

THE WATERBORNE SYMPOSIUM

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Undergraduate Abstracts



A Study of the Influence of Hydrogen Bond Clusters on the Bulk Physical Properties of Hyperbranched Polymers

John Cunningham, Samantha Daymon, Sergei Nazarenko*

Hyperbranched polymers (HBP's) based on 3-hydroxy-2-(hydroxymethyl)-2-methylpropionic acid (bis-MPA) have been widely studied due to their commercial availability and chemical stability. These materials are used in a variety of applications but the relationship between their structure and bulk physical properties have still not been fully explored. More specifically, due to the high concentration of hydroxyl groups available, bis-MPA based HBPs can form extensive intra and inter molecular hydrogen bonds (H-bonds) which play an important role in defining their bulk properties. The dielectric properties of bis-MPA based HBPs are highly influenced by the presence of water, likely due to an increase in available H-bond donors and acceptors provided by water molecules. These HBP systems already form extensive H-bond networks on par with pure water, and it's hypothesized that water in small enough quantities can act as a chain extender for these networks, increasing their long-range cooperation and ultimately their dielectric constant. Utilizing both computational and experimental approaches, HBP's of the second generation were examined to probe the effect of water on the polymer's hydrogen bonding capabilities.

Developing Degradable Polymer Networks Using the Dual Trigger and Gate Strategy

Rylan Price, Surabhi Jha, William D. Walker and Derek L. Patton*

It is crucial to design degradable polymers as replacements for conventional polymers that persist in the environment for centuries. However, a challenge with degradable polymers is the unintentional scission of degradable linkages, resulting in undesirable loss of properties during storage or use. We report a strategy to combine thermal and photo-stimuli as a dual trigger "AND" gate enabling the creation of a stable thermoset with triggered spatiotemporal control of degradation. Thioether networks are synthesized using commercial thiol and bisallyl benzylidene acetal monomers in a one-pot two-step process with 5% excess thiol. First, the excess thiol is thermally protected, resulting in a stoichiometric thiol-ene resin, which is subsequently photocured in the presence of photoinitiator. In the absence of any protecting group, thermosets readily degrade under UV irradiation with thiyl radicals from excess thiols acting as polarity reversal catalysts to abstract the electron-rich acetal hydrogen atom and affect cataclysmic degradation of acyclic benzylidene acetals to benzoate esters within seconds, as previously reported by our research group. The presence of a thermal protecting group prevents photolysis of the benzylidene acetal in ambient conditions. However, the network readily degrades within a few minutes when subjected to a dual thermal and photo trigger. Thermolysis of the model protecting group was also explored. Thermal deprotection kinetics were quantified via NMR and real-time FT-IR experiments. Electronic effects were explored on the thermal protecting group to tune network-degradation rates, creating a network with enhanced control on degradation.

Mechanically Robust 3D-printed Carbon from Commercial Polyethylene

Ethan Bounds, Paul Smith, Kaleb Jones, Anthony Griffin, Jeff Aguinaga, Derek Patton, Zhe Qiang*

Additive manufacturing (AM) stands as a pivotal force in the continual evolution of new products and technologies. Despite significant advances in the field of AM technologies for diverse material systems including polymers, metals, ceramics and even composites, processes for creating macrostructured carbon materials through AM are still emerging. Current systems involve the deposition and post-treatment of carbon containing slurries or the use of polymeric carbon precursors with multiple processing steps. Recently, we reported a process using fused filament fabrication (FFF) to 3D print polypropylene (PP) structures that could undergo sulfonation to induce crosslinking and later pyrolysis, resulting in simple access to large-scale carbon structures. In this work, we look to further expand the capabilities of this system through material selection to different polyolefins, specifically, polyethylene (PE). PE is demonstrated to act as an effective precursor system using this approach, undergoing a crack-assisted diffusion phenomenon which allows for efficient crosslinking. Additionally, the effects of processing conditions such as sulfonation temperature and carbonization procedure are elucidated on the morphology and mechanical properties of the final carbon materials. Tuning of PE sulfonation conditions allows for increased crosslinking kinetics and a reduction in cracking, creating smoother, more continuous carbon relative to PP counterparts.

