



2020 Gulf Coast Undergraduate Research Symposium

Chemical & Biomolecular Engineering Abstract
Book

Abstracts are presented in the order of presentation. If an abstract does not appear, it is because the student has requested it not be published.

Quantitative Analysis of Dispersion State for Two-dimensional Systems

Rhyu, Jinwook^{1, ‡}, Kim, Dongjae^{1, ‡}, Nam, Jaewook¹

1. Department of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea

([‡] These authors equally contributed to this work.)

Abstract

Various studies have proven that the relation between performance and dispersion states in nearly two-dimensional systems, such as films, elastomers, and nanocomposites. In this respect, many researchers have attempted to quantify the dispersion state of microstructures inside a given system. Several algorithms for analyzing micrographs are proposed to evaluate indicators reflecting dispersion states. The values of these indicators can correlate several performances of a given system, to some degree. This research proposes a new indicator, degree of dispersion (*DoD*), that assesses the dispersion state by combining a random walk simulation with cloud overlap estimation. Based on numerical experiments, we confirm that the proposed indicator possesses various features that need to be satisfied during the proper evaluation of dispersion states: Stability, effectivity, and flexibility. Besides, *DoD* can consider inter- and intra-cluster dispersions naturally. Furthermore, the indicator has an adjustable parameter that can reflect different contexts of various applications.

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. NRF-2018R1A5A1024127 and NRF-2020R1A2C2008141).

Simple and Accurate Experimental Determination of Reactivity Ratios in Nonterminal Terpolymerization Systems.

Adams, Cameron P¹, Uruchurtu Patino, Diego¹, Lynd, Nathaniel A¹

1. McKetta Department of Chemical Engineering, Cockrell School of Engineering, University of Texas at Austin, Austin, Texas

Abstract

The copolymer differential equation introduced by Mayo, Lewis, and Wall in 1944 has since served as the basis for interpreting copolymerization data through the reactivity ratios, which describe the tendency for each monomer to self-propagate. Although significant progress has been made in the intervening decades to accurately measure the composition of copolymers, less progress has been made to accurately extract the reactivity ratios describing copolymerization reactions from compositional kinetic data; relying instead on methods based on the original work from 1944. In 1964, Meyer and Lowry integrated the differential copolymer equation for the terminal copolymerization model. Based on the Meyer-Lowry approach and inspired by more recent advances, we have developed a method to estimate the reactivity ratios of a non-terminal three-monomer system. Terpolymerizations are widely used in research and industry but unlike their copolymer counterparts, there have previously been no accurate methods to extract their reactivity ratios. Knowing the reactivity ratios of a terpolymerization system is key to control of structure-property relationships in multicomponent polymer materials.

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Uruchurtu Patino, Diego¹, Adams, Cameron P¹, Lynd, Nathaniel A¹

1. McKetta Department of Chemical Engineering, Cockrell School of Engineering, University of Texas at Austin, Austin, Texas

Abstract

The copolymer differential equation introduced by Mayo, Lewis, and Wall in 1944 has since served as the basis for interpreting copolymerization data through the reactivity ratios, which describe the tendency for each monomer to self-propagate. Although significant progress has been made in the intervening decades to accurately measure the composition of copolymers, less progress has been made to accurately extract the reactivity ratios describing copolymerization reactions from compositional kinetic data; relying instead on methods based on the original work from 1944. In 1964, Meyer and Lowry integrated the differential copolymer equation for the terminal copolymerization model. Based on the Meyer-Lowry approach and inspired by more recent advances, we have developed a method to estimate the reactivity ratios of a non-terminal three-monomer system. Terpolymerizations are widely used in research and industry but unlike their copolymer counterparts, there have previously been no accurate methods to extract their reactivity ratios. Knowing the reactivity ratios of a terpolymerization system is key to control of structure-property relationships in multicomponent polymer materials.

Electrocatalytic Reduction of TNT by Fe-Salen Ligand Complexes

Miller, Joshua L¹, Janik, Michael J¹, Wong, Andrew J¹, Perdue, Brandon S¹

1. Department of Chemical Engineering, Pennsylvania State University, University Park, PA.

Abstract

Trinitrotoluene (TNT) is a well-known explosive material and environmental hazard. Given these properties, TNT detoxification is important for military and environmental applications, including treating water contaminated by TNT. A common route of detoxifying TNT entails converting its nitro groups to amines to produce triaminotoluene (TAT). In the reaction mechanism, one nitro group is fully reduced to an amine before the next nitro group is reduced.³ For each nitro group, there are two key intermediates: a nitroso (NO) species and a hydroxylamine (NHOH) species. The reduction takes place in an electrochemical cell to simplify the reaction conditions. We wanted to determine if iron-salen ligand complexes can serve as useful catalysts for the electroreduction of TNT. These complexes feature a central iron atom coordinated to four nitrogen atoms and surrounded by ligands.^{1,2} They can undergo oxidation and reduction to modify their catalytic behavior. We applied Density Functional Theory (DFT), an electronic structure method, to analyze the catalytic activity of iron-salen ligand complexes in the electrocatalytic reduction of TNT.

DFT results demonstrated that the fully reduced iron-salen ligand complex can be readily deprotonated. The first oxidation occurred at an equilibrium potential of -1.245 V. In this oxidation, a hydrogen was removed from a nitrogen near the iron atom, causing an oxygen on a nearby ligand to coordinate with the iron atom. The second oxidation took place at an equilibrium potential of -0.896 V. Once a hydrogen was removed from a second nitrogen, another oxygen coordinated with the iron atom. This fully oxidized version of the salen complex was the most stable version of the compound. However, since there were six atoms coordinated to iron, TNT could not interact with this form of the catalyst. Reducing this complex, though unfavorable thermodynamically, freed a coordination site for TNT binding because one of the ligands detached from the iron atom. The resulting partially reduced salen complex could be used as a catalyst for TNT reduction. TNT binding to this complex resulted in an adsorption energy of -0.839 eV, delineating that the salen complex provided significant energy stabilization. A relative energy diagram was constructed for the reduction of TNT by the partially reduced salen complex. As the reaction coordinate increased, the relative energy of the TNT-salen system steadily decreased. A further study utilizing a microkinetic model could be used to examine the kinetics of TNT electrocatalytic reduction. This would help corroborate initial findings that the salen complex is an effective catalyst for TNT reduction.

