

Activities and Engagement 2021



Georgia Tech
**Renewable Bioproducts
Institute**



Executive Director's Statement

I am pleased to share with you the calendar year **2021 Activities and Engagement Report** for Georgia Tech's Renewable Bioproducts Institute. As one of ten Interdisciplinary Research Institutes at Georgia Tech, RBI's mission is to catalyze a community of exceptional individuals committed to developing thought leadership in biomass and bioproducts technology. The 2021 year was a very productive one for the faculty, students and staff of RBI. Through the generous endowment made possible by the Institute of Paper Chemistry Foundation, RBI supported 28 Ph.D. students in 2021, who worked on projects in our core research thrusts of (i) Paper, Packaging and Tissue, (ii) Biorefining and Bioindustrial Manufacturing, and (iii) Circular Materials. This group of students published 28 peer reviewed articles in archival journals in 2021, which have been reproduced here for your convenience. Among these 28 students are 8 new fellowships awarded in fall of 2021. A brief description of each current student's project and advisors is included in this report. The faculty have utilized research results from fellowship support to write external proposals exceeding \$32 million to federal agencies and industrial partners, and RBI committed to cost-sharing over \$800,000 in support through the endowment fellowships.

RBI offered two virtual workshops in 2021, on the topics of circular packaging (spring) and the role of bioproducts in meeting the United Nation's Sustainable Development Goals (fall). The attendance at these workshops was the highest in RBI's history and included stakeholders from academia, national labs including the Forest Products Laboratory and the National Renewable Energy Laboratory, industry, and non-profit organizations like Two Sides and GreenBlue.

We couldn't do it without the active engagement our industrial members. I thank each of them for their time and effort over the prior year in guiding our research priorities, partnering on external proposals, and participating as key speakers and panelists in our workshops.

I also thank the RBI faculty, staff, and students and the administration within the Executive Vice Provost for Research Office for their hard work.

Sincerely,



Carson Meredith
Executive Director, *Renewable Bioproducts Institute*
Professor, *School of Chemical & Biomolecular Engineering*

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RBI Fellows

RBI Fellow	School	Research Title	Advisor(s)
Nurlan Amirov	ChBE	Lignin-derived biodegradable biolatex	Will Gutekunst, Pamela Peralta-Yahya
Connor Armstrong	ME	Enabling direct ink write edible 3D printing of food purees with cellulose nanocrystals	H. Jerry Qi, Yulin Deng
William Berkley	CHEM	Upcycling of carbohydrates to yield furan-containing building blocks as platforms chemicals and precursors to value-added fuels, materials, and products	Stefan France, Chris Jones
Krista Bullard	CHEM	Utilizing cyclodextrin to compatibilize the polymer and CNC Interface	Will Gutekunst, Mohan Srinivasarao
Woosung Choi	MSE	Unique recyclable cellulose-derived photo-crosslinkable biopolyesters with outstanding barrier properties for next-generation packaging	Zhiqun Lin, Sankar Nair
Jonathan Cotler	ChBE	Photodegradable polymers for recyclable and sustainable packaging	Blair Brettmann, Stefan France
Sumner Dudick	ChBE	Fabrics with three-dimensional wetting gradients for improved dewatering	Victor Breedveld, Dennis Hess
Natalie Duprez	ChBE	Cost-effective, aqueously degradable poly (ethylene terephthalate) coating for paper cups	Chris Luettgen, Donggang Yao
Yacine Feliachi	ChBE	Novel polymers for membrane-based separations of crude sulfate turpentines and tall oil	Ryan P. Lively, M. G. Finn
Qiang Fu	ChBE	Separation of complex multicomponent organic mixtures: Addressing a critical gap in biorefining and chemical recovery from pulping processes	Sankar Nair, Scott Sinquefield
Dogukan Karahan	ME	Dynamics of fiber motion in complex flows	Cyrus Aidun, Devesh Ranjan
Jinhyuen Kim	ChBE	Data-driven and hybrid modeling of integrated paper production systems	Kamran Paynabar, Fani Boukouvala, Chris Luettgen
Jungin Kim	ME	Design of degradable bio-based polymeric coating materials for cellulose products	Yan Wang, Karl Jacob
Geng-Sheng Lin	ChBE	Robust, antifouling, sensory biomass-derived adsorption membrane for wastewater metal removal and detection	Julene Tong, George Lan
Ojelade Opeyemi	ChBE	Valorization of Kraft Black Liquor: Conversion of enriched hydroxy acids to high-value lubricants and waxes	Sankar Nair, Christopher Jones
Sarah Paluskiewicz	MSE	Is it really just creep? Cyclic fatigue accumulation mechanisms in paper	Chris Muhlstein
Jimin Park	ChBE	Production of active pharmaceutical ingredients from lignin	Andreas Bommarius, Carsten Sievers, Marta Hatzell
Annie Pham	ME	High-performance lightweight nanocellulose composites through scalable manufacturing for high volume applications	Kyriaki Kalaitzidou, Karl Jacob, Tequila Harris
Erin Phillips	CHEM	Mechanocatalytic depolymerization and upgrading of lignin	Carsten Sievers, Marta Hatzell

Udita Ringania	ChBE	Scalable, low cost, and energy-efficient nanocellulose drying using ultrasonic transducers	Saad Bhamla
Javaz Rolle	ChBE	Advancing nanocellulose-based barrier packaging: performance and manufacturability via hybrids with soluble polysaccharides and metal oxides	Carson Meredith, Natalie Stingelin
Fariha Rubiya	MSE	Understanding electromechanical coupling in cellulose for single component Auxetic-Piezoelectric energy harvesters	Meisha Shofner, Lauren Garten
Helen Wong	ChBE	Incorporation of cellulose-based materials into flexible energy storage devices for smart packaging and the internet of things	Elsa Reichmanis, Nian Liu
Andrew Wu	MSE	Designing tunable chemistries targeted for recyclable multilayer packaging	Natalie Stingelin, Kyriaki Kalaitzidou, Karl Jacob
Kaung Su Khin Zaw	ChBE	Black Liquor concentration using graphene oxide membrane	Sankar Nair, Meisha Shofner, Scott Sinquefield
Li Zhang	ChBE	Controlled durability and degradation in cellulosic products	Mark Losego, Todd Shulchek
Mingyue Zhang	ChBE	Cellulose-based nanocomposites with ambient-light-activated biocidal properties for food packaging	Zhiqun Lin, Yulin Deng

ChBE School of Chemical Biomolecular Engineering

CHEM School of Chemistry & Biochemistry

ME School of Mechanical Engineering

MSE School of Materials Science & Engineering

RBI Workshops

RBI Workshops

RBI has a long tradition of connecting our premier researchers with company executives, and researchers in academia and national labs who are searching for new innovative products and processes, as well as solutions to some of today's toughest challenges in the areas of bioproducts and bioprocessing.

Our annual events are organized with that goal in mind. A key purpose of our workshops is to identify the areas of greatest shared opportunity in the developing bioeconomy — in other words, to identify how we can best work together with companies in various industries that need our expertise. The sessions are designed to encourage engagement in determining how we can build a collaborative partnership to further strategic goals.

GT Faculty and external experts lead our discussion in a variety of areas based on a selected theme. RBI's Ph.D. Fellows take discussions a step further, presenting research being conducted in these very areas.

We bring in company leaders who are beneficiaries of our research to share their experiences, and we offer an ample amount of time to network with experts and innovators, as well as our faculty and students and other private sector stakeholders.

Our vision is to create and strengthen relationships, both internally and externally. This will maximize the impact of our research in real-world applications benefitting our world — your world. Your involvement in the discussion is key to our success.

Achieving Sustainable Development through Renewable Bioproducts

A workshop sponsored by: Georgia Tech's Renewable Bioproducts Institute



Overview

Join us for a workshop entitled **Achieving Sustainable Development through Renewable Bioproducts** on September 17, 9:30am - 12:00pm.

The workshop is free.

This unique workshop is a venue for understanding and discussing how companies and organizations are utilizing bioproducts to approach the U.N. Sustainable Development Goals (SDGs) and how research can advance their progress.

Bioproducts from forest and agricultural resources include paper and tissue that comprise many products critical to education, personal care and healthcare. Access to these products in both developed and developing nations is critical to achieving equal access to education for all (SDG #4), gender equity (SDG #5), sanitation (SDG #6), and responsible consumption and production (SDG #12). By expanding renewable bioproducts into applications traditionally held by synthetic materials, they can enable sustainable food packaging (SDGs #1 and #12) and reduced greenhouse gas emissions (SDG #13).

The workshop will involve talks to introduce the topics followed by a panel discussion with experts who seek to champion innovation that makes an impact on the U.N. SDG's. The goal of the workshop is to identify **R&D needs for meeting these commitments.**

AGENDA :: 9:30AM – Noon

Andre Calmon, College of Business *Overview of SDGs* 20 min

Carson Meredith, Exec. Director, RBI *SDGs and Bioproducts* 15 min

Panel Discussion: *R&D Opportunities* 60 min

Lisa Morden,

VP of Safety, Sustainability and Occupational Health,
Kimberly Clark Corporation

Andre Calmon, Assistant Professor, Scheller College of Business

Savannah Seydel, Better Earth Inc.

Breakout Sessions *Challenges to address* 25 min

Report Back *Summarize reporting* 15 min

Ángel Cabrera, President, Georgia Tech *Closing remarks*

Achieving Sustainable Development through Renewable Bioproducts Attendees

Auburn University

Becompostable

City of Atlanta

Dow

Georgia Pacific

Greif

Interface

Jamestown, L.P.

Kimberly-Clark

McGrath

M&I Materials

Morehouse College

Murata

NREL

Piana Nonwovens

Pulmac

Rayonier Advanced Materials

San Jacinto College

Silpara Tech

Solenis

Southwire

Suzano

Tate and Lyle

UPS

USDA

Westrock

Winpak

2021 Circular Paper and Packaging Virtual Workshop



Join us for a **Circular Paper and Packaging Virtual Workshop, April 1-2**, sponsored by Georgia Tech's Renewable Bioproducts Institute.

The workshop will feature talks from **WestRock, Printpack, Forest Products Laboratory, Greenblue, NCASI, Two Sides, and Georgia Tech.**

April 1 session: 1:00pm - 3:45pm EDT

WORKSHOP OVERVIEW:

In this workshop we will explore several key questions:

- (1) How is paper-based packaging already approaching circularity? What are the challenges that need to be addressed?
- (2) How can paper- and fiber-based products be used to substitute for single-use plastics?

We will hear from a panel of experts that includes:

Pat Lindner (Westrock)

Megan Robison (Printpack)

Kathi Rowzie (TwoSides)

Nina Goodrich (GreenBlue)

Caroline Gaudreault (NCASI)

Jinwu Wang (Forest Products Laboratory, USDA)

Blair Brettmann (ChBE, Georgia Tech)

Meisha Shofner (MSE, Georgia Tech)

Bernard Kippelin (ECE, Georgia Tech)

Chris Muhlstein (MSE, Georgia Tech)

Participants will also have access to a poster session highlighting the cutting-edge research being performed by Georgia Tech Paper Science & Engineering PhD students.