Barrier Coatings for Polyphenylene Sulfide Carbon-Fiber Reinforced Composite Structures

Jaylen Phillips, Richard Ferguson and James Rawlins*

The project's purpose was to develop and evaluate a suitable protective coating for polyphenylene sulfide (PPS) carbon fiber composite in aerospace applications. PPS has good bulk resistance to UV light exposure; However, it will cause surface degradation. Our hypothesis is that a coating with good adhesion, sufficient hiding, and UV absorbers will mitigate the degradation. Urethane coatings were formulated using acrylic, polyester, and silicone modified polyester resins in clears, and at two pigment loading levels with and without UV inhibitors. Adhesion was evaluated on steel and composite substrates using pull off and cross hatch. The Xenon chamber experiment was used to simulate out-door exposure to evaluate discoloration and surface degradation.

Elucidating the Effect of Backbone Structure on Dynamic Exchange in Poly(benzoxazine) Imine-based Vitrimers

Elania Booker, Jo D. Arrington, John J. Peyrefitte, Levi J. Hamernik, Jeffrey S. Wiggins *

Vitrimers, a type of covalent adaptable network, exhibit dynamic bond exchange at elevated temperature. In addition to the glass transition temperature observed for traditional polymer networks, vitrimers possess a topology freezing temperature (T_v). Above T_v , vitrimers can be reshaped and welded like thermoplastics, unlike traditional non-dynamic polymer networks. The dynamic nature of vitrimers adds to the complex structure-property relationships observed in polymer networks. Dynamic bond exchange is impacted by factors such as chain rigidity and adjacent structure to dynamic bonds, which may vary depending on the type of dynamic bond employed. In order for vitrimers to be utilized in applications such as coatings, films, and fiber-reinforced composite materials, the impact of structure on dynamic properties must be well-understood. Due to the synthetic modularity of poly(benzoxazine) networks, the impact of structure on the properties of imine-based vitrimers can be investigated through the modulation of precursor structure. In the present work, polymer network structure was modulated in imine-containing poly(benzoxazine) networks to investigate the resulting impact on the rheological and thermal properties, such as T_v and apparent activation energy (E_a).

Understanding the Thermal Properties Through Atomistic Changes of High Char Polymers

Ian Beall, Trey Schneider, and Jeffery Wiggins*

This work studies matrix properties from monomers to polymers by changing the heteroatom in a five-membered ring. From the monomer, we studied thermal characterization for oxygen and sulfur backbones, and for the polymers, we examined mechanical changes through the use of dynamic mechanical analysis (DMA). These matrices were then carbonized through thermo gravimetric analysis (TGA) and the carbon left over was then studied utilizing scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS). Between these two methods, we calculated the degradation temperature and char yield via TGA, and atom composition via SEM-EDS. This work strives to improve the carbon yield of polymers by finding newer methods to better understand char yield matrices. This work studies both furfurylamine and thiopheneamine chemistries, comparing carbon yields. Through this study, we attempted to provide insight into the thermal properties and carbon composition/yields through the changing of heteroatoms

