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"Why am I muted?"
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https://www.acs.org/content/acs/en/acs-webinars/videos.html

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Learn from the best and brightest minds in chemistry! Hundreds of webinars on diverse topics presented by experts in the chemical sciences and enterprise.

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Live Broadcasts of ACS Webinars® continue to be available to the general public several times a week generally from 2-3pm ET!

A **collection of the best recordings** from the ACS Webinars Library will occasionally be rebroadcast to highlight the value of the content.

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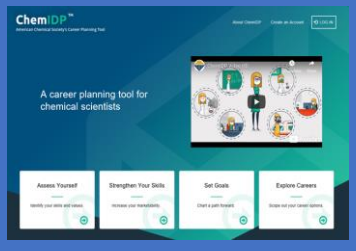

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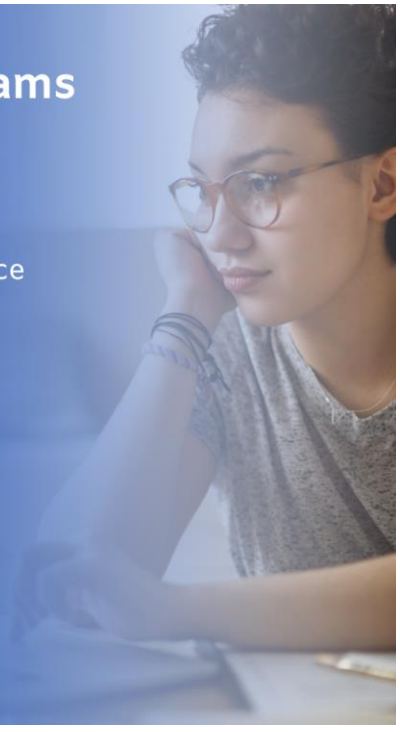


ACS Career Navigator: Your Home for Career Services

Whether you are just starting your journey, transitioning jobs, or looking to brush up or learn new skills, the **ACS Career Navigator** has the resources to point you in the right direction.

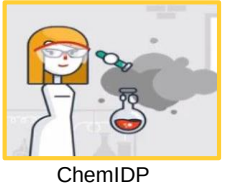
We have a collection of career resources to support you during this global pandemic:

Professional Education

Virtual Career Consultants

ACS Leadership Development System

Career Navigator LIVE!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FAST OR SLOW
Chemistry Makes It Go!
OCTOBER 17–23, 2021
#NCW
ACS Chemistry for Life
American Chemical Society
Visit www.acs.org/ncw
On Sunday, August 1st, 2021 discover how to get a big reaction out of your community for National Chemistry Week!
#NCW

Join us in our efforts to increase the diversity of chemistry.
Valued donors like you have sustained ACS educational programs that are welcoming students from diverse backgrounds into our profession.
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A Career Planning Tool For Chemical Scientists

ChemIDP is an Individual Development Plan designed specifically for graduate students and postdoctoral scholars in the chemical sciences. Through immersive, self-paced activities, users explore potential careers, determine specific skills needed for success, and develop plans to achieve professional goals. **ChemIDP** tracks user progress and input, providing tips and strategies to complete goals and guide career exploration.

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ACS Bridge Program

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The ACS Bridge Program offers:

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Email us at bridge@acs.org

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ACS Department of Diversity Programs

Advancing ACS's Core Value of Diversity, Inclusion & Respect

We believe in the strength of diversity in all its forms, because inclusion of and respect for diverse people, experiences, and ideas lead to superior solutions to world challenges and advances chemistry as a global, multidisciplinary science.

Contact Us:
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acsvoices.podbean.com/

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Register for a Professional Education course that meets your training needs!

