

Polysaccharide Based Delivery Vehicles for Controlled Release of Agrochemicals and Biologically Active Compounds

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Abstract:

Aqueous solubility and controllable release are key factors for determining the efficacy of a bioactive molecule. In the case of oral drug delivery, the poor aqueous solubility of a drug gives rise to a correspondingly low bioavailability. Thus, a greater quantity of the drug is required to achieve a therapeutic concentration in systemic circulation. For agrochemicals such as pesticides, poor aqueous solubility means that less of the pesticide will be absorbed into the plant. Thereby increasing the amount of pesticide lost to the environment. Controlled release is critically important to pesticides as a regulated release rate reduces the need for multiple pesticide applications to crops by extending the duration of effective concentration. The aqueous solubility and release rate of a bioactive molecule can be improved with the conjugation of a carrier molecule, to form a pro-active delivery system. Polysaccharides have great potential as carriers since they are biodegradable, nontoxic, and readily available. We have hypothesized that amphiphilic derivatives of cellulose and dextran can be synthesized and utilized as carrier molecules for delivery of bioactive molecules in both agricultural and medicinal applications. Commercially produced hydroxypropyl cellulose was oxidized with sodium hypochlorite and reacted with primary amines to form a Schiff base imine bond. Successful conjugation to both tert-butylamine and diethylamine was confirmed with ¹H and ¹³C NMR spectroscopy.

Emissions in Extrusion-based Additive Manufacturing: Impact on Food, Energy, and Water

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KEYWORDS: additive manufacturing (or material extrusion), volatile organic compounds, ultrafine particles, acrylonitrile butadiene styrene, polylactic acid, thermoplastic polyurethane, cellulose nanocrystals

Abstract

Material extrusion based additive manufacturing is an emerging form of product manufacturing and is gaining exponential popularity in the industry, work offices, and homes. Material extrusion is an interdisciplinary advancement that will grow fields such as agriculture, renewable energy, and clean water engineering. Water deficiency is an ongoing issue in arid parts of the world, thus there is a pressure to increase the production and capability of desalination membranes through controlled structure and on-site manufacturing capability. Food safety can be made more efficient by extruding thin trackers and sensors that can be embedded in packaging. Material extrusion is an energy conserving process due to its decrease in waste production. However, the material extrusion process has the potential to emit ultrafine particles and volatile organic compounds. The purpose of this study is to call into question the safety of the process in respects to the health of the user, along with the potential global impacts of the water cycle and the impact of this pollution on agriculture and air quality. Research has been conducted on the rate of emissions from material extrusion and the effects of ultrafine particles and volatile organic compounds on the human respiratory system. This study uses thermo-gravimetric analysis, infrared spectroscopy, and gas chromatography/mass spectrometry to evaluate the chemical composition of ultrafine particles and volatile organic compounds from material extrusion. Across different filament-color combinations, water vapor and carbon dioxide were the most prominent emission components. The emission of different chemical compounds at lower concentrations can be found based upon the additives used in filament formulation.

**Plant-Signaled Delivery:
Water and Fertilizer on Demand**

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Abstract

This study aimed to synthesize and characterize novel acetal containing, polyethylene glycol (PEG) based photo-cured hydrogel networks. A series of three different PEG oligomers were synthesized by the acetalization of two smaller PEG oligomers, hydroxyl terminated PEG 2000, and tri(ethylene glycol) di-vinyl ether. This series included two vinyl ether end-capped PEG oligomers with molecular weight 25k and 10k as well as a hydroxyl end-capped oligomer with molecular weight 10k. NMR spectroscopy confirmed acetalization as well as end-capping, and the molecular weight was determined with APC size exclusion chromatography. The hydroxyl end-capped oligomer was functionalized with acrylate end-groups. Additionally, a PEG10k di-acetal acrylate was synthesized. These novel polymers were crosslinked via ultra-violet irradiation producing a set of hydrogels with swelling properties linked to their crosslinking method. pH dependent degradation studies show high hydrogel stability at pH 8 as well as the degradation of the hydrogels at pH 4-5. The number of acetal functionalities impacts the rate the hydrogels degrade in acidic environments. These acid degradable hydrogels have promise in the implementation of plant signaled fertilizer delivery.

