient transport of designated ions through IEMs, quantified as membrane selectivity and throughput, respectively. Unfortunately, a trade-off between these properties impedes membrane performance, wherein highly selective membranes typically have low throughput and vice versa. As a result, for technologies using IEMs either the membrane selectivity or throughput commonly limit a module's energy efficiency or intensity. Our prior research identified that the volumetric charge density of IEMs essentially defines the upper bound of the performance trade-off. So, to improve IEMs universally, we sought to design materials with significantly higher charge densities than those of currently available membranes.

It is synthetically challenging to prepare membranes with high charge densities because hydrophilic IEM polymers expand as they swell with water. To minimize swelling without sacrificing the charge density of the membrane, we synthesized a series of cross-linkable charged monomers. We polymerized the monomers using synthetic strategies capable of finely tuning and maximizing the charge density of the resultant IEM. The performance of these membranes was probed by measuring the NaCl ionic conductivity and salt permeability, which allowed calculation of the counter-ion throughput and selectivity. To add context, we characterized the performance of 40 commercially available IEMs and surveyed structural properties from ~1,000 reported IEMs. Many IEMs prepared from these specialized monomers achieved ultrahigh charge densities (~5 M), greatly exceeding every charge density surveyed in the literature (<4 M). As a result, select membranes simultaneously achieved substantially higher selectivities and throughputs than all 40 commercial IEM controls. With such favorable performance, this class of ultrahigh charge density membranes promises significantly improved energy consumption in IEM-based technologies.

Generation of Blocky Sulfonated PEEK With Multiple Sulfonations Per Sulfonated Monomer

Mark McCrary

Session 1, 10:00-10:15, Pond

Poly(ether ether ketone) (PEEK) is a mechanically strong and chemically resistant semicrystalline polymer. When PEEK is sulfonated, it can be manufactured into a robust ion-conducting membrane for use in hydrogen and methanol fuel cells. Sulfonated PEEK (SPEEK) is typically synthesized by dissolving PEEK in highly concentrated sulfuric acid, forming a PEEK-SPEEK copolymer with a random microstructure. Recent work in our group has demonstrated that when PEEK is sulfonated in the heterogeneous gel state using a solution of chlorosulfonic acid, sulfonated PEEK with a blocky microstructure (BSPEEK) is formed. BSPEEK is a valuable ion-conducting material because it retains its crystallinity and insolubility in water even at high degrees of sulfonation. It has been suggested by many previous researchers that the sulfonation, an electrophilic aromatic substitution reaction, occurs almost exclusively on the electron dense hydroquinone units of PEEK, with minimal if any substitution on the benzophenone units. However, utilizing 2D-NMR to characterize our BSPEEK, we have recently found that sulfonation of PEEK in the gel state increases the prevalence of multiple substitutions per sulfonated monomer, with all secondary and tertiary sulfonations taking place on PEEK's benzophenone aryl rings. This discovery has led to a more accurate method of calculating SPEEK's degree of

sulfonation using proton NMR, where previous methods used by our group and others in the field neglected these secondary and tertiary sulfonations and underestimated the degree of sulfonation by up to 36%.

Functional Materials

Sensor- and Machine Learning-guided High-throughput Characterization of Hydrogel Rheological Properties

Lester Anderson

Session 1, 11:00-11:15, Anderson ABC

High-throughput characterization (HTC) is a critical aspect of modern accelerated materials discovery workflows, which aim to identify, validate, and optimize formulation parameters from large domains, such as associated with functional materials and associated applications thereof. However, HTC processes often generate big data, requiring integrated data analytics for both data interpretation and guidance of iterative experimentation. Here, we demonstrate that the integration of machine learning and HTC processes enables autonomous formulation of hydrogels and investigation of material phase behavior. This presentation provides a comprehensive overview of a novel sensor- and AI-guided HTC system for high-resolution discovery of hydrogel phase behavior via autonomous iterative experimentation in 96-well plate formats. The methodology has the potential to significantly accelerate the discovery, optimization, and engineering of soft functional materials, thereby accelerating materials design for a range of associated applications, including energy storage, biomedical devices, drug release, soft robotics, and bioelectronics.

Additive Manufacturing of Multifunctional Polymer-Metal Composite Structures with Tunable Internal Structure and Physical Properties

Jinyu Bu

Session 1, 10:15-10:30, Pond

Additive manufacturing of hybrid composite that combines polymers and metals has attracted significant research attention. However, the incompatibility of additive manufacturing processes and conditions for polymers and metals is a substantial limitation for multi-material 3D printing and the fabrication of polymer-metal 3D hybrid structures. Here, we explore the possibility of using extrusion-based additive manufacturing to 3D-print the Field's metal (FM)-polymer composite material. The composite material is fabricated by a facile one-step probe sonication method which breaks the bulk FM into sub-micron particles and disperses the particles well in the polymer matrix at the same time. The composite material was extruded into filaments suitable for FFF 3D printing by a single screw extruder. Various complex 3D geometries were printed to validate the excellent printability of such FM-polymer composite material. The as-printed hybrid material shows electrical insulating behavior, while the same material with post-treatment showed up to nine orders of magnitude decrease in the electrical resistance. Due to the phase change of FM, the hybrid material also showed reversible mechanical properties switching below and above FM's melting point (~ 62 °C). We observed an 80% increase in the modulus at low temperatures compared with high temperatures. The electrical conductivity recovery, along with the temperature-dependent mechanical properties allows on-demand programming of the hybrid material to form a variety of composites from rigid insulators to elastic conductors, or any combinations in between.

Understanding Heterogeneous Dynamics in Filled Rubber with Functionalized Additives

Hakan Aras

Session 1, 10:45-11:00, Pond

Functionalized chain additives have been used along with coupling agents to improve the macroscopic dynamics of silica-filled styrene butadiene rubber (SBR) to obtain more sustainable tires by enhancing the interaction between filler and the polymer matrix. We have synthesized well-defined linear or star-shaped polymeric chain additives and their nonfunctional analogs to probe how changing the chemistry of the filler/polymer interface changes the microscopic response of the filler particle network and thus the macrodynamics. This requires investigating the filler network structure over a wide range of length scales, from that characteristic of networked agglomerates down to the nanoscale details of the filler/polymer interfaces. We then observe the microscopic response of the filler network of the nanocomposites using in situ X-ray Photon Correlation Spectroscopy (XPCS) while the sample is under dynamic (oscillatory) strain. These measurements probe the rate of change in the filler network as the sample is cycled. Scattering intensity snapshots are collected as the measurement progresses. Correlations of the intensities for every pair of snapshots in the series are calculated. Visualization of these correlations provides information on microscale changes in the silica filler network. The microscopic responses of the samples that contain functionalized chain additives are different from those of samples that have nonfunctional chain additives. These results can be applied to develop tires with better gas mileage, wet grip, and wear resistance properties to move toward more sustainable transportation.