Structural Evolution of Silicon Oxycarbide Polymer-derived Ceramics

Isabell Duplantis, Virginia Lewis, and Jeffrey S. Wiggins *

The future of humanity lies in the stars, and in the polymer scientists and engineers working tirelessly to make space travel safe and affordable for the public. Thermal protection systems (TPS) are essential to the success of aerospace and hypersonic endeavors, so using materials that exhibit mechanical stability at high temperatures is imperative. Polymer-derived ceramics (PDCs) are used for high temperature and high impact applications because of their durability and resistive properties. PDCs are amorphous ceramics made using advanced ceramic manufacturing techniques that design and control a ceramic product's molecular structure. From heat treatment in an inert atmosphere (pyrolysis), PDCs become amorphous microstructures containing nanodomains that dictate heat, creep, and oxidation resistance, among other mechanical properties. Thermal pyrolysis of organic preceramics such as polysiloxanes and polysilsequioxanes produce silicon-based PDCs, specifically silicon oxycarbide and silicon carbonitride. Silicon oxycarbide PDCs have been found to have a negative enthalpy during crystalline formation, meaning they are thermodynamically stable during and after pyrolysis, ideal for TPS applications. This research systematically modifies cure environment and heteroatom substitution to produce silicon oxycarbide matrices. The resulting thermal performance, elemental composition, and phase morphology were analyzed.

Influence of Purity on Thermal and Mechanical Properties of Aromatic Diamine Based Polybenzoxazines

Isaac Fisher, Jonathan Burris, Charles Davis
and Jeffery Wiggins*

Polybenzoxazines are a class of thermosetting polymers with a growing interest as aerospace composite matrices due to their low cost, high glass transition temperature, and tailorable molecular design. Crude benzoxazines monomers are easily synthesized, however, the purification of the monomers is resource intensive. Due to these factors, literature about the influence of monomer purity on the resulting polymer properties is lacking. This research aims to elucidate the influence of purity on thermal and mechanical properties of aromatic diamine based polybenzoxazine networks. Several benzoxazines with slight molecular alterations were synthesized through a facile one pot method, and subsequently purified through a silica plug. Both crude and purified polybenzoxazine networks were probed through thermal and mechanical characterization methods including differential scanning calorimetry (DSC) and tensile testing.

Improving the Melt Processability of High Tg Poly(benzoxazine) Imine-based Vitrimers

Jo D. Arrington, Elaina Booker, John Peyrefitte, Levi Hamernik, and Jeffrey Wiggins*

In glassy thermosetting polymers with Tg exceeding 100 °C, the monomers used typically exist as highly viscous liquids. High viscosity can impart difficulty when processing such polymers to achieve the final cured parts such as coatings, films, or fiber-reinforced composites. Vitrimers, a type of dynamic polymer network, contain dynamic covalent bonds that enable reshaping and welding above their topology freezing temperature (Tv), unlike traditional non-dynamic polymer networks. Similar to traditional non-dynamic polymer networks, realizing robust mechanical properties and high Tg in vitrimers often involves the use of high viscosity liquid monomers. Although increasing processing temperature can reduce monomer viscosity, sustained exposure to elevated temperature can progress the extent of cure, which can result in additional increases in viscosity. Aside from modulation of processing temperature, careful incorporation of reactive diluents can reduce viscosity while minimizing the impact on Tg and other properties. The investigated imine-benzoxazine vitrimers undergo cross-linking through benzoxazine ring-opening, while dynamic bond exchange is facilitated by the presence of imine bonds in the cross-linked network. With the motivation of increasing Tg, rigid aromatic backbone structures are associated with high monomer viscosity for the investigated imine-benzoxazine vitrimers. The present work encompasses reducing monomer viscosity and improving processability of high Tg imine-benzoxazine networks through the incorporation of chemically similar monofunctional benzoxazine monomer that act as a reactive diluent.

Evaluating the Role of Benzoxazine Purity on Processability

Keith Dusenberry, Benjamin Morasch, Jeffrey S. Wiggins*

Polybenzoxazines are an attractive alternative to traditional thermosetting chemistries including epoxy and phenolic resins for applications including coatings, adhesives, composites, and flame-retardant materials due to high thermal stability, high glass transition temperatures, and modularity in molecular design. Herein, we describe the synthesis of high purity crystalline benzoxazine monomers and systematic evaluation against a commercially relevant equivalent. Following purification routes spanning those industrially relevant to those feasible on a lab-scale, nuanced differences in network formation and the impact on processability were quantified. Additionally, rheological and resulting thermomechanical properties were investigated and reported. This work provides insight into the role of purity and assesses relevancy of transitioning chemistries from a lab to an industrially relevant process.

