

Improved templating of porous TiO₂ by pH change of CNC-H₂O Solution on control of CNC-Titania dispersion

Kylie DeClue, Nizar Zahed, Dr. Carolina Tallon

ABSTRACT

Cellulose nanocrystals (CNC) has shown an increased potential for an array of applications, partly due to its renewability, mechanical properties, compatibility, surface chemistry, and structure. Using CNC's as an organic filler creates efficient and easier reactions when using Titanium (IV) Isopropoxide (TTIP) as a precursor. This study aims to understand the effects that pH and the addition method of TTIP on the porosity of Titanium Dioxide. The solution's pH was changed to 3 and 11 prior to adding TTIP. Samples were characterized by solution separation, pH measurements, and scanning electron microscopy (SEM). From those images, it can be concluded that pore size and frequency is effected by the starting pH of the solution, as well as how the sample is prepped without the precursor of TTIP. Increasing control over porosity yields diverse applications that are more beneficial and efficient.

Loratadine Solubility Enhancement by Amorphous Solid Dispersions with CCAB
Brittany Anderson

Abstract

Loratadine (Lor) is an antihistamine drug used to treat allergy symptoms and hives. However, Lor has low solubility under acidic conditions but improved solubility under neutral pH levels. Amorphous solid dispersion (ASD) has been demonstrated to be an effective strategy to improve solubility of drugs and thus improve bioavailability. Cellulose is the most abundant polysaccharide that is found in nature and its derivatives are very important to pharmaceutical industries. 6-carboxy-cellulose acetate butyrate (CCAB) is a highly new commercial cellulose derivative. Using cellulose derivatives can prevent recrystallization after the drug is released into the GI tract. The goal of this study is to enhance the solubility of Lor using amorphous solid dispersion (ASD) with CCAB. The ASD formulations were prepared by spray drying and analyzed using Ultraviolet- Visible spectroscopy to examine the solubility over an eight-hour drug release study. Using cellulose derivative polymer with Lor did increase should increase the water solubility of this drug.

Vat Photopolymerization of Biodegradable PLGA-based Personalized Dosage Pharmaceuticals

Corey Davis, Emily M. Wilts, and Dr. Timothy E. Long

Department of Chemistry, Macromolecules Innovation Institute, Virginia Tech, Blacksburg, VA

24061

Abstract

Three dimensional (3D) printed pharmaceuticals tailor to meet patients' specific needs. While many patients taking traditional, non-personalized medicines suffer from adverse side effects, personalized dosage pharmaceuticals strive to not only cure these diseases, but also alleviate these side effects. Through the evolution of 3D printing, personalized dosage pharmaceuticals improve both drug therapy and drug release profiles. The focal point of this research is the characterization and synthesis of poly(lactic-co-glycolic)acid (PLGA) photoactive precursors. Characterization through thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and ^1H NMR spectroscopy elucidates the chemical and thermal properties of the synthetic tri-block copolymers. This study utilizes the food energy water system (FEWS) theme through bio-sourced and biodegradable monomers and polymers. Subsequently, this research aims at producing personalized oral tablets with dissimilar release rates by establishing a range of degradation rates.

Post-synthetic modification of porphyrinic zirconium metal-organic frameworks for energy efficient desalination

Miranda De La Garza, Brittany Bonnett, Dr. Amanda Morris



Figure 1: Illustration demonstrating the connection between the food, energy, and water nexus and MOF-545 for desalination.

Abstract:

Incorporating multidisciplinary advancements into producing a viable reverse osmosis (RO) membrane for desalination can lead to innovative technologies and solutions to combat the exhaustion of water resources for lacking communities. However, high-energy consumption, poor molecular selectivity, excessive prices, and fouling of films have obstructed extensive usage of RO membranes. Thin film nanocomposite (TFN) RO membranes comprise of nanoparticles, which allow variance in modifying the selectivity of the film, have become an intriguing technique in improving such drawbacks of membranes. Additionally, the

assimilation of a porous and crystalline material such as metal-organic frameworks (MOFs) can increase RO membrane selectivity and inhibit fouling. Known for its distinctive characteristics, MOF-545, a porphyrinic zirconium MOF, is hydrolytically stable and improves the robustness of membranes. Through research and investigation, the incorporation of attributes displayed by MOFs into the development of RO membranes appears to be a promising avenue to remove unwanted pollutants from unorthodox water supplies. This study encompasses the synthesis of MOF-545, post-synthetic modification (PSM) of the MOF, and examines the effects loading rates of MOF-545 to myristic acid (MA, 0.1 M) have on the perm-selectivity of the MOF structure. The study correspondingly highlights the examination of a MOF loading rate for membrane casting and effectiveness in purifying contaminated water. Analysis revealed that as the MOF was being loaded with increasing amounts of MA, the mesopores became increasingly clogged and had a decline in the quantity of gas absorbed. Additionally, the RO membrane added with modified MOF-545 with a 10:1 loading rate of myristic acid nearly doubled the water flux when compared to an unmodified membrane while maintaining a high salt rejection percentage.