Chemically enabled labeling of disordered cellulose in fibrils and nanocrystals via advanced microscopy

Mica Pitcher

Session 1, 11:00-11:15, Pond

The nanostructure of cellulose has long been hypothesized to comprise “alternating” crystalline and disordered regions, which are distributed regularly along the fibril. The most cited evidence of disordered cellulose is the repeatable production of highly crystalline cellulose nanocrystals, first observed via strong acid hydrolysis in 1951; however, the exact position and nature of these dislocations has not been completely discerned. They are often disregarded in nanocellulose chemistry when the entirety of disordered cellulose is fully disintegrated, effectively missing the opportunity to reap the potential for new and interesting properties originating from disordered cellulose chains. In this work, we investigate the selective chemical modification and labeling of disordered cellulose via top-down and bottom-up approaches. In the top-down approach, labeling cellulose nanofibrils using two methods, i.e., gold nanoparticle and fluorescent labeling, is conducted and complemented with advanced microscopy, including transmission electron microscopy (TEM) and stochastic optical reconstruction microscopy (STORM). In the bottom-up approach, the labeling of hairy cellulose nanocrystals (HCNC), nanocelluloses in which the disordered regions are partially preserved, is investigated to bridge the gap between length scales and provide further information on the changes in disordered regions upon chemical modifications. The results of both approaches lead us to believe that disordered regions are distributed semi-regularly along cellulose fibrils, becoming larger and more frequent upon further chemical modification, acting as starting points for the formation of HCNC.

Functional Zwitterionic Coatings for Marine Anti-fouling Applications

Boyi Song

Session 2, 3:00-3:15, Anderson D

Zwitterions are a series of materials that show super-hydrophilic properties and strong resistance to biofouling including proteins, cells, bacteria, microorganisms, and marine micro/macro species. However, their poor wettability on hydrophobic surfaces such as polyurethane, as well as their strong tendency of dissolving in an aqueous environment makes them difficult to be stabilized on conventional hydrophobic substrates, limiting their applications as coatings for practical applications. Here we discuss the development of a functional zwitterionic coating, which shows significantly improved antifouling performance compared with commercial antifouling paints. This functional zwitterionic coating exhibited long-term durability in shearing water for more than one month, almost 'zero' microbial adhesion, and improved mud resistance capabilities. Especially, this functional zwitterionic coating showed excellent anti-fouling capabilities in a field test in the Atlantic Ocean (Cape Charles, VA). Further technical work is ongoing to validate the practical applications and potential commercial adoption, including large-scale applications and further adjustment of fabrication parameters.

Biocidal Potency of Polymers with Bulky Cations

Yang Lou

Session 2, 3:15-3:30, Anderson D

The performance of antimicrobial polymers depends sensitively on the type of cationic species, charge density, and spatial arrangement of cations. Here we report the first example of antimicrobial polymers bearing bulky tetraaminophosphonium groups as the source of highly delocalized cationic charge. The bulky cations drastically enhanced the biocidal activity of amphiphilic polymers, leading to very potent activity in the sub-micromolar range. The cationic polynorbornenes with pendent tetraaminophosphonium groups killed over 98% *E. coli* at a concentration of 0.1 $\mu\text{g/mL}$ and caused 4-log reduction of *E. coli* within 2 hrs at a concentration of 2 $\mu\text{g/mL}$, showing very rapid and potent bactericidal activity. The polymers are also very hemolytic at similar concentrations, suggesting a biocidal activity profile. Polymers of similar chemical structure but with more flexible backbones were made to examine the effects of the flexibility of polymer chains on their activity. We also explore variants with different spacer arm groups separating the cations from the backbone main chain. The antibacterial activity was comparably potent in all cases, but the polymer with short spacer arm groups showed more rapid bactericidal kinetics. Interestingly, pronounced counterion effects were also observed. Tightly bound PF₆⁻ counter anions showed poor activity at high concentrations due to gross aggregate formation and precipitation from the assay media, whereas loosely bound Cl⁻ counterions resulted very potent activity which monotonically increased with increasing concentration. In this paper, we reveal for the first time that bulky phosphonium cations are associated with markedly enhanced biocidal activity, which provides a new strategy to develop more effective self-disinfecting materials.

Polymer-based Chirped Broadband Reflectors and Thermal Management

Joseph Mushyakov

Session 2, 4:00-4:15, Anderson D

Space cooling consumes 10% of current global electricity demands and is expected to more than triple in the next 30 years, thus efficient building heat management is required. To reduce energy consumption in buildings,

passive cooling techniques, such as incorporating chirped broadband reflectors in windows can selectively reject the near-infrared radiation while maintaining visible transparency. Chirped broadband reflectors are multilayered photonic structures that alternate two materials with highly contrasting refractive indexes. The thickness of the layers decreases further away from the substrate to reflect a different wavelength range in each interface, resulting in a broadband reflector with a highly reflective stopband that is highly transparent otherwise. As of now, most chirped reflectors are fabricated using inorganic dielectrics and metals mainly due to the broad refractive index range that they offer. Efforts have been made to circumvent the incompatibility of these materials with large-area and flexible applications by employing organic materials, but their narrow and low refractive index range leads to a small refractive index contrast between adjacent layers and poor reflectivity. Here, we present the design and fabrication of fully solution-processed polymer-based chirped reflectors using a high-refractive-index titanium oxide hydrate/poly(vinyl alcohol) hybrid and commodity poly(methyl methacrylate). By using this inorganic/organic hybrid material, we attain a larger refractive index contrast and remarkably higher reflectivity than that offered by their all-organic counterparts. The solution-processed chirped reflectors presented here offer a readily accessible and simple alternative for heat management purposes, including windows for passive cooling comparable to the commercial highest standard Low-E 366.

