CROSSLINKING CO$_2$-SWITCHABLE POLYMERS FOR PAINTS AND COATINGS APPLICATIONS

RAZ ABBASI

The emission of volatile organic compounds (VOCs) from solvent-based paints and coatings, with its adverse effects on both human health and the environment, has prompted this industry to shift towards more eco-friendly alternatives. Water-based paints and coatings, however, require a complex film formation process involving the coalescence of colloidal polymeric particles in the aqueous medium which adversely affects the critical properties of the film. Despite the advances in water-based formulations, they are still outperformed by solvent-based coatings, particularly in high performance applications. Our group previously demonstrated the potential of CO$_2$-switchable polymers in paints and coatings applications to achieve an aqueous zero-VOC formulation that uses the same film formation process as solvent-based formulations. The normally water-insoluble CO$_2$-switchable polymer can be fully dissolved in carbonated water rather than organic solvents. Subsequently, upon application of the solution to a surface, the polymer switches to a water-insoluble form as the CO$_2$ and water evaporate. This technology offers both environmental friendliness and high performance.
In this study, we focus on improving the solvent resistance of the resulting coatings by utilizing a crosslinking reaction. In order to achieve a 1K crosslinking system, the crosslinking reaction should be hindered when CO\textsubscript{2} is present to achieve stability and occur during the film formation process as the CO\textsubscript{2} evaporates. To accomplish this goal, possible reactions are initially investigated using model compounds that mimic the structure of the polymer and crosslinking agent in terms of their reactivity in the presence and absence of CO\textsubscript{2}. The promising candidates were then applied in a coating formulation and evaluated in terms of the performance of the crosslinked coatings and the stability of the formulation.

The proposed approach for enhancing the solvent resistance of coatings made from CO\textsubscript{2}-switchable polymers should lead to the development of a new environmentally friendly and high performance coating and contribute significantly to reducing VOC emissions arising from the paints and coatings industry. Furthermore, the crosslinking chemistry that relies on CO\textsubscript{2} switching could bring significant advantages to the field of CO\textsubscript{2}-switchable polymers beyond paints and coatings applications.
The tertiary amine group of 2-(dimethylamino)ethyl methacrylate (DMAEMA) imparts stimuli-responsiveness to polymer products for novel coatings, biomedical, conductive and environmental applications. The responsiveness of these materials to pH depends on both the amount of DMAEMA in the polymer and the distribution of the functionality among as well as along the polymer chains. Thus, the synthesis of these polymers, either by conventional free-radical or reversible-deactivation radical polymerization, is impacted by monomer ionization and hydrolysis in aqueous solution. When polymerized at the natural system pH of 10.1, a significant fraction of the non-ionized monomer is consumed by a competing hydrolysis reaction. While lowering pH decreases the loss of monomer by hydrolysis, the rates of termination and propagation of the protonated version of the monomer differ from the unprotonated monomer. Thus, a better understanding of DMAEMA polymerization kinetics is needed to guide process and product development.
As a first step towards this goal, a kinetic model is developed to capture the influence of hydrolysis and monomer protonation on polymerization. The model is used to guide experiments, with nuclear magnetic resonance (NMR) spectroscopy used as a tool to study the kinetics of hydrolysis and polymerization as a function of pH and temperature. In addition, the pulsed laser polymerization/size exclusion chromatography technique is used to evaluate the influence of solvent on DMAEMA propagation kinetics. As improved estimates of key rate coefficients are obtained, the model will be used to guide reactor selection and suitable operating conditions to produce DMAEMA-containing polymers.
While Cu-mediated polymerization has proven to be a method to engineer complex polymer microstructures in the lab for research applications, efforts are still required to scale-up the chemistry in a cost-effective manner for commercial production\(^1\). We are developing a robust process that is compatible with current operating practices and the wide range of acrylates and methacrylates used to produce acrylic coatings resins. Our process runs at low temperatures (40 to 60 °C) and low solvent content using inexpensive reagents to produce block copolymers to high conversion (> 90%) with a reaction time under 4.5 h. The one-pot process uses the same semi-batch operating strategy and reaction times used commercially to produce random acrylic copolymers by conventional free-radical polymerization at much higher operating temperatures. These mild operating conditions for the Cu-mediated process are enabled by using ascorbic acid or Ascorbyl Palmitate as an environmentally benign reducing agent to speed up the reaction while also reducing the level of copper catalyst in the final solution to less than 50 ppm.\(^1\) The advantages of the process will be outlined using the 12 Principles of Green Chemistry.\(^2\)
The process has been developed using methyl acrylate (MA) and diethylene glycol di(ethylene glycol) methyl ether methacrylate (DEGMEMA) as representative acrylate and methacrylate monomers. The efficient production of acrylate-acrylate (MA with either butyl acrylate or 2-methoxyethyl acrylate) and DEGMEMA-MA methacrylate-acrylate block copolymers has been demonstrated. Work is ongoing to further reduce the copper levels in the process while maintaining robust operation, different solvents, as well as to demonstrate the ability to operate the process with functional monomers.