Metal sequestration using sulfonamide-based macrocycles

Roger Dias, Elliot Shelton, Brady Hall, Dr. Michael Schulz

Macromolecules Innovation Institute REU at Virginia Tech 2018

Abstract

Heavy metal pollution of water and a shortage of precious metals is a pressing issue, affecting places from Flint, Michigan to India. In high concentrations, heavy metals such as cadmium, chromium, copper, and lead all produce serious health problems ranging from nausea to death. While toxic, these metals are essential in industries that produce contaminated wastewater such as metal plating, mining, and pickling. While there are many techniques to remove heavy metals from wastewater, many metal chelators are not optimized for this process. In this study, preliminary results of the synthesis of a metal-chelating macrocycle based on the benzenesulfonamide moiety are discussed.

A Comprehensive Study on the Effect of Acetaminophen in Powder Bed Jet Printing

By Charles Ellis

Abstract

The inclusion of an active drug in powder bed binder jet printing is studied in the pursuit of customizable pharmaceutical distribution. The ability to create uniquely customized drugs for an individual is the next innovative step in personalized pharmaceutical care. This field of study creates new methods to effectively treat patients with pharmaceuticals specifically designed for the individual. Unique characteristics include customized rate of dissolving, inclusion of multiple active ingredients in a single pill, and exact dosage conditions dependent on the patient. In this study, acetaminophen is the single active ingredient being reviewed. The question answered within this study is: Will the inclusion of the active pharmaceutical ingredient (API) prevent pills from being printed. In this study several tests were performed as follows: the maximum solubility level of acetaminophen in both ethanol and water was discovered, multiple variations of pills were printed, surface tension and viscosity of binder with API was measured, crushing strength of the pills was measured, and the presence of API in the printed pills was proven.

Morphological Characterization of Cellulose Nanocrystal and Cellulose Nanofibril Composites

George Funk¹, Cailean Pritchard^{2,3}, Dr. Michael J. Bortner^{2,3}

¹Department of Chemical Engineering, University of Minnesota

²Macromolecules Innovation Institute, ³Department of Chemical Engineering, Virginia Tech

Abstract

The morphologies and thermal properties of cellulose nanocrystal (CNC) and cellulose nanofibril (CNF) composite films were characterized. Films of varying concentrations of CNC and CNF were cast in glass petri dishes and oven dried. The morphology of these composite films was characterized using polarized light microscopy (PLM) and atomic force microscopy (AFM). CNC birefringence revealed its location in the composite films and showed localized agglomeration. AFM revealed that the films possessed concentration-dependent morphologies that transitioned from rigid and rod-like to fibrous as CNF concentration increased. Additionally, AFM confirmed CNC agglomeration, specifically in films with higher CNC concentrations. Thermogravimetric analysis (TGA) showed composite degradation temperatures characteristic of both pure CNCs and pure CNFs. Composite degradation rate at 220-240 °C decreased with increasing CNC concentration, suggesting a possible shielding effect, while the degradation rate at 285-320 °C increased with CNC concentration. PLM, AFM, and TGA results suggest that we can tailor CNC/CNF composite morphology to target specific mechanical performance and thermal stability.

Elucidating the Effect of Polymer Architecture on Heavy Metal Chelation

By Sherrie Heinz-Kunert

Abstract

Heavy metal contamination in wastewater is becoming an increasingly pressing issue as industrial pollution continues to increase. Access to clean water is essential for many areas. Although heavy metal removal techniques are available, an alternative method that is inexpensive, effective, and available on an industrial-scale is preferred. By modifying polymer architecture and functionality, we propose that polymers can sequester heavy metals. In this paper we will report the binding abilities of methylphosphonate (MP) to Cu (II) on linear, branched, and bottlebrush polymer architectures.

Dynamic-Mode Cantilever Sensing in Hydrogels

Miharu Koh¹, Alexander P. Haring², and Blake N. Johnson³

Allegheny College¹, Department of Industrial and Systems Engineering²⁻³,
Macromolecules Innovation Institute²⁻³

Virginia Polytechnic Institute of Technology²⁻³, Blacksburg, VA 24060

Abstract

With the increasing demand for efficient, low-cost, and mass food production, securing safe food is still an obstacle to the modern society. Thus developing reliable foodborne pathogen sensors that can be used in actual food samples is critical. In this paper, the fabricated piezoelectric-excited millimeter-sized cantilever (PEMC) sensors, which have been reported as in-liquid biochemical sensors, were investigated to monitor real-time in variable hydrogel medium: alginate and poly(ethylene glycol) dimethacrylate (PEGDA). The cantilever sensor produced distinct resonance peaks in air, deionized water, uncured precursor, and cured hydrogel, disrupting prior assumptions that PEMC sensors would be damped out in non-fluid mediums. Phase angle shifts during curing correlated with hydrogel concentration and mechanical properties. Following curing, the resonance peak was present and stable. Although further investigation is needed, this suggests that the cantilever sensors can be used as biosensors in non-fluid samples such as food.