Synthesis, characterization, and application of polydopamine analogues for surface engineering

Jiwon Lim

Session 2, 3:00-3:15, Wolverine

Mussel-inspired polydopamine (PDA) has attracted massive attention due to the surface-independent coating capability via a simple and environmentally friendly processing in a basic aqueous solution. However, establishing a comprehensive understanding of the binding and polymerization mechanism of PDA is still demanding owing to the abundant reactive sites of the dopamine monomer and the insoluble nature of the resulting polymer film. Here, we rationally designed a series of PDA derivatives and prepared their corresponding polymers to investigate the role of each building block as well as bonding mechanisms on different substrates by systematically characterizing the obtained polymers. Among the PDA analogues, poly(3,4-dihydroxybenzylamine) exhibited a smooth coating with abundant primary amine functionality, leading to versatile surface amine functionalization. We also found that the smooth coating of poly(3,4-dihydroxybenzylamine) on graphene reduces thermal resistance at the interface between graphene and poly(acrylic acid), resulting in enhanced thermal conductivity (87%) of the polymer-graphene composites. Finally, we investigated dithiol crosslinkers in connection with phenols to develop a new coating system of PDA derivatives. The resulting new copolymers have the same surface-independent coating capability even without having amine moiety, extending potential coating materials from dopamine to other phenols.

The air/water synthesis of 2D polymers for atomically precise hybrid structures prepared by the layer-by-layer deposition

Pratik Kasbe

Session 2, 3:15-3:30, Wolverine

Atomically precise hybrid structures composed of Two-Dimensional (2D) polymers and Two-Dimensional layered materials have shown a promising horizon in many applications. 2D polymers have shown limited lateral growth and lack of easy synthesis and transferability onto various substrates. Here we have used the Langmuir-Blodgett technique to photopolymerize the monomer units into 2D polymer, additionally we

employed layer-by-layer method for the preparation of atomically precise hybrid structures. Such atomically precise hybrid structures can be used to fine tune their properties depending on the application. The successful photopolymerization of 2D polymer was confirmed by the XPS and FTIR analysis, which had a thickness of 1.2 nm. Here, such atomically precise hybrid materials have been fabricated by layer-by-layer deposition of such 2D polymers with graphene. The prepared hybrid structure showed a stable structure which was then used to study the adhesion of the PDMS lens over such 2D polymer films (34.3 mJ/m²), the results showed a better adhesion and screening effect of the films from the SiO₂ substrate (54.2 mJ/m²).

Effect of Crosslink Homogeneity on the Mechanochemical Activation of Elastic Polymer Networks

Victoria Kong

Session 2, 3:30-3:45, Wolverine

To successfully design functional soft crosslinked elastomeric materials, understanding the effects that variables such as crosslink heterogeneity and network topology have on molecular scale force distributions is critical. Here, we use a force-responsive naphthopyran mechanophore as a covalent crosslinker in randomly and regularly crosslinked elastic butyl acrylate networks to investigate how network homogeneity impacts molecular-scale force distributions.

Tetrafunctional n-butyl acrylate star polymers are coupled to form regularly crosslinked networks, while randomly crosslinked networks are formed by conventional free-radical polymerization. Through simultaneous tensile tests and optical measurements, we find that networks with similar bulk properties, but different crosslink homogeneities, exhibit differences in the onset of mechanochemical activation. These results suggest the impact of network topology on the molecular scale force distribution in crosslinked networks and the role that network heterogeneity may play in determining the mechanical behavior of elastic polymer networks.

Photocaged R-Alkoxysilanes for On-Demand Functionalization and Polymerization Control

Mahmud Rashed

Session 2, 3:45-4:00, Wolverine

R-alkoxysilanes are the monomer workhorses of silicon-based sol-gel chemistry and are used as the building blocks for materials from silicas to silicones. However, since their inception, the sol-gel and siloxanes communities have struggled with uncontrolled hydrolysis, premature condensation, and overall polymerization control. This study focused on the development of new silicon sol-gel chemistry methodologies which utilize photoremovable protected R-alkoxysilanes (PPGs) to control the synthesis of distinct silicon-based materials. We started our investigation with the synthesis and characterization of 2-nitrobenzyloxy based PPG systems from ethyl and phenyl derivatives (R_x-(alkoxy)ysilanes, with x=0-3 and y=1-4). Through these systems, we have explored the photochemical responses for PPG removal including kinetics, removal efficiency, and tin catalyzed coupling of products to induce polymerization. We have found that applicable removal of the photoremovable protecting groups was achieved, giving a new avenue to generate silicon-based polymeric materials. Furthermore, a crude study has found that it is possible to directly 3D print with these materials.

Hierarchical Porous Carbons from Thermoplastic Elastomers

Anthony Griffin

Session 2, 4:00-4:15, Wolverine

Ordered mesoporous carbons (OMCs) have enormous utility in many applications due to the union of carbon properties (chemical stability, electrical and thermal conductivity, etc.) and porosity, which enables the transport of molecules into the material. OMCs have been used in catalysis, water remediation, and the adsorption of harmful gases like CO₂. Recently, a new platform for OMC synthesis using thermoplastic elastomers was established. This fabrication method employs a sulfonation-induced crosslinking process to selectively crosslink the olefinic majority phase of a nanostructured thermoplastic elastomer in the bulk. In doing so, the minority phase can be decomposed at elevated temperatures to form pores, while the majority phase is converted to carbon without destroying the well-ordered nanostructure. In this work, we extend this design principle to thermoplastic elastomer blends for the development of hierarchical macro/meso-porous carbons. We will discuss how to enable controlled reaction rate and assembly dynamics through altering blend composition; these advantageous features will then be leveraged to engineer the nanostructure of the final carbon products, with tailored pore structures, geometry, and framework chemistry. Finally, we will demonstrate the practical use of thermoplastic elastomer-derived OMCs for addressing environmental challenges, such as CO₂⁻ capture from flue gas.

Effect of smart charge switching polymers on cariogenic oral bacteria

Rajani Bhat

Session 2, 3:45-4:00, Anderson ABC

Streptococcus mutans is a dominant species in cariogenic biofilms that cause acidic microenvironments. Herein, we report a pH-responsive, charge-switching smart copolymer to selectively target and eradicate bacteria in cariogenic biofilms. To that end, we designed a random copolymer, Poly-1A, consisting of cationic ethyl ammonium group, a carboxylic group, and a hydrophobic group in the side chains that can be activated in an acidic environment. The net charge of Poly-1A remained neutral at physiological pH of 7.4, but in acidic pH of 4.5, it switched to be cationic due to the protonation of carboxylic groups. Poly-1A with a net positive charge bound to the anionic surface of oral bacteria by electrostatic interactions and disrupted the bacterial membranes, causing bacterial death. Thus, Poly-1A reduced the cell viability of planktonic and biofilm *S. mutans* at pH 4.5, while it was not bactericidal at pH 7.4. Poly-1A did not reduce the cell viability of human gingival fibroblasts and periodontal ligament stem cells for a 1 h incubation.