References:

1. Lytvynenko et al., *Modeling of catalytically active metal complex species and intermediates in reactions of organic halides electroreduction*. Phys. Chem. Chem. Phys., 2015. 17: p. 5594-5605.
2. Lytvynenko et al., *Redox-Active Porous Coordination Polymers Prepared by Trinuclear Heterometallic Pivalate Linking with the Redox-Active Nickel(II) Complex: Synthesis, Structure, Magnetic and Redox Properties, and Electrocatalytic Activity in Organic Compound Dehalogenation in Heterogeneous Medium*. Inorg. Chem., 2014. 53 (10): p. 4970-4979.
3. Soomro et al., *Highly sensitive shape dependent electro-catalysis of TNT molecules using Pd and Pd-Pt alloy based nanostructures*. RSC Adv., 2016. 6: p. 44955-44962.

Modeling the Crosslink Density of Materials Photopolymerized in Additive Manufacturing Processes

Soukaseum, Mya¹, Thomas, Jessica², Korley, LaShanda T. J.^{1,2}

1. Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware
2. Department of Materials Science and Engineering, University of Delaware, Newark, Delaware

Abstract

Liquid based additive manufacturing (AM) is a process in which each layer of a photopolymerizable resin is uniformly cured upon exposure to light to achieve a predetermined part geometry. AM is useful for the rapid production of bio-inspired materials, such as actuating hydrogels. By changing the printing parameters directly, properties of the final material can be tuned. An important physical property of cured samples is crosslink density (ν_c): the moles of crosslinks per unit volume measured via dynamic mechanical testing. Given that this technique does not relate any printing parameters (i.e. part height, intensity, exposure time) to ν_c , data from literature are fitted and statistically analyzed to develop models that capture the influence of critical AM photocuring parameters on crosslink density.

Briefly, cure depth is expanded as a function of wavelength and initiator concentration and related to light intensity, and the initiator concentration is related to the rate of polymerization via Fourier transform infrared spectroscopic conversion (FTIR) data. The expanded intensity function is used in the relationship between energy density and ν_c (A) and the relationship between light intensity, Young's Modulus, and ν_c (B).

Statistically significant models for data fitted via pathways A and B are obtained. Both models show a positive correlation between ν_c and light intensity, exposure time, and distance towards the incident light as predicted in literature. Model A exhibits a distinct plateau after one hour of exposure, representing a maximum in ν_c and the formation of the polymeric network, but a weak dependence on light intensity. Model B did not exhibit a plateau, but is more sensitive to all of the photocuring parameters previously stated and provides greater control over crosslink density. Future work will be aimed towards solidifying the trends exhibited by Model B by fitting experimental data collected in the lab following this model development process.

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Innovative Ceramic Membrane with Ozonation for Wastewater Reuse

Pimentel, Anthony L¹, Liu, Bryan¹, Owen Evan¹, Linden, Karl¹

1. Department of Civil, Architectural, and Environmental Engineering, College of Engineering and Applied Science, University of Colorado Boulder, Boulder, Colorado

Abstract

Wastewater reuse is a growing application in many areas of the world as water scarcity is becoming a major issue due to climate change and exponential population growth. Due to increased water scarcity and engineered technological advancements, wastewater effluent is more commonly treated further than regulated to reuse the water in direct and indirect settings. Membrane filtration is commonly used in these settings to physically separate larger contaminants, but membrane fouling in wastewater is of high concern. Advanced Oxidation Processes (AOPs) such as ozonation and UV can transform organic contaminants and inactivate pathogens, along with the enhancement of micropollutant removal, which are of growing concern.

This study investigated the combined effects of ceramic microfiltration with pre-ozonation compared with other AOPs secondary wastewater effluent treatment. When injecting ozone into wastewater effluent, ozone can react with natural organic matter (NOM) and produce hydroxyl radicals, which are very strong nonselective oxidants and can degrade micropollutants such as pesticides (Wojnarovits and Takacs, 2014) and pharmaceuticals (Yan and Song, 2014). Direct ozone and hydroxyl radical oxidation were studied by measuring total organic carbon (TOC) and ultraviolet absorption 254 (UVA₂₅₄) reduction in secondary wastewater effluent. Ozonation with ceramic microfiltration was compared to other AOPs such as ultraviolet irradiation with hydrogen peroxide treatment (UV/H₂O₂ which is also used to degrade select trace contaminants in drinking water and wastewater applications). In addition to ozone decomposition with the presence of NOM, ozone decomposition can be catalyzed by the surface interaction with select metal oxides, such as those which ceramics are composed of, to produce hydroxyl radicals. A quantitative study of hydroxyl radical production via catalytic ozonation was warranted, as hydroxyl radicals have an extremely rapid half-life (10⁻⁹ s) and are very challenging to track directly. Two methods for measuring hydroxyl radical formation were studied: using para-chlorobenzoic acid (pCBA) as a probe compound and the NASH method. The pCBA method studies the degradation of pCBA via hydroxyl radicals by high performance liquid chromatography (HPLC), while the NASH method investigates the formation of formaldehyde (CH₂O) in the presence of hydroxyl radicals and an ammonium acetate/acetyl acetone solution. Hydroxyl radicals can enhance the abatement of organic contaminants in water in addition to degrading bio foulants on the membrane surface. These bio foulants physically block membrane pores and lead to an increased transmembrane pressure (TMP) needed to push water through the membrane, as well as irreversible membrane fouling, which means the membranes will not be able to recover their original flux, even after intense chemical cleaning. Less membrane fouling leads to less frequent backwashing and chemical cleaning of the membranes, thus lowering costs and extending the lifetime of the membranes. The study found that ozonation coupled with ceramic microfiltration was the most efficient treatment process in reducing TOC (~35-40%) and UVA₂₅₄ (~60-70%) compared to lone ozonation and UV/H₂O₂. Ozonation also effectively extended the ceramic membrane cycle time by reducing the rate of TMP increase and allowed longer times between required backwash cycles. This study proved that AOPs and membrane filtration can enable more efficient and sustainable processes for water reuse applications.