Key words: *hydrogel, polyethylene glycol, polyacetals, acid cleavable, thiol-ene click, acid cleavable, plant signaling.*

3D Printing Tissue Scaffolds with Varying Pore Sizes Using an AMPS-PEGDA Photopolymer

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Abstract

Current agricultural practices and standards are not sustainable for the Earth and its inhabitants of the future. Cellular agriculture has spawned an agriculture revolution and additive manufacturing has spawned a manufacturing revolution that competes with the current dominating traditional or subtractive manufacturing practices. The livestock (meat) sector within agriculture industry is the most wasteful, least efficient, and most harmful to the environment. Cultured meat has shown to be a viable solution for meeting the demands of the future while being environmentally friendly. Current efforts are to combine the benefits of the emerging technology of 3D printing and the science of cultured meat in the most effective and efficient way possible. More specifically, much effort works to find an appropriate biocompatible scaffold with an architecture that maximizes cell proliferation in the least amount of time. Experiments were conducted with a photopolymer mix of AMPS and PEGDA and a custom-made mask projection microstereolithography (MP μ SL) machine to test how different pore sizes affect cellular response. The pore size that maximizes surface area will theoretically yield the best response. However, of the pore sizes tested the experimental data suggests that a pore size of around 500 microns yields the best cellular response.

Material interference to minimize photon excitation of riboflavin for protecting milk nutrients and flavor quality

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Abstract

Light-emitting diode lights (LED) are becoming more common in retail use due to long-lasting and energy saving capabilities. However, the effect LED lights have on fluid milk quality has not been thoroughly studied, including flavor and nutritional analysis. The objective is to analyze the interaction between packaging material, light intensity, and exposure time through riboflavin analysis and headspace volatile analysis. Packaging tested includes glass, translucent high density polyethylene (HDPE), white HDPE pigmented with 4.9% TiO₂, clear polyethylene terephthalate (PET), white PET pigmented TiO₂, and a PET control and HDPE control, which were wrapped in aluminum foil to prevent light exposure. Electronic nose headspace analysis and riboflavin degradation analysis indicated higher levels of photooxidation at higher light intensities and longer storage times.

Packaging Efficacy for Protecting Milk Freshness Stored in High Energy LED Retail Conditions

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Keywords: LED, light-protective additives, packaging, oxidation, milk

Abstract

As retailers have transitioned from fluorescent lighting to LED, to reduce energy consumption, there has become a need for packaging to protect milk quality from light energy in order to keep the milk fresh. We compared three HDPE and three PET packages representing traditional packaging materials, light-blocking innovations, and a light-blocking control treatment (foil-overwrap) along with glass, against different LED light intensities, 1052 ± 484 and 5691 ± 512 lux to see the effects on 2% milk after a period of four hours and 24 hours. Dissolved oxygen and thiobarbituric acid reactive substances (TBARS) were the analyses used to measure the success of each type of package under the different light intensities. Ideally, packaging would completely block light; however, for consumer acceptance, PET with light-protective additives provide significant protection to improve milk freshness.

PEDOT:PSS Electrodes in 3D Printed Flexible Biosensors for Food and Water Safety

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Abstract

The inability to detect water-borne toxins and pesticides in water sources and on agricultural products poses a significant problem worldwide, especially in countries where water sanitation and food quality monitoring systems are lacking. In this work, we propose a simplistic model for a conformal and robust biosensor constructed solely through additive manufacturing techniques. The development of a 3D conformal sensor optimizes the detection interface between the detecting components of the device and uniquely-shaped biological surfaces of agricultural products. Employing the conductive polymer, poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS), with optimized dopant and annealing conditions, we demonstrate its role as an inexpensive alternative to conductive nanoparticle inks. Overall, the development of this proof of concept device suggests a solution to food and water safety issues worldwide through reliable quality control and the accessibility of monitoring devices.

Recycling and Managing Heat Energy Using Advanced Poly(pyrrole) Network and PNIPAm Hydrogel

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ABSTRACT

Heat transfer is one of the most common forms of energy waste, and to help reduce industrial energy loss, our research team desires to utilize the principles of thermoelectricity and thermal switch to find different materials that can be used to reduce and recycle heat waste in various fields and industries. The first part of our research is the synthesis of poly(N-isopropylacrylamide) hydrogel using redox-initiation polymerization process. The goal of this experiment is to characterize the thermal switch, thermo-responsiveness, and thermal diffusivity of the hydrogel for future applications. For the second part, we attempt to synthesize a conductive polymer network, particularly poly(pyrrole) network, under the form of a thin film and analyze its resistivity and thermoelectricity. To achieve desirable product, we apply electropolymerization for the poly(pyrrole) synthesis and basic organic reactions to obtain double gyroid template for the network.

An exploration of phosphonated poly (ether ether ketone) properties for desalination applications

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Abstract

As access to fresh water decreases in many areas of the world, more people will rely upon desalination for their water supply. Some of the most energy efficient desalination methods use semipermeable polymer membranes, including forward and reverse osmosis. Although these methods can be efficient, the membranes must withstand high temperatures and pressures, limiting the materials that can be used. Another problem is low water flux of the semipermeable membranes. This experimentation seeks to address these problems with phosphonated poly(ether ether ketone), synthesized through post-polymerization functionalization. The phosphite functional groups are divalent, so the ionomer is more highly charged than other ionomers with monovalent functional groups at the same degree of functionalization. The phosphonated poly(ether ether ketone) exhibits strong chemical resistivity and desirable thermal properties, making it a strong candidate for future desalination studies.