Therapeutic Applications of Polymers

Bi-layered hydrogels to recapitulate dynamic and reversible tissue folding patterns in vitro

Avinava Roy

Session 1, 10:00-10:15, Anderson Draani

Abnormal folding of mucosal tissues, such as within the epithelium of the upper respiratory airways is often a consequence of diseases, including chronic injury and fibrosis. Studying the influence of these tissue abnormalities on cellular function is challenging due to the lack of cell culture platforms that can mimic tissue folding in vitro. To address this, we developed bilayer folding systems composed of tough double network (DN) and rigid covalent hydrogels to generate tissue-like patterns based on mechanical instabilities. DN hydrogels were further mixed with micromagnetic particles to provide dynamic patterning.

DN hydrogels were fabricated through simultaneous crosslinking of polyacrylamide (12 wt%) and alginate (Alg, 2 wt%). To induce dynamic patterns, DN hydrogels were equally mixed with neodymium microparticles (NdFeB, 5 μm diameter), crosslinked, and magnetized within customizable molds. Pre-stretched (150% – 200% strain) or magnetized DN hydrogels were coated with a 200 μm thick layer of methacrylated hyaluronic acid (MeHA) pre-gel (3-5wt.%) and photo-crosslinked (ultraviolet light, 5 mW/cm, 3-5 mins). Human lung fibroblasts (hLF, $8 \times 10^6/\text{mL}$) were embedded into the MeHA hydrogel and co-cultured with bronchial epithelial cells (hBEC, $1 \times 10^6/\text{cm}^2$) atop, for up to 5 days.

Different pre-strain ratios of the DN hydrogel, and the MeHA hydrogel elastic moduli values generated characteristic static ridges, wrinkles and folds as dictated by mechanical instabilities. Embedding of magnetic microparticles inside the DN pre-gel enabled generation of similar but dynamic and reversible patterns through a fluctuating magnetic field. Co-culture of hBECs with hLFs significantly increased cell coverage and cell-to-cell contacts when compared to hBEC mono-culture.

Mechanical instabilities and magnetic microparticles generated suitable static and dynamic platforms for co-culture of cells. Reversible patterning holds promise to recapitulate mucosal tissue-dynamics. Ongoing work is to transition from a 2D substrate towards dynamic patterning of 3-D tubular structures with a precise control over the architecture and magnitude of patterning.

Synthesis of norbornene-modified hyaluronic acid hydrogels via water-based DMTMM coupling

Eleanor Plaster

Session 1, 10:15-10:30, Anderson D

Introduction: Synthesis of chemically modified hyaluronic acid (HA) polymers has enabled the fabrication of hydrogels, such as norbornene-modified HA (NorHA) hydrogels, that can provide tunable mechanical properties. However, current protocols for NorHA synthesis rely on dimethyl sulfoxide (DMSO)(1), a solvent that is cost-intensive and requires extensive dialysis for removal. Thus, we developed a DMSO-free synthesis based on triazine derivative 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM)(2) and tested the degree of norbornene substitution, hydrogel mechanics, and embedded cell viability towards their use for biomedical applications.

Methods: HA was modified with 5-norbornene-2-methylamine using DMTMM, precipitated with ethanol, and the degree of substitution (DS) was determined using proton nuclear magnetic resonance (^1H NMR). NorHA hydrogels were prepared via UV light thiol-ene reaction using dithiothreitol (DTT)(1). Mechanical analysis was performed using oscillatory photorheology, and cell viability investigated through Live/Dead staining.

Results: NorHA polymers were synthesized through the activation of HA carboxylic acids with DMTMM, and the reaction time and temperature of the synthesis were altered to tailor the degree of substituted norbornenes (DS). Increasing the temperature from 20°C to 37°C yielded a two-fold increase in DS, and increased reaction times were coincident with higher DS that increased over 48 hours. While the crosslinker concentration had little influence on the storage modulus (G') for low substituted NorHA polymers (DS 10.5%), high substitutions (DS 38.5%) resulted in stiffer hydrogels shown by an increase in G' for increasing DTT. High viability of encapsulated human mesenchymal stromal cells was observed after 24 h of culture (>75.5%)

Conclusions: The use of water-soluble DMTMM eliminates the need for extensive dialysis while maintaining

the tunability and cytocompatibility of crosslinked hydrogels. Moreover, reducing the use of solvents provides promise as means towards the development of green and sustainable syntheses.

References: 1(Gramlich, W.M. et al. Biomaterials 2013), 2(Loebel, C. et al. Carbohydrate Polymers 2015).

Catechol-functionalized polymers: from bulk adhesive to adhesive hydrogels

Alexandre Lancelot

Session 1, 10:30-10:45, Anderson D

Closure techniques typically employed in surgery, such as suture and staples, still remain invasive and are prone to infections.[1] Some skin adhesives, such as Dermabond®, have been developed and approved by the FDA. However, they can only be applied on superficial dry wounds, show limited adhesion, and may provoke erythema. Notwithstanding, Nature shows us many examples of non-toxic and strong adhesion in wet atmospheres. Indeed, mussels, can strongly attach to marine substrates using adhesive proteins that contain the unusual amino acid 3,4-dihydroxyphenylalanine. This amino acid contains a catechol moiety that was identified to be the main functional group responsible for underwater adhesion.[1]

Various innovative mussel-bioinspired copolymer adhesives that randomly alternate catechol-derived monomers with other monomers have been synthesized. They showed high adhesive performance in both, wet and humid environments. Recently, Prof. Wilker's group scaled-up the synthesis of poly(vinylcatechol-styrene) using suspension polymerization. After tuning the reaction conditions, polymer chains with Mw higher than 150 kg·mol⁻¹ have been obtained. This polymer showed adhesive strengths up to 4 MPa in dry condition and 3 MPa when used underwater.[2]

In order to prepare new alternatives for biomedical closures, hydrogels based on Pluronic® F-127 have been functionalized with catechol moieties. Pluronic is an FDA approved thermoresponsive polymer that passes from sol to gel with temperatures comprised between 25 and 37 °C, an idoneous temperature range for medical application. Acrylate-terminated Pluronic derivatives, previously developed by Dr. Sierra group[3], have been added to the hydrogels in order to enhance crosslinking and obtain better mechanical properties.