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DMSO Assembling Virus Cages Solubilize UCNPs

Xie, Amberly H¹, Cadena-Nava, Ruben D², Tsvetkova, Irina¹, Dragnea, Bogdan¹

1. Department of Chemistry, Indiana University, Bloomington, IN

2. Center of Nanoscience and Nanotechnology, National Autonomous University of Mexico, Mexico City, Mexico

Abstract

While virus capsid assembly has been extensively studied in environments mimicking *in vivo* conditions, such as with the synthesis of virus-like particles (VLPs), not much is known about virus assembly in buffers containing organic solvents. In this study, Brome Mosaic Virus (BMV) capsid proteins were assembled around both gold nanoparticles (GNP) as well as upconversion nanoparticles (UCNP), which have the unique ability to absorb low energy IR light and emit higher energy visible light. While GNPs can easily be modified to be stable in aqueous buffers, UCNPs are usually only stable in organic solvents. Because of this, assemblies were conducted in different concentrations of DMSO to try and encapsulate the UCNPs. Analysis of assemblies utilized techniques such as transmission electron microscopy, dynamic light scattering, fluorescence measurements, and circular dichroism. It was found that increasing the concentration of DMSO did not affect GNP-VLP assembly nor the BMV capsid proteins themselves. Assembly around UCNPs in buffers with DMSO ultimately proved successful, with the UCNP retaining their optical properties. Not only can these UCNP-VLP be used in medical imaging and cell targeting, but the success of assembly in non-biological conditions opens the door to studying virus assembly in a multitude of environments.

Acknowledgement

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Multiplex Genome Engineering of Yeast Using CRISPR-Cas Technology

Chen, Maple N¹, Gong, Franklin L², Li, Sijin²

1. Department of Biomedical Engineering, Cornell University, Ithaca, NY

2. Department of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY

Abstract

Tetraterpenoids are a class of phytochemicals with great pharmaceutical potential due to their antioxidative and anti-inflammatory properties. Synthesis of tetraterpenoids is native to plants, but the long growth periods and low yield often make it prohibitively expensive to produce high concentrations of tetraterpenoids in plants. As an alternative, yeast can be genetically engineered using the CRISPR-Cas9 system to produce tetraterpenoids with lower associated costs. One tetraterpenoid of interest is zeaxanthin, a carotenoid which has been correlated with lower incidence of eye disease.

Zeaxanthin synthesis is not a native pathway in yeast and requires the integration of many enzymes that convert terpenoid precursors into zeaxanthin. Metabolic flux needs to be redirected towards creating terpenoid precursors in the mevalonate pathway, then genes such as *ERG20* and *BTS1* must be integrated in order to produce the precursor to tetraterpenoids. After that, genes such as *crtYB* must be integrated for tetraterpenoid synthesis. Usually, this would require multiple rounds of integration, however, the use of the delta-integrated CRISPR-Cas9 system could allow us to integrate multiple genes at once into repeated delta sites.

The goal of my work is to validate the delta-integrated CRISPR system, called Di-CRISPR (Shi et al. 2019), by integrating a gene cassette leading to mCherry fluorescent protein expression into yeast. Di-CRISPR takes advantage of the delta transposon site, which is repeated 109 times throughout the yeast genome. By designing the CRISPR guide RNA to target the delta site, up to 109 double stranded breaks can be induced simultaneously, leading to many homologous recombination events that will integrate high copy numbers of the desired gene into the yeast genome. Compared to typical CRISPR integrations, Di-CRISPR has the potential to introduce much higher copy numbers of a gene in a single integration.

A plasmid harboring the Cas9 protein was successfully constructed with a guide RNA targeting the delta site. After the guide RNA for the delta site was ligated into the plasmid backbone harboring the Cas9 protein, Sanger sequencing confirmed the plasmid's successful construction. Secondly, our mCherry plasmid needed to be modified by adding a stop codon to the 3' end of the coding sequence. After creating a corrected coding sequence using PCR, the sequence was assembled into a pE plasmid using Gibson assembly, and Sanger sequencing confirmed the successful insertion of the stop codon.

Six experiments were conducted to validate the successful integration of mCherry into yeast at delta sites. After successful integration, future steps in this project include the integration of multi-gene inserts containing the zeaxanthin synthesis pathway into yeast followed by a feeding assay to quantify the concentration of zeaxanthin produced.

References:

Shi S, Liang Y, Ang EL, Zhao H. Delta Integration CRISPR-Cas (Di-CRISPR) in *Saccharomyces cerevisiae*. *Methods Mol Biol*. 2019;1927:73-91. doi: 10.1007/978-1-4939-9142-6_6. PMID: 30788786.