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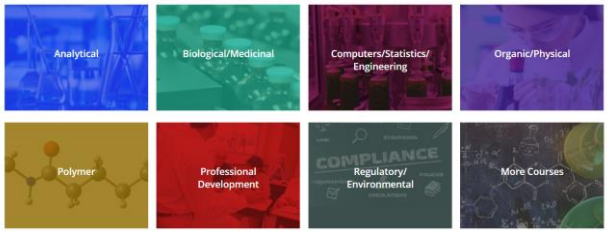
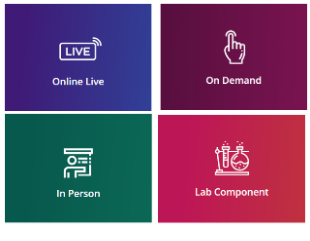
ACS member and early bird discounts are available. **Explore courses in a variety of topics and delivery methods.**

Course Categories



Course Formats



https://www.acs.org/proedweb

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Polymer Chemistry: Principles and Practice

ACS Chemistry for Life®
American Chemical Society

December 5-10, 2021 | Blacksburg, VA

Learn about polymer chemistry through a novel combination of lectures and labs.

Are you a research chemist, engineer, physicist, or technician who works with polymers and their applications? This workshop is for you!

This popular course is taught by Virginia Tech faculty experts and is designed for all education levels. Space is limited!

Register today at **ACS.org/PolymerLab**

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LA MARAVILLA DE LA BIODIVERSIDAD

A TRAVÉS DEL PRISMA DE LA CROMATOGRAFÍA

Fecha: Miércoles, 29 de Septiembre @ 2-3pm ET (1-2pm CT)
Ponente: Elena Stashenko, Universidad Industrial de Santander
Moderadora: Ingrid Montes, Universidad de Puerto Rico, Recinto de Río Piedras y American Chemical Society

Registrarse Gratuitamente

Lo Que El Público Aprenderá:

- Junto con la biodiversidad biológica existe una diversidad molecular bastante amplia para cuyo estudio son indispensables las técnicas de cromatografía y espectrometría de masas
- Los llamados metabolitos secundarios desempeñan papeles importantes para la comunicación, la adaptación, y la supervivencia de las plantas
- El color de algunas flores está asociado con la capacidad antioxidante de sus colorantes

Co-producido con: Sociedad Química de México y *Chemical & Engineering News*

This collaboration with the Mexican Society of Chemists will be in Spanish.

Who Will Win the #ChemNobel?

Predicting the 2021 Nobel Laureate(s) in Chemistry

Date: Thursday, September 30, 2021 @ 2-3pm ET
Speakers: Angela Zhou, CAS / Andrés Cisneros, University of North Texas / Rigoberto Hernandez, Johns Hopkins University / Frank Leibfarth, University of North Carolina
Moderator: Laura Howes, *Chemical & Engineering News*

Register for Free!

What You Will Learn:

- Who are our front-runners for this year's Nobel Prize in Chemistry and why
- Big ideas in chemistry that we think should someday win the prize
- Nobel trivia, different divination techniques, and much more

Nobel Collections Website: Every October, the Nobel Committee for Chemistry awards the field's biggest prize. C&EN asks experts for predictions on who will win, covers the annual prize announcement, and examines Nobel trends over the years.

Co-produced with: *Chemical & Engineering News*

Catalyze the Vote!

2022 ACS President-Elect Candidates

ACS Committee Younger Chemists
CATALYZE THE VOTE

Date: Wednesday, October 6, 2021 @ 2-3pm ET
Speakers: Judith Giordan, ecosVC and the Chemical Angel Network and John C. Warner, Zymergen
Moderator: Amber Wilson, Green Analytics, LLC

Register for Free!

What You Will Learn:

- Meet the ACS President-Elect Candidates
- Listen as the candidates speak to topics relevant to young chemists
- Ask your questions for the candidates

Co-produced with: ACS Younger Chemists Committee

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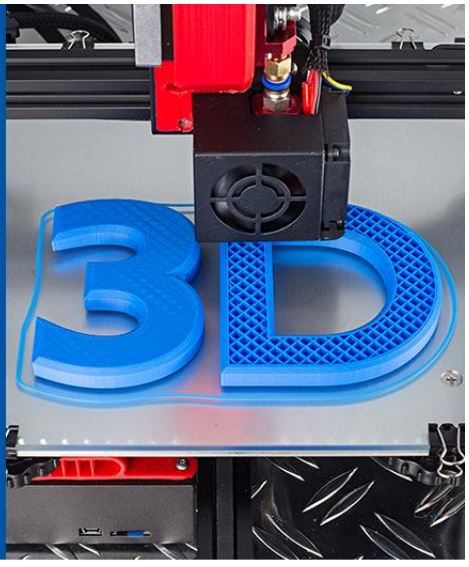
Co-produced with: **ACS Professional Education**

Molecules to Manufacturing to Marketplace

3D Printing of Sulfonated Polyesters for Controlled Release



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ACS Chemistry for Life®

Molecules to Manufacturing to Marketplace: 3D Printing of Sulfonated Polyesters for Controlled Release

BRYAN TWEEDY
Senior Portfolio Manager, Learning and Career Development, American Chemical Society

TIMOTHY LONG
Center Director & Professor, Biodesign Center for Sustainable Macromolecular Material and Manufacturing (SM3), Arizona State University

MICHAEL BORTNER
Associate Professor and College of Engineering Faculty Fellow, Department of Chemical Engineering, Virginia Tech

Presentation slides available now! Today's recording will be made available to all registrants for 24 hours before moving to www.acs.org/acswebinars as soon as possible.

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Ira A. Fulton Schools of Engineering

VIRGINIA TECH

TIMOTHY E. LONG

Center Director & Professor,
Biodesign Center for Sustainable Macromolecular Material and Manufacturing (SM3),
Arizona State University

MICHAEL J. BORTNER

Associate Professor,
Macromolecules Innovation Institute,
Department of Chemical Engineering,
Virginia Tech

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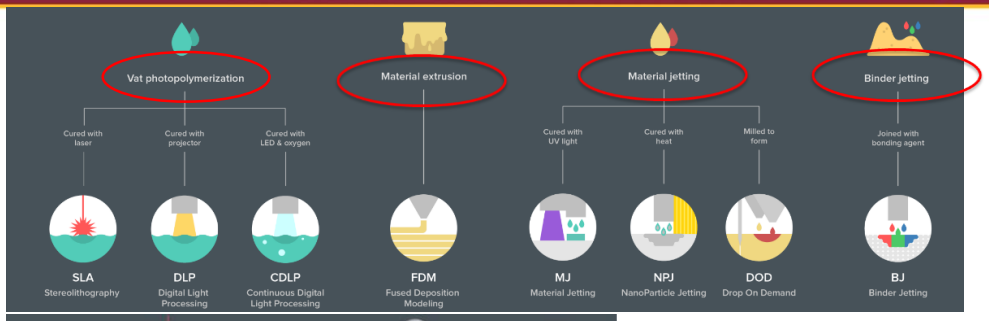
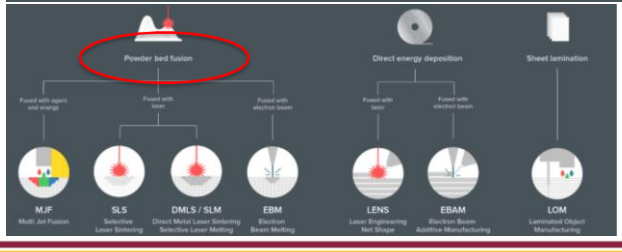
From Molecules to Manufacturing





- The **first 3D printer appeared in 1987** from Chuck Hull (3D Systems) employing a "stereolithography" (SLA) process.
- **Advanced manufacturing now demands advanced materials design**

www.3dhubs.com/what-is-3d-printing#additive-manufacturing-infographic

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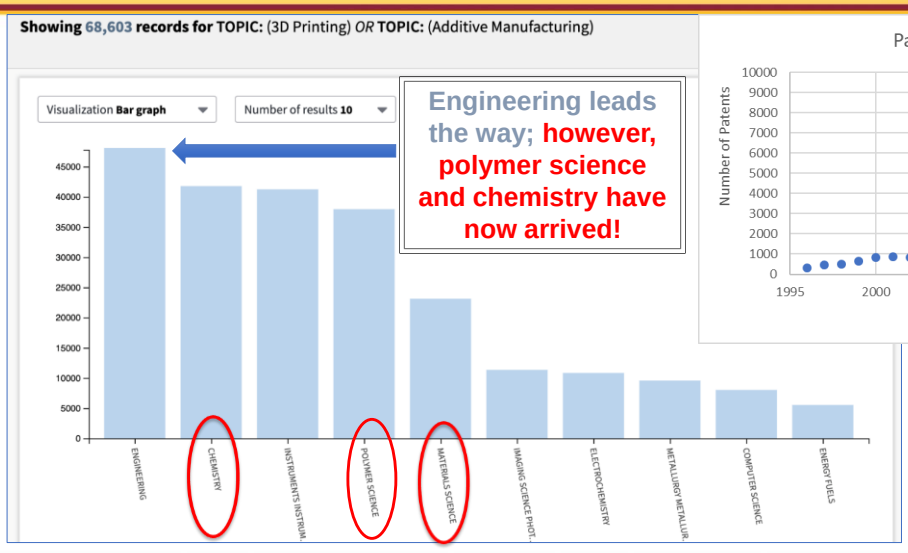
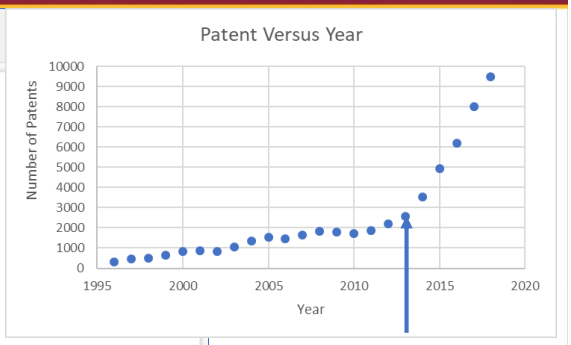
Additive Manufacturing or 3D Printing: Patents
(Web of Science Derwent Innovation Index)



Engineering leads the way; **however, polymer science and chemistry have now arrived!**



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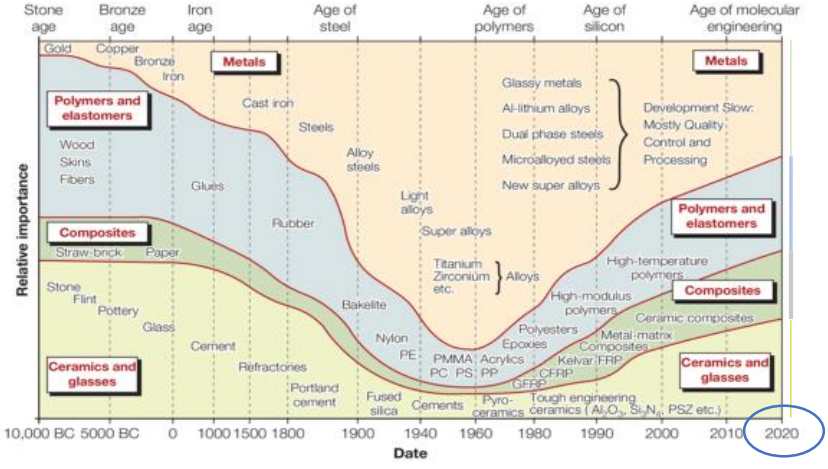
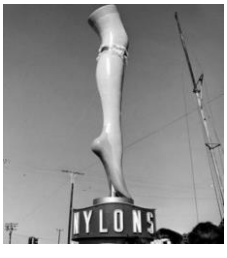
Leveraging the age of molecular engineering: polymers, composites, and ceramics

Ashby, M. F. *Materials Selection in Mechanical Design*, 4th Edition.; Elsevier, 2011



Polymer design from the 1950s are not tuned for the additive manufacturing of 2020



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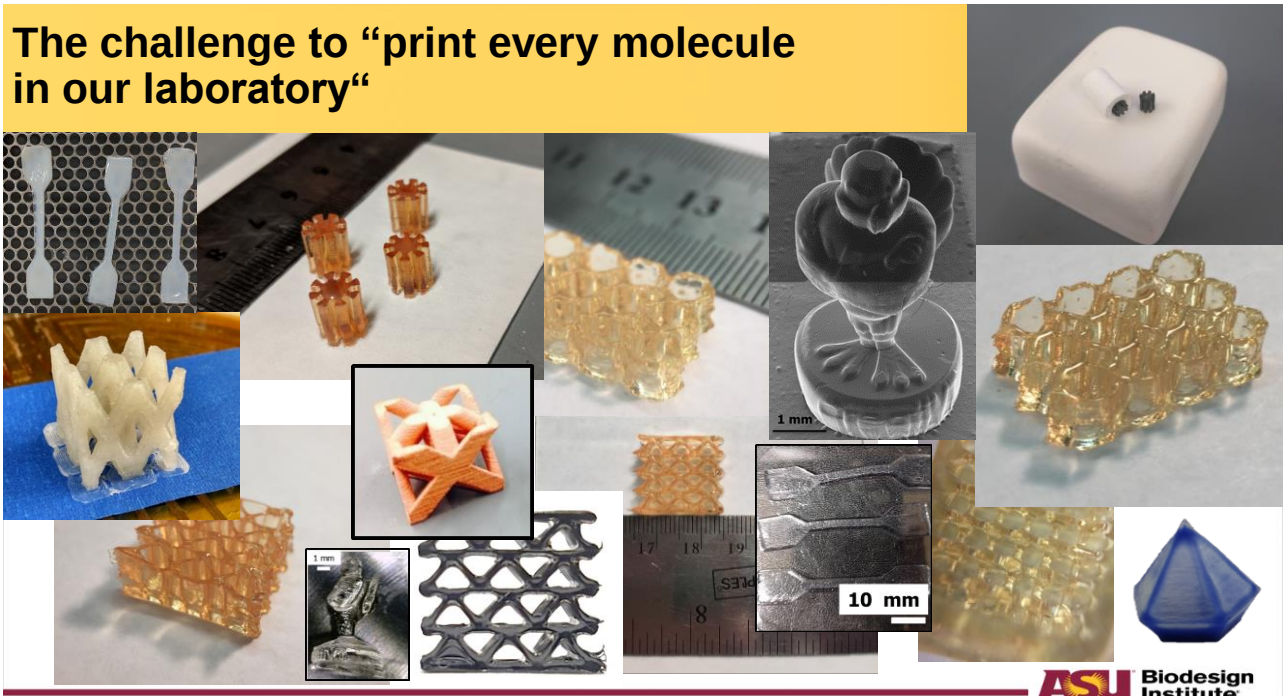
The challenge to "print every molecule in our laboratory"



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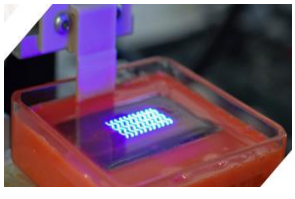
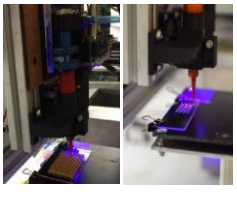
Understanding viscosity ranges for commercial 3D printing platforms

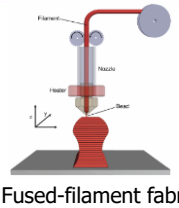
Ink-jetting



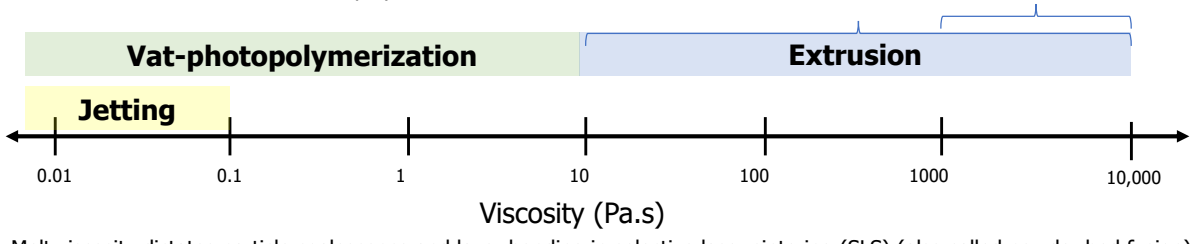
Vat Photopolymerization



Direct-ink-write



Fused-filament fabrication (melt viscosity)



- Melt viscosity dictates particle coalescence and layer bonding in selective laser sintering (SLS) (also called powder bed fusion)
- SLS-grade-nylon-12 reports 60 Pa·s (melt viscosity)

Gibson, I., David, W. R., Brent, S. *Additive manufacturing technologies*; Springer: New York, 2014; Vol. 17.

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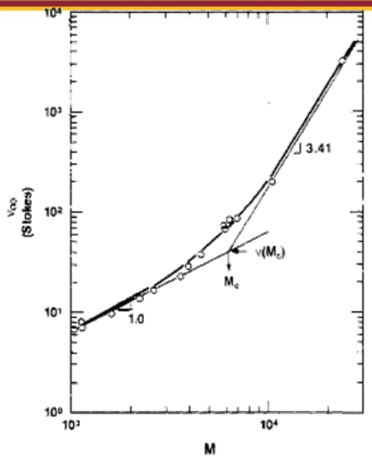
Polymer viscosity is directly proportional to molecular weight

Our overarching question:

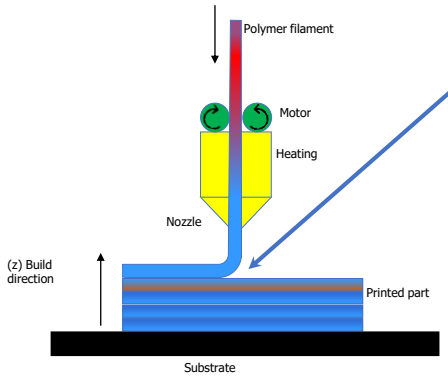
How do we decouple the relationship between molecular weight from viscosity to enable new directions in AM?



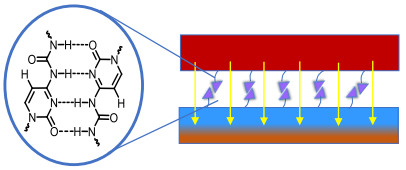
Colby, R. H.; Fetters, L. J.; Graessley, W. W.*Macromolecules* **1987,** *20* (9), 2226-2237.

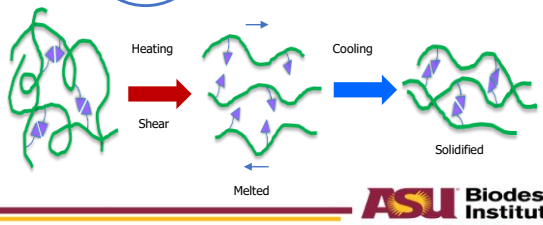
Lest we forget the role of entanglements and physical crosslinks

Supramolecular polymers are promising candidates for extrusion additive manufacturing



- Tunable viscosities/shear thinning
- Thermo-reversible physical crosslinks
- Rapid solidification upon extrusion





Challenge: mechanical anisotropy (weak bonding strength in the build direction)

Kishore, V. *et al. Addit. Manuf.* **2017**, *14*, 7 Shaffer, S. *et al. Polymer (Guildf).* **2014**, *55*, 5969

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Staying on the "road"

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Extrusion-based Processes

Fused-Deposition Modeling (Stratasys)

Positives:

- Cheap
- Robust, strong parts
  - 85% strength of conventional ABS
- Easy post-processing
- Office-friendly
- Sandable, paintable, tap-able
- Little material waste
- Easy material change

Challenges:

- Slow
  - Viscosity
  - Filling cross-sections
- Poor surface finish
- Anisotropic parts
- Poor resolution
- Porous
- Difficult to make point-like depositions

Thanks to Chris Williams

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Versatility of Extrusion AM

- 3D dispensing is highly versatile with respect to its extraordinarily wide choice of materials ranging from polymers to ceramics and metals.

- 3D dispensing of **polymer melts** and solutions, polymer **latex**, **thermoplastic elastomers**, ceramic precursors, cements, pastes of inorganic and organic particles, biopolymers, reactive resins (i.e., thermosets), liquid rubbers, and even hydrogels and polyelectrolytes

See distribution statement on the title page

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Necessity for Solidification in Fused Filament Fabrication

- Amorphous polymers are printed above the glass transition temperature
- Semi-crystalline polymers are printed above melting temperature
- Reversible crosslinks enable the melt extrusion of thermosets
- **Solidification processes are based on crystallization and entanglement/physical interactions** (supramolecular assembly)

See distribution statement on the title page

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Parameters for Extrusion AM

Process

- Layer thickness
- Nozzle speed
- Extrusion feed rate
- Nozzle temperature
- Environment temperature
- Fill pattern and layer timing
- Road width

Machine

- Nozzle diameter
- Filament diameter
- Nozzle height
- Maximum pressure

Material

- Viscosity (function of temperature and shear rate)
- Stiffness
- Thermal conductivity
- Glass transition temperature
- Coefficient of thermal expansion

Courtesy of Chris Williams

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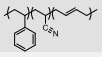
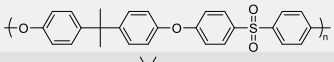
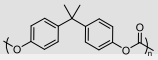
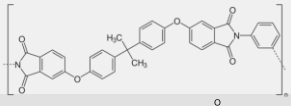
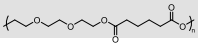
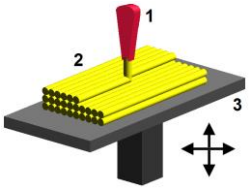
Thermoplastic Polymers for Extrusion

Any thermoplastic material with proper melt viscosity is potentially suitable for extrusion

POLYMER TYPE	CHEMICAL STRUCTURE	PROPERTIES
Acrylonitrile-Butadiene-Styrene (ABS)		High toughness and impact resistance
Polysulfones		Heat/chemical resistance, dimensional stability
Polycarbonates		High impact resistance/tensile strength, low scratch resistance
Polyetherimides		High temp applications (T_g = 216 °C), similar to PEEK
Polyesters		Biocompatible and biodegradable



Gibson, I.; Rosen, D. W.; Stucker, B.; Springer: New York, 2010, pg. 159

Images - http://en.wikipedia.org/wiki/Fused_deposition_modeling

http://blog.lib.umn.edu/thors394/3701/assets_c/2013/10/DSC_2569-thumb-800x529-167617.jpg

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Thermoplastics Investigated for Fused Filament Fabrication (FFF)

- Acrylonitrile-Butadiene-Styrene copolymers (ABS)
- Polyamides (PA)
- Polypropylene (PP)
- Poly(ether esters) elastomers
- Polylactide (PLA)
- Polycarbonate (PC)
- Polyetherimides (PEI)
- Polysulfones (PSF)
- Water soluble polymers (as supports)

Common grades include:
ABS plus
ABS-M30
ABS-M30i
ABSi
PC-ABS
PC
PC-ISO
PPSF/PPSU
ULTEM 9085

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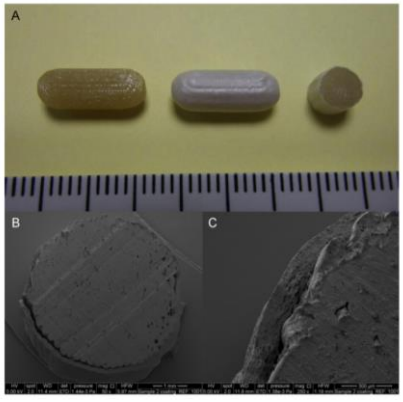
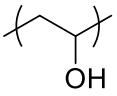
Water-soluble polymers for materials extrusion AM remain limited

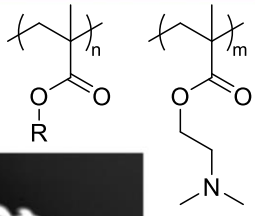
Poly(vinyl alcohol)