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Preoperative Surgical Planning via Patient-specific, Tough and Anti-drying Hydrogel-based Cardiac Mimic

Joanne Hwang

Session 1, 10:45-11:00, Anderson D

Surgical procedures can be extremely challenging due to the complexities and variances between each patient's anatomy and medical condition. Therefore, detailed preoperational planning is required for successful treatments. Accordingly, imaging tools including CT and MRI have been utilized to visualize the targeted tissue. Scanning outputs are reconstructed to build 3D images and printed out as physical models via 3D additive manufacturing. As these organ mimics provide clinicians the opportunity to perform preoperative practice, the material properties should be carefully tailored to resemble real tissue. Silicone based rubber has been a

common material for surgical training kits yet is often too stiff and lacks interstitial water to mimic native tissue properties, leading to the search of new materials for this application.

Hydrogel has emerged as an alternative due to their high water content and tissue-like softness, which offers a more realistic tactile feeling. Though conventional hydrogels are brittle and cannot endure surgical manipulations, our group developed a tough and stretchable single-component polyacrylamide hydrogel. Its toughness allowed needle penetration without any crack propagation. However, this hydrogel is still limited by dehydration, which induces changes in the microstructure hence mechanical properties and result in a high-stiffness glassy polymer which hinders its use as suture models.

To solve this problem, we integrated glycerol to our hydrogel to facilitate anti-drying property. We were able to 3D print an unique tough and anti-drying hydrogel in one-batch synthesis and successfully fabricated heart mimics showing a healthy and a diseased model with ventricular septal defect (VSD) respectively. Then, the printed models were examined by CT scans to evaluate the printing precision. By printing with our anti-drying tough hydrogel, we were able to create suturable and anti-drying organ models with tissue-like properties to provide better understanding on different cases and establish next-generation surgical simulations that will further improve healthcare.

Crosslinked Polyethylenimine: A Novel Drug Delivery System for Acidic Drugs

Kristen Kelsall

Session 1, 11:00-11:15, Anderson D

Poor solubility limits oral bioavailability for many pharmaceuticals. Crystalline drugs with low solubility have the potential to benefit from delivery in the amorphous form; however, poor physical stability of amorphous forms is a persistent problem. Amorphous solid dispersions (ASDs), in which polymeric excipients are mixed with an active pharmaceutical ingredient (API) to inhibit crystallization, overcome this problem though the number of FDA-approved polymeric excipients is low. In this work, crosslinked polyethylenimine (cPEI) is investigated for delivery of an acidic biopharmaceutical classification system (BCS) class II drug; cPEI was chosen for its potential for high API loading due to the abundance of basic nitrogen functionality. Amine group capping is employed to increase hydrophobicity of the crosslinked materials. In order to develop PEI, commonly used for gene delivery, as a drug delivery vehicle, this work shows novel cPEI design and optimization, ASD formation with a BCS class II drug, the identity of the drug species at different drug loadings, improved dissolution rate and solubility relative to crystalline drug, and promising physical stability data. The development of strong intermolecular interactions between the drug and polymer are expected to lead to physically stable dispersions. These findings motivate the broadening of polymer classes employed in ASD formation to allow tunability for drug acidity and enable loadings not readily achieved with existing polymers.

Polymer Upcycling and Sustainability

Upcycling Virgin and Waste Polyethylene to Reprocessable Dynamic Covalent Networks via Free-Radical Grafting of Dialkylamino Disulfide Bonds

Logan Fenimore

Session 1, 10:00-10:15, Wolverine

Plastics enable modern life through their advantageous properties and broad applicability. Regardless of their type or use, plastics are challenging to recycle efficiently. Current methods for recycling spent thermoplastics such as re-extrusion with additives result in property degradation over time and the relegation of these downcycled polymers to low-value applications. Plastics may be permanently cross-linked into thermosets, yet permanent cross-links prevent these plastics from being processed and molded into new shapes at high

temperature. An emerging avenue to mitigate these sustainability problems involves enriching waste plastics with dynamic covalent bonds as chemical cross-links. By introducing dynamic covalent cross-links, previously thermoplastic materials exhibit robust mechanical properties characteristic of conventional thermosets yet maintain their reprocessability at high temperatures. Not only can the incorporation of dynamic bonds be achieved during polymer synthesis to produce reprocessable step-growth networks like polyurethanes and addition-type networks like polymethacrylates, but also it can be achieved via post-polymerization modification to upcycle spent polyolefins for higher value applications. Using reactive batch processing, we upcycled virgin and waste low-density and high-density polyethylene into covalent adaptable networks (CANs) via melt-state, free-radical grafting of a cross-linker capable of dynamic dialkylamino disulfide (BiTEMPS) chemistry onto polymer chains. Unlike PE thermosets, our PE CANs are reprocessable and recover their thermomechanical properties after reprocessing. We have further shown that, in the absence of crystallinity, high-temperature creep behavior of the CANs is dominated by the exclusively dissociative reversible dynamic chemistry of the cross-linker. This observation also demonstrates the utility of this dissociative dynamic chemistry of high activation energy at suppressing creep in networks exhibiting different viscoelastic behavior. We will also describe cases of other thermoplastics that are able to be upcycled into CANs using our simple method.

One pot synthesis of stereoblock copolymer, poly-syndio-block-iso-3-hydroxybutyrate, with tacticity controlled by exogenous donors

Ziyan Yu

Session 1, 10:15-10:30, Wolverine

Poly-3-hydroxybutyrate (P3HB) is a promising biodegradable substitute for petroleum-based plastics; however, its mechanical properties (i.e., brittleness) limit its applicability. Incorporating polymer blocks with different tacticity (i.e. stereoblock copolymers) can potentially produce high-performance materials with improved physical and mechanical properties, yet methods for achieving this from a single racemic monomer remains challenging. Herein, we report a one-pot synthesis of syndio-block-iso stereoblock P3HB by its simplest racemic monomer, β -butyrolactone (BBL), from a cooperative, multi-catalyst approach through donor-modulated ROP. Mechanistic studies reveal that exogenous donors can perturb the activity of two catalysts which rapidly and reversibly undergo chain-transfer events. The stereoblock copolymers feature low dispersity ($M_w/M_n < 1.3$), high block fidelity, and a high proportion of racemic dyads (~83%) and meso dyads (~73%) in each block. The resulting copolymers are rigorously characterized, including their thermal properties. Our studies indicate that stereoblock copolymers synthesized through these methods offer unprecedented opportunities to tune the miscibility and thermal properties of P3HB.