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Investigating the Effects of RNA Regulators on Metal Nanoparticle Biosynthesis in *Deinococcus Radiodurans*

Patel, Sonia M¹, Chen, Angela², Gonzales, Natalia², Contreras, Lydia²

1. Department of Biochemistry, University of Texas at Austin, Austin, TX.

2. Department of Chemical Engineering, University of Texas at Austin, Austin, TX.

Abstract

Nanoparticles exhibit special properties that enable them to have a variety of applications such as drug delivery, electronics, and antimicrobials. These applications are strongly dependent on nanoparticle size, shape, and morphology and nanoparticles are typically synthesized through chemical methods. However, since this chemical process can be toxic to the environment and humans, recent studies have shifted towards nanoparticle biosynthesis. Nanoparticle biosynthesis is an environmentally friendly alternative that uses microorganisms, such as bacteria, to facilitate metal reduction and form nanoparticles as a stress response mechanism to the presence of toxic metal ions. In bacteria specifically, many stress responses are controlled by RNA regulators which have the ability to dynamically control gene expression and have been utilized previously to metabolically engineer organic products such as amino acids and biofuels.

Our goal was to determine whether RNAs could play a significant role in nanoparticle biosynthesis and the resulting nanoparticle morphology and properties produced by *Deinococcus radiodurans*, an extremophilic bacterium renowned for its high resistance to oxidative stresses.

First, genetic knockouts were generated using PCR and homologous recombination to replace the RNA regulator of interest with an antibiotic resistance gene in the wildtype *Deinococcus radiodurans*. These different strains were then cultured, and silver nanoparticles were synthesized by adding AgNO₃ to the cell-free supernatant. The yield of silver nanoparticles was assessed using UV-vis spectroscopy and we found that some RNA regulators significantly affected the yield, supporting the hypothesis that RNA regulators indeed play a role in nanoparticle biosynthesis. After observing changes in the yield, we were interested in determining if the RNA regulator knockouts also impacted other properties such as antimicrobial and catalytic activity. Antimicrobial activity was characterized through well-diffusion and minimum inhibitory concentration assays. The catalytic activity was then determined by monitoring the ability of the nanoparticles to reduce several organic dyes (methylene blue or congo red) through an optimized colorimetric assay. Together, these characterization results gave insight on the functionality of the nanoparticles produced from the different RNA regulators as we observed changes in the antimicrobial activity and catalytic degradation rates.

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Phylogenetic Analysis of Literature-Induced Mutations of the Cocaine Aptamer via Re-rooting Method

Aziaklo, Alexander F¹, Stovall, Gwendolyn M¹

1. Department of Chemistry: Freshman Research Initiative, University of Texas at Austin, Austin, Texas

Abstract

Aptamers are short strands of nucleotides, formally called oligonucleotides, capable of having a strong affinity to specific macromolecules, discriminating between targets based on a single amino acid or functional group. They act as tags for researchers to track the movement and production of a target for therapeutic and diagnostic applications with significantly more advantages in comparison to utilizing antibodies (Song et al., 2012). Within aptamer literature, there is a distinct lack of consistency pertaining to selection details researchers need to provide when publishing (Dunn et al., 2017). Omission or unexplained alteration of the sequence or procedures within the production of the publication results in unclear instructions for future labs. The purpose of the Aptamer Phylogeny project is to construct a timeline of inconsistencies and missing details across such literature using the snapshot and re-rooting methods and promote stricter guidelines for research paper submissions. With the snapshot method, such a timeline begins with the identification of target-specific papers currently on Google Scholar and denoting the earliest one as the root paper. Relevant information such as the type of nucleic acid, its sequence, and modifications made are recorded and ensuing papers that cite this root are added to a datasheet. Alteration of the sequence in a daughter paper can be thought of as a node that branches off from the root. Figures are then constructed to map the publication errors made by these nodes in forms such as deletions, insertions, and unexplained modifications. The re-rooting method functions to test the hypothesis that errors within literature propagate throughout by establishing each node from the snapshot method as a root and following the timeline of errors in papers that cite this work. It's through the findings of the re-rooting method by the current phylogeny team that a follow-up paper is to be drafted utilizing identical target-specific aptamers to validate the methodology and problematic irregularity within the aptamer community as described by the Alex Miller paper. In this publication, guidelines such as requiring papers to clearly refer to the root paper and placing the aptamer sequence in the materials and methods section have already been devised. Ultimately, gaining awareness and improving the methodology behind these reports will reduce the incorrect reproduction of experiments and bolster aptamer applications in future works.

Acknowledgement – All Aptamer Stream research is supported by the FRI, CNS, as well as HHMI and NIH grants. This work is derived from the research and publication efforts made from Alexandra Miller and the Snapshot Phylogeny Team.

Synthesizing Novel Biobased Molecules for Enhanced Polymer Properties

Trettin, James L, Carter, Prerana, Tessonnier, Jean-Philippe, Shanks, Brent, Cochran, Eric
1. Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa
Center for Biorenewable Chemicals (CBiRC), Ames, IA

Abstract

Biobased molecules are promising building blocks for polymer synthesis as they can provide new and unique properties that are unavailable from conventional petrochemicals. The overarching goal of this research is to explore the chemistry of muconic acid, an unsaturated diacid that is produced from biomass by fermentation using metabolically-engineered bacteria. A cyclic monomer, CH1DA, is produced from a Diels-Alder reaction between trans,trans muconic acid and gamma-Valerolactone (GVL). This monomer is then incorporated as a novel biobased monomer for tuning the properties of PA6,6. While adipic acid and hexamethylenediamine are polymerized in equal proportions to produce PA6,6, varying molar percentages of the adipic acid can be replaced by the novel monomer (10 mol% to 25 mol%) to produce CBAN. Thermogravimetric analysis (TGA) on the new polymer shows that the melting temperature of CBAN decreased compared to conventional nylon 6,6, which implies easier processing for the new biobased polymer. Water uptake tests were conducted and showed an increase in hydrophobicity for CBAN, which is preferable since nylons are susceptible to water absorption that degrades the mechanical properties of the polymer.