AGENDA

DAY 1: April 1, Sessions A-B 1:00pm-3:45pm

Today's Agenda

Session A: **"How Paper is Circular: Now and Future"**

- 1:00pm (5 min) Opening remarks and Welcome Carson Meredith and Chris Luetzgen, (Renewable Bioproducts Institute)
- 1:05pm (15min) Pat Lindner (WestRock)
- 1:21pm (15min) Megan Robison (Printpack)
- 1:37pm (15min) Caroline Gaudreault (NCASI)
- 1:53pm (15min) Panel Discussion
- 2:09pm-2:25pm BREAK

Session B: **"Opportunities in Broadening Paper Packaging into Plastic Markets"**

- 2:26pm (15min) Nina Goodrich (GreenBlue)
- 2:42pm (15min) Chris Muhlstein (Materials Science and Engineering/Georgia Tech)
- 2:59pm (15min) Bernard Kippeplén (Electrical & Computing Engineering)
- 3:15pm (15min) Jinwu Wang (Forest Products Laboratory)
- 3:31pm (15min) Panel Discussion

DAY 2: April 2, Sessions A-B 10:00am-12:00pm

Today's Agenda

Session A: **"Challenges in Broadening Paper Packaging into Plastic Markets"**

- 10:00am (15min) Meisha Shofner (Materials Science and Engineering/Georgia Tech)
- 10:16am (15min) Kathi Rowzie (Two Sides)
- 10:32am (15min) Blair Brettmann (Chemical and Biomolecular Engineering/Georgia Tech)
- 10:48am (15min) Panel Discussion

Session B: **RBI Fellowship Students Poster Session in Gatherly**

"Future Workforce: Company Needs and Student Training"

11:05am-12:00pm Poster Session in Gatherly (an online engagement platform--details to be provided to registrants)

Circular Paper and Packaging Virtual Workshop Attendees

Applied Materials
Applied Paper Technology
Arkema
C2P Sciences
Dow
DuPont
Ecolab
EDT Enzymes
Exponent
First Quality
Georgia Forestry Commission
Graz University of Technology
GreenBlue
Imperial College
International Paper
Kimberly-Clark
Koroza
Le Groupe Bel
Liquid IV
NCASI
NCSU
NREL
Printpack
Purdue
Purpose Built Brands
Ranpak
SAPPI
Seventh Generation
Simon Miller
Solenis
SUNY-ESF
Surface Measurement Systems
Suzano
Suzano Canada
Two Sides
University of Maine
University of Miami - Ohio
University of Tennessee-Knoxville
USDA Forest Products Lab
Westrock
Zero Waste

Publications

Pulp & Paper

Kraft black liquor concentration with graphene oxide membranes: Process simulations and technoeconomic analysis

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Funding information

Georgia-Pacific LLC; International Paper Company; Office of Energy Efficiency and Renewable Energy/RAPID Institute, Grant/Award Number: DE-EE0007888-7-5; Renewable Bioproducts Institute, Georgia Institute of Technology; SAPPI; WestRock

Abstract

Black liquor (BL) dewatering by multi-effect evaporation in the kraft paper-making process is highly energy-intensive. It was previously shown that graphene oxide (GO) nanofiltration membranes can remove lignin, other organics, and inorganic salts from BL while exhibiting stability in caustic BL conditions. Here, we design and simulate several candidate dewatering processes and evaluate their technoeconomic characteristics. All processes concentrate BL from 15 to 30 wt% solutes while producing aqueous permeate. Two process options were analyzed—option A including “last-mile” permeate treatment to reduce solutes to 0.2 wt%, and option B excluding this treatment and producing a 3–4 wt% solutes stream. These processes were simulated in custom-built ASPEN Plus flowsheets interfaced with Microsoft Excel and MATLAB. All processes deliver large (>40%) energy savings. Detailed technoeconomic analysis showed that option A processes are profitable in mills equipped with condensing turbines, but unprofitable with only purchased fuel savings. Option B processes are profitable in both situations, but require the caustic permeate to be utilized in other kraft process units. They are also profitable with electricity generation when operated at smaller scales matching the requirements of other process units. Monte-Carlo sensitivity analysis shows that Option A can yield median 20-year NPVs up to ~\$10MM and Option B up to ~\$25MM. Overall, GO membrane-based BL dewatering is economically promising, assuming successful slipstream piloting and scale-up campaigns. It would have immediate sustainability benefits from large energy savings, and broader implications for biorefinery processes due to the ability to fractionate biomass feedstock components under harsh conditions.

KEYWORDS

biorefining, graphene oxide membranes, kraft process, process design, pulp and paper, separations, technoeconomic analysis

Dewatering of Cellulose Nanofibrils using Ultrasound

Udita Ringania

Georgia Institute of Technology

Joseph Harrison

Georgia Institute of Technology

Robert J. Moon

USDA Forest Service Region 8: USDA Forest Service Southern Region

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Georgia Institute of Technology <https://orcid.org/0000-0002-9788-9920>

Research Article

Keywords: dewatering, ultrasonic dewatering, cellulose nanofibrils, energy-efficient, continuous, platform

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Reactive melt processing of poly(ethylene terephthalate) waste into calcium terephthalate

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Abstract. Recycling of waste poly(ethylene terephthalate) (PET) has attracted much attention in recent years because of the pressure from the environment. However, the cost-effective conversion of waste PET into value-added products by eco-friendly methods remains to be a challenge in the industry. In this work, a method for converting PET into calcium terephthalate by reactive melt processing was developed and investigated. Specifically, PET pellets were blended with calcium hydroxide powders using reactive melt processing, and the resulting mixture was converted into calcium terephthalate by simple hydrolysis in water. Physicochemical characterizations for morphologies, chemical compositions, and thermal properties were conducted to investigate intermediate components produced during the process, as well as the mechanisms of this new process. The results indicate that the effective transformation of molten PET into calcium terephthalate may be attributed to several factors, including the strong mechanical interaction during melt mixing, the thermal decomposition of PET chains to form carboxylic end groups, and the catalytic nature of calcium hydroxide in PET hydrolysis. This research can lead to a cost-effective route for the upcycling of waste PET into a value-added product that may be useful in demanding and emerging applications.

Keywords: recycling, polyethylene terephthalate, reactive processing, hydrolysis

1. Introduction

Poly(ethylene terephthalate) (PET) has been industrially produced at large volumes, particularly for packaging (including beverage bottles) and textile applications, because of its superior mechanical strength, thermal stability, and chemical resistance [1]. However, the enormous consumption of non-degradable PET contributes to the accumulation of solid waste at an alarming rate. Although landfill and incineration are currently used to contain or reduce the amount of waste PET, the occupation of land resources and the emission of toxic gases make them ecologically and economically unacceptable [2].

In order to promote the utilization of PET wastes, mechanical and chemical recycling have been proposed and investigated in recent years. In particular,

mechanical recycling can treat waste PET on a large scale through washing, separating, and melt processing (by molding, extrusion, or fiber spinning) [3]. The reproduced PET, however, typically undergoes a significant reduction in molar mass, intrinsic viscosity, and mechanical properties, making it restricted to down-cycling production [4]. In contrast, waste PET can also be depolymerized into its monomers and then reused in synthesis. The conventional methods for depolymerization of PET are hydrolysis, glycolysis, and methanolysis. Among these methods, hydrolysis is considered to be relatively safe and cost-effective, which can be conducted in water under alkaline, acidic and neutral conditions to convert waste PET into terephthalate acid (TPA) [5, 6]. However, PET hydrolysis generally entails pure PET feedstock, and

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Structure–Property Relationship in Capillary Foams

Omotola Okesanjo, J. Carson Meredith,* and Sven H. Behrens*

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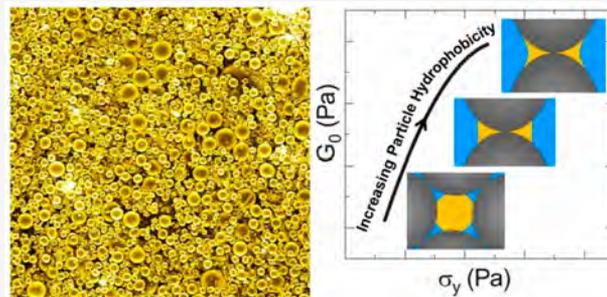


Article Recommendations



Supporting Information

ABSTRACT: The recently discovered capillary foams are aqueous foams stabilized by the synergistic action of colloidal particles and a small amount of oil. Characteristically, their gas bubbles are coated by a particle-stabilized layer of oil and embedded in a gel network of oil-bridged particles. This unique foam architecture offers opportunities for engineering new foam-related materials and processes, but the necessary understanding of its structure–property relations is still in its infancy. Here, we study the effects of particle wettability, particle volume fraction, and oil-to-particle ratio on the structure and selected properties of capillary foams and use our findings to relate measured foamability, foam stability, and rheological key parameters to the observed foam microstructure. We see that particle wettability not only determines the type of gel network formed but also influences the prevalence of oil droplets included within the foam. Our results further show that the stability and rheology of capillary foams are mainly a function of the particle volume fraction whereas the foamability and observed microstructure are sensitive also to the oil-to-particle ratio. These insights expand our fundamental understanding of capillary foams and will greatly facilitate future work on new foam formulations.



1. INTRODUCTION

Ternary systems composed of fluid/fluid/particle mixtures display different types of structures that are determined by the constituent volume fractions and wetting behavior.^{1–3} Pickering emulsions, liquid marbles, and bijels are examples of different ternary states obtainable when particles interact at fluid–fluid interfaces.^{4–6} Understanding the nature and properties of ternary colloidal multiphase systems plays a big role in material design and processing in the ceramics, food, pharmaceutical, and cosmetics industries. In many of the ternary fluid/fluid/particle systems, capillary interactions and particle wettability also play a major role in determining and stabilizing the observed structure.^{2,7} Recently, Velankar categorized the obtainable morphologies of fluid/fluid/particle mixtures in a state diagram as a function of mixture composition and particle wettability.⁸ Many of these ternary systems are composed of immiscible fluids, usually water, a water-immiscible solvent (“oil”) or air, and solid particles of different surface characteristics, but liquid phases formed by immiscible polymer melts are also of interest and allow for convenient structure analysis after solidification.³

Ramsden and Pickering first reported in the early 20th century that particles with appropriate wettability can stabilize fluid interfaces.^{9,10} Since then, it has been well-understood that colloidal particles, in the absence of insurmountable kinetic barriers, tend to adsorb irreversibly to fluid interfaces, provided that the particle wettability does not favor one fluid over the other to an extreme degree. This is because the minimum energy ΔE required to remove a single adsorbed particle of size

R from the interface of two fluids with interfacial tension γ is given approximately by

$$\Delta E = \pi R^2 \gamma (1 - |\cos \theta|)^2 \quad (1)$$

where θ is the contact angle between the fluid interface and the particle surface, and typical values of ΔE exceed the thermal energy scale, kT , by orders of magnitude. Both interfacial tension and particle wettability, for which θ is a measure, are important in the formation and stability of ternary systems; however, the particle wettability has a stronger influence on the system morphology. The values of θ in ternary systems range between 0° to 180° , where both extremes indicate complete wetting of the particles by one of the two fluids. Much attention has been given to systems stabilized by particles with near-neutral wetting (θ close to 90°).^{11–13} More recently, work has been devoted to understanding ternary systems in which one fluid preferentially wets the particles, which commonly occurs *e.g.* in capillary suspensions.¹⁴

Capillary suspensions are particle suspensions that include a small amount of an immiscible secondary liquid. The addition of the secondary liquid and mixing leads to the formation of a space spanning network of particles bridged by the secondary

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Bilevel interactive optimisation for rebatching scheduling problem with selectivity banks in high variety flow line production

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ABSTRACT

Mass customization enables the integration of traditional flow line production with product platforms to accommodate abundant product-process varieties. These platform-based flow lines explore common process routes while highlighting rebatching scheduling with selectivity banks (RBS) to handle large process varieties across production stages at minimum setup cost. Given the inherent coupling between decision making in job diverging and retrieval quality, an interactive optimization approach is necessary for the RBS problem. This study proposes a bilevel interactive optimization (BIO) model for RBS to accommodate high variety flow line production. The model addresses the conflicting goals of lane occupancy cost, process setup cost, and job divergence and retrieval efficiency. Regarding job divergence at the leader-level, a vehicle routing problem with precedence constraints is formulated and solved by a constructed genetic algorithm (GA). Concerning job retrieval at the follower-level and the ongoing characteristic of selectivity banks, a dispatching problem with various batch size preference and dynamic time window is established and dealt with a restricted dynamic programming (RDP) algorithm after balancing search efficiency and accuracy. Thus, to solve the BIO, a hybrid GA-RDP is developed and implemented. A practical application to an automotive painting shop illustrates the operational benefits of the BIO model for the RBS problem.