Functionalization of Cellulose Nanocrystals With β -Cyclodextrin as Water Treatment Binding Bisphenol A

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Abstract

Cellulose as a natural polymers are abundant on the earth with its eco-friendly and low cost features. Nanoscaled materials with its various potential benefits have also been investigated in the past several decades. Cellulose nanocrystals are found excellent potential properties on the material engineering fields, such as its low toxicity, biodegradable, and easy modified surface properties. Cyclodextrins are well known by their high encapsulation capacity of their hydrophobic cavity as an active adsorbent. In this paper, functionalized cellulose nanocrystals with β -cyclodextrin would rapidly remove bisphenol A served as filtration for water treatment . Cellulose nanocrystals served as a backbone to chemically graft with β -cyclodextrin through amidation reaction forming a nanoscaled adsorbent material. Lipophilic cavity of cyclodextrin encapsulate bisphenol A which is a highly toxic industrial pollutant to form an ideal water treatment model in which to detect the adsorption speed and capacity of cyclodextrin-based materials in the aqueous condition. UV-vis spectrophotometer evaluated the final yield of cyclodextrin binding efficiency on the surface of cellulose nanocrystals and the capacity of encapsulation for removing bisphenol A in the aquatic system.

Corrole-Based Zr-Metal-Organic Frameworks for Light Capture

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ABSTRACT

Tris(4-carboxyphenyl) corrole was incorporated into a zirconium-based framework to yield a novel metal-organic framework with predicted formula $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TCPC})_4]$ using modulator-mediated solvothermal conditions. The properties and characteristics of this framework were investigated using powder X-ray diffraction (PXRD) to determine crystallinity and lattice spacing. The ligand 5,10,15-tris(4-carboxyphenyl) copper corrole (CuTCPC) was characterized using ¹H NMR, electronic absorption spectroscopy, fluorimetry and atmospheric-pressure chemical ionization (APCI) mass spectroscopy, followed by base-catalyzed ester hydrolysis to yield a triacid compound for the first time. Electronic absorbance spectra showed the λ_{max} blue shift when TCPC was coordinated with Cu. ¹H NMR of the resultant CuTCPC complex revealed a shift to lower ppm for all aromatic peaks compared to TCPC, characteristic copper increasing electron density around the macrocycle. Comparison of fluorescence spectra indicated chelation of copper quenches fluorescent properties of free-base TCPC.

A study of nanoparticle binder's impact on the binder jetting additive manufacturing process

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Abstract

Binder jetting copper can produce conductive, complex shapes that can be used to maximize thermal/electrical energy. Nanoparticle binder rheology, jettability, and interaction with powder were investigated. The rheologies of the nanoparticle inks were varied to determine their effect on ink jettability and overall part densification. Nanocopper suspensions were prepared by dispersing copper nanoparticles in various binders and dispersants. The viscosity and surface tension of the inks were tested to determine the inks jettability. A relationship between rheology and droplet size was established through a MicroFab inkjet printing test. Droplets of the inks were deposited onto the powder and characterized to determine the inks wetting and dispersion behavior through the use of optical microscopy. The presence of copper nanoparticles decreased the surface tension, increased the viscosity, decreased the drop volume, increased the absorption time, and increased the spread of droplet onto powder.

Novel Model of Carbon Nanotubes for High Performance Filtration Systems

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We present a novel implementation of the Lennard Jones 12:6 potential in modeling inter-molecular interactions in Carbon Nanotube(CNT)/Polymer systems. CNT/Polymer systems have shown promise in many nano-technological applications, such as desalination membranes. Following standard course-graining procedures, we describe the CNT as a bead-spring chain. This allows the study of larger systems as (5,5) CNTs have around 100 Carbon atoms per nanometer. Intra-molecular interactions are determined by equating continuum mechanics to full atom simulations utilizing conservation of energy principles. Inter-molecular interactions have plagued other notable CNT models in the literature. The use of an unmodified LJ potential, leads to corrugation at the surface of the course-grained CNT. This unphysical defect forced previous models to neglect shear properties of CNT bundles. We wish to alleviate this issue, as we intend to study shear properties at CNT/Polymer interfaces. In studying these interactions we wish to quantify the microscopic origin of macroscopic defects, such as delamination and crack propagation. We have shown that the corrugation could be significantly reduced. More work is currently being done.