Enhancement of Polyacrylonitrile Production using Aqueous Photoiniferter Reversible Addition Fragmentation Chain Transfer Polymerization

Mac McCormick, Evan Stacy, Penelope Jankoski, Tristan Clemons*

Polyacrylonitrile (PAN) has remained the industry standard for the precursor to carbon fiber production due to its mechanical and thermal stability, along with a high carbon yield upon graphitization. However, free radical solution polymerization of acrylonitrile has remained a limitation due to lower conversion and chain transfer side reactions, making more controlled polymerization reactions of high interest for PAN production. In addition, most solvents used for processing PAN, such as N,N-dimethylformamide, dimethyl sulfoxide, and ethylene carbonate, are toxic to the environment and have high boiling points, making polymer purification difficult. Thus, in this work, aqueous photoiniferter reversible addition fragmentation chain transfer polymerization (PI RAFT) of acrylonitrile is reported. A high concentration of inorganic salts (sodium thiocyanate and zinc chloride; ~7M) was used to solubilize both the monomer and polymer, which allows high molecular weights to be achieved (target ~25000 g/mol). Using photoinitiation as opposed to traditional thermal RAFT polymerization techniques also provides opportunities for performing these polymerizations at lower temperatures, which could help reduce termination rates and limit polymerization exotherm. Polymerization kinetics were reported using proton nuclear magnetic resonance spectroscopy, and molecular weight and dispersity were determined using gel permeation chromatography and matrix assisted laser desorption/ionization mass spectrometry. Tacticity at the varying reaction temperatures was determined using carbon-13 NMR based on the triad peaks corresponding to the chiral carbon centers.

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Graduate Abstracts



Investigation of the Self-assembly and Dye Encapsulation of “Janus-type” Linear Dendritic Block Copolymers Containing Stereoisomeric Glycopolymers for Utilization in Biomedical Applications

Kevin Green Penelope Jankoski, Thomas Newton, Blaine Derbigny, Anuja Kulkarni, Davita Watkins, Tristan Clemons, Lisa Kemp and Sarah Morgan*

The use of near infrared (NIR) fluorophore dyes in noninvasive biological imaging has shown promise due to minimal interfering absorption and enhanced tissue penetration depth. However, many NIR dyes are not water soluble. The self-assembly of amphiphilic Janus dendrimers (JD) into Janus dendrimersomes (JDS) comprised of a hydrophilic/hydrophobic bilayer has enhanced the capabilities for small molecule drug/dye encapsulation and transport. To further improve the biocompatibility of self-assembled structures, JDs have been decorated with saccharide groups, which upon self-assembly, form non-toxic Janus glyco-dendrimersomes (JGDS). Due to distinct lectin binding interactions, saccharide stereochemistry plays an important role in carbohydrate functions such as biological recognition and peptide aggregation pathways. Thus, the stereospecific arrangements of pendant saccharide groups may be used for cell targeting in vivo. This work explores the use of synthetic glycopolymers as the hydrophilic block of JGDS to amplify the structures' hydrogen bonding capabilities, potentially enhancing the self-assembly kinetics and structural stability. Linear glycopolymers were synthesized through reversible addition fragmentation chain transfer (RAFT) at varying target molecular weights and with different pendant saccharide groups, glucose and galactose, and were then subsequently characterized using nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The glycopolymers were then photo-coupled to polylactic acid (PLA) dendrons at different molecular weight ratios. Following the self-assembly of these amphiphilic structures in water, nanostructures were characterized through dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). During the self-assembly process, either hydrophilic (methyl orange) or hydrophobic (curcumin) dyes were introduced to the system and the resulting encapsulation data was then determined by their absorbance spectra and compared to known calibration curves.