As the world combats climate change, novel innovative energy storage solutions are needed to ensure a smooth transition away from fossil fuels. Batteries and supercapacitors are two potential energy storage solutions, each with their advantages and disadvantages. Hence, there is considerable research on their hybridization to combine the benefits of both technologies and provide a high energy and power density energy storage solution. Many hybrid systems, however, tend to use transition metals, such as vanadium, which are scarce and difficult to recycle. There is a growing need to explore alternative redox-active species such as nitroxide radicals like 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) which is particularly attractive due to high redox potentials and fast reaction kinetics. In this work, we report a novel ionic liquid-based battery-supercapacitor hybrid that utilizes bipolar TEMPO to enhance its energy density. Reduced graphene oxide (rGO) aerogels, self-assembled via hydrothermal reduction, are used to provide binder-free and high specific surface area electrodes. 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF₄) is selected given its high ionic conductivity relative to other ionic liquids, making it an ideal supercapacitor electrolyte. We demonstrate that EMIM BF₄ is capable of long-term aminoxy anion stabilization, allowing for the exploitation of all three oxidation states of TEMPO. The resulting device can operate at exceedingly high current densities while maintaining redox functionality that improves energy density over a typical supercapacitor, and exhibits exceptional cycling stability, providing an environmentally friendly alternative to metal-based battery-supercapacitor hybrids.
Free-radical photopolymerization is a pivotal method in the production of films, coatings, and a variety of optical, dental, and microelectronic applications. A dynamic model is proposed for the photopolymerization of 1,6-hexane-diol diacrylate (HDDA) with a bifunctional initiator bisacylphosphine oxide (BAPO) in the presence of oxygen. This partial-differential-equation (PDE) model predicts time- and spatially-varying vinyl-group conversion as well as concentrations of monomer, initiator, oxygen, and seven types of radicals. Additionally, diffusivities of oxygen, BAPO and HDDA are obtained experimentally. Oxygen-kinetic and free-volume related parameters are estimated using real-time Fourier-transform infrared (FTIR) conversion data. FTIR experiments were conducted using a range of film thicknesses (8 – 17 μm), BAPO levels (1 – 4 wt%) and light intensities (200 – 6000 W/m²). The model predicts qualitative trends. Conversion predictions for runs with high intensities (≥ 5000 W/m²) and high BAPO (4 wt%) are accurate with a root-mean-squared error (RMSE) of 0.04. Larger RMSE (0.13) for runs with lower intensities and BAPO indicates that improved parameter estimates are required. Parameter estimates will be updated in future using a model that accounts for shrinkage during polymerization.
The increasing carbon dioxide (CO₂) concentration in the atmosphere brings challenges to the global ecological environment. Electrochemical CO₂ conversion (ECC) to chemicals and fuels is one of the efficient CO₂ utilization technologies because of the mild reaction environment and high-value-added products. However, the traditional ECC system requires highly pure and compressed CO₂ as the reaction feedstock, leading to extra energy expenditures for gas purification, compassion and transportation. In this work, we designed a system that integrates CO₂ capture and electro-reduction technologies, which is able to electro-reduce CO₂ from capture media to products. Furthermore, we came up with a novel catalyst that is capable of maintaining a highly active surface for hydrocarbon production. In particular, 60% Faradic efficiency (FE) of methane production could be achieved at a current density of approximately 500 mA/cm², and an over-600-hour benchmarked operation with around 70% FE was stably obtained at a current density over 200 mA/cm² as well. Towards an industrial perspective, the scalability of this system was evaluated by feeding it with a simulated CO₂ concentration of flue gas into the capture media. Additionally, the system’s adaptability to intermittent operation modes, specifically day-on and night-off cycles, was assessed to facilitate the integration of solar energy utilization. This work provides a promising avenue for the industrial application of ECC, leveraging renewable energy for sustainable CO₂ utilization.
Due to the intricate microbial processes involved in anaerobic digestion (AD), predicting and modeling outcomes can be challenging, and the utilization of machine learning (ML) holds promise for enhancing comprehension and management of co-digestion processes. This study aims to model and optimize the process of anaerobic co-digestion of wastewater activated sludge (WAS) and food waste (FW). For this purpose, three type of ML models including random forest (RF), XGBoost, and artificial neural networks (ANN) are applied on data collected from the last two decades (754 data) to predict methane yield and to analyze the impact of substrate characteristics and operational parameters on methane production. Also, mixing ratio of substrate and co-substrate is highly significant. All the previous research on co-digestion have focused to find optimum mixing ratio for distinct characteristics of WAS and FW. This study extends optimization efforts, employing dual annealing for global optimization. Results indicate the superiority of regularized ANN over its unregularized counterpart, addressing overfitting issues. The model was fitted with R² value of 0.86 and NRMSE of 0.31 on the entire dataset and was used for optimization on seven candidate points with fixed features to find maximum methane yield for an optimum mixing ratio.
MAPPING THE JOURNEYS OF SCIENCE-BASED ACADEMIC ENTREPRENEURS IN THE QUEEN'S UNIVERSITY ECOSYSTEM