Photoresponsiveness of Polymer Ionic Liquid Composites Analyzed Through UV-Vis and Fluorescence Spectroscopies

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Abstract

The needs for more energy storage and energy harvesting are ever growing in relation to the world's population. Our research focuses on the development and characterization of a new polymer based electrolyte synthesized from the polyanion poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) as well as select ionic liquids. The MIC has previously been analyzed for its applications to energy, as it is a composite gel, which houses the characteristics of high conductivity ($8 \text{ mS}\cdot\text{cm}^{-1}$), high modulus (up to 3 GPa), high temperature threshold (up to 300 °C), and an electrochemical window up to 6 V.¹ These characteristics make the MIC suitable for use as a polymer electrolyte in high energy density batteries, however there are other properties of the MIC that are yet to be as thoroughly defined, such as its notable optical properties when exposed to white light. This initial investigation on the molecular ionic composite's optical properties involves exploration through fluorescence and ultraviolet-visible spectroscopies on samples of PBDT, choice ionic liquids, and MICs. The purpose of this experimentation was to define the absorption spectra and fluorescence spectra of the MIC and its components in order to explain its optical phenomena. We hypothesized that the MICs fluorescent nature was attributed to the ionic liquids in the sample.² Our UV-Vis results indicate that PBDT, ionic liquids, and the MIC absorb light in the visible range, and that there is some absorption within the MIC that is explicitly caused by the PBDT and IL within. For the fluorescence both the fluorescence excitation and emission, we found that the MIC expressed a combination of both the PBDT and IL, however investigation into the full spectra of the MIC and its components is ongoing.

Synthesis and Design of Polyetherimide Nanoparticles for Improved Efficiency in Composite Manufacturing

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Abstract

Polyetherimide composite materials are widely used in industry, particularly in aviation applications where materials are required to have high thermal, chemical, and mechanical stability. A method for preparing nanoscale polyetherimide particles has been developed through homogenization of solvent-water mixtures containing the polyetherimide, followed by removal of the solvent. and chemical stability, as well as resistance to damage. We have synthesized a series of poly(amic acid) ammonium salts with targeted molecular weights and used them as suspending agents for polyetherimide nanoparticles in water. The poly(amic acid) salts were synthesized from Ultem dianhydride, phthalic anhydride, m-phenylenediamine, and dimethylaminoethanol. Silane coupling agents were investigated to functionalize carbon fibers with amines so that they would bind to the poly(amic acid) salts on the surfaces of the polyetherimide nanoparticles.

Taking Charge: Incorporating Energy-Harvesting Piezoelectrics into Large-Area Projection
Microstereolithography 3D Printing

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KEYWORDS: piezoelectric, stereolithography, 3D printing, polymer, energy-harvesting,
sustainable, alternative energy

Abstract

With the need for more energy sources as the population rises, piezoelectric materials could provide a renewable, environmentally-friendly relief to anticipated energy demands. However due to the brittleness of traditional piezoelectric ceramics, these materials have not warranted broader consideration in applications coupled with limitations in fabrication of complex shapes. Therefore the work of our group has been motivated to incorporate piezoelectric ceramics into polymeric frameworks that can be printed by stereolithography (SLA) to provide flexibility, resilience, and high piezoelectric response with processability to complex shapes. Surface functionalization of piezoelectric nanoparticles to enhance mechanical coupling, incorporation into polymer resin, and subsequent SLA printing and testing of structures has been characterized primarily by Infrared Spectroscopy. Nuclear Magnetic Resonance, Thermo gravimetric Analysis, and Dynamic Light Scattering have also been primary characterization methods in evaluating functionalization. It is demonstrated through our experiments that functionalization improves the piezoelectric response, but further studies are needed to improve the dispersion and piezoelectric response of particles throughout the printed structures.

Sustained Release of Hydrogen Sulfide via Polymeric Donors

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Abstract

Hydrogen sulfide (H₂S) is an important endogenous signaling molecule in plants that increases resistance to drought, salt, extreme temperatures, soils containing heavy metal, and osmotic stress.¹ Exogenous delivery of H₂S through polymeric donors may allow for controlled release depending on the molecular weight (MW) and functionality. Here we describe the use of *N*-thiocarboxyanhydrides (**NTAs**) as H₂S releasing functional groups appended to a biodegradable polycarbonate backbone synthesized using ring-opening polymerization. The biodegradable, H₂S-releasing polymers were modified using poly(ethylene glycol) (PEG) chains of various sizes to create a water soluble H₂S-releasing polymer, which is expected to show a tunable release rate based on polymer MW and PEG content. Applicably, these polymers may help to improve plant or crop growth in arid climates or in high-salinity soils.