A Sprayable Hydrogel for Potential Drug Delivery Applications

Xianjun Wang, Lisa Kemp, Sarah Morgan*

Every year, a lot of people get tick-borne disease, and tick resistance to acaricides is becoming a huge economic problem for livestock industries. Gene-modification technology has shown great success in the laboratory and could be used to control tick-borne diseases in the future. However, traditional gene delivery methods (i.e., such as soaking ticks in solution or microinjection) are tedious and restricted to use in the laboratory. Our approach is to use a bio-adhesive hydrogel as a drug delivery vehicle to support transcuticular delivery in the tick's native environment. For this research, we prepared a hydrogel and tested its in-situ gelation after spraying. We evaluated the hydrogel rheological properties and tackiness. A passive diffusion model was created to mimic how dsRNA polyplex transports through the hydrogel network using a pair of ionic dyes.

Evaluating Graphene-based Additives in Polyurethane Films for Magnetic, Conductive, and Morphological Properties

Zoe Lequeux, Christopher Faulkner, Lisa Kemp, Dane Wedgeworth, Steven Price, John Newman, Sarah Morgan*

Due to the increased use of technology, including WIFI and smartphones, electromagnetic (EM) pollution has risen exponentially. This pollution can cause interference and occasional malfunction of sensitive electronic devices as well as possible detrimental effects on human health due to prolonged exposure. Metals have been used to shield equipment by reflecting EM radiation, but it does not reduce overall pollution. Additionally, metals are expensive, have low flexibility, and are prone to corrosion. For these reasons, interest has begun to shift towards polymer composites due to their tunability, low weight, and low cost. Specifically, graphene-based polyurethane (PU) composites have become a focal point due to their ease of manufacturing at commercial scale. Tailoring the polyurethane morphology to force the additive to pack into a percolated network can increase the EM properties of the film while reducing the amount of additive needed. This project serves to investigate the effects of various graphene-based nanoscale additives on the conductive, magnetic, and morphological properties of polyurethane composite films.

Surface Modification of Poly(vinylidene fluoride) Microfiltration Membranes Using Polydopamine in Combination with Organic or Inorganic Hydrophilic Agent to Improve Oil Fouling Resistance

Moustafa Zagho, Shifa Shaikh, Mohammad Hassan, Sergei Nazarenko*

Membrane technology is widely utilized for producing industrial-grade water for numerous applications. Poly(vinylidene fluoride) (PVDF) is one of the most commonly used polymers in various separation membranes due to its high mechanical strength, low cost, superior thermal stability, and excellent chemical resistance properties. However, PVDF membranes mainly suffer from oil fouling due to their hydrophobic nature. In this regard, a simple surface modification method based on dopamine polymerization to polydopamine (PDA) is applied to enhance the hydrophilicity and oil antifouling behavior of PVDF membranes. PDA makes strong adhesion to organic and inorganic substrates due to the formation of strong covalent and noncovalent bonds in addition to the presence of abundant surface hydrophilic functional groups such as amines and hydroxyl groups. Modification of PDA is recommended to further enhance the hydrophilicity of the membranes. Herein, we investigated a facile approach which is based on a co-addition of PDA with another either organic (Boltorn™ fourth (H40) pseudo-generation 2,2-bis(hydroxymethyl)propionic acid based hyperbranched polyol) or inorganic (MXene) hydrophilic agents. Comparisons are drawn between the effects of incorporating Boltorn™ H40 hyperbranched polyol and MXene in combination with PDA on the oil separation performance of PVDF membranes while treating oil-in-water emulsions with a detailed surface characterization of the modified membranes. The incorporation of H40 hyperbranched polyoldemonstrated a remarkable boost in the separation of oil from water in tight emulsions while displaying high resistance to fouling over multiple runs versus unmodified, PDA, and PDA/MXene modified PVDF membranes. The reported functionalized microfiltration membranes, especially the PDA/H40/PVDF membrane, can be recommended for water/oil separations.