2Cyclic hydrogel actuators based on an enzyme-substrate feedback system

Kristofer A. Kristofferson¹, Laura E. Hanzly², and Justin R. Barone^{1,2,3}

*¹Macromolecules Innovation Institute, ²Biological Systems Engineering, ³Center for Soft Matter and Biological Physics
Virginia Tech
Blacksburg, VA 24061*

Abstract:

A biocompatible and biodegradable starch-amylase hydrogel cyclic actuator was engineered to function as biological engine fueled by renewable energy. Ideally, this system utilizes naturally occurring polymers, such as proteins, enzymes, and carbohydrates, to form a gel system that bends and unbends via changes in osmotic pressure, a readily available and renewable source of energy input. In order to achieve this cyclic actuating system, a previously devised hydrogel bilayer system consisting of gelatin layers crosslinked with glutaraldehyde was used. Differences in crosslinking between gelatin layers causes the bilayer actuator to bend when swollen. In an attempt to create a soft actuator that can be manipulated to cycle between bent and unbent stages, starch was directly added to the active layer of the gelatin bilayer actuator, in hopes that the polysaccharide would prevent the gelatin matrix from swelling and bending. From there, the enzyme alpha-amylase was added to digest the starch, which would enable the digested starch fragments to diffuse out of the gelatin matrix and allow the actuator to swell and bend. It was found that the equilibrium swelling ratio, Q , of the gelatin layer decreased with increasing starch content. However the addition of alpha-amylase into the system caused the gelatin-starch layer to disintegrate completely, suggesting the starch became an integral part of the structural integrity of the gelatin layer. Future work will focus on exploring different ways of introducing

the starch to the system, such as drying the sample first and then attempting to diffuse the starch into the layer as it swells in distilled water.

Metal-containing Poly (ether imide)s: The Effects of Divalent Metal Cations as Ionic Crosslinkers on Mechanical and Thermal Properties

Elle McKenzie¹, Ben Stovall², Dr. Guoliang Liu²

¹Department of Chemistry, Vassar College, Poughkeepsie, NY

²Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA
Virginia Tech Macromolecules Innovation Institute REU 2018

Abstract

The introduction of metals into polymers has shown to have significant effects on its mechanical and thermal properties, such as an increase in the tensile strength or thermal stability. Within this study, we observed the trends and properties resulting from the incorporation of sulfonate salts of alkaline earth metals/ zinc (Ca, Ba, Sr, and Zn) ionically crosslinked into the backbone of poly(etherimide) (PEI) by varying the cation size and ratio, creating a facile and novel approach compared to conventional incorporation methods. Group 2 metal/ zinc salts of 2,4-diaminobenzenesulfonic acid (DABS-M) were prepared and combined with *m*-phenylenediamine (*m*-PD) to synthesize an ionically crosslinked PEI of approximately 12,000 Da. The metal-crosslinked PEI samples were synthesized with varying percents of DABS-M monomer (10-40%). It was then characterized using TGA and DSC, before being melt pressed and tested for mechanical properties, such as tensile strength.

Synthesis and characterization of bioderived polyureas for controlled ammonia release

John Migliore, B. Tyler White, Timothy E. Long

Macromolecules Innovation Institute, Department of Chemistry, Virginia Tech, Blacksburg, VA

24061

ABSTRACT

Overuse of ammonia in agricultural fertilizers presents a significant threat to surrounding ecosystems due to nitrogen runoff in streams. Controlled and sustained release of ammonia in fertilizer provides a promising solution to mitigate this issue. This study utilizes a recently developed food-energy-water systems (FEWS) approach, while incorporating Green Chemistry principles, to produce novel polyureas for controlled ammonia release. Renewable and biologically-sourced starting materials provide a route for the isocyanate-free synthesis of polyureas through melt polycondensation, allowing for less reactive, nontoxic working conditions. Analysis of Poly(tetramethylene oxide) (PTMO)-based polyureas revealed their chemical and physical properties. The ability to form creasable films suggested that high molecular weight was achieved. Thermal analysis displayed multiple melting temperatures dependent on composition, crystallinity, and hydrogen bonding interactions within segmented polyureas. Tensile testing of segmented polyureas revealed high strain capabilities (300-800%) with tunable stress at break dependent on polyurea composition. These isocyanate-free, bioderived polyureas demonstrate potential for use as controlled ammonia release vehicles for agricultural applications.