ARTICLE HISTORY

Received 13 September 2020
Accepted 16 May 2021

KEYWORDS

Manufacturing; rebatching problem in manufacturing; selectivity banks in manufacturing; bilevel interactive optimisation; bilevel algorithm

1. Introduction

The extent of 'market-of-one' has been recognised as a driving force for the manufacturing economies, which transforms the conventional mass production to mass customisation by offering more product variants to satisfy market niche segments (Pirmoradi, Wang, and Simpson 2014). This abundant of product variety propagates from product domain to production domain, which leads to an increase of process variety to challenge the reduction of production cost (Jiao, Zhang, and Wang 2007; Zhang, Lee, and Akhtar 2020). The flow line production has been widely recognised as an efficient approach to produce high volumes of products with high production rates and low costs (Ashraf and Hasan 2018). This production decomposes the product fulfilment procedures into multiple production stages based on the precedence relationship among the processes. It can enable economies of scale by reusing the common process structure and satisfy the diverse product expectations by concurrently reconfiguring the common process

routings (Jiao, Zhang, and Wang 2007). Based on the common process structure shared by the product variants, an appropriate product order can cluster the similar process routes into a batch to minimise the setup efforts and maximise the reuse of manufacturing resources (Bataia, Dolgui, and Guschinsky 2020). Because the flow line explores the common process routing based on various features across production stages, this process differentiation entails a product rebatching problem, which analyses the upstream product orders and resequences these orders into batches to balance workload or minimise setup efforts at downstream (Ko, Han, and Choi 2016; Taube and Minner 2018). Moreover, apart from the predefined process requirement, the random injection of products caused by unexpected disruptions also make the rebatching for downstream workstations necessary.

A critical aspect of practical rebatching applications is regarding capacity planning and optimal decisions of job dispatching, which is commonly referred as rebatching scheduling (Stadtler and Sahling 2013). The rebatching

Thermally Stimulated Wettability Transformations on One-Cycle Atomic Layer Deposition-Coated Cellulosic Paper: Applications for Droplet Manipulation and Heat Patterned Paper Fluidics

Yi Li, Jamie P. Wooding, Emily K. McGuinness, Yici Sun, and Mark D. Losego*



Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 13802–13812



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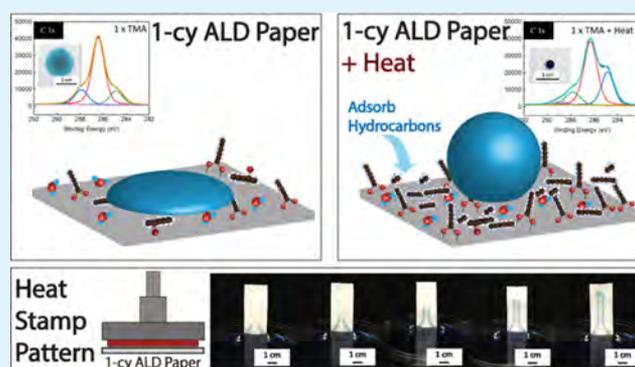
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Supporting Information

ABSTRACT: Cellulosic materials are widely used in daily life for paper products and clothing as well as for emerging applications in sustainable packaging and inexpensive medical diagnostics. Cellulose has a high density of hydroxyl groups that create strong intra- and interfiber hydrogen bonding. These abundant hydroxyl groups also make cellulose superhydrophilic. Schemes for hydrophobization and spatially selective hydrophobization of cellulosic materials can expand the application space for cellulose. Cellulose is often hydrophobized through wet chemistry surface modification methods. This work reports a new modification method using a combination of atomic layer deposition (ALD) and atmospheric heating to alter the wettability of purely cellulosic chromatography paper. We find that once the cellulosic paper is coated with a single ALD cycle (1cy-ALD) of Al_2O_3 , it can be made sticky superhydrophobic after a 150 °C ambient post-ALD heating step. An X-ray photoelectron spectroscopy investigation reveals that the ALD-modified cellulosic surface becomes more susceptible to adsorption of adventitious carbon upon heating than an untreated cellulosic surface. This conclusion is further supported by the ability to use alternating air plasma and heat treatments to reversibly transition between the hydrophilic and hydrophobic states. We attribute the apparent abruptness of this wetting transition to a Cassie–Wenzel-like phenomenon, which is also consistent with the sticky hydrophobic wetting behavior. Using scanning probe methods, we show that the surfaces have roughness at multiple length scales. Using a Cassie–Wenzel model, we show how a small change in the surface's Young's contact angle—upon adsorption of adventitious carbon—can lead to an abrupt increase in hydrophobicity for surfaces with such roughnesses. Finally, we demonstrate the ability to spatially pattern the wettability on these 1cy-ALD-treated cellulosic papers via selective heating. This ALD-treated hydrophobic paper also shows promise for microliter droplet manipulation and patterned lab-on-paper devices.

KEYWORDS: atomic layer deposition (ALD), wettability transition, cellulose, Cassie–Wenzel transition, paper-based fluidics



1. INTRODUCTION

Cellulosic products are attractive for their biodegradability, low cost, and mechanical flexibility. Paper-based devices continue to gain attention for applications as varied as energy storage devices,^{1,2} microfluidics,³ sensing,⁴ and analytical detection systems.^{5,6} These applications take advantage of paper's mechanical flexibility, low density, renewable sourcing, and usefulness in working with small sample volumes. Many of these devices rely on the capillary flow of water through the paper's hydrophilic fibrous structure. Directing this capillary flow within the paper via hydrophobic patterning has a number of potential applications.^{7–9} Here, we examine new methods, using <1 nm metal oxide atomic layer deposition (ALD) coatings to create a hydrophobic paper.

Hydrophobicity occurs when the spreading of water over a material's surface is not energetically favored. Both chemical and structural conditions can cause hydrophobicity.¹⁰ Several

mathematical frameworks have been developed to predict surface wetting properties. The most frequent mathematical framework, Young's equation, assumes a smooth ideal surface, which is isotropic and homogeneous. Under these assumptions, the wetting process is not energetically favored (i.e., hydrophobic) when the surface energy of the liquid–solid interface is higher than the surface energy of the water–vapor interface. Mechanistically, this is how surface chemistry modification, such as the addition of hydrocarbons, creates

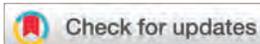
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Biorefining and Bioindustrial Manufacturing



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Production of active pharmaceutical ingredients (APIs) from lignin-derived phenol and catechol

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Active pharmaceutical ingredients (APIs) constitute a significant and growing global market. In the past few decades, labor costs, concerns regarding chemical waste, and more stringent regulations in developed countries have shifted the production of APIs to emerging economies, notably India and China. Nowadays, Europe and North America rely on imports for the majority of pharmaceuticals. The recent COVID pandemic as well as logistical challenges have called this model into question and have raised the interest in rebalancing distributed global API supply chains and possibly reshoring some API production to Europe and North America. API production often suffers from unfavorable Green Chemistry metrics, owing to complex routes, outdated chemistry for established entities, or lack of maturity of routes for newer entities. The environmental footprint of API synthesis routes benefits from renewables as starting materials. One such abundant renewable material is lignin, which can be converted to phenol and catechol. In addition, waste could be reduced by co-producing APIs in an integrated plant and the use of advanced catalysts. This Perspective demonstrates green production routes from phenol or catechol in four large scale examples: paracetamol (Tylenol®), acetyl salicylic acid (Aspirin®), amoxicillin (as sole API or as combination with potassium clavulanate (Augmentin®)), and epinephrine (adrenaline, also as trademark Adrenaline®). We compare conventional routes with more modern routes with respect to Green Chemistry metrics. Overall, API production from renewable materials stands to combine low environmental footprint with high quality and economical manufacture of pharmaceuticals.

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Introduction

Active pharmaceutical ingredients (APIs) constitute a significant global market of USD 190 billion in 2020 projected to compound annually by 6.6%.¹ This growth is attributed to the aging population and higher incomes in emerging economies.¹ In the past few decades, the high cost of manufacturing as well as the more stringent environmental regulations in developed countries has shifted the production of APIs, resulting in the reliance of many regions on API imports for their supply. As demand for APIs continues to increase, distributed global API supply lines become more important.

In recent years, the dependence of various countries on API imports has become more apparent. According to the FDA, 70%

of facilities that supply APIs to the USA are overseas.² Europe has similar API supply concerns, most generic medicines being imported from China and India. Even for locally produced APIs in Europe, most of the raw materials originate overseas.³ India, one of the world's largest drug exporters, relies on imports from China for 70% of its raw materials.⁴ In addition, recent availability and access issues surrounding the Covid-19 pandemic have raised concerns about the reliability of current API supply chains, which could impact national security.⁵

These recent events have renewed interest in reshoring drug production in various developed countries. Many pharmaceutical processes have been outsourced from Europe and North America in parallel with regulations such as Europe's Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) legislation, which have tightened environmental restrictions and made the domestic production of certain APIs less viable.⁶ New initiatives, such as the FDA's Emerging Technology Program (ETP), have tried to reduce barriers to advanced manufacturing techniques that can make domestic production more economically attractive.² A collaboration between the FDA and the Biomedical Advanced Research and Development Authority (BARDA) is trying to develop

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Closing the Anthropogenic Chemical Carbon Cycle toward a Sustainable Future via CO₂ Valorization

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Concerns over the massive increase in CO₂ emissions induced by overconsumption of fossil fuels have driven the rapid development of CO₂ valorization techniques. Carbon capture and utilization (CCU) technology, which emerged as a promising strategy to relieve increasing environmental concerns and create more carbon feedstocks simultaneously, hold great promise to close the anthropogenic chemical carbon cycle. Herein, recent breakthroughs related to the two predominant techniques involved in returning CO₂ into a useful state, namely CO₂ capture and CO₂ conversion are systematically overviewed. Initially, CO₂ capture principles, recent advances, as well as future challenges of state-of-the-art adsorbents/adsorbents and membrane separation technology are summarized. Furthermore, innovative catalysts related to the CO₂ conversion technologies (including thermo-driven CO₂ hydrogenation, photo-and electrochemical CO₂ reduction, and enzymatic CO₂ conversion) are discussed, emphasis is focused on the catalytic performance, design principles, and economic efficiency. Finally, a perspective regarding the future research opportunities toward CCU technologies is provided. This review aims to stimulate innovation and accelerate interdisciplinary integrations toward CCU related technologies via a discussion of fundamental mechanisms, recent breakthroughs, current associated difficulties as well as future directions.