BRUNA GUARINO MORAES

Societies are looking to universities to solve pressing global problems and provide economic opportunity through the generation and transfer of research informed knowledge. Previous research has shown that Canada invests significantly in university-anchored research but underperforms in business-related research. Additionally, assessments of technology transfer historically have tended to focus on more readily measurable outputs (e.g., invention disclosures and patents) that don’t necessarily provide a comprehensive view of the transfer to impact of university research. The objective of this study is to delve deeper and identify significant factors and pathways influencing academic entrepreneurs in STEM and Health Science fields in the Queen’s University ecosystem. Survey and interview data gathered in this study, which include examining the phases of venture formation and growth and founder entrepreneurial journeys, will provide contextual data to identify important factors and interventions for university science-based research commercialization. Utilizing process-oriented case study analysis alongside modern data visualization tools will enable the clustering of variables and the creation of visual and conceptual models to elucidate academic entrepreneurial pathways. This approach is underpinned by insights derived from coding and the comprehensive assessment of interview and survey data. A quantitative and statistical analysis from the survey along with a multivariate regression model will complement the study to develop a better understanding of the frameworks influencing the Queen’s University anchored innovation ecosystem and provide policy and programming recommendations.
ON RELU NEURAL NETWORKS AS PIECEWISE LINEAR SURROGATE MODELS