External stress-free characterization of inherent reversible bond exchanges in vitrimer network

Yuming Wang

Session 1, 10:30-10:45, Wolverine

Vitrimer, an emerging class of associative covalent adaptable network, is reprocessable due to the nature of their dynamic crosslinking chemistry. The onset temperature when the network rearrangement occurs can be defined as topology freezing transition temperature, or T_v , characterized by a sharp reduction in materials viscosity. Over the years, several methods have been demonstrated for detecting T_v , including non-isothermal creep, multi-frequency rheological test, and use of free volume-sensitive guest molecules, such as aggregation-induced emission fluorophores. However, these methods are most indirect measurements and have several limitations, such as the need of introducing external stress. Here, we will discuss a universal, easy, and precise method by

measuring the thermal expansion coefficient change of vitrimer films as a function of temperature. Specifically, we found that the thermal expansion coefficient of vitrimer film can change significantly upon surpassing T_v . Two different vitrimer systems, including benzoxazine and maleic anhydride-epoxy systems, will be discussed to confirm the generalization of our approach. Moreover, we will discuss other material parameters, such as catalyst loading and film thickness. Impact the T_v of vitrimers.

Thermophysical Property Prediction of Polyethylene Binary Mixtures

Maria Ley Flores

Session 1, 10:45-11:00, Wolverine

The accurate determination of bulk properties of polymer mixtures in the melt is a topic of critical academic and industrial interest. However, the ability to predict multi-molecule processes in polymer systems remains challenging for molecular modeling. In this work, we propose a workflow to understand and predict thermophysical properties of binary mixtures of polyethylene with n-alkanes using supervised Machine Learning (ML) techniques. First, we generate a data set by combining SAFT- γ -Mie equations of state and atomistic molecular dynamics simulations. Then, we train a ML model to predict both transport and thermodynamic properties for binary mixtures of polyethylene in n-alkanes of different molecular weights at different concentrations. Our results show how quantitative predictive models can aid the design of polyethylene hydrocracking systems for chemical recycling.

Conversion of Extremely Brittle Polypropylene into Toughened Dynamic Networks

Mikaela Sadri

Session 1, 11:00-11:15, Wolverine

Upcycling polypropylene (PP) at industrial scale is typically done through pyrolysis, which could be energy intensive. While there have been recent reports of directly functionalizing PP to create higher performance plastic materials, their use in addressing low molecular weight (MW) PP is underexplored. Low MW PP can be produced upon mechanically recycling PP due to chain scission, and are extremely fragile materials with poor mechanical properties and limited applications. By adapting scalable reactive extrusion-based dynamic crosslinking methods, this work effectively addresses this challenge and upcycles brittle low MW PP into dynamic networks (vitrimers) with enhanced thermal and mechanical properties. While previous works have focused on small molecule crosslinkers, here polyethylene glycol-based polymeric crosslinkers are employed as dynamic linkages in order to act as toughening agents. Specifically, the impact of crosslinker amount and MW on the dynamic network crystalline structures, thermal, mechanical, and viscoelastic responses will be discussed. It is found that increasing the MW of the dynamic crosslinkers can result in PP vitrimers with increased fracture toughness by over 50 times. Additionally, in contrast with the substantial embrittlement that comes from blending low MW PP with high MW PP (PPh), blends of PPh and our PP vitrimers show comparable mechanical properties and material toughness to neat PPh, demonstrating the robust capability of using polymeric dynamic crosslinkers as a method of upcycling extremely brittle PP waste into higher-value products.

Guiding Pyrolysis Reactor Design: Mechanistic Microkinetic Modeling of High-Density Polyethylene Pyrolysis

Alexander Best

Session 2, 3:00-3:15, Anderson ABC

We are facing one of the largest global challenges of our time as improperly discarded plastics harm the environment and pollute natural resources, be it large plastic products drifting across oceans or microplastics leaching into the topsoil and drinking water. One of the leading plastic pollutants is high-density polyethylene (HDPE), a commercial packaging plastic. While HDPE can be recyclable, it has a limited number of lifecycles before the desired properties are lost. The pyrolysis of HDPE is an alternative technique for upcycling spent plastic into higher-value fuels or chemicals, with product composition strongly dependent on operating conditions. While this approach has been studied empirically, limited research has concentrated on creating a comprehensive model that captures the HDPE depolymerization mechanism under various iso-thermal and ramped temperature conditions. To date, models have focused on global measures, such as mass loss, and thus lack descriptions of the detailed product distribution and its dependence on polymer properties. The challenge to developing mechanistic models of polymer pyrolysis is the large number of species that exist, as radical and dead species with various functionalities (e.g., mid- versus end-chain radicals, saturated versus unsaturated ends) and polymer chain lengths form during pyrolysis. Therefore, the number of species that need explicit tracking grows exponentially. To overcome these computational challenges, we have developed a mechanistic model with functionality-defined species classes and ability to track distributions of molecular weights via the method of moments. Using kinetic parameters from literature or estimated using structure-reactivity correlations, rate constants are posed in Arrhenius form and are calculated at each time-step, thus allowing explicit modeling of non-isothermal conditions. These simulations can guide selection of optimal conditions for HDPE pyrolysis. This study developed a microkinetic model for HDPE pyrolysis that was validated using experimental data from the literature and expanded to model non-isothermal reactor conditions.

Low carbon concrete with recycled PE rope fibers and industrial by-products

Mengjun Hou

Session 2, 3:15-3:30, Anderson ABC

Fibers have been used widely in fiber-reinforced concrete (FRC) to overcome the brittle nature of conventional concrete. Engineered cementitious composites (ECC), as one member of FRC family, possesses at least 2% tensile strain capacity with a fiber volume fraction of no more than 2%. The ductility of ECC is about two orders of magnitude higher than that of conventional concrete. However, the high energy consumption and carbon emissions of synthetic fibers hinder the application of ECC in infrastructure facilities. In this study, the waste polyethylene (PE) rope was recycled to explore the potential in ECC materials. In the meanwhile, more sustainable raw materials, including waste industrial by-products (fly ash, crumb tire rubber), and desert sand, were introduced into the ECC mixture design to enhance its sustainability. The experimental results showed that waste PE fiber was compatible with the developed ECC, and the tensile ductility can be achieved to 10%. PE fiber restrained the crack initiation and propagation, and the crack width can be controlled below 50 μm under the loading conditions. The induced durability improvement was verified by the following durability test, including the alkali-silica reaction (ASR) study, sulfate attack study, and accelerated corrosion test. ECC with recycled PE fibers showed superior performance over the control mortar group. Besides, the fatigue test showed that the developed ECC exhibited multi-cracking, strain-hardening characteristics and satisfying fatigue durability at high load levels. The sustainability analysis showed that the carbon emissions of the developed ECC were reduced significantly due to the sustainable raw materials, and comparable to the conventional

concrete. The superior mechanical and durability performance combined with the enhanced sustainability ensure the potential of the developed ECC in infrastructure applications.