Use of Finite Element Analysis to Predict Graphene Polymer Nanocomposite Mechanical Properties

Bryant Grove, Boran Ma, and Derek Patton*

Computational methods have served as feasible alternatives to experimental methods for decades. Among the most accurate and powerful of these methods is finite element analysis (FEA), which works by discretizing representative objects into individual components or elements, solving said elements for corresponding functions, and then reassembling said functions to describe the discretized whole. FEA simulations can be utilized to predict mechanical properties of polymer nanocomposites, which can be derived from simulations of composites as representative volume elements (RVEs), or the smallest unit of a composite that has properties considered uniformly representative of said composite. By modeling composites on the microscale with sufficient accounting of filler and matrix mechanical properties, filler dimensions, and filler-matrix interactions, FEA modeling can provide the means to predict composite properties. Additionally, FEA simulations can be used to replicate experimental testing procedures like short beam shear testing (SBS) to derive the mechanical performance of composite materials with multi-layered structures. In this work, we performed FEA simulations on graphene polymer nanocomposites. We will present the effects of filler volume fraction, orientation, and dispersion state on composite mechanical properties such as Young's modulus and tensile strength. We will also demonstrate how the mechanical performance of a multi-layered laminate structure can be tuned by designing the orientation of filler in individual layers.

Thermocleavable Sidechain Containing Donor Materials Towards High Stability Organic Solar Cells

Andrew Bates, Soumya Kundu, Haoyu Zhao, Jordan Shanahan, Wei You, Xiaodan Gu*

The power conversion efficiency of organic solar cell(OSC) devices has been optimized over time and has now reached a commercially viable value. The lack of thermal stability in OSC devices is the primary issue preventing the commercial use of this technology. Over the course of a few months at a realistic operating temperature, the efficiency of the devices will drop by half or more due to phase separation and other phenomena occurring in the active layer. Previous work has shown that thermocleavable sidechains (TCSs) in the donor material impart increased thermal resistance to the OSC devices after cleavage while allowing the materials to keep their attractive solution processibility before cleavage.

Here, we create OSC devices using a TCS containing donor material (a PffBT4T derivative) and perform isothermal annealing at 100C °C for a period of a month to see the effect sidechain cleavage has on stability. We correlate the performance data with morphology using atomic force microscopy coupled with infrared spectroscopy (AFM-IR). Thermocleavage results in a more stable morphology and thus efficiency over time. Issues such as decreased thickness and void space after cleavage are addressed by backfilling the top portion of the active layer with a similar noncleavable donor. This research could provide the needed breakthrough for the creation of flexible and thermally stable solar cells.

Influence of Carbon Nanotubes on Poly (phenylene sulfide) Crystallization Kinetics and Multiscale Semi-Crystalline Morphology

Nick Enos and Jeffery Wiggins*

Interest in thermoplastic composites for aerospace applications has been driven by the need for high-volume manufacturing of materials that display excellent mechanical, thermal, and solvent resistive properties. Poly (phenylene sulfide) (PPS) is a semi-crystalline polymer with high potential as a thermoplastic polymer matrix for aerospace composites and relies on the crystalline portions of the matrix for its improved thermomechanical properties. Common thermoplastic melt processing methods such as induction welding and automated tape placement (ATP) rely on electrically conductive domains in polymer composites, such as carbon fibers or carbonaceous nanomaterials, which also influence the crystallization kinetics and morphology of semi-crystalline polymers through changes in nucleation behavior and local diffusion rates. Herein, PPS/Carbon Nanotube (CNT) Composites are prepared via high-temperature compounding to determine CNT influence on PPS electrical conductivity, rheological properties, crystallization kinetics, and oxidative degradation. This work gives greater insight into the influence of CNTs on the processibility and crystallization behavior of PPS which, in turn, dictate morphology and resulting material performance.

Understanding the Thermal Properties of a High-Char Polymer Compared to a Polymer Ceramic Hybrid.