Oceanic and Atmospheric Administration, atmospheric CO₂ concentration has dramatically increased from 280 ppm to ≈414 ppm since the first industrial revolution, and is predicted to reach ≈590 ppm, which will result in an increase of the global mean air surface temperature of ≈1.91 °C by the end of the 21st century. Therefore, anthropogenic CO₂ production is responsible for a growing detrimental effect on our environment and is a catastrophic threat to our current society and future generations.^[2] To take action against global warming caused by greenhouse gas (GHG) emission, 195 sovereign nations signed the 2015 Paris Climate Agreement to restrict GHG emissions and limit the rise of global temperatures to lower than 2 °C above preindustrial levels.^[3] In this context, numerous efforts have been devoted to stabilizing global atmospheric CO₂ concentrations. Developing carbon emission-free energy generation technologies is a widely recognized solution; nevertheless, the annual global investment in fossil energy remains dominant

and the proportion of energy collected from sustainable sources is scarce.^[4] Indeed, recent studies also indicated that this emissions reduction strategy alone is not enough to keep global warming within 2 °C. The concept of “anthropogenic chemical carbon cycle” based on CO₂ capture and recycling to fuels and materials is therefore proposed as a supplement to the natural photosynthesis-based carbon cycle to provide sustainable, and renewable carbon feedstocks on which we depend so much.^[5] As the core of the “anthropogenic chemical carbon cycle,” the carbon capture and utilization (CCU) technology has gathered extensive interest from both researchers and policy-makers owing to its great promise in controlling atmospheric CO₂ concentrations.^[6]

Two major processes, namely CO₂ capture and CO₂ conversion, are included in the CCU.^[7] As the first step for CCU, CO₂ capture has already been commercially utilized since the 1950s as a pretreatment for cryogenic air separation, and a series of novel materials for CO₂ capture have been developed over the past decades.^[8] Another key process, CO₂ conversion, has received increasing attention over the past decades due to its potential to simultaneously store intermittent energy and control CO₂ concentrations by returning CO₂ to a useful state (e.g., chemicals and fuels). Typically, the CO₂ conversion process is scientifically challenging due to the robust nature of C=O

1. Introduction

Over the past centuries, fossil fuels have played an essential role in the unprecedented development of the human civilization, but rapid fossil fuels combustion since the industrial revolution results in over 35 gigatonnes CO₂ emission annually, which gradually disrupts the balance of the natural carbon cycle and causes serve climate issues including but not limited to the climate change, rising sea-levels, and decreasing food security.^[1] According to the latest data from the National

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Application of Density Functional Tight Binding and Machine Learning to Evaluate the Stability of Biomass Intermediates on the Rh(111) Surface

Chaoyi Chang and Andrew J. Medford*

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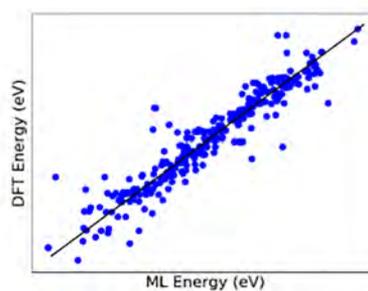
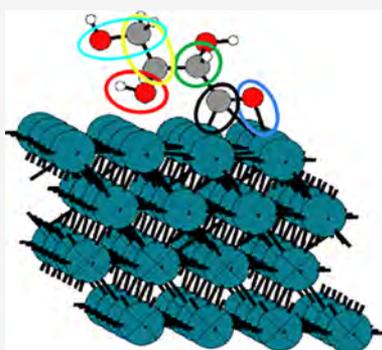
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ABSTRACT: Biomass compounds adsorbed on surfaces are challenging to study due to the large number of possible species and adsorption geometries. In this work, possible intermediates of erythrose, glyceraldehyde, glycerol, and propionic acid are studied on the Rh(111) surface. The intermediates and elementary reactions are generated from first two recursions of a recursive bond-breaking algorithm. These structures are used as the input of an unsupervised Mol2Vec algorithm to generate vector descriptors. A data-driven scheme to classify the reactions is developed, and adsorption energies are predicted. The lowest mean absolute error of our prediction on adsorption energies is 0.39 eV, and the relative ordering of different surface adsorption geometries is relatively accurate. We show that combining geometries from density functional tight-binding calculations with energies from machine-learning predictions provides a novel workflow for rapidly assessing the stability of various molecular geometries on the Rh(111) surface.

INTRODUCTION

Biomass compounds play a key role in biorenewable products and are the basis of a sustainable economy. For example, the US Department of Energy has listed the 10 top biorefinery products with the highest potential impact.¹ Selective conversion between these products and other small-molecule products are important if biomass compounds are to form the basis of a sustainable economy. Rh is a commonly used transition-metal catalyst for conversion of biomass compounds and has been the subject of numerous experimental studies. For example, Rh catalysts have been used for succinic acid conversion to fumaric acid,² hydrogenolysis of furfural to 1,2-pentanediol,³ and production of C1 compounds from ethanol.^{4–6} However, there have been relatively few systematic computational studies of biomass intermediates on Rh surfaces.⁷ Density functional theory (DFT) is the most common theory used to study the adsorption and reaction of biomass compounds.^{8–10} However, complex molecules have multiple binding sites and various geometries, and DFT calculations of larger molecules are expensive and require significant computational effort to converge. Thus, previous

studies often utilize empirical and machine learning (ML) methods to relate reaction properties of biomass molecules or intermediates to their structures, physical properties, and even experimental conditions.^{9,11–13} Most of these ML methods could reach a mean absolute error (MAE) of adsorption energies/transition-state energies within 0.4 eV,^{7,13,14} with some examples of predictions as accurate as 0.2 eV using a combination of physical and structural features along with feature selection methods.^{12,15}

As mentioned previously, a key challenge with biomass molecules is their complexity, and “model compounds” are often used to simplify systems of interest. A “model compound” refers to a relatively small molecule (typically

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Designing the bioproduction of Martian rocket propellant via a biotechnology-enabled in situ resource utilization strategy

Nicholas S. Kruyer¹, Matthew J. Realff¹, Wenting Sun², Caroline L. Genzale³ & Pamela Peralta-Yahya^{1,4}  

Mars colonization demands technological advances to enable the return of humans to Earth. Shipping the propellant and oxygen for a return journey is not viable. Considering the gravitational and atmospheric differences between Mars and Earth, we propose bioproduction of a Mars-specific rocket propellant, 2,3-butanediol (2,3-BDO), from CO₂, sunlight and water on Mars via a biotechnology-enabled in situ resource utilization (bio-ISRU) strategy. Photosynthetic cyanobacteria convert Martian CO₂ into sugars that are upgraded by engineered *Escherichia coli* into 2,3-BDO. A state-of-the-art bio-ISRU for 2,3-BDO production uses 32% less power and requires a 2.8-fold higher payload mass than proposed chemical ISRU strategies, and generates 44 tons of excess oxygen to support colonization. Attainable, model-guided biological and materials optimizations result in an optimized bio-ISRU that uses 59% less power and has a 13% lower payload mass, while still generating 20 tons excess oxygen. Addressing the identified challenges will advance prospects for interplanetary space travel.

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CATALYSIS

Two steps to sustainable polymers

Medium-chain linear α -olefins are commodity chemicals; however, manufacturing α -olefins from biomass is challenging due to inefficient removal of the last oxygen atoms. Now, a two-step biological-chemical catalysis strategy to produce medium-chain linear α -olefins provides a route to sustainable polymers.

Shaafique Chowdhury and Pamela Peralta-Yahya

Unlike most chemical processes, chemical synthesis using engineered microbes occurs in aqueous conditions, at ambient temperature and pressure, enhancing the sustainability of the overall manufacturing process. Over the last decade, our ability to engineer microbes to produce value-added chemicals from renewable biomass has dramatically improved in terms of biosynthetic productivity (that is, titres, yields and rates) and chemical complexity. As a field, we are moving beyond producing biofuels and natural products, to engineering microbes for the synthesis of chemicals that more closely resemble 'petroleum-like' hydrocarbons, such as medium-chain linear α -olefins, that can be 'dropped in' to existing chemical processes, such as polymer synthesis.

α -Olefins are commodity chemicals that are used as plasticizers and are also a starting material used for the synthesis of other chemicals. A key challenge in the completely biological synthesis of α -olefins is the inefficient removal of the last oxygen atoms. Biological systems are proficient at converting biomass (for example, glucose, $C_6H_{12}O_6$) into 'biological hydrocarbons' (for example, octanoic acid, $C_8H_{16}O_2$). Removal of the last oxygen atoms to produce alkenes

either requires additional reducing power (NADH) and energy (ATP), which throws cellular metabolism off balance and results in lower biosynthetic productivities, or there are simply no known enzymes to perform the desired reaction.

Chemical catalysis can reduce biological hydrocarbons to petroleum-like ones. Heterogeneous chemical catalysis offers the added benefit of high selectivity, yields and ease of separation. Indeed, two-step biological-chemical heterogeneous catalysis strategies have been applied to the production of other chemicals, such as adipic acid¹. Key to this two-step process is the identity of the biological hydrocarbon. The microbe should produce a chemical that is as close to the final product as possible while maintaining high biosynthetic productivity. The biological hydrocarbon should be chemically upgraded using a catalyst that is inexpensive, suffers only limited poisoning in the presence of biological contaminants, and operates at low temperatures and pressures.

A team led by Zhen Q. Wang and Michelle C. Y. Chang have now developed a two-step biological-chemical catalysis strategy to produce medium-chain linear α -olefins by engineering a microbe to metabolize glucose to linear medium-chain

3-hydroxy acids, with a subsequent reduction to α -olefins via heterogeneous chemical catalysis² (Fig. 1). In this work, Wang, Chang and co-workers make two key contributions to the field. First, the identification of 3-hydroxy acids as the optimal biological hydrocarbon for chemical upgrading to α -olefins. The 3-hydroxy moiety functions as a leaving group to ease decarboxylation/dehydration, which is readily accomplished by solid acid catalysts, including earth-metal-based ones, which are compatible with sustainable chemical catalysis. Second, the discovery of a new thiolase-dependent medium-chain fatty acid synthesis cycle that is more energy efficient than traditional fatty acid synthesis (FAS), which requires one ATP per 2-carbon extension. This thiolase-dependent cycle allows the cell to keep using FAS to produce C_{16} – C_{18} fatty acids to support cell growth and maintenance, thus reducing cell toxicity, and enabling higher medium-chain fatty acid yields.

The discovery of the thiolase-dependent cycle hinged on the identification of a medium-chain (C_8 – C_{10}) iterative thiolase from *Mycobacterium* (PaaJ), which did not cluster with known short-chain (C_4 – C_6) thiolases involved in polyhydroxyalkanoate synthesis or broad-specificity (C_2 – C_{18})

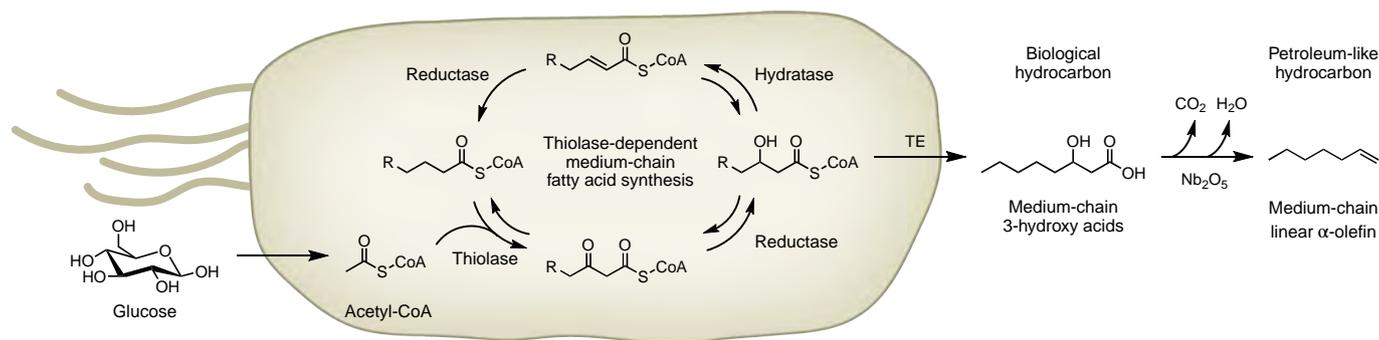


Fig. 1 | A two-step biological-chemical catalysis strategy for the production of medium-chain α -olefins. A microbe was engineered to metabolize glucose to linear medium-chain 3-hydroxy acids using a thiolase-dependent fatty acid synthesis cycle. Key to the cycle are the iterative thiolase, irreversible reductase, and medium-chain acyl-CoA specific thioesterase (TE). In a second part of the process heterogeneous chemical catalysis converted the 3-hydroxy acids to medium-chain α -olefins.