While CHDA (1,4-cyclohexanedicarboxylic acid) is commercially available and used in polyester synthesis, our novel biobased monomer, CH1DA, contains an unsaturated double bond that improves rigidity and can be used for polyamide synthesis. Due to the presence of an unsaturated bond in the cyclic monomer, the molecule can be functionalized to impart different enhanced properties, such as flame retardance. As a proof of concept, the flame retardant molecule DOPO will be reacted on to the monomer to produce a novel biobased polymer with enhanced properties. The resulting polymer will be characterized by various thermal and mechanical tests. CH1DA will also be polymerized in 50 mol%, 75 mol%, and 100 mol% replacement of adipic acid to test the effect of molar percentage on mechanical and hydrophilic properties.

No acknowledgments to state

Charge Density Rules For Nature-Inspired Materials

Tjo, Hansen¹, Perry, Sarah L.^{1,2}

1. Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA

2. Institute for Applied Life Sciences, University of Massachusetts Amherst, Amherst, MA

Abstract

Stabilization of thermo-responsive biomolecules represents a long-standing engineering problem. For instance, the effectiveness of vaccine campaigns is limited by the quantities of vaccines that can be transported under refrigerated conditions. In nature, cells store proteins in stress granules through an associative phase separation process termed *complex coacervation*, whereby oppositely-charged macro-ions phase separate into two liquid phases. By inducing complex coacervation in both synthetic and biological macromolecular systems, we look to circumvent this need for refrigeration. However, this effort requires extensive analysis of the phase behavior of our proposed materials.

Using polyelectrolyte-micelle complexes, which are ideal phase-separating platforms due to their physicochemical tunability, we seek to extrapolate design principles governing self-assembly in a broad range of coacervate systems. Electrostatic interactions govern coacervate phase behavior, with an expected 1:1 charge ratio between the charged macro-ions. Nonetheless, the mixed-micelle nature of polyelectrolyte-micelle coacervates results in a ternary system that introduces an additional variable Y : the micellar charge fraction. The critical micellar charge fraction Y_c , where complexation is induced, is a parameter frequently used to characterize polyelectrolyte-micelle systems and has been shown to vary as a function of polymeric and micellar chemistries.

We hypothesize that the charge densities of both the polymer and micelle affect overall phase behavior, which we can test by varying polymeric charge densities and by using steric exclusion to decrease the apparent micellar charge density. Specifically, we use turbidimetry coupled with optical microscopy to characterize the phase behavior of a series of cationic random copolymers of varying charge densities with a panel of anionic mixed-micelles with different neutral hydrophilic head group sizes. Preliminary results support our hypothesis: for a given mixed-micelle, we saw a positive shift in Y_c with decreasing polymer charge density. In other words, a polymer of a lower charge density requires a micelle of a higher surface charge density in order to form coacervates. Moreover, for a given polymer we observed that increasing levels of micelle steric exclusion correlated with increases in Y_c ; we believe these steric effects functionally decrease the micellar surface charge density. We are now applying electrophoretic light scattering to quantify the relationship between the zeta potentials of each cationic co-polymer and anionic mixed-micelle with the critical micellar charge fraction Y_c of their corresponding polymer-micelle complex. Our goal is to establish design rules accounting for the effective charge density of each macro-ion to facilitate the tailored design of materials for biomedicine.

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Effect of Gas-Particle Partitioning on Source Apportionment of Ambient Mass Spectrometry Data

Dinh, Andrew T¹, Bhandari, Sahil¹, Hildebrandt-Ruiz, Lea¹

1. McKetta Department of Chemical Engineering, Cockrell School of Engineering, University of Texas at Austin, Austin, Texas

Abstract

As a part of the Delhi Aerosol Supersite (DAS) campaign, submicron organic aerosol (OA) was measured in spring 2018 in Delhi, India using an Aerodyne aerosol chemical speciation monitor. Previously, we conducted source apportionment using positive matrix factorization (PMF) on this particle phase-only dataset. We obtained three factors: a hydrocarbon-like OA (HOA) factor, a biomass burning OA (BBOA) factor, and an oxidized organic aerosol (OOA) factor. Typically, relative factor contributions are taken from this particle phase-only analysis. However, recent research suggests that the inclusion of either measured or modeled gaseous organic compounds allows improved characterization of sources by accounting for the non-linearity effects of gas-particle partitioning.

Here, we estimated gas phase concentrations corresponding to particle phase-only PMF factors HOA, BBOA, and OOA by using volatility basis set (VBS) parameters and assuming phase equilibrium conditions. We applied PMF to the combined gaseous and particle-phase data using the EPA PMF tool. This combined PMF yielded three factors similar in mass spectra to the particle phase-only analysis but different in relative contributions and absolute loadings. Particularly, compared to the particle phase-only analysis, the combined analysis amplifies the contributions of the HOA and BBOA factors, especially during nighttime. Conversely, the loadings of these factors are significantly amplified, especially during daytime. This combined particle-gas phase source apportionment of mass spectrometry data may more accurately reflect the relative importance of different sources contributing to particulate matter formation. Further testing with different VBS parameters and PMF error estimation methods showed that the source apportionment is robust. When comparing the gas phase estimates with the combined PMF analysis, the factor contributions agreed well, suggesting that combined PMF analysis is not needed and that the VBS-based gas phase estimates is sufficient for the purpose of source apportionment.

Thermoset Blends of an Epoxy Resin and Polydicyclopentadiene

Oladipo, Arafat O, Sontgerath, Stephanie, Berg, Rosalie, Robertson, Megan L

Department of Chemical Engineering, Cullen College of Engineering, University of Houston,
Houston, Texas

Abstract

Polymer blending is an effective strategy to develop new materials that possess beneficial properties, combining desirable attributes of two or more polymers. The mechanical properties of two thermoset polymers were manipulated through the development of thermoset blends. The thermoset blend system was made of epoxy resin contributing to high tensile strength and modulus and polydicyclopentadiene (PDCPD) which has a higher toughness and impact strength as compared to other thermoset polymers. Ultra-small-angle and small-angle X-ray scattering analysis was used to probe the structure of the thermoset blends as it evolved during the curing process. To further understand how the structure of the sample evolves and how the phase separation progresses certain variables such as interparticle distance, volume fraction of hard spheres as they change with time are studied.

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Engineering an Inexpensive, Temperature-Controlled Instrument for the Accurate Deterministic Transfer of 2D Materials

Diaz-Arauzo, Santiago¹, Murillo, Melanie², Sanchez, Daniel³, Lu, Nanshu⁴

1. McKetta Department of Chemical Engineering, Cockrell School of Engineering, University of Texas at Austin, Austin, TX
2. Walker Department of Mechanical Engineering, Cockrell School of Engineering, University of Texas at Austin, Austin, TX
3. Department of Material Science and Engineering, Cockrell School of Engineering, University of Texas at Austin, Austin, TX
4. Department of Aerospace Engineering and Engineering Mechanics, Center for Mechanics of Solids, Structures and Materials, The University of Texas at Austin, Austin, TX

Abstract

After the discovery of 2D materials, such as graphene, methods to isolate and place 2D materials on foreign substrates with high precision continues to be one of the most important breakthroughs in the research of 2D materials. As a result, the development of these methods led to the creation of stacked, unlike 2D materials, known as van der Waals heterostructures (vdWs). The investigation of these structures requires expensive mechanical and optical instruments to effectively identify them, further preventing the progress of research on 2D materials. Despite the discovery and publication of a low-budget system for transfer ranging between 7000-8000 USD, this price can still hamper the implementation of the system for effective, conventional studies. Thus, the goal aimed to construct an inexpensive transfer system with a temperature-controlled stage, allowing for the efficient transfer of 2D materials onto foreign substrates.

The first step in the assembly of these TGBs involves the exfoliation of graphene onto silicon oxide treated wafers with Scotch tape. The crystals adhered to the surface of the tape are transferred to the surface of the silicon and annealed at 100°C for two minutes. Then the surface of the silicon oxide wafer is inspected under an optical microscope to locate a flake for transfer. Afterwards, a polypropylene carbonate (PPC) coated polydimethylsiloxane (PDMS) block is mounted on a glass slide to pick up graphene and release 2D materials. Using a micromanipulator, the x , y , and z axes can adjust to locate the 2D material through a camera. By tuning the temperature above the boiling point of water and the glass transition of the polymer, graphene flakes can be picked up or dropped down. Higher temperatures throughout the transfer process prevent delamination of PPC from PDMS as PDMS can be plasma-treated to promote strong adhesion between the polymer block. Temperatures above 110°C favor vdWs adhesion between another 2D material, hexagonal boron nitride (hBN) and graphene. At 40 °C, hBN can be lifted off a substrate using the polymer block. As such, by tuning the temperature at which different adhesions are promoted, located graphene flakes can be picked up and deposited onto foreign substrates.

An inexpensive, temperature-controlled instrument allowed for the precise transfer of graphene onto foreign substrates capable of forming TGBs. The understanding of interactions between electrons and phonons in atomically thin structures is crucial for the manufacture of 2D devices. Moreover, the study of interlayer coupling in stacked graphene structures remains a novel study and the use of an instrument capable of fabricating such structures will enable the investigation into the relationship of TGBs.

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Engineering Thermo- and Photo-Responsive Fluidic Pumps using Liquid Crystal Elastomers

Cetinkaya, Sueda H¹, Barnes, Morgan G², Verduzco, Rafael^{2,3}

1. Department of Biochemistry & Cell Biology, Rice University, Houston, TX
2. Department of Materials Science & Nanoengineering, Rice University, Houston, TX
3. Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX

Abstract

Liquid crystal elastomers (LCEs) are loosely cross-linked polymer networks with unique optical, mechanical, and physical properties that enable them to shape-shift with thermal stimuli. These unique elastomers have a nematic phase where the liquid crystalline molecules have orientational order at low temperatures and an isotropic phase where there is no order at elevated temperatures. Recent work has demonstrated that dual-network LCEs can be initially cured in the isotropic state, and shape programmed in the nematic state through UV curing. When heated above or cooled below the nematic to isotropic transition temperature, T_{NI} , the LCE can reversibly shape shift between the initially cured and the mechanically programmed shape.

Current applications of LCEs range between soft robotics, 4D printing, and biomedical devices. We attempt to expand the potential applications of LCEs by making self-pumping fluidic devices. We program an LCE device to have a collapsible fluidic channel capable of pumping water in response to higher temperatures. In addition, we expand current chemistries to include a photo-responsive dye and additional monomers to produce LCEs with tunable T_{NI} values. The resulting pumps can be controlled using a cascading laser or uniform heat source to yield a bidirectional or one directional pumping, respectively. In the future, the fabrication of these functional LCE fluidic pumps can be translated to a smaller scale in order to create microfluidic devices for alternative applications.

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Computer Modeling of Aerosol Particle Transport through Lung Mucosa

Bartlett, Blake A¹, Feng, Yu¹, Fromen, Catherine A², Ford Versypt, Ashlee N¹

1. School of Chemical Engineering, College of Engineering, Architecture, and Technology, Oklahoma State University, Stillwater, OK
2. Department of Chemical and Biomolecular Engineering, College of Engineering, University of Delaware, Newark, DE

Abstract

Diseases of the lung are some of the most common and deadly in the world, accounting for 4 of the top 10 global causes of death according to the World Health Organization. Existing treatments, if any exist, tend to be extremely rigorous, invasive, and time-consuming. Further, due to the poor bioavailability of drugs traditionally administered orally or through injection, these treatments are not very effective. Technology is emerging that allows an aerosolized drug dosage to be delivered directly to the diseased area; however, the mucus layer separating the airways from the tissue (and the blood) remains a barrier to this method. In order to combat this, we have constructed a physics-based computer model of the mucosal interface between the airways and the lung tissues, providing a much-needed insight into how a vaccine, antibiotic, or other drug must behave to effectively reach the target tissue in various lung regions.

The lung has a phenomenal system called the mucociliary clearance mechanism in place to clear foreign particles (including cigarette ash, dust, and bacteria), prevent infection, and keep the lungs healthy. A layer of mucus on the surface of the inner lung is constantly pushed upward towards the throat by a bed of cilia, and most particles that impact on the mucus are cleared from the lungs quickly and without incident. However, when it fails to prevent a disease from being contracted, it remains a barrier to drug delivery, as those particles must cross the same thick, non-Newtonian mucus layer.

The model uses COMSOL Multiphysics software to visualize the mucosa as a cross-section. Data from the literature is used to determine details like dimensions, velocity, and viscosity. The mucus layer moves upwards towards the throat in laminar flow, imitating the mucociliary effect, and the underlying periciliary layer has slower net movement due to the regular beating of the cilia that move the mucus. The viscoelastic properties of mucus are accounted for in the model, with its shear-thinning effects parametrized to a Carreau fluid model. The “drug” particles enter from the airway side and move through the fluid by convection. The Stokes-Einstein equation is used in conjunction with a hydrodynamic and steric hindrance model to calculate an effective diffusivity through the network of glycoproteins that comprises the mucus. Given these inputs, the model outputs an image showing how much, if any, of the administered particles diffuse through the mucosa and reach the tissue. The model is extremely customizable, easily modified to simulate other drugs or any other particle (including pathogens) so long as some properties are known. Variables have been parametrized to find more complex relationships, like effective diffusivity, from an input of more readily available information, like particle radius. Lung conditions can also be quickly altered to meet the needs of the user (for example, the mucus layer is much thinner in the alveolar region, and the mucus of cystic fibrosis patients is much denser than average). Thus, the model can quickly provide greater insight into the efficacy of new lung treatments, biomechanics of pathogens, and capacity of prophylactics. We are currently extending this work to consider treatments and vaccines for SARS-CoV-2.

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Artificial Intelligence in the Diagnosis of Glaucoma using Tomography Angiography (OCTA)

Awkal, Jacob A,^{1,2,3} Shariff, Muhammed A,³ Montillo, Albert,⁴ Angirekula, Ashika,¹ Zuberi, Hafsa,¹ **Kooner, Karanjit S**¹

1. Department of Ophthalmology, University of Texas Southwestern Medical Center, Dallas, TX
2. Department of Pharmacology, University of Texas Southwestern Medical Center, Dallas, TX
3. Department of Biomedical Engineering, University of Texas at Dallas, Richardson, TX
4. Department of Bioinformatics, University of Texas Southwestern Medical Center, Dallas, TX

Abstract

Glaucoma is the leading cause of irreversible blindness worldwide and is characterized by progressive neurodegeneration of the retinal ganglion cells. The etiology is poorly understood, but prevalent theories connect damage to elevated intraocular pressure (IOP), mechanical insult, and vascular insult. Current diagnosis of glaucoma relies on visual field testing, visualization of the optic disc, and measurements of IOP, which are all inherently inconsistent and subjective. Optical coherence tomography angiography (OCTA) is an imaging technique that offers objective measures of structural and vascular parameters of the optic nerve head and retina, but the deluge of raw data produced from each scan poses a challenge for comprehensive clinical assessment. Therefore, the purpose of our study was to develop a machine learning (ML) algorithm based clinical decision support tool to help clinicians differentiate between normal and glaucomatous eyes as well as characterize the severity of glaucoma in patients.

In this Institutional Review Board (IRB) approved retrospective study, 1371 eligible eyes, which include 462 healthy eyes (HE) and 909 glaucomatous eyes (GE) (377 ocular hypertension, 160 mild, 156 moderate, 216 severe) from 735 subjects seen at a UT Southwestern glaucoma clinic were used. Parameters collected included demographic data, retinal nerve fiber layer thicknesses and vessel densities. Models were divided into two problem categories: i) a two-class problem to distinguish between HE and GE and ii) a four-class problem to distinguish between HE, mild, moderate, and severe glaucoma. A rigorous *nested* stratified, group 5x10 fold cross validation strategy was applied to partition the data. The performances of six ML algorithms were compared using both classical and deep learning approaches. Over 2500 ML models were optimized using random search, with model performance compared using mean validation accuracy. Final performance is reported on held out test data using accuracy and F1 scores. Decision trees and feature importance were produced for the final model.

Amongst the six algorithms, XGBoost achieved the highest test performance for both the two-class problem (F1 score 83.8%; accuracy 83.9%) and the four-class problem (F1 score 62.4%; accuracy 71.3%). Additionally, our highest performing model identified inferior temporal vessel density, a feature unique to OCTA, as the most important feature to distinguish controls from glaucoma, followed by inferior hemisphere vessel density and inferior temporal retinal nerve fiber layer (RNFL). However random forest and decision trees identified RNFL peripapillary thickness as the most important feature.