Trey Schneider, Ian Beall and Jeffery Wiggins*

High char-yielding polymer systems find use in thermal protection systems (TPS) such as atmospheric re-entry vehicles used by NASA. To create these TPS, polymers are subjected to high temperatures (1000 °C plus) creating a carbon-carbon (C-C) matrix able to withstand re-entry conditions. Creating these TPS can take up to months or even a year or more to make. The reason for this, is each time a part is pyrolyzed (turned into its carbon form) it loses mass and creates voids which then need to be refilled and re-pyrolyzed. This process is repeated until a desired density is achieved. This work strives to improve the carbon yield (char yield) of polymers by finding methods to covalently incorporate ceramic moieties into the polymer backbone and ideally improve the overall char. By improving the carbon yield, it will take less pyrolyzation steps to create the same desired part while also saving time and money overall.

Phase development of Polymer-derived Ceramics

Virginia Mullens and Jeffery Wiggins*

The demand for more powerful and efficient aircraft translates to harsher operating conditions and more hostile environments. The challenge to create heat resistant materials has led to studies of ceramics with over 8,000 patents related to aerospace-grade ceramics obtained since the early 1980s. Polymer-derived ceramics (PDCs) are a class of materials created by the solid-state thermolysis (pyrolysis) of organosilicon polymer precursors precursor which allows tailoring of the ceramic's chemical composition by modification of the precursor. While progress has been made in understanding the nanoscale structure and energetics of single source precursor derived PDC, attaining the same level of understanding for more complex PDCs such as nanocomposites remains a challenge of both fundamental and practical importance. This research studied the phase development of a preceramic polymer matrix as the polymer underwent ceramization. Analysis of heat flow during the cure process was conducted using DSC, and thermal stability was measured using TGA.

Biobased Building Blocks for Rigid, Sterically Congested Epoxy-amine Thermosets

Ethan Rose, Chloe Donaldson and Derek Patton*

Biomass is a largely untapped candidate feedstock for replacement of petroleum-based feedstocks used to synthesize epoxy monomers. Herein, we explore a series of thermally stable, bio-based epoxy amine networks containing a rigid component derived from citric acid. The rigid bridge derived from citric acid endows thermosets with improved thermal and chemical stability when compared to properties of similar networks derived from heterocyclic structures of isohexides. Bifunctional epoxy monomers were synthesized using the citric acid derivative and were purified via flash chromatography. Epoxy monomers were cured with either isophorone diamine or 4,4-diaminodiphenylsulfone to compare thermo-mechanical performance (T_d , T_g , E'). This work expands the scope of bio-derived monomers for epoxy-amine thermoset and will provide opportunities to explore degradable systems to address end-of-use challenges.

Photo-Induced RAFT Polymerization to Generate Peptide-Functionalized Gene Delivery Vehicles

Evan Stacy, Penelope Jankoski, and Tristan Clemons*

Current methods of treating cancer, including chemotherapy, are accompanied by debilitating side effects primarily due to their lack of specificity toward cancer cells. In recent years, a class of polymers known as polyplexes have demonstrated their ability as promising alternatives to viral gene therapeutics due to their relatively low cost as well as a high degree of tuneability and characterization. Polyplexes are block copolymers that incorporate a polycationic block, allowing self-assembly into micelles in the presence of mRNA, resulting in the nucleic acid payloads being protected from enzymatic degradation. In this work, imparting targeting capability to polyplexes was explored by employing a chain-transfer agent (CTA) developed via solid-phase peptide synthesis, incorporating the GE11 sequence which has been shown to target the Epidermal Growth Factor Receptor (EGFR) that is highly overexpressed in several types of cancer. The CTA was then utilized in Photoinduced Electron/Energy Transfer Reversible Addition-Fragmentation Chain Transfer (PET-RAFT) polymerization to prepare diblock copolymers of poly(oligoethylene glycol) methyl ether methacrylate (pOEGMA) and 2-(dimethylamino)ethyl methacrylate (pDMAEMA) for electrostatic binding with green fluorescent protein (GFP) mRNA. Micelle self-assembly and payload encapsulation efficiency of non-targeted and GE11 functionalized block copolymers at varying N/P ratios were assessed by Dynamic Light Scattering (DLS) and agarose gel electrophoresis. Biocompatibility of polyplex nanoparticles was assessed in vitro with HEK293 cells utilizing a lactate dehydrogenase assay. Transfection efficiency was also assessed in HEK293 cells by measuring GFP expression.