Non-covalent, Photocleavable Enzyme Nanogels via NIPAM Copolymerization with Acrylic Acid

Brock Hosier

Session 2, 4:00-4:15, Anderson ABC

Enzyme nanogels have become an increasingly viable option for delivering biological therapeutics while protecting them from external stressors. Many methods have been developed for creating these enzyme nanogels, but most recently, the creation of non-covalent enzyme nanogels using a photocleavable linkage has become a method of interest because of its potential for controlled drug release. Thus far, non-covalent enzyme nanogels with a photocleavable linkage have been demonstrated to effectively protect enzymes from external stressors while still retaining enzyme functionality, but there is still research to be done on using different polymerizations and different proteins. Here, we work to expand on the preparation of non-covalent enzyme nanogels with a photocleavable linkage using the free radical polymerization of N-isopropylacrylamide (NIPAM), which has “smart” properties compatible with drug delivery. Specifically, NIPAM copolymerized with acrylic acid has a low critical solution temperature (LCST) of 32°C, close to that of human body temperature, meaning the temperature of the human body will cause the nanogel to collapse and release its payload. Additionally, copolymerization with acrylic acid will allow for pH control, as the nanogel will swell or collapse at tuneable pH values. Thus, with temperature and pH control, a non-covalent enzyme nanogel using NIPAM copolymerized with acrylic acid will allow for a more well-controlled drug release system. This can allow for a certain drug to be delivered to only a specific region of the body or for a more controlled release over an interval of time. Moreso, we begin by using lysozyme as a model enzyme for this system and then apply this system to glucagon, which is an important peptide hormone critical in illnesses like hypoglycemia. Through this exploration we expand the applications of this system and further the amount of known polymerizations and proteins that this system is compatible with.

General

NIR laser-assisted stereolithography of polymer-derived ceramics

Evelyn Wang

Session 2, 3:30-3:45, Anderson D

The use of stereolithography (SLA) in making 3D structured polymer-derived ceramic (PDC) materials has greatly improved the precision, production efficiency, and ability to create intricate shapes from ceramic materials. However, traditional UV-assisted SLA faces challenges when working with new material systems due to stringent material requirements such as UV transparency, resistance, and curing mechanisms. A new NIR-assisted thermal SLA printing technology is introduced in this work to overcome these limitations in the UV-based SLA of PDC materials. This thermal method uses a high-intensity NIR laser to create localized thermal effects, leading to the rapid solidification of the resin during scanning due to a thermal cure mechanism. The technology was demonstrated using a gantry-based platform and a resin pool in a top-down SLA configuration. To enhance the printed parts, a post-processing technique called polymer infiltration and pyrolysis (PIP) was applied, resulting in excellent mechanical strength in the ceramic parts. This approach allowed for the creation of reinforced ceramic matrix composite materials made mainly of SiC, SiOC, and SiCN. The use of heat instead

of UV also opens more opportunities in traditional SLA, as additional mechanisms like hydrosilylation, epoxides ring opening, and esterification are also made possible in the printing process.

Making cellulose-based films work in high humidity

Tanner Hickman

Session 2, 3:45-4:00, Anderson D

Petroleum-based plastics are ubiquitous in society, but their slow degradation and limited recyclability present significant environmental concerns. Solid waste accumulation, energy consumption, and carbon emissions associated with virgin plastic manufacturing have driven extensive research efforts to develop sustainable alternatives for traditional plastics. Cellulose, the most abundant polymer on earth, has been widely studied as a sustainable plastic alternative for applications in packaging, composite materials, and printed electronics. However, the properties of cellulose and its derivatives are sensitive to moisture and relative humidity (RH), limiting their performance in many applications. In this work, we investigate different approaches to control swelling and water vapor transmission in cellulose-based films using commercially available cellulose derivatives: 1) by crosslinking cellulose with renewable small molecules to chemically bind polymer chains together, and 2) blending cellulose with other renewable polymers to form an electrostatically bound network. We find that crosslinking reduces swelling of cellulose-based films, and the water vapor transmission rate of crosslinked films can be tuned over approximately four orders of magnitude by varying the crosslinker content. The lowest measured water vapor transmission rates are comparable to poly(ethylene terephthalate), but only up to 65% RH. Comparatively, blends of cellulose and chitosan are less sensitive to moisture and exhibit lower water vapor transmission rates at high RH due to complexation between the oppositely charged polymers. The two approaches explored here to control swelling and water vapor transmission in cellulose-based films are therefore promising for potential applications as sustainable alternatives to petroleum-based plastics.

Physical aging behavior of polymer brush thin films

Sneha Srinivasan

Session 2, 3:00-3:15, Wolverine

Thin films in the brush morphology consist of polymer chains attached to a substrate by a single end. Due to this morphology, polymer brushes allow for control of film thickness and molecular packing. The ability to control both parameters in polymer brushes lends itself to interesting comparative studies with spin-coated films. Previous work in thin films has demonstrated that confinement and molecular packing strongly impact the glass transition temperature, among other material properties. However, less focus has been given to the combined influence of these two parameters on the physical aging response of thin films. In this study, we elucidate the physical aging behavior of polymer brushes via ellipsometry and fluorimetry. In particular, we investigate the role of confinement on physical aging of polymer brushes by decreasing film thickness at a constant grafting density. Our results show that upon confinement, both polymethylmethacrylate brushes and spin-coated films have decreased physical aging rates, with similar aging profiles obtained at certain temperatures. Ultimately, this work will help to design new ways to alter thin film properties for critical applications ranging from antifouling materials for water treatment purposes to organic optoelectronic devices.