AMIRHOSSEIN HOSSEINI

Continuous piecewise linear (CPWL) surrogate models are increasingly used in process systems engineering to accurately represent complex, nonlinear data relationships. Neural Networks with ReLU activation functions (ReLU-NN) have become a common method to represent CPWL models. However, the intricacies of the linear pieces generated by these networks have yet to be fully explored. In this study, we proposed exact mathematical expressions for linear functions and linear regions of small rectifier networks. Moreover, we analyzed the performance of the rectifier networks from a polyhedral perspective and introduced the three major challenges associated with these models: redundancy, degeneracy, and low efficiency. Furthermore, we explore Difference-of-convex continuous piecewise linear (DC CPWL) approximation as an alternative representation of CPWL functions and compare it to ReLU-based shallow and deep Neural Networks across industrial case studies. Our findings demonstrate that DC CPWL consistently yields highly efficient models without the issues of redundancy and degeneracy while ReLU-NN representation generates less efficient models with several inefficient linear regions.
Polyhydroxyalkanoates (PHAs) are naturally occurring biopolymesters that are promising alternatives to petroleum-based polymers. There are two major types of PHA, short-chain-length (scl) and medium-chain-length (mcl). Copolymers featuring both scl and mcl repeating units have been found to possess superior physical properties conducive to industrial processing and applications. The incorporation of subunits with vinyl functional groups will further increase their potential applications, allowing the synthesis of graft copolymers, attachment of bioactive molecules, and/or controlled crosslinking. Previous studies have shown the production of scl PHA with vinyl groups using a costly fatty acid as carbon source, renders the product uneconomical.
*Pseudomonas putida* is a well-known bacterial strain for mcl PHA production. A mutant *P. putida* strain was constructed previously, by deleting the *phaC* genes from *P. putida* KT2440 and introducing with the *phaPCJ* genes from *Aeromonas hydrophila*, a scl-mcl producer. The specificity of the *A. hydrophila phaC* synthase and the strain’s resistance to fatty acids were studied by feeding it with various fatty acids, including butyric acid, valeric acid, caproic acid, hexanoic acid, and octanoic acid, across different concentrations. The synthase exhibited a preference towards acyl-CoA with chain length ranging from 3-hydroxybutyrate (3HB) to 3-hydroxyhexanoate (3HHx). Chemostat studies were conducted to optimize the feeding conditions to study the production of scl-mcl PHA with vinyl groups from less expensive carbon sources. These studies also demonstrated the relatively high substrate specificity of the *Aeromonas hydrophila* PHA synthase.
Understanding the orientation of polymer molecules under flow is advantageous in designing high performance composites; however, detailed knowledge is scarce, as opposed to those at rest, since there are only a few techniques that are able to measure it. One of these techniques is small-angle neutron scattering (SANS), but the literature on orientation distributions remains limited as only two traditional perspectives are considered (tangential and radial positions). In this paper, we aim to learn more about molecule orientation during flow by analyzing the system from different positions. We use worm-like micelles as our model system which is subjected neutron scattering coupled with a rheometer (rheo- SANS). We expand upon the traditional radial and tangential rheo-SANS measurements to include intermediate scattering positions from which we are able to measure the polydispersity of micelle orientation. We call this method rheo-SANS slices. We anticipate that the development of this comprehensive analysis technique will lead to a better understanding of material alignment dynamics; validation of our technique will be performed on a suspension of self-assembling protein fibrils under flow.
The valorization of carbon dioxide (CO₂) via electrochemical CO₂ reduction (ECR) has attracted great interest as a pragmatic approach to tackle greenhouse gas emissions. Multiple carbon (C₂+) products, such as ethylene, ethanol and propanol are highly valuable chemicals and of great demand. Copper (Cu)-based catalysts are so far the only electrocatalytic material that allows CO₂ reduction to C₂+ products at industrially relevant current densities. However, most Cu-based catalysts are unstable for long-term reactions (> 100 h), with the main reasons being the potential-induced surface reconstruction, deposition of impurities, catalyst aggregation and leaching, among others. Consequently, we report an in situ catalyst regeneration strategy that can extend the operation time of Cu-based catalysts. Applying this strategy on a Cu catalyst - which is stable for ~5 h towards C₂+ products during a continuous electroreduction under neutral-pH conditions, we were able to extend the operating time to ~120 h.
This study presents the fabrication and characterization of ionic liquid (IL)/polymeric ionic liquid (PIL) mixtures for supercapacitors intended for wearable electronics. PIL was synthesized and characterized by NMR spectroscopy and GPC to ensure molecular structure and measuring the molecular weight. Rheological properties of these series IL/PIL mixtures were investigated to optimize mechanical properties and conductivity. Additionally, gel polymer electrolytes (GPEs) based on IL/PIL were also synthesized to be used as solid state electrolyte. This has been done by employing an IL based crosslinker in the formulation. The specific capacitance of the fabricated supercapacitors was measured, and their mechanical properties and conductivity of the mixture of IL with linear and crosslinked PILs have been compared. It has been found out that the storage modulus and dynamic viscosity of the GPEs in higher that linear PILs, maintain their relatively high conductivity even at high crosslinking density.
Water-based polymerization methods, such as emulsion polymerization, offer improved sustainability by reducing or eliminating volatile organic compound use.\textsuperscript{1} The US paints and coatings market has exhibited a yearly increase in demand, with the waterborne segment leading the largest market share. The demand for eco-friendly products is expected to have a positive impact on market growth in the coming years.\textsuperscript{2,3} Both academia and industry have shown interest in cellulose nanocrystals (CNC), derived from biological sources, typically using sulfuric acid hydrolysis. One of the recent technologies considered simple and “greener” than acid hydrolysis is oxidation with hydrogen peroxide.\textsuperscript{4} The peroxide treatment yields a CNC surface with carboxylic acid groups rather than sulfate half-esters.
Carboxylated CNC (cCNC) has previously been added into pressure-sensitive adhesive formulations and appears to exhibit improvements in adhesive properties. Despite these findings, the enhancement effects in high-performance latex-based coatings have not been studied. This study focuses on enhancing the properties of a high solids polymer content commercial-level performance coating formulation through the incorporation of cCNCs via in situ seeded semi-batch emulsion polymerization. The work investigates the effects of CNCs with different surface chemistry through rheological, water whitening and water absorption characterizations. The superior results obtained from the coatings based on cCNC latex nanocomposites broaden their potential industrial applications.