Bioactive Surfaces Through Affinity TAG Protein-Polymer Conjugation

Alyssa Shaw, Monica Rahman, Tristan Clemons*

Proteins, with their high catalytic activity and substrate specificity, have found their dominance in a myriad of industrial and medical applications. A widely used strategy to enhance protein stability involves covalent conjugation of polymers to proteins. However, such covalent conjugates often encounter limitations such as reduced catalytic activity, either from the indiscriminate conjugation or disruption of the protein's folded structure after conjugation. Thus, a surface conjugated with protein may become completely inactive from these covalent attempts. Recombinant proteins are often expressed with six Histidine residues (His-tags) at either the N- or C-terminus of proteins to facilitate protein purification through utilizing the high binding affinity of His-tags for metal ions (usually Ni²⁺). This research focuses on a dual approach to both immobilize active His-tagged proteins to a surface, but also stabilize these proteins through conjugation with hydrophilic polymers and the noncovalent divalent metal ion – His tag interaction. To demonstrate this, we synthesized poly(N,N-dimethylacrylamide) by reversible addition-fragmentation chain transfer (RAFT) polymerization utilizing a metal chelating nitrilotriacetic acid modified chain transfer agent. Through reducing the Z-group of the polymer to a thiol, the polymer was then conjugated to a glass surface via thiol-ene click chemistry, which in the presence of divalent metal ions, could then non-covalently tether model His-tagged proteins to the polymer functionalized surface. Chemical content and surface modification was investigated using X-ray photoelectron spectroscopy (XPS) as well as contact angle measurements. Conjugation and protein activity were probed using NATIVE gel electrophoresis and relevant enzyme activity assays, respectively. Taken together, we demonstrate the utility of His-tag affinity chemistry to be repurposed for the facile, non-covalent preparation of protein-polymer conjugates and ultimately, bioactive surfaces.

Investigating Nanostructural Evolution in Thermoplastic Elastomers during Mesoporous Carbon Synthesis

Mark Robertson, Andrew Barbour, Anthony Griffin, Alejandro Guillen Obando, Paul Smith, Zhe Qiang*

Many applications, like energy storage, drug delivery, and heterogeneous catalysis benefit from the unique properties of ordered mesoporous carbon (OMCs). Specifically, the large pore sizes and surface areas facilitate the mass transport of guest molecules into the carbon matrix enhancing the number of interactions for specific applications. Synthesizing OMCs from commodity, thermoplastic elastomer precursors has recently been enabled through a simple, sulfonation-induced crosslinking method that has excellent potential for scaled production. The sulfonation-induced crosslinking reaction selectively crosslinks polyolefin majority phases of thermoplastic elastomers, while the polystyrene minority phases are not crosslinked, allowing them to be thermally decomposed. While the polystyrene phases do not crosslink, they do react with the crosslinking agent, resulting in significant nanostructural changes which directly impact the pore structure of the carbonaceous products. In this work, in situ small angle x-ray scattering and chemical evolution investigations are employed to deconvolute the contributions of the simultaneous reactions within the thermoplastic elastomer nanodomains. It has been determined that preferential sulfonation of the polystyrene minority phase results in swelling of the polymer nanostructure which is mediated through kinetic trapping as the majority polyolefin phase crosslinks. Furthermore, the crosslinked thermoplastic elastomers are converted to OMCs to establish a processing-structure relationship for future rational system design.



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