Order-Disorder Transition Effects on the Rheology of Lamellar Structured Concentrated Surfactant Solutions

Parth Kelkar

Session 2, 3:15-3:30, Wolverine

Global consumer product companies that manufacture surfactant-based liquid laundry detergents and shampoos are striving to create products with lower environmental footprints by using more concentrated feedstocks. The handling and processing of concentrated surfactant feedstocks is challenging without altering their lamellar microstructure and/or incurring higher production costs. Unless multiscale relationships between processing, structure, property, and performance (PSPP) for concentrated feedstocks are developed, industry will continue to waste valuable resources on inefficient and unsustainable manufacturing processes.

In this university-industry collaboration, the rheo-physical behaviour of concentrated surfactant solutions was investigated. As a follow-up study to Caicedo-Casso et al.¹, industrially relevant additives – sodium chloride, and propylene glycol – were separately added in varying concentrations (0.25-20 wt.%) to lamellar-structured 70 wt.% sodium lauryl ether sulfate (SLES) aqueous solutions. Structure-property-processing relationships were experimentally established for each additive-SLES mixture. Oscillatory temperature ramps and complementary calorimetry experiments were conducted to evaluate the flow behaviour across processing and end-use relevant temperatures. Contrary to the behaviour of typical polymeric solutions, lamellar-structured samples displayed an unusual viscosity peak spanning at least one order of magnitude with increasing temperature in a narrow range from 7.5°C to 12.5°C. The effects of additives and reversible order-disorder transitions in lamellar bilayers on this unusual viscosity peak were investigated. Confocal microscopy and small-angle X-ray scattering were employed to quantify microstructural differences with variation in additive concentration and processing history.

Outcomes from rheometry, microscopy, calorimetry, and scattering shed light on the sensitivity of order-disorder transitions on key processing-relevant parameters including critical shear rates and transition temperatures. This study helps answer unexplained processing behaviour for concentrated feedstocks and will have implications in improving the sustainability of surfactant-based consumer products.

1 Caicedo-Casso, et al., *Rheologica Acta*. 58, 467 (2019).

Microphase separation and crystallization cooperatively enable toughness and thermal resistance in fully renewable poly(L-lactide) triblock copolymers

Daniel Krajovic

Session 2, 3:30-3:45, Wolverine

Poly(L-lactide) (“PLLA”) is among the most widely produced renewable plastics and a promising candidate for replacing petroleum-derived analogues. However, PLLA is inherently brittle, which has motivated considerable research into blends of PLLA with rubbery toughening additives. Historically, most of these additives have been petroleum-based, and their large droplet sizes prevent optical clarity, a desirable attribute in the rigid packaging market. Additionally, few blends have retained mechanical property improvements following PLLA crystallization, which is necessary for high thermal resistance. Block polymers of PLLA have been studied as compatibilizers for such blends but have not been widely evaluated as neat materials with respect to these technological goals. Here, we report on a series of fully renewable ABA triblock copolymers with PLLA as the majority-fraction “A” endblocks and poly(γ -methyl- ϵ -caprolactone) (“P γ MCL”), a compostable, lignin-derivable rubbery polymer, as the “B” midblock. X-ray scattering shows that these triblocks microphase

separate in the melt, producing rubbery P γ MCL domains inside a PLLA matrix. The P γ MCL domains do not scatter visible light owing to their nanoscale size, and the triblocks maintain optical translucency even after crystallization of the PLLA endblocks. During mechanical deformation, the rubbery domains facilitate various composition-dependent energy-dissipative processes, significantly improving ductility and toughness. These enhancements are retained after crystallization, endowing the triblocks with toughness, high heat distortion temperature, and translucency with a single thermal history. These findings provide new insight on the unique advantages of neat PLLA block polymers as tough, renewable plastics.

Tri-Cure Hybrid Organo-Silicon Coatings

Cory Sims

Session 2, 3:45-4:00, Wolverine

A novel tri-cure coating system was developed for the protection of stone, glass, metal, wood, and other building materials from environmental degradation while offering graffiti resistance on smooth surfaces. This technology utilizes three distinct curing methodologies to undergo a rapid (30-minute), photo-initiated cure upon exposure to UV light which is quickly followed by a secondary amine-epoxy surface adhesion and sol-gel alkoxy silane crosslinking. The design of the system allows it to be stored as a one-pot solution for over one year with repeated usage. Surfaces are enhanced with hydrophobicity, oxidative and flame resistance, anti-fouling capabilities, and chemical, photo, and thermal stability. The nature of this coating allows for modifiability including the addition of R-alkoxy silane groups to achieve specific characteristics.

Biaxial Deformation of Poly(p-phenylene sulfide) by Cross-Rolling and Subsequent Annealing

Nathan McMullen

Session 2, 4:00-4:15, Pond

Despite the many advantages poly(p-phenylene sulfide) (PPS) possesses in high performance applications, one limiting aspect is its relatively low impact toughness. Blending or reactive extrusion of PPS with a higher toughness phase has been proposed as a way to obviate this problem; however, there is still interest in improving the mechanical properties of PPS without relying on blending (i.e. intrinsic toughening). Well established in commercial steel manufacturing, plastic deformation by cold roll milling has also been proven to enhance the toughness and strength of semicrystalline polymers. Furthermore, the effect of annealing after plastically deforming a semicrystalline polymer below the glass transition temperature (T_g) is known to drastically influence mechanical properties but the mechanism is not well understood.

This work seeks to combine a thermodynamic and microstructural understanding of thermal treatment following plastic deformation of PPS by roll milling for the first time. Melt pressed 6.35 mm plaques of unfilled linear FORTRON® were fed through a counter-rotating roll mill with the gap reduced by 0.32 mm and the plaque rotated 90° alternately clockwise and counterclockwise on each pass (i.e. cross-rolling). Modulated differential scanning calorimetry (MDSC), dynamic mechanical analysis (DMA), and broadband dielectric spectroscopy (BDS) were used to study the effect of cross-rolling on the T_g and cold crystallization behavior. Wide-angle x-ray diffraction (WAXD) was used to observe the effect of rolling and annealing on micro and nanostructure. The mechanical properties of rolled PPS sheets subject to various annealing histories were measured in tension tests.

It was found that the ductility of PPS could be improved by rolling and further enhanced by annealing above T_g . The yield strength conversely could be improved by sub- T_g annealing after rolling. The kinetics of cold

crystallization were increased by cross-rolling and the crystal structure could be partially recovered by annealing above T_g .