Article

Greenhouse Gas Impact of Algal Bio-Crude Production for a Range of CO₂ Supply Scenarios

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Abstract: Refined bio-crude production from hydrothermal liquefaction of algae holds the potential to replace fossil-based conventional liquid fuels. The microalgae act as natural carbon sequestrators by consuming CO₂. However, this absorbed CO₂ is released to the atmosphere during the combustion of the bio-crude. Thus, the life-cycle greenhouse gas (GHG) emissions of refined bio-crude are linked to the production and supply of the materials involved and the process energy demands. One prominent raw material is CO₂, which is the main source of carbon for algae and the subsequent products. The emissions associated with the supply of CO₂ can have a considerable impact on the sustainability of the algae-based refined bio-crude production process. Furthermore, the diurnal algae growth cycle complicates the CO₂ supply scenarios. Traditionally, studies have relied on CO₂ supplied from existing power plants. However, there is potential for building natural gas or biomass-based power plants with the primary aim of supplying CO₂ to the biorefinery. Alternately, a direct air capture (DAC) process can extract CO₂ directly from the air. The life-cycle GHG emissions associated with the production of refined bio-crude through hydrothermal liquefaction of algae are presented in this study. Different CO₂ supply scenarios, including existing fossil fuel power plants and purpose-built CO₂ sources, are compared. The integration of the CO₂ sources with the algal biorefinery is also presented. The CO₂ supply from biomass-based power plants has the highest potential for GHG reduction, with a GHG footprint of −57 g CO₂ eq./MJ refined bio-crude. The CO₂ supply from the DAC process has a GHG footprint of 49 CO₂ eq./MJ refined bio-crude, which is very similar to the scenario that considers the supply of CO₂ from an existing conventional natural gas-based plant and takes credit for the carbon utilization.

Keywords: algae; direct air capture; bio-crude; hydrothermal liquefaction; catalytic hydrothermal gasification; life cycle analysis



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1. Introduction

The sustainable production of advanced biofuels from algal biomass faces several challenges. These include algae productivity, the sustainable supply of carbon dioxide (CO₂), and the use of fossil-based energy in algal conversion processes [1–3]. Among these, the sustainable supply of CO₂ is often overlooked, or it is assumed that CO₂ would be readily available at the algal biorefinery site without any substantial emissions associated with the supply of CO₂. Patel et al. [4] developed a cradle-to-gate attributional life cycle

Circular Materials



Enabling zero added-coalescent waterborne acrylic coatings with cellulose nanocrystals

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ABSTRACT

Waterborne acrylic coatings contain volatile and non-volatile coalescents. Volatile organic compound (VOC) coalescents enable film formation of hard acrylic polymers at ambient temperature, but their evaporation results in air pollution and health concerns. Non-volatile alternatives are available, but they remain in the coating long-term and as a result films are often tacky and lack adequate hardness. Reinforcing mineral fillers are available, but are associated with sustainability challenges inherent to mineral mining. An alternative approach demonstrated here utilizes a renewably-sourced, plant-based hardening filler dispersed in the water phase, with soft polymer latexes that don't require VOCs for film formation. We reinforced coalescent-free and ambient film-forming butyl acrylate/methyl methacrylate/methacrylic acid latexes with cellulose nanocrystals (CNCs) by a post-synthesis blending approach. CNCs possess high elastic modulus and tensile strength, making them promising candidates to improve the mechanical performance of soft ambient film-forming acrylic latexes. CNCs form aggregates within the interstices between latex particles as water dries, however film coalescence is not compromised. Films with 15 wt% CNC showed almost 230 % improvement in Koenig hardness and 10x improvement in the nanoindentation hardness compared to neat films, achieving properties similar to hard VOC-containing acrylic binders in a zero-added VOC formulation.

1. Introduction

Paints and coatings with a market of ~43 million tons in 2016 [1], have annual volatile organic compound (VOC) emissions of ~2 million tons [2]. Reducing VOC release has driven development of waterborne paints, but despite advances many interior waterborne products contain 250 g/L VOCs [3]. In addition to inherent health effects [4], VOCs react with atmospheric nitrogen oxides, forming ground-level ozone [5] that contributes to global warming and harms health [6]. Coating producers are under increasing pressure to decrease VOC content because of legislation and customer demand. However, transitioning to low VOC products brings a challenge known as the “film formation dilemma”, in which the VOC organic coalescents are needed to plasticize individual latex particles so that they form hard, durable coatings following VOC evaporation.

Acrylics are the most used binder resin in waterborne coatings.

Hardness of the acrylic is an important aspect of coating durability. Soft latex particles that easily coalesce to form a film lack adequate hardness. Latexes are often formulated with copolymers with high glass transition temperature (T_g) but VOC coalescents are added to temporarily plasticize the particles to enable film formation at ambient conditions [7]. Industry also employs non-evaporative plasticizers that provide coalescence. However, the film remains tacky after curing. Thus, alternative approaches are desired to achieve the performance of high T_g acrylic latex coatings in the lower VOC formulations of today.

One approach is to add a hardening filler to the polymer matrix. Mechanically robust nanoscale fillers have been shown to improve polymer mechanical performance [8], including nanoscale fillers such as clay [9], silica [10], and carbon nanotubes [11]. Cellulose nanocrystals (CNCs) are proposed as a renewable filler to enhance mechanical performance of soft latex films, due to their high crystallinity, strength, and modulus, low density (relative to mineral fillers), and optical transparency (when

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Photostability of Ambient-Processed, Conjugated Polymer Electrochromic Devices Encapsulated by Bioderived Barrier Films

Augustus W. Lang, Yue Ji, Anna C. Dillon, Chinmay C. Satam, J. Carson Meredith, and John R. Reynolds*



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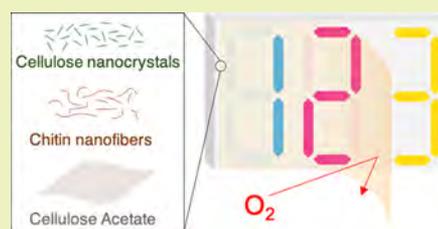
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Supporting Information

ABSTRACT: Polymer-based electrochromic devices (ECDs) are a promising technology for enabling low-voltage, disposable displays, yet are currently limited by photo-oxidative bleaching of the active materials. Here, renewable barrier films composed of cellulose and chitin are presented as an alternative to poly(ethylene terephthalate) (PET) for encapsulating ECDs. To assess barrier film effectiveness, lateral ECDs composed of poly(3,4-propylenedioxythiophene-(CH₂OEtHx)₂) (P(ProDOT)) active layers were constructed and encapsulated with a multilayer barrier consisting of chitin nanofibers and cellulose nanocrystals spray cast onto a cellulose acetate substrate (oxygen transmission rate (OTR) = 29 cm³ m⁻² day⁻¹), a commercially available PET film (OTR = 8.5 cm³ m⁻² day⁻¹), and a high-performance PET-Al₂O₃ multilayer barrier film (OTR < 1 cm³ m⁻² day⁻¹). The photodegradation of the P(ProDOT) active layer was determined by measuring the evolution of the colorimetric contrast (ΔE^*) and switching speeds as a function of light exposure (100 mW cm⁻², AM 1.5 G light). Photodegradation was found to proceed at a similar rate for all encapsulated devices (roughly 10 times more slowly than unencapsulated devices), highlighting the opportunity for replacing petroleum packaging with bioderived barrier films. Analysis of the switching kinetics, the shifts in optical absorbance, and evidence of chemical degradation indicate that both photochemical breakdown of the electrolyte and cross-linking of the P(ProDOT) active material are key drivers for loss of device performance when oxygen flux to the active material is limited. Pathways toward better understanding photodegradation are then proposed with sustainability in mind for future ECD design.

KEYWORDS: bioderived barrier films, conjugated polymer photostability, electrochromic device encapsulation, nanochitin, nanocellulose, green electronics



INTRODUCTION

Each year, roughly 150 million tons of flexible plastic packaging are produced for a range of consumer goods from food to pharmaceuticals to electronics.¹ The majority of these plastic packages are composed of polyethylene, polypropylene, and poly(ethylene terephthalate) (PET), each derived from petroleum. These materials offer many benefits in terms of their cost, processability, and gas barrier properties, yet pose a sustainability challenge due to greenhouse gas emissions associated with their production and their long-term persistence in the environment. While recycling offers a partial solution to this challenge, the rise of single-use packaging and commoditized cost of these materials has rendered recycling efforts largely a failure as estimates suggest only 9% of petroleum-based plastics have ever been recycled.¹ To address this challenge, we must find renewable substitutes that provide sufficient strength, durability, and gas barrier properties with much lower environmental impact over the course of their life cycle.

To fulfill these sustainability criteria, materials derived from biomass become an obvious choice, especially those abundant in natural supply that can be processed with sustainable and

energy-efficient processing.² Cellulose nanocrystals (CNCs), extracted from woody biomass, offer a number of advantageous properties for packaging materials. Due to their high crystallinity, ease of derivatization, and propensity to self-assemble into a chiral nematic liquid crystalline phase, CNCs have attracted significant attention as oxygen barrier coatings.^{3–5}

Chitin has also generated recognition as a promising biomass-derived alternative to petroleum products for packaging.^{5–10} Chitin offers the advantage of being widely available as a waste product from the crustacean industry at roughly 8 million tons per year^{11–13} and is present in insect exoskeletons and microorganisms such as fungi.¹⁴ Crystalline chitin nanofibers (ChNFs) can be extracted from crab, shrimp, or lobster shells via deproteination with base and demineraliza-

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Scalable coating methods for enhancing glass fiber–epoxy interactions with cellulose nanocrystals

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Abstract Two scalable coating techniques, slot die and spray coating (SC), are used to apply cellulose nanocrystals (CNCs) to the surface of glass fibers with the goal of enhancing interfacial interactions between glass fibers and epoxy and, consequently, the strength of fiber-reinforced composites. The quality of the cellulose coatings and the interfacial shear strength, assessed via the single fiber fragmentation test, are determined as a function of the method and conditions used to coat the fibers. In addition, a comparison with

glass fibers coated with identical CNC formulations using a laboratory-scale dip coating (DC) technique is provided. Results from both scalable methods were found to be comparable or superior to the DC technique, with SC outperforming DC by up to 18% on average depending on the coating applied. Further analysis was conducted on coating morphology, fracture behavior, elemental composition, and surface loading. The observed differences can be used to determine which technique is most appropriate for a given application. This work demonstrates the viability in adapting existing, scalable processes for CNC

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TEMPO-CNF suspensions in the viscoelastic regime: capturing the effect of morphology and surface charge with a rheological parameter

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Abstract TEMPO cellulose nanofibril (TEMPO-CNF) suspensions in the viscoelastic regime are often used as rheological modifiers and additives to prepare composites and hydrogels. Therefore, understanding their rheology is important, including the role of morphology and surface charge. The viscosity of TEMPO-CNF suspensions decreases with higher homogenization pressure or number of homogenization passes, and higher surface charges. To compare the effects of morphology and surface charge more robustly, a rheological “flow index” parameter is developed. Zero-shear viscosity η_0 is first determined

from the Cross model, and the flow index k is defined through the scaling relation $\log_{10}(\eta_0) = k \cdot c - \log_{10}(\eta_{water})$, c being concentration and η_{water} the viscosity of pure water. The flow index decreases with higher homogenization energy and higher surface charge. The flow index condenses many viscosity points into a single parameter, establishing a clear and concise one-to-one relationship between TEMPO-CNF rheology and fibril characteristics, which can be used for quality control and/or benchmarking.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10570-020-03572-1>) contains supplementary material, which is available to authorized users.

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Synergistic Reinforcement of Composite Hydrogels with Nanofiber Mixtures of Cellulose Nanocrystals and Chitin Nanofibers

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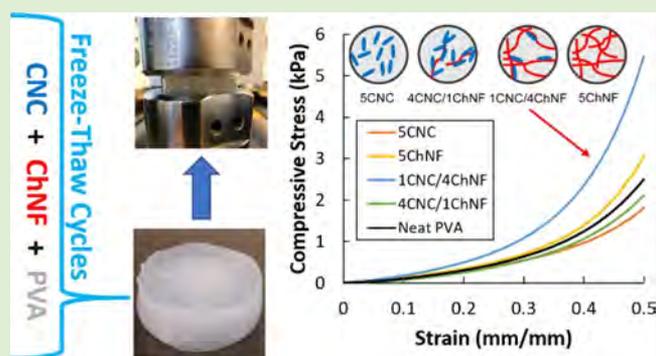


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Supporting Information

ABSTRACT: Simultaneous incorporation of cellulose nanocrystals (CNCs) and chitin nanofibers (ChNFs) into a polyvinyl alcohol (PVA) matrix opens possibilities for customization of more environmentally friendly composite materials. When used in tricomponent composite hydrogels, the opposite surface charges on CNCs and ChNFs lead to the construction of beneficial nanofiber structures. In this work, composite hydrogels containing CNCs, ChNFs, or their mixtures are produced using cyclic freeze–thaw (FT) treatments. When considering different compositions and FT cycling, tricomponent composite hydrogels containing a specific ratio of CNCs/ChNFs are shown to have promising mechanical performance in comparison to other samples. These results together with results from water absorption, rheological, and light scattering studies suggest that the CNC/ChNF structures produced property improvement by concurrently accessing the stronger interfacial interactions between CNCs and PVA and the longer lengths of the ChNFs for load transfer. Overall, these results provide insight into using electrostatically driven nanofiber structures in nanocomposites.



1. INTRODUCTION

Since renewable materials are derived from natural resources, they continue to garner popularity in the research community and have developed into a large field of study.^{1–6} One such renewable material that has been closely studied in recent years is nanocellulose. Sourced from trees, other plant life, and even bacteria, cellulose is the most abundant biopolymer and is composed of repeat units of two anhydroglucose rings that align themselves into a ribbon-like conformation.^{7,8} Cellulose nanocrystals (CNCs), a type of nanocellulose, are rod-like, highly ordered particles that can be isolated from cellulose through a sulfuric acid hydrolysis process that preferentially dissolves disordered regions of the cellulose chain. The size of CNCs often varies from batch to batch, but they generally have lengths of 50–500 nm and widths of 3–5 nm.⁷ This processing method also leaves sulfate half ester groups on their surface, which give the CNCs a negative charge.^{8–11} Their incorporation into polymer composites allows for the development of materials that can be structurally strong while reducing the environmental impact of synthetic polymers.³

Chitin, another abundant natural polymer, is a renewable material found primarily in the exoskeleton/shells of arthropods including crustaceans and insects, as well as fungi,^{12,13} and contains molecular repeat units of *N*-acetyl-*D*-glucosamine.^{14,15} When produced through high-pressure homogenization,¹⁶ chitin can be separated into long, wispy

chitin nanofibers (ChNFs) with approximate widths of 5–20 nm and lengths up to several micrometers. In contrast to CNCs, in mildly acidic media, ChNFs possess a net positive surface charge as a result of protonation of primary amine groups that are the product of deacetylation of the *N*-acetyl groups.¹² This surface functionality imparts electrostatic stabilization in acidic aqueous media. ChNFs, as well as highly deacetylated chitosan, have been used in biomedical applications such as sutures and wound dressings, as well as in a hydrogel form in tissue engineering.¹⁷ Of particular interest in this work, the positive surface charge also provides potential for attractive electrostatic forces to drive interactions between CNCs and ChNFs.^{18,19}

Polymer composites can be generated in a variety of different constructs, such as hydrogels, that facilitate the addition of nanofillers to achieve customized performance for different applications. Hydrogels are three-dimensional structures primarily made up of water, though they display solid-like properties because of the structure of the dispersed

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Dewatering Cellulose Nanomaterial Suspensions and Preparing Concentrated Polymer Composite Gels via Reverse Dialysis

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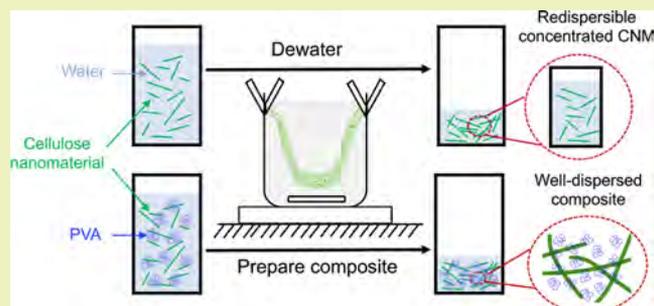
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Supporting Information

ABSTRACT: Cellulose nanomaterials (CNMs) are typically produced in aqueous suspensions at low concentrations, which require subsequent dewatering to reduce transportation cost or as a preprocessing step for applications that require higher CNM loadings such as rheological modifiers and composites. Reverse dialysis is an effective method that avoids common dewatering issues like irreversible aggregation and sample heterogeneity. In this study, samples for dewatering were placed inside a dialysis bag and immersed in poly(ethylene glycol) (PEG) solution. The water removal process is driven by the osmotic pressure difference. Dewatered TEMPO-cellulose nanofibril (TEMPO-CNF) was redispersible after allowing for time to rehydrate; the original viscosity was recovered after a dewatering-redilution cycle. The generalizability of reverse dialysis was demonstrated by also dewatering suspensions of cellulose nanocrystal and chitin nanofiber. Furthermore, concentrated and well-dispersed poly(vinyl alcohol) (PVA)/TEMPO-CNF composite gels were obtained via reverse dialysis at loadings that were difficult to achieve by other methods. Reverse dialysis thus increases the processing range for these sustainable nanomaterials while preserving their beneficial morphological properties. Reverse dialysis can be added to manufacturing processes; recycling of the PEG solutions via ultrafiltration can be used to create an energy-efficient, sustainable, closed-loop dewatering process for cellulose nanomaterials that are hard to redisperse.

KEYWORDS: reverse dialysis, TEMPO-CNF, cellulose nanocrystal, chitin nanofiber, composite, rheology, viscosity



INTRODUCTION

Cellulose nanomaterials (CNM) are produced from abundant cellulose sources and include cellulose nanocrystal (CNC), cellulose nanofibril (CNF), and TEMPO-oxidized cellulose nanofibril (TEMPO-CNF).¹ Due to their large aspect ratios and physical properties, these sustainable nanomaterials are attractive as rheological modifiers² and as reinforcing agents in a polymer matrix.³ CNM are typically first produced in dilute aqueous suspensions due to gelation at low concentrations (1–3 wt % for CNF, 10 wt % for CNC).⁴ Subsequent dewatering is therefore necessary to reduce storage and transportation costs or as a preprocessing step for applications that require high CNM concentrations, such as fiber spinning, hydrogels, and composites.^{5,6} Dewatering has been identified as a key barrier to the successful commercialization of CNM.⁷

Methods to efficiently dewater CNM suspensions to reach high concentrations while maintaining good redispersibility are currently lacking. Ultrafiltration is used in the industry for purifying and dewatering CNM suspensions during manufacturing.^{8–10} However, in tangential flow ultrafiltration, the most common implementation of the process, the viscosity increase, and gelation that occur during dewatering of CNM suspensions limit the final CNM concentrations that can be

achieved.^{9–11} In current ultrafiltration processes, concentrations are only increased to around 5 wt % for CNC and 0.5 wt % for TEMPO-CNF.^{8,9} Evaporation is another common dewatering method, which can be used to dewater suspensions and—if desired—all of the way to the dry state. However, evaporation is energy intensive and known to cause significant aggregation at the vapor–liquid interface where water is removed, especially for nanofibril materials due to their large surface area and hydrogen bonding.^{10,11} Such aggregates are formed while the overall CNM concentration is still fairly low and they often persist during redispersion, which greatly reduces the benefits and applicability of the CNM. Other dewatering techniques that avoid vapor–liquid interfaces include centrifugation, filtration, and pressing. These methods have been used to dewater CNM and microfibrillated cellulose (MFC),¹⁰ but they present the common challenge that large

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Challenges and Advances in Aerosol Jet Printing of Regenerated Silk Fibroin Solutions

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Silk fibroin materials are manufactured using printing and coating techniques at resolutions 1–2 μm . However, current processes are unstable, of low printability and versatility, and of limited feature size, and often require use of additives to process, which can impact material functionality and performance. Although there exist well established material synthesis and formulation approaches for making processable solutions from silkworm cocoons, these approaches do not translate to the emerging fabrication processes, such as aerosol jet printing (AJP). Here, a new approach is introduced to formulate silk-worm solutions for AJP and subsequently analyze the processing limits, due to defects such as overspray, pooling, and cloudiness. It is found that the degumming step is critical and can lead to defects such as gelling and pooling. Furthermore, it is found that there exists a narrow processing window (sheath rate as a function of ink rate) for AJP formulations without defects. As with other materials (such as metal inks), overspray is an issue during the fabrication process; however, it is minimized within the processing window. This work stands to open a pathway for manufacturing new and emerging biodegradable materials suitable for pharmaceuticals, food packaging, and electronics, among others.

Silk fibroin produced by silkworms has been used commercially as biomedical sutures for centuries, due to its unique combination of mechanical properties, biocompatibility, and biodegradability. More recently, research is being conducted on regenerated silk fibroin (RSF) solutions in order to exploit these unique properties for applications in drug delivery, packaging, wound treatment, layer-by-layer fabricated capsules, scaffolds for tissue microenvironment, and biosensors like optical waveguides.^[1–6] These biomaterials have been found to be a better alternative to other existing materials. However, the silk fibroin solution

must be fabricated with high resolution, in various forms including films, coatings, sponges, and nanofibers.^[4–6] For these biomaterials, additive manufacturing techniques, rather than conventional techniques for microfabrication, are considered more efficient production processes, with higher volume throughput and sustainability in the long run.^[7]

Techniques that have been utilized to fabricate silk fibroin mainly include lithographic-related approaches and direct-write printing beyond the conventional approach of spinning or casting.^[8] Inkjet printing (IJP), which is a direct-write printing method, is a more broadly accepted approach due to its maturity and ubiquity.^[9] Among different types of IJP, the piezoelectric-based inkjet is more commercially accepted due to the fact that it processes the material without damaging the labile chemical compounds in the ink.^[10] An alternative noncontact IJP fabrication method, electrohydrodynamic

printing, has the highest resolution to date at 1–2 μm ; however, the jet instability of the solution has been a major challenge.^[11]

Currently, the major challenge for utilizing silk fibroin is its low printability, which can be improved by mixing RSF solutions with other polymers in order to fine-tune the viscosity of the ink.^[12] Typically, drop-on-demand inkjet printing process inks in the viscosity range of 10–40 centipoise.^[13] Therefore, viscosity modifiers are often used to adapt functional inks to the printing environment by increasing the viscosity of dilute solutions, thus increasing printability. However, viscosity can inhibit the printability in some cases of silk fibroin.^[14] This study provides a pathway to overcome the current challenges, thus enabling aerosol jet printing (AJP) of regenerated silk fibroin solutions without the use of additives and without clogging the nozzle. Furthermore, an optimum operating window is developed by investigating the effect of the process parameters on the printed pattern morphology and feature size, based on defect generation.

A delicate balance between the material preparation steps (degumming, dissolution, dialysis, and centrifugation) and the material fabrication steps (atomization, tuning, and printing) must be maintained in order for the RSF solution to be printable (**Figure 1**). Slight alterations in the material preparation protocol, during the first two steps, will cause gelation before or during atomization, rendering the solution unprintable, as reported also elsewhere.^[12] In this case of premature gelation,

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Water treatment via non-membrane inorganic nanoparticles/cellulose composites

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Nanomaterials offer innovations in water purification technology with decreased operational and capital cost, reduced dosage, and improved pollutant selectivity. In particular, inorganic nanoparticles (NPs)/cellulose hybrid nanocomposites have attracted growing interest due to the unique properties of cellulose and high specific surface area of NPs and their pollutant selectivity. The integration with cellulose brings benefits to inorganic NPs for water treatment, including preventing agglomeration, ensuring colloidal stability, and allowing for separation by magnetic nanoparticles after purification. In this review, firstly, conventional water treatment technologies are introduced (Section 1). Following this, an overview of inorganic NPs/cellulose composites for water treatment (Section 2) is presented. Moreover, engineering of such hybrid composites is discussed (Section 3). Furthermore, water purification of inorganic NPs/cellulose through adsorption of pollutants (Section 4) and non-adsorption (catalytic, photocatalytic, and antibacterial) activities (Section 5) are highlighted. Finally, conclusions and outlook are provided (Section 6).

Keywords: Nanoparticles; Cellulose; Water treatment; Adsorption; Catalyst; Antibacterial

Introduction

Over the past several decades, research on water treatment has remained salient due to the tremendous increase in demand for clean water. Water treatment facilities traditionally operate based on several treatment stages, including chemical coagulation, gravity sedimentation and filtration [1–9]. Fig. 1 illustrates the process flow of a water treatment plant, showing a common sequence of these stages, from natural water sources to household water consumption. First of all, chemical coagulants remove colloidal inorganic particles or clay by neutralizing negatively charged particles after being added to water and mixed vigorously, causing the particles to aggregate and precipitate. Gravity sedimentation promotes settling of solids, and flotation is often performed concurrently to remove floating debris [10]. Filtration processes are performed using pressure sand filters, activated carbon filters, hollow fibres, or membranes. Finally, a

disinfectant aeration stage is applied to refine the biological and chemical composition of water intended for general usage. During aeration, water and air interactions increase as bubbles are introduced to remove volatile organic matter and gases such as CO₂, as well as to oxidize and precipitate dissolved metals [11]. Activated sludge mainly composed of bacteria may be added to the aeration tank to oxidize carbonaceous biological pollution and nitrogenous matter, which requires cost-intensive dewatering and disposal [12]. Pathogens are also removed by adding oxidants throughout the water treatment stages, which inactivate pathogens and prevent their replication [13]. Common oxidants include chlorine, chlorine dioxide, and ozone [14].

However, even after undergoing these treatment stages, water may still contain residual dyes, heavy metals, and pathogens. Moreover, the chemical disinfection step forms unwanted disinfection by-products (DBPs) such as chloroform, chlorinated organics, and oxo-anions with high mutagenic and/or carcinogenic potential. Traditional water supply systems face enormous challenges due to recently imposed regulations for lower pollu-

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REVIEW

Recent advances in polysaccharide-based hydrogels for synthesis and applications

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Engineering, Georgia Institute of Technology,
Atlanta, GA 30332, USA.
Email: zhiqun.lin@mse.gatech.edu**Abstract**

Hydrogels are three-dimensional (3D) crosslinked hydrophilic polymer networks that have garnered tremendous interests in many fields, including water treatment, energy storage, and regenerative medicine. However, conventional synthetic polymer hydrogels have poor biocompatibility. In this context, polysaccharides, a class of renewable natural materials with biocompatible and biodegradable properties, have been utilized as building blocks to yield polysaccharide-based hydrogels through physical and/or chemical crosslinking of polysaccharides via a variety of monomers or ions. These polysaccharide-derived hydrogels exhibit peculiar physicochemical properties and excellent mechanical properties due to their unique structures and abundant functional groups. This review focuses on recent advances in synthesis and applications of polysaccharide-based hydrogels by capitalizing on a set of biocompatible and biodegradable polysaccharides (i.e., cellulose, alginate, chitosan, and cyclodextrins [CDs]). First, we introduce the design and synthesis principles for crafting polysaccharide-based hydrogels. Second, polysaccharide-based hydrogels that are interconnected via various crosslinking strategies (e.g., physical crosslinking, chemical crosslinking, and double networking) are summarized. In particular, the introduction of noncovalent and/or dynamic covalent interactions imparts polysaccharide-based hydrogels with a myriad of intriguing performances (e.g., stimuli–response and self-recovery). Third, the diverse applications of polysaccharide-based hydrogels in self-healing, sensory, supercapacitor, battery, drug delivery, wound healing, tissues engineering, and bioimaging fields are discussed. Finally, the perspectives of polysaccharide-based hydrogels that promote their future design to enable new functions and applications are outlined.

KEYWORDS

applications, double-network, dynamic covalent interactions, noncovalent interactions, polysaccharide-based hydrogels

INTRODUCTION

Hydrogels represent a class of materials that are composed of crosslinked hydrophilic polymer networks filtered with solvents (e.g., water, organic solvent/water mixture). They find a broad spectrum of applications in biomedical,^[1] self-healing,^[2] sensory,^[3] energy, and water sustainability fields.^[4] These hydrophilic polymer networks can be produced via in situ physical and/or chemical crosslinking. Generally, chemical crosslinking can be achieved using redox-, thermal-, photo-, or radiation-initiated free radical polymerization. On the other hand, noncovalent interactions (e.g., hydrogen bonding, metal coordination, hydrophobic

interaction, and host–guest interaction) have also been widely employed to construct physical networks, thereby imparting hydrogels with attractive self-healing properties.^[5] This intriguing characteristic can be used to distinguish the hydrogels formed via covalent or noncovalent crosslinking. Due to the low binding strength of single polymer chains, and weak noncovalent interactions, hydrogels usually display poor tensile strength. Many strategies, such as double-network,^[6] topological structure,^[7] multi-interaction,^[8] and nanocomposite^[9] have been implemented to improve mechanical properties. However, most synthetic polymer hydrogels cannot concurrently render biocompatibility and high strength in emerging biological materials.

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REVIEW

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Towards sustainable production and utilization of plant-biomass-based nanomaterials: a review and analysis of recent developments

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Abstract

Plant-biomass-based nanomaterials have attracted great interest recently for their potential to replace petroleum-sourced polymeric materials for sustained economic development. However, challenges associated with sustainable production of lignocellulosic nanoscale polymeric materials (NPMs) need to be addressed. Producing materials from lignocellulosic biomass is a value-added proposition compared with fuel-centric approach. This report focuses on recent progress made in understanding NPMs—specifically lignin nanoparticles (LNPs) and cellulosic nanomaterials (CNMs)—and their sustainable production. Special attention is focused on understanding key issues in nano-level deconstruction of cell walls and utilization of key properties of the resultant NPMs to allow flexibility in production to promote sustainability. Specifically, suitable processes for producing LNPs and their potential for scaled-up production, along with the resultant LNP properties and prospective applications, are discussed. In the case of CNMs, terminologies such as cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) used in the literature are examined. The term cellulose nano-whiskers (CNWs) is used here to describe a class of CNMs that has a morphology similar to CNCs but without specifying its crystallinity, because most applications of CNCs do not need its crystalline characteristic. Additionally, progress in enzymatic processing and drying of NPMs is also summarized. Finally, the report provides some perspective of future research that is likely to result in commercialization of plant-based NPMs.

Keywords: Lignin nanoparticles (LNPs), Cellulosic nanomaterials (CNMs), Cellulosic nano-whiskers (CNWs), Cell wall deconstruction, Fibrillation

Background

Plant biomass is renewable and can be sustainably produced in large quantities in many regions of the world [1, 2]. Utilization of plant biomass to produce biofuels, biomaterials, and biochemicals to replace petroleum-based energy, materials, and chemicals is critically important

for a future that employs a sustainable, effective circular economy. Plant biomass consists of three major components: cellulose (30% to 45% wt/wt), lignin (15% to 30% wt/wt), and hemicelluloses (15% to 35% wt/wt) [3, 4]. Internationally, considerable research effort has focused on the production of biofuels and biochemicals following the conversion of lignocellulosic plant biomass to fermentable sugars [5, 6] and aromatic compounds [7, 8]. This endeavor has been very challenging considering that plant biomass has evolved to resist biological deconstruction.

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Dynamic Chiro-Optics of Bio-Inorganic Nanomaterials via Seamless Co-Assembly of Semiconducting Nanorods and Polysaccharide Nanocrystals

Saewon Kang, Gill M. Biesold, Hansol Lee, Daria Bukharina, Zhiqun Lin, and Vladimir V. Tsukruk*

This study demonstrates a novel chiral organization of multi-materials from semiconducting quantum nanorods (QNRs) co-assembled into chiral nematic polysaccharide (cellulose) nanocrystals for active manipulation of chiro-optical light emission properties in elastomeric materials. Highly emissive anisotropic QNRs with dimensions and surface chemistry commensurate with those of biological nanocrystals facilitate seamless co-assembly into an integrated chiral nematic organization due to preferable enthalpic interactions and pairing processes. The resulting freestanding highly emissive bio-inorganic elastomeric materials exhibit vivid iridescence and emission with a strong optical activity that manifests itself in active and tunable chiral photoluminescence with unusually large asymmetry. Intriguingly, large-strain reversible mechanical deformation of physically crosslinked elastomers endows fully reversible alternation of helical structural configuration and corresponding linearly and circularly polarized photoluminescence. This study provides a platform to render dynamic optical functionality with reconfigurable light propagation/emission in bio-inorganic elastomers for futuristic applications in chiral lasing, biosensing, optical gauges, and holographic display.

1. Introduction

Semiconducting nanocrystals such as quantum dots (QDs), ribbons, and nanorods are intriguing candidates for efficient light emission due to their high quantum yield (QY), good thermal and chemical stability, long lifetime, narrow spectral bandwidth, and tunable emission wavelength.^[1,2] Recently, the development of chiral luminescent semiconducting nanocrystals with new optical functionalities has garnered great interest for potential applications in the fields of chiral recognition, biological sensing, 3D displays, information storage, and optical security.^[3–5] In order to utilize semiconducting

nanocrystals with optical activity, several approaches have been implemented to date, such as supramolecular assemblies,^[6] enantioselective synthesis,^[3,7,8] and chiral ligand exchange.^[9–12] For example, doping achiral quantum nanocrystals into a chiral supramolecular system has opened up possibilities for the design of functional photoluminescent materials with induced chiro-optical behavior.^[9,13] However, such assembly approaches require sophisticated multi-stage fabrication and render relatively weak optical activity (with an asymmetry factor of left/right circular polarization intensity within 10^{-2} – 10^{-4}).^[11,12,14,15]

Coupling the optoelectronic properties of individual semiconducting nanocrystals with photonic structures could enable the development of novel optically functional materials with circularly polarized light (CPL) emission with large asymmetry of circular polarization. Chiral biopolymers, such as polysaccharides, DNA, and

proteins, can be attractive bio-templates that provide optical elements with built-in solid-state chiral organization. Among polysaccharide nanocrystals, cellulose nanocrystals (CNCs) with high aspect ratio and spindle-shape are most widely explored for chiral bio-templates.^[16,17] Aqueous CNC dispersions can form a chiral nematic liquid crystal (LC) phase with a left-handed helical structure.^[18] Integrating optically active synthetic components into a helical structure can create nanostructures with intriguing optical functionalities via a host-guest co-assembly process.^[19–21] Among these appealing nanostructures, QDs, metal nanoparticles, and organic dyes have been employed to control the light polarization of chiral photonic structures, resulting in chiral photoluminescence.^[22–26] For instance, chiral emissive CNC composites incorporating semiconducting QDs (i.e., carbon dots, CdSe QDs) have been fabricated, and the resulting chiral photonic composites exhibited selectively reflected left-handed CPL, leading to strong right-handed emission.^[21,27] Although this synergistic integration endows the composites with the unique optical functionality of emissive QDs, the composites exhibit weak emission with static optical activity and thus a limited ability to adapt quickly to a changing environment.

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Encapsulation of cellulose nanocrystals into acrylic latex particles via miniemulsion polymerization

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ABSTRACT

Cellulose nanocrystals (CNCs) show promise for enhancing properties of waterborne latexes and coatings. Miniemulsion polymerization is a promising route to obtaining well-controlled latex distributions sufficient to encapsulate CNCs in the monomer phase. Here, we demonstrate the first miniemulsion polymerization resulting in encapsulation of CNCs that incorporates costabilizer, water soluble initiator, and comonomer mixtures, aspects that are important for practical implementation. CNCs were added to the monomer phase as either unmodified (umCNC) or one of two functionalized forms: modified with isocyanatoethyl methacrylate (mCNC, containing a polymerizable vinyl group) or grafted with butyl acrylate/methyl methacrylate copolymer (gmCNC). The gmCNCs were incorporated successfully into acrylic particles. In contrast, the umCNCs were located outside the formed latex particles. Interestingly, the mCNCs coagulated during the polymerization, highlighting the challenge of utilizing polar and reactive acryloyl CNC surface modifiers that lead to migration from the droplet phase.

1. Introduction

Polymer colloids are essential precursors used in various industrial applications. These colloid systems have been used in the paper, leather, and construction industries and in printing inks, coatings (decorative, protective, automotive), and adhesives [1]. Interest in the research and applications of waterborne polymer colloids has increased in the last decades, as opposed to traditional solventborne technologies, since market and regulatory trends are moving more towards eco-friendly materials [2].

An aqueous polymer colloid or a latex is a dispersion of submicron polymer particles in water. The most commonly used method to produce latexes is conventional emulsion polymerization. Emulsion polymerization is a heterogeneous free radical polymerization where the monomer is initially contained in droplets stabilized by a colloidal stabilizer (typically surfactant) in water. Surfactants used above the critical micelle concentration (CMC) stabilize the monomer droplets (~10 μm) and also form micelles (~10 nm) in the aqueous phase [3]. Emulsion polymerization employs monomers having a slight water solubility and

a water-soluble initiator to initiate the polymerization in the aqueous phase. Monomers diffuse from relatively larger monomer droplets to the aqueous phase to supply the polymerization that occurs in the continuous aqueous phase (homogeneous nucleation), in monomer-swollen micelles (micellar nucleation), or (very slightly) in the monomer droplets (droplet nucleation).

Miniemulsion polymerization is another route to synthesize latexes. Both conventional emulsion polymerization and miniemulsion polymerization result in polymer particles ranging from 50 to 500 nm; however, the mechanism for particle growth differs. Miniemulsions contain smaller (<1 μm) monomer droplets obtained by a high shear emulsification step and use a costabilizer to prevent Ostwald ripening. A low surfactant concentration is used so that no micelles form in the aqueous phase after the emulsification step. Reducing the droplet sizes increases the surface area for polymerization, enabling droplet nucleation to become the dominant mechanism for the growth of particles. The identity of droplets is maintained with an effective surfactant and costabilizer system during the polymerization. Whereas surfactants stabilize droplets against coalescence as in emulsion polymerization,

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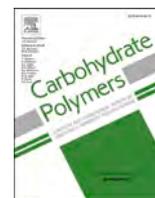
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Increasing efficiency of the homogenization process for production of chitin nanofibers for barrier film applications

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ABSTRACT

Chitin nanofibers (ChNFs) are of interest for barrier materials but are often extracted by high pressure homogenization (HPH) with high energy utilization. We studied the influence of deacetylation (DA) and pressure on HPH of shrimp chitin and the resulting solution cast films. Deacetylation to 72% DA resulted in improved ChNF suspension and film light transmission, strain at break, and tensile strength compared to chitin with DA of 89%. The oxygen permeability (OP) of the films was not affected by the modification and remained at low values of 1.9–2.4 cm³ μm²/day/kPa. We also show that deacetylation enables HPH intensity to be reduced during extraction of ChNFs from crab shell chitin (63% lower pressure and 73% reduction in number of passes), while achieving a low OP. Deacetylation pretreatment reduces HPH process intensity required to achieve oxygen barrier properties in ChNF films.

1. Introduction

High pressure homogenization (HPH) is an effective method for size-reduction of natural fibers, including producing nanofibers from polysaccharides like cellulose and chitin (Dufresne, 2013; Ono, Ogura, Kaku, Fujisawa, & Isogai, 2020). Chitin is an abundant biological material that occurs in the form of nanofibrils and microfibers in skeletal structures of fungi, diatoms, sponges, arachnids, crustaceans and insects (Kumar, 2000; Brunner et al., 2009; Kaya et al., 2017; Machalowski et al., 2019; Tsurkan et al., 2021). Within crustacean exoskeletons chitin occurs as microfibrils consisting of individual nanofibers of 2–5 nm diameter and 300 nm length embedded in a protein matrix (Ifuku & Saimoto, 2012). These can be extracted as nanofibers of 10–20 nm width and 1 to 4 μm in length (Ifuku & Saimoto, 2012; Wu, Zhang, Girouard, & Meredith, 2014). Chitin exists as a random block co-polymer of β-(1-4)-linked N-acetyl-glucosamine and N-glucosamine (Zhang & Rolandi, 2017). Structurally, the backbone is similar to cellulose, except with an acetamide group (–NHCOCH₃) or amine (–NH₂) at the C2 position. The existence of amine groups allows protonation under acidic conditions, making chitin a cationic polyelectrolyte. Chitin nanofibers and nanocrystals are of interest because of their ability to be fabricated into films with excellent gas barrier properties (Satam et al., 2018; Wu et al., 2014), high tensile strength and Young's modulus (Ifuku & Saimoto,

2012; Zeng, He, Li, & Wang, 2012), and transparency (Ifuku et al., 2013; Ifuku & Saimoto, 2012; Satam et al., 2018; Wu et al., 2014).

Homogenization processes use shear and impact forces to reduce size of particles in colloidal suspensions, often driven by pressure (Lim & Gong, 2018). In HPH a suspension at high pressure is forced through an orifice or valve resulting in pressure drop, turbulence, and cavitation that provide energy for size reduction of the particles (Chowdhury, Clarkson, & Youngblood, 2018; Levy, Okun, & Shpigelman, 2020). Smaller nozzle diameters lead to greater pressure drop and hence greater shear forces on the particles. However, smaller nozzle diameters also place an upper limit on the particle size that can pass through the homogenizer without clogging the nozzle. HPH can separate large hierarchical fibers (10–50 μm depending on source) into smaller constituent nanofibers with diameters <100 nm that have high fiber aspect ratio close to the original source fiber (Nechyporchuk, Belgacem, & Bras, 2016). HPH is associated with elevated energy usage (Nechyporchuk et al., 2016; Spence, Venditti, Rojas, Habibi, & Pawlak, 2011; Zimmermann, Bordeanu, & Strub, 2010) and chemical pretreatments have been explored to reduce energy intensity required to defibrillate materials (Dufresne, 2013; Zimmermann et al., 2010). Homogenization of cellulose suspensions, closely related to chitin, has been widely studied and reviewed (Dufresne, 2013; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Nechyporchuk et al., 2016; Spence et al., 2011;

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Acryloyl-modified cellulose nanocrystals: effects of substitution on crystallinity and copolymerization with acrylic monomers

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Abstract Cellulose nanocrystals (CNCs) are crystalline nano-rods that have high specific strength with hydroxyl surface chemistry. A wide range of chemical modifications have been performed on the surface of CNCs to increase their potential to be used in applications where compatibilization with other materials is required. Understanding the surface chemistry of CNCs and critically examining the functionalization technique are crucial to enable control over the extent of modification and the properties of CNCs. This work aims to optimize the surface modification of wood-derived CNCs with isocyanatoethyl

methacrylate (IEM), a bifunctional molecule carrying both isocyanate and vinyl functional groups. We studied the effect of modification reaction time and temperature on the degree of substitution, crystallinity, and morphology of the CNCs. We found that the degree of modification is a strong and increasing function of reaction temperature over the range studied. However, the highest temperature (65 °C) and the longest time of reaction (6 h) resulted in shorter, thinner, and less crystalline CNCs. We obtained surface hydroxyl conversion of $60.1 \pm 6\%$ and percent crystallinity of 84% by keeping the reaction shorter (30 min) at 65 °C. Also, the copolymerization ability of modified CNCs was verified by polymerizing attached IEM groups with acrylic monomers via solution polymerization. The polymer-grafted CNCs (6% w/w) dispersed better in an acrylic polymer matrix compared to unmodified CNCs (umCNCs), resulting in approximately 100% improvement in the tensile strength and about 53% enhancement in the hardness of the acrylic, whereas addition of 6% w/w umCNCs did not influence the strength and hardness.

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Controlled Dispersion and Setting of Cellulose Nanofibril - Carboxymethyl Cellulose Pastes

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Abstract This work investigated the redispersion and setting behavior of highly loaded (~ 18 wt.% solids in water) pastes of cellulose nanofibrils (CNFs) with carboxymethyl cellulose (CMC). A single-screw extruder was used to continuously process CNF + CMC pastes into cord. The adsorption of CMC onto the CNFs was assessed through zeta potential and titration which revealed a surface charge change of ~ 61% from - 36.8 mV and 0.094 mmol/g COOH for pure CNF to -58.1 mV and 0.166 mmol/g

COOH for CNF + CMC with a CMC degree of substitution of 0.9. Dried CNFs with adsorbed CMC was found to be fully redispersible in water and re-extruded back into a cord without any difficulties. On the other hand, chemical treatment with hydrochloric acid, a carbodiimide crosslinker, or two wet strength enhancers (polyamide epichlorohydrin and polyamine epichlorohydrin) completely suppressed the dispersibility previously observed for dried-untreated CNF + CMC. Turbidity was used to quantify the level of redispersion or setting achieved by the untreated and chemically treated CNF + CMC in both water and a strong alkaline solution (0.1 M NaOH). Depending on the chemical treatment used, FTIR analysis revealed the presence of ester, N-acyl urea, and anhydride absorption bands which were attributed to newly formed linkages between CNFs, possibly explaining the suppressed redispersion behavior. Water uptake of the differently treated and dried CNF + CMC materials agreed with both turbidity and FTIR results.

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3D-Printed Anisotropic Polymer Materials for Functional Applications

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Anisotropy is the characteristic of a material to exhibit variations in its mechanical, electrical, thermal, optical properties, etc. along different directions. Anisotropic materials have attracted great research interest because of their wide applications in aerospace, sensing, soft robotics, and tissue engineering. 3D printing provides exceptional advantages in achieving controlled compositions and complex architecture, thereby enabling the manufacture of 3D objects with anisotropic functionalities. Here, a comprehensive review of the recent progress on 3D printing of anisotropic polymer materials based on different techniques including material extrusion, vat photopolymerization, powder bed fusion, and sheet lamination is presented. The state-of-the-art strategies implemented in manipulating anisotropic structures are highlighted with the discussion of material categories, functionalities, and potential applications. This review is concluded with analyzing the current challenges and providing perspectives for further development in this field.

heterogenous structures or ingredients.^[1] For example, tooth enamel has highly mineralized collagen fibers perpendicular to the tooth surface, which makes it the hardest mineral substance in human body. Inspired by this structure, aligned reinforcements are constructed in load-bearing materials to achieve maximal possible mechanical performance in the demanded direction.^[2] The bioinspired design is widely applied in engineering to fabricate anisotropic materials that enable directionally dependent enhancement in mechanical, electrical, or thermal properties and perform specific functionalities such as tunable shape morphing and polarized patterning. These anisotropic materials have attracted long-term research interest in aerospace, sensing,

soft robotics, and tissue engineering applications because of their high efficiency in material utilization and specified functional modification.^[2–3]

The inherent features of anisotropic materials inevitably set limitations and constraints in their fabrication using conventional manufacturing processes including molding, templating, freeze-casting, self-assembly, etc.^[4] 3D printing, or additive manufacturing (AM), opposed to other technologies or processes, provides unparalleled freedom in the design and fabrication of anisotropic materials, especially polymers, which are widely used in engineering applications owing to their high processability, lightweight, and decent mechanical and physical properties.^[5] A layer-wise manner is adopted to construct 3D objects with the help of computer-aided design. Such manner grants 3D printing the ability to flexibly manufacture architectures for desired anisotropic functional performances. This manner, however, generally results in inherent undesired anisotropy due to discontinuous construction of materials across layers, which can be reduced by adjusting the printing parameters.^[6] Over decades of development, several 3D printing techniques, such as material extrusion (ME), vat photopolymerization (VP), powder bed fusion (PBF), and sheet lamination (SL), have been widely applied to fabricate anisotropic polymer materials by the programmable control of intricate structures, where the manipulation ranges from unidirectional to multidirectional. A large proportion of the research in anisotropic polymer manufacture focus on the ME. To better elucidate this technique, ME is divided into two parts, fused filament fabrication (FFF) and direct ink writing (DIW), based on the feedstock, which are reviewed with the other techniques in this paper (Figure 1).

1. Introduction

Nature has served as an inspiring source for the development of anisotropic functional materials that show various mechanical or physical properties in different directions through

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