Synthesizing Tapered (Cone-Shaped) Bottlebrush Polymers by Sequential Addition of Macromonomers

Ami K. Patel

Abstract

Bottlebrush polymers, or molecular brushes, are a type of graft polymer comprised of a linear backbone and polymeric side-chains. Moreover, bottlebrush polymers of different morphologies have been explored because of their unique properties and applications. In this work, tapered (cone-shaped) bottlebrush polymers were synthesized to study their effectiveness in templating nanoparticles. A series of macromonomers with different molecular weights were synthesized by photoiniferter polymerization using norbornyl functionalized chain transfer agents. These macromonomers had molecular weights ranging from 1.5 to 7.1 kg mol⁻¹ in 1.5 kg mol⁻¹ intervals. Using ring-opening metathesis polymerization (ROMP), while also employing the sequential addition of macromonomers (SAM) approach, tapered bottlebrush polymers were synthesized. Further research will involve synthesizing bottlebrush polymers in the shape of an hourglass, and a cone, to later assess their abilities to be used as templates to form nanoparticles in those shapes to evaluate their plasmonic properties.

Optimizing chitosan and γ -cyclodextrin blends for electrospinning: A sustainable alternative for active food packaging

Emily Plunkett[†], Deepak Poudel[‡], Dr. Cristina Fernández Fraguas[‡]

[†]Department of Chemistry, University of Virginia, [‡]Department of Food Science and Technology, Macromolecules Innovation Institute, Virginia Tech

Abstract

The amount of plastic and food waste produced are two big issues that our world faces. Electrospinning has the potential to address both of these problems. This process can produce biodegradable films to replace plastic packaging as well as active packaging films that can reduce the amount of food wasted due to spoilage. Natural, biodegradable polymers like chitosan can be mixed with active molecules and then spun into a film to make active packaging. Cyclodextrins can also be included in an electrospinning solution to encapsulate and protect fragile active compounds. This study aims to optimize a food-grade chitosan/ γ -cyclodextrin solution in acetic acid for electrospinning nanofiber films. Chitosan/ γ -cyclodextrin blends were characterized by examining rheology and conductivity of the solutions. Adding γ -cyclodextrin is shown to affect the viscosity, viscoelasticity, entanglement concentration, and conductivity of the chitosan solutions. Attempts at electrospinning chitosan/ γ -cyclodextrin blends did not produce well-formed fibers. More work is needed to identify the optimum ratios of the components in this blend in order to produce films made of smooth nanofibers.

Improving the durability of Portland cement concrete using poly(dimethylsiloxane-ethylene oxide) admixtures

By: Mary Shingler, Dr. Kristie Caddick, Dr. Timothy Long



Abstract

Concrete is an energy and water intensive industry, using over 4.4 million BTU of energy per ton of concrete produced, and requiring 2 gigatons of water every year. Because the concrete industry has a significant impact on the environment, mechanisms to reduce that impact, such as improving the durability and longevity of concrete, are important. This project serves to create a more durable Portland cement concrete by improving the hydrophobicity and flexibility, so that less concrete needs to be produced every year, thereby lowering the energy and water consumption during production. Two types of poly(dimethylsiloxane-ethylene oxide), PDMS-PEO, (50-55% and 80-85% PEO) were added to a control concrete mixture in varying percentages by weight of Portland cement, to determine the effects on the compressive and splitting tensile strength and contact angle measurements of the cured concrete. Scanning Electron Microscopy and Energy Dispersive Spectroscopy were used to determine mineral structure and the location of the polymer in the polymer modified concrete. It is shown that the addition of 10 wt % of the 50-55% PDMS-PEO produces a hydrophobic concrete with an initial contact angle greater than 90° . Splitting tensile strength ratios increased with the addition of 0.1 wt % of the 80-85% PDMS-PEO, and 0.25 and 10 wt % of the 50-55% PDMS-PEO.

Studying Intermolecular Interactions within Molecular Ionic Composites

By: Adrienne Smiley, Curt Zanelotti, Dr. Louis A. Madsen

Abstract:

Combining a highly aligned polymer with room-temperature ionic liquids (RTILs) can increase the efficiency and durability of ion-conducting materials used for battery electrolytes. In this study, poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), a rigid rod polyelectrolyte, is dissolved in water and then completes an ion exchange with 1-ethyl-3-methyl imidazolium $[C_2mim]^+$ trifluoromethanesulfonate $[TfO]^-$ to form molecular ionic composites (MICs). Once the MICs were formed, ATR-FTIR analysis was used to investigate the ion-ion and ion-polymer interactions. A schematic depiction was able to be produced from the data gathered.

Graphical Illustration:

