2022

Fourth Quarter

PTC Newsletter

PTC Polymer Technology Consortia

UPCOMING EVENTS

Mark Your Calendars for the PTC Fall meetings!

Scratch Behavior of Polymers Consortium-SCRATCH

SCRATCH Spring meeting-March 23rd, 2023
Texas A&M University-College Station, TX

Polymer Technology Industrial Consortium-PTIC

PTIC SPRING meeting—March 23rd-24th, 2023
Texas A&M University-College Station, TX

Inside the Newsletter

"3D Printed CO2-Based Triblock Copolymers and Post-Printing Modification"

Emily Pentzer

Materials Science and Engineering

A collaborative research endeavor between two PTC faculty has led to the production of porous materials of varied mechanical properties, based on block copolymers of polycarbonates prepared from CO_2 gas. The groups of Dr. Emily Pentzer, associate professor of materials science and engineering, and Dr. Don Darensbourg, distinguished professor of chemistry and recently elected member of the National Academy of Science, worked collaboratively on this project. The work was published in Angewandte Chemie and the lead author on the study is Dr. Peiran Wei from the Texas A&M Soft Matter Facility; co-authors include Dr. Gulzar A. Bhat (TAMU chemistry), Ciera Cipriani (TAMU materials science and engineering), Dr. Hamza Mohammad (TAMU chemistry), and Krista Schoonover (TAMU chemistry).

A series of triblock copolymers consisting of soft and hard blocks were prepared by the alternating co-polymerization of CO_2 and epoxides, leveraging chemistry developed in the Darensbourg lab. The hard blocks of the polymer contained pendant alkene groups of that could be used for chemical modification. Thixotropic inks suitable for direct-ink-write (DIW) additive manufacturing were formulated by dissolving the block copolymers in the organic solvent *N*,*N*-dimethylformamide (DMF) and then adding in NaCl particles of controlled size and concentration. The inks were loaded into a syringe and then printed and submerged in water to both remove the solvent and the NaCl from the printed objects.

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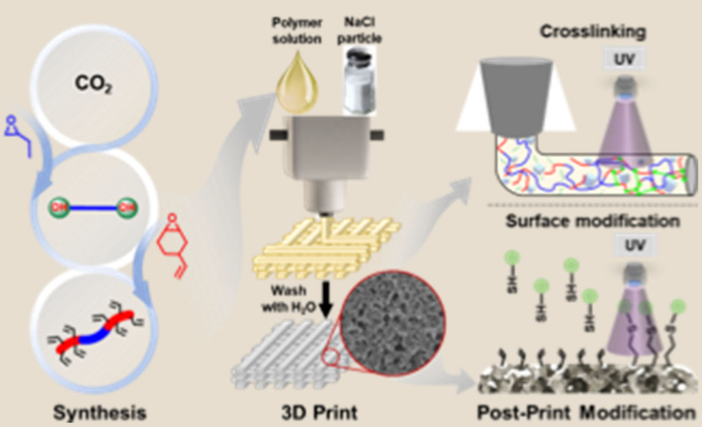
The printed porous polycarbonate structures had mechanical properties dependent on the ratio of the hard and soft blocks. Characterization of the surface and cross-section by SEM revealed an open-cell porous foam-like structure throughout. Compression tests performed with a dynamic mechanical analyzer (DMA) revealed that the stiffness and strength of the materials increased with an increased proportion of hard block of the copolymer. Further, a 15-pound (~6.8 kg) weight could be supported by a porous printed lattice composed of ~0.2 g of the polycarbonate containing a 1:1 molar ratio of the soft and hard blocks, highlighting the high strength of the printed copolymers.

The chemical composition of the polymer feedstock, specifically the alkene groups of the hard block, could be used as handles for chemical modification or cross-linking. The printed and washed porous structures were modified using UV-initiated thiol-ene click reactions with primary thiols, giving coverage with, e.g., alkylbromides, as confirmed by FTIR spectroscopy, XPS, and SEM-EDS. Further, incorporation of the a tetrathiol in the ink, along with UV curing of the printed object enabled the hard blocks of the porous structure to be chemically cross-linked. By temporally controlling this cross-linking, the stability of the printed object could be tailored: the non-cross-linked regions could be dissolved in organic solvent, but the cross-linked polymer regions could not. However, the cross-linked polycarbonate regions could be chemically degraded in < 24 h upon submersion in an aqueous solution of sodium hydroxide.

The ability to tune the composition of the copolymer and the structure of the printed objects will enable tough and lightweight polycarbonates to be used for a variety of applications, such as organ culture or bone regeneration. Moreover, the surface of the printed object could be modified with, e.g., cell growth factors to induce bone formation. In complement, chemical crosslinking of the polymers can be used increase mechanical strength, making them more suitable for weight-bearing applications or structural components.



Scheme 1: Schematic illustrating the triblock copolymer synthesis, ink formulation, 3D printing, and UV-induced crosslinking and surface modification.

"Polymer Rheology-driven Process Parameter Selection for Material Extrusion Additive Manufacturing"

Chukwuzubelu Ufodike
Department of EngineeringTechnology & Industrial Distribution

Dr. Chukwuzubelu Ufodike is an Assistant Professor and Charlotte and Walter Buchanan Faculty Fellow in the Department of Engineering Technology & Industrial Distribution at Texas A&M University. He holds a joint (courtesy) appointment in the Department of Multidisciplinary Engineering. Dr. Ufodike completed his doctoral degree in Industrial and Manufacturing Engineering, at Florida A&M University (through a joint degree program with Florida State University) in May 2020. He is the Director of the Digital Manufacturing and Distribution Lab (DMD-Lab) at the Texas A&M Engineering Experiment Station (TEES). His research group (Professor Ufodike Research Group – **PURG**) focuses on theoretical and computational materials science, advanced manufacturing, and distribution. Dr. Ufodike's group represents one of the world's leading teams in the field of computational and numerical modeling of the polymer flow in Fuse Filament Fabrication (FFF) Additive Manufacturing (AM). It is difficult to predict the FFF thermoforming process using conventional theories and models developed for traditional thermoforming processes. This has created a huge drawback for the adoption of FFF as a mainstream manufacturing process due to the lack of in-depth theoretical understanding and potential disconnect of material and process aspects. Dr. Ufodike's team has made significant contributions to this challenging multidisciplinary research field, by integrating novel experimentation, theoretical, and computational models specifically for FFF AM.

Dr. Ufodike's accomplishments in the investigation of thermal evolution and fluid flow in the hot-end of a material extrusion 3d printer provided a new Computational Fluid Dynamics (CFD) melting model developed specifically for the FFF process (**Figure 1**) recently published in Additive Manufacturing https://doi.org/10.1016/j.addma.2021.102502. It is hypothesized that the new CFD melting model will improve the overall understanding of coupled heat transfer and fluid flow in the FFF 3D printing hot-end and process control. The new CFD melting model as applied on the 3D FFF printer, proves to be a powerful tool to easily implement the effect of the air gap between the filament and the liquefier wall. This further aid in identifying the true position of the melting front at the liquefier center, and the exact location where melting begins at the entrance inside the heating wall.

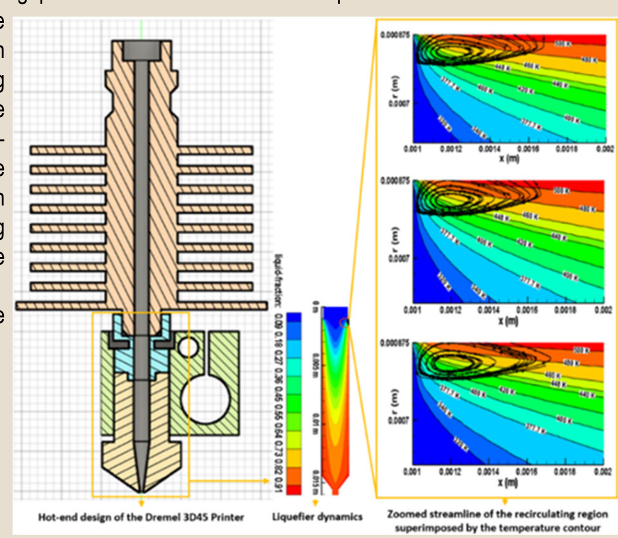


Figure 1. Thermal evolution and fluid flow in the hot-end of a 3D Printer using a novel CFD melting model.

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Such information is very useful to the design engineers and improves the understanding of the coupled heat transfer and fluid flow in the FFF 3D hot-end.

In an attempt to successfully reach the optimum material, and process aspects required for manufacturing quality and consistent 3D printed parts, Dr. Ufodike's team developed a numerical model to predict pressure, temperature, outlet melt viscosity, strain rate, and velocity in the hot-end of a FFF system (**Figure 2**) recently published in the Journal of Manufacturing Processes (by Society of Manufacturing Engineers - SME) https://doi.org/10.1016/j.jmapro.2022.08.029. The numerical model accounted for the velocity of the solid filament in the liquefier. The numerical model was thoroughly validated by comparing the model predictions with experimentally measured feeding force data. The predicted numerical results closely approximated the experimentally measured feeding force. Then the model was also validated with extrudate temperature, measured with a thermal imaging camera, and the results obtained are in good agreement. Outlet capillary diameter, feeding rate, and heat flux (quantified in terms of Nusselt number) were varied to determine the response of pressure field, temperature, velocity, viscosity, and strain rate in the liquefier. The model presented in this work can easily be used to simulate any material to reduce manufacturing iteration and recommend process parameters such as nozzle set temperature, printing speed, and design of a new liquefier for new high-temperature material.

This exciting development in Dr. Ufodike's recent works will establish a new paradigm for FFF (computational design for additive manufacturing - CDAM), impacting, directly and indirectly, all the industries (e.g., automotive, healthcare, aerospace, defense, and transportation) associated with additive manufacturing processes.

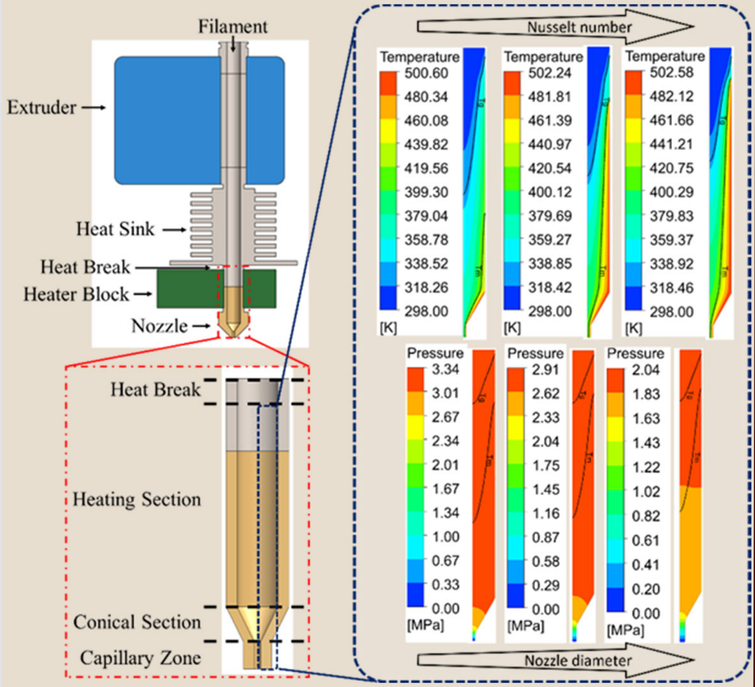
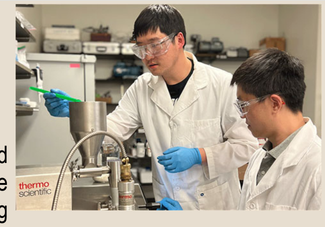


Figure 2. *Numerical modeling of the effect of nozzle diameter and heat flux on the polymer flow in fused filament fabrication.*

Manufacturing metal-organic framework-based composites for efficiency



Dr. Qingsheng Wang, associate professor and George Armistead '23 Faculty Fellow in the Artie McFerrin Department of Chemical Engineering at Texas A&M University, and his team of researchers have spent over three years finding more efficient ways to manufacture metal-organic framework (MOF)-based composites for industrial applications such as flame retardants.

Currently, most MOF-polymer composites are prepared by a discretely bottom-up principle that requires complex chemical reactions blended within different polymers in solutions. This multistep process entails significant time, energy and money to produce minimal quantities.

By combining parts of the MOF's development process, Wang's team has discovered a one-step method using reaction extrusion to produce MOF-based composites on a larger scale safely and effectively. Together with the heating condition, applied shear and compressive forces, MOFs can meet the required reaction conditions for mechanochemical synthesis.

Full story: **https://bit.ly/3doTdzo**

Balbuena named 2022 Electrochemical Society Fellow

Dr. Perla Balbuena has been selected as a 2022 fellow of The Electrochemical Society (ECS).

"I'm extremely happy to be named an Electrochemical Society Fellow," said Balbuena. "The ECS Fellow is one of the highest honors for a professional in the fields of electrochemistry and solid-state science and technology. The selection process is extremely thorough and requires true peer recognition."

Balbuena is one of 15 ESC members selected for the 2022 class. She has served as an ECS member for many years. During her time in ECS, she has organized and chaired meeting symposia at national and international conferences. In April 2021, she was appointed the associate editor of the *Journal of The Electrochemical Society*.

Full story: **https://bit.ly/3BmLn1m**

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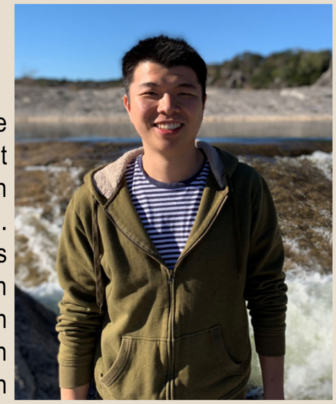
Dr. Mingzhen Zhao
PTC—Ph.D. Graduate from China



Mingzhen Zhao received his Ph.D. degree from the Department of Materials Science and Engineering at Texas A&M University in August 2022. Mingzhen joined Dr. Hung-Jue Sue's group since 2017. Mingzhen has been conducting research on Synthesis and Structure-Property Relationship of Polyolefin Nanocomposites. As a graduate student, Mingzhen received Graduate research assistantship. Mingzhen also cooperated with Dr. Joshua Yuan's group on developing lignin-based degradable and recyclable polymer composites. He also completed a Polymer Specialty Certificate offered by Texas A&M Engineering Experiment Station. Mingzhen will work as a Postdoctoral researcher at Shanghai Jiaotong University in China.

Lorenzo De Nonii
Ph.D. Visiting Scholar from Milano Italy

Lorenzo De Noni is currently doing a PhD at Politecnico di Milano and he spent 6 months in the laboratory of Professor Hung-Jue Sue as a visiting scholar. During this period, he had the chance to work on scratch behavior and scratch visibility of polymeric materials using new methodologies and techniques. The reason he chose the Texas A&M University was to grow and learn new ways to approach scientific research in a new international working environment. Most importantly, he met wonderful people and made new friends who helped him have a comfortable and enjoyable time in College Station. This made the experience one of the best of his life.

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Polymer Specialty Certificate Updates

Students that have applied for the Polymer Specialty Certificate	87
Students that have received the Polymer Specialty Certificate	75

For more information, please visit: http://ptc.tamu.edu/polymer-specialty-certificate/

Have Questions?

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