Recycling thermosets has been a big challenge due to their three-dimensional network of bonds. We investigate the potential of reprocessing 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO)-mediated peroxide-crosslinked high-density polyethylene (XHDPE) as a sustainable strategy for waste management. Because of its superior thermal and chemical properties, XHDPE has gained extensive use in various industries. However, crosslinking restricts the material's ability to be reprocessed through conventional methods. Crosslinking is achieved by mixing HDPE with the desired amount of dicumyl peroxide (DCP) and AOTEMPO in an Advanced Polymer Analyzer (APA) at 160°C for 1 hour. Rheological studies and gel content confirm that XHDPE can be part-de-crosslinked by treating the samples at different temperatures in sequence, from 160°C to 230°C, then to 160°C, for 1 hour each in an APA. In addition to a reduction in gel content, the storage modulus (G') dropped significantly. Finally, we studied the dynamics of de-crosslinked HDPE powder with virgin HDPE for re-processibility.
SURFACE MODIFICATION OF CHITOSAN NANOCRYSTALS VIA NITROXIDE-MEDIATED POLYMERIZATION

CARLOS ANTONIO RAMIREZ FOYO

The global plastic manufacturing sector is worth $1.2 trillion, but 79% of the plastic waste ends up in landfills or the environment. Chitosan nanocrystals (ChsNCs) are a renewable and biodegradable resource attracting recent research interest due to their outstanding physical, chemical, and mechanical properties, representing an alternative to synthetic polymers. ChsNCs are obtained from chitin, which is the second most abundant biobased polymer in the world after cellulose. The main commercial source of chitin is marine food production waste.

ChsNCs exhibit promising commercial potential as reinforcing materials in polymer-based nanocomposites. However, the hydrophilic nature of ChsNCs poses a major challenge for implementing them in commercial applications due to their poor dispersion in nonpolar polymer matrices and organic solvents. Due to the interest in using them in nonpolar matrices, the ChsNCs surface must be modified to address this problem.

In this work, ChsNCs were initially functionalized with glycidyl methacrylate to provide a reactive surface group that enables the polymer graft modification of ChsNCs with welldefined synthetic polymers. Polystyrene and poly(methyl methacrylate) were first synthesized via NMP (nitroxide-mediated polymerization), and the polymers were then “grafted to” the ChsNCs surface. The functionalized materials are characterized using 1H NMR, FT-IR, GPC, and TGA.
Although the basic mechanisms of free radical polymerization (FRP) are largely understood, there remains the need to determine key polymerization rate coefficients to improve the reliability of models used to aid the synthesis of new products and the development of new processes. Emulsion polymerization is a widely utilized (and modeled) industrial polymerization method that uses water as an environmentally benign solvent. Despite extensive research into emulsion polymerization mechanisms, most models do not consider the substantial difference in the (co)polymerization kinetics of monomers in the continuous aqueous phase and the non-polar polymer particles. Although solvent influences have been studied for highly water-soluble monomers, it is vital to measure the propagation rate coefficients and copolymerization reactivity ratios of hydrophobic monomers such as butyl acrylate (BA) and methyl methacrylate (MMA) in aqueous solution, in order to develop an improved understanding of the aqueous-phase kinetic processes important to particle formation and radical entry process in emulsion (co)polymerizations. To achieve this objective, the Pulsed-Laser Polymerization coupled with Size Exclusion Chromatography (PLPSEC) analysis of the resulting polymer and the in-situ NMR technique are employed. Given the hydrophobic nature of these monomers (MMA and BA), the approach taken in this study is to investigate the copolymerization of similar non-functional model monomers possessing enhanced water solubility with carboxylic acid monomers. Di(ethylene glycol) methyl ether methacrylate (DEGMEMA) can be considered as a model monomer for MMA and methyl acrylate (MA) for BA.
With increasing public awareness surrounding the impacts of pollution on the environment and human health, alternative methods to produce important materials, such as protective coatings that prolong the lifetime of materials, are needed more than ever. Waterborne paints, adhesives, sealants, and other coatings produced through emulsion polymerization are an ideal substitute for solvent-based coatings given that harmful emissions are eliminated. Despite the advantages of emulsion polymerization, the requirement of an amphiphilic stabilizer molecule to prevent phase separation of a thermodynamically unstable oil-in-water mixture is often viewed as a “necessary evil”. Conventionally used small-molecule surface active agents (surfactants) readily diffuse to interfaces, leading to poor performance properties of products such as water sensitivity. This has motivated the development of larger, polymeric stabilizers that cannot readily diffuse to interfaces.

Our group has developed highly hydrophobic “block-random” copolymers aimed at providing efficient stabilization while allowing industrially relevant solids contents (polymer fraction in water) to be reached. Despite being >70 mol% polystyrene, the unexpectedly facile dispersion of these materials in water as well as the unique and robust behaviour observed when these materials are used as stabilizers in emulsion polymerization makes these materials an intriguing alternative to small-molecule surfactants. This talk will focus on the impact of changing the block-random copolymer structure and composition (i.e., acrylic acid content, molecular weight, block ratio) on the aqueous solution properties and emulsion polymerization particle formation mechanism and stabilization performance. The findings of this work will guide the design of block-random copolymers for use as stabilizers in emulsion polymerization, as well in other fields such as catalysis and biomedicine.
controlled degradation of polypropylene (CPP) is used to convert high molecular weight (M_w) polypropylene (PP) grades to lower M_w PP grades via peroxide-induced degradation reactions. The CPP process causes predominantly isotactic PP to exhibit decreases in isotacticity, which affects its crystallinity. A novel deterministic model is developed to predict these tacticity changes. The proposed model relies on the assumption that the lifetimes of polymeric free radicals are short compared to the residence times of the PP in the extruder. The model determines instantaneous rates of formation of defective pentads as the PP moves through the extruder and accumulates these pentads using dynamic material balances. Predictions from this deterministic model agree with those from a previous kinetic Monte Carlo model, and require substantially lower simulation times. Two versions of the deterministic model are proposed, one that assumes chain-walking reactions occur via 1-6 isomerization and one that assumes 1-8 isomerization reactions. Kinetic parameters for chain-transfer-to-polymer and chain-walking reactions are estimated for the first time using industrial 13C-NMR data obtained using different levels of free-radical initiator. The 1-6 isomerization model results in a better fit to the data and is able to predict six of the eight types of defective pentads that are observed experimentally.
Plastic products are overwhelming produced from petroleum-based sources. This dependence on petroleum has significant environmental ramifications, with about 80% of the plastics produced in modern society ending up as persistent waste. To combat this, herein we aim to investigate the potential of microalgae as a sustainable, bio-based, and biodegradable material for bioplastic production. Microalgae are known for their high protein content and health benefits, with applications in the food, cosmetics, and pharmaceutical industries. However, their use in bioplastics formulation and production is still untapped and warrants further exploration. Specifically, our research explores the extraction and purification of protein fractions from two types of microalgae: spirulina and chlorella. Following extraction, we investigate the formation of ordered protein aggregates through high temperature, low pH mediated assembly protocols. Factors such as incubation time, temperature, and biomass concentration are varied in order to understand their impacts on protein aggregation kinetics, morphology, and physicochemical properties. Techniques including dynamic light scattering, circular dichroism spectroscopy, and atomic force microscopy are used to characterize the protein aggregates. This foundational work hints at the feasibility of using microalgae-derived protein aggregates for sustainable bioplastics, with future research directed towards developing bio-based inks for 3D printing and other additive manufacturing processes, enhancing our understanding of the relationship between protein aggregate structure and the mechanical properties of resulting composites.