Our large-scale analysis from 1371 ethnically diverse eyes is one of the first to apply classical and deep learning approaches to OCTA parameters. We demonstrated the ability for demographic and OCTA parameters to aid clinicians in staging glaucoma diagnoses. Our unique developmental algorithms characterized by using demographically diverse data sets in conjunction with standard OCTA protocols will aid clinicians in staging glaucoma diagnoses with high accuracy.

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Utilizing Spectroelectrochemical Detection to Improve Sensitivity in the Shear Enhanced Lab on a Chip Device

Burgula, Shweta¹, Zhenglong Li²

1. Department of Chemical and Biological Engineering Rensselaer Polytechnic Institute, Troy, New York
2. Department of Chemical and Materials Engineering, New Jersey Institute of Technology, Newark, New Jersey

Abstract

Pathogen detection is currently limited by a lack of widespread access to equipment that is portable and accurate. Point of care detection techniques strive to make detection more accessible for healthcare applications. One example is a lab-on-a-chip device which detects changes in properties of the chip, including electrical resistance and optical absorbance, after running a sample through the channel. Substrates in the chip would bind to biomarkers of interest from the sample, and thus change the overall properties of the chip. These devices are often effective in either detecting molecules in a sample (called sensitivity) or differentiating similar molecules (called selectivity). However, they may fail to achieve high sensitivity and selectivity simultaneously, thus reducing accuracy by either creating false negatives or false positives, respectively. In order to achieve higher sensitivity a new technique is being developed, in which carbon nanotubes (CNT) or other materials are packed into the channel, creating a web through which the sample has to navigate. This creates turbulent flow to enhance mixing and creates more active locations for the biomarkers to bind. Additionally it enhances the shear force of the device, thus improving selectivity by washing away different molecules with similar structures.

Until now, the device only utilizes one type of detection, which limits the sensitivity. This paper addresses the potential of optical detection to be used as a secondary measure to further enhance sensitivity. In order to add an optical component, it is necessary to replace CNT with another optically reactive nanotube. This involves testing for an appropriate electrochemical response, ensuring an ability to functionalize the nanotube, and gathering data for optical reactivity. Due to its versatile properties such as being a dielectric and highly optically reactive, rhenium disulfide (ReS_2) was chosen as a potential replacement.

By replacing the CNT with the optically reactive nanotubes ReS_2 , it was found that the change in current through the chip caused by an induced AC voltage varied based on the concentration of the sample. This variation in the chip's properties was consistent with the data gathered for chips packed with CNT. The similarities remained regardless of different electrode configurations and sample concentrations, indicating that ReS_2 is electrochemically similar to CNT. Therefore, these substances can be used for spectroelectrochemical detection in place of CNT, as the electrochemical detection will act similarly to CNT. Spectroelectrochemical analysis can greatly improve sensitivity and with further testing, the shear enhanced lab on a chip design can incorporate multiple detection methods. Future works include testing for changes in optical properties caused by biomarker build up and functionalizing ReS_2 to improve selectivity.

Overall, the use of ReS_2 , a dielectric material with excellent optical properties, in place of CNT can allow for a secondary detection technique of optical detection. Utilizing spectroelectrochemical detection can greatly enhance sensitivity of the chip and allow for more accurate results. The work in this paper proves that ReS_2 is a suitable candidate for electrical and optical detection.

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Development of A Vascularized Tissue-Engineered Skeletal Muscle Containing Adipocytes

Howland, Kennedy K¹, Acosta, Francisca M^{1,2}, Rathbone, Christopher R¹

1. University of Texas at San Antonio, 12346, Department of Biomedical Engineering and Chemical Engineering, San Antonio, Texas, United States, 78249-1644
2. UTSA-UTSA Joint Graduate Program in Biomedical Engineering, One UTSA Circle, San Antonio, Texas, United States, 78249-1644.

Abstract

Tissue-engineered skeletal muscle (TE-SkM) is a promising tool for applications in disease modeling and regenerative medicine. While numerous TE-SkM models have been created utilizing various techniques and cell sources, further work is needed in creating a model that accurately mimics the *in vivo* environment and metabolic function of diseased skeletal muscle. Two key components for studying this are adipose tissue and vessels. Fat has been observed to infiltrate skeletal muscle in various pathological settings, while vessels are necessary for meeting the high energetic demand in muscle activity. In the current study, a triculture TE-SkM model was developed that contains myogenic precursor cells (MPCs), adipocytes, and microvessels derived from adipose tissue (microvascular fragments (MVs)). This objective was accomplished by culturing MPCs with and without MVs in two different adipogenic media conditions. Consequently, we demonstrated the ability to recapitulate skeletal muscle in different pathological states using a combination of cellular inputs and culture conditions.

The most notable mechanical characteristics included compaction, which was higher in constructs containing MPCs and MVs (MPCMVF), although significantly lower in adipogenic conditions; and young's modulus and ultimate tensile strength which were greater in MPCMVF constructs compared to MPCs alone, although they decreased in adipogenic conditions. These results indicate that adipogenesis negatively impacts mechanical properties. Histological staining with BODIPY and GS-Lectin I, to assess lipid droplets and vessels, respectively, indicated that adipocyte formation occurred in constructs under the MM/AM and MM/AM+ conditions with more adipogenesis in MM/AM+. Additionally, we found addition of MVs increased adipocyte formation in MPCMVF constructs more than MPC only, which may be attributed to adipogenic precursors within MVs. Finally, all MPCMVF samples showed vessel growth; however, the vessel structure and integrity decreased in MM/AM and even more in MM/AM+ which may be indicative of complex intercellular communication affecting angiogenesis in the presence of adipocytes.

The results of this study indicate that an *in vitro* culture of MPCs, MVs, and adipocytes confers significant changes to TE-SkM metabolism and mechanical characteristics as compared to constructs with MPCs alone. Future research should focus on the adaptation of these conditions to mimic disease states and optimization of constructs for applications in personalized medicine.

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