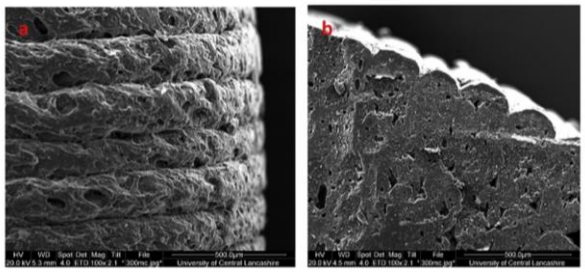




Printing parameters:
190 °C, 90 mm/s

Eudragit EPO





Printing parameters:
135 °C, 90 mm/s

Goyanes, Alvaro, et al. *International journal of pharmaceutics* 496.2 (**2015**): 414-420

Sadia, Muzna, et al. *International Journal of Pharmaceutics* 513.1 (**2016**): 659-668.

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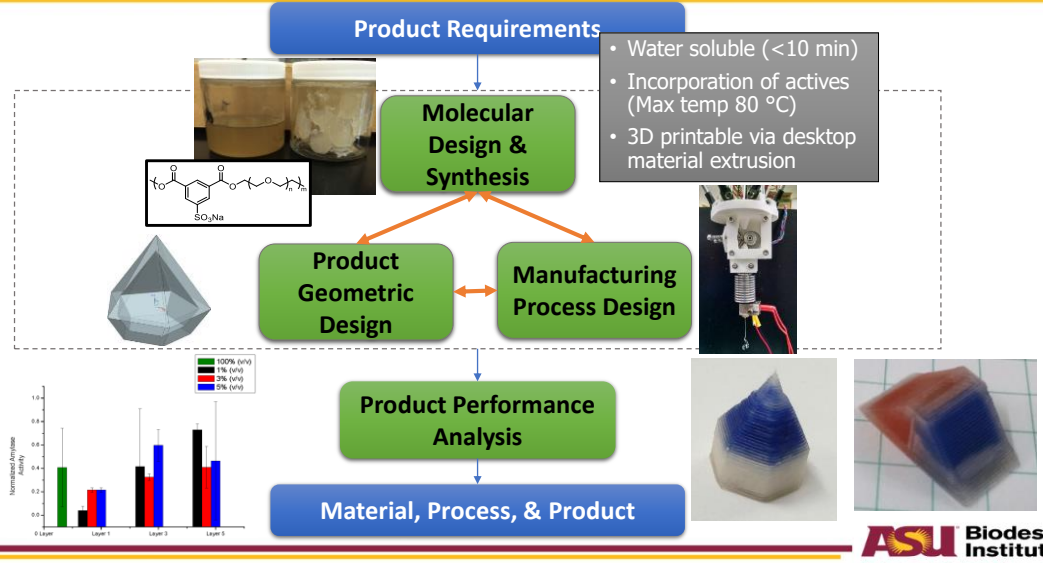
Tailored dissolution of extrusion printed polymers with temperature-sensitive biologics



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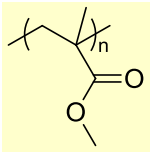
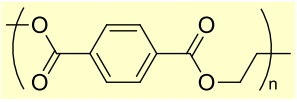
Acrylic Esters *versus* Main Chain Polyesters

Acrylics



- Tunable monomer performance for PSA applications
- **Solvent-based chain growth polymerization**
- MWs > 100,000 g/mol
- Controlled radical and living polymerizations for block copolymer formation
- **Non-biodegradable**
- **Limited bio-based mono-substituted monomer choices**

Polyesters



- Tunable monomer performance for PSA applications
- **Solvent-free step-growth polymerization**
- MWs < 100,000 g/mol
- Segmented block copolymers from preformed polyols
- **Hydrolytically degradable**
- **Vast bio-based alcohol, carboxylic acid, and ester monomer possibilities**

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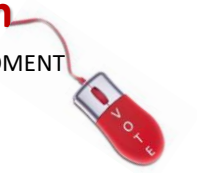
Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



A plot of log zero shear viscosity versus log weight-average molecular weight reveals a steeper dependency at a critical molecular weight, what is this observation due to?

- Phase of the moon
- Polymer end group effects
- Entanglement
- Free volume increases
- Other (let us know if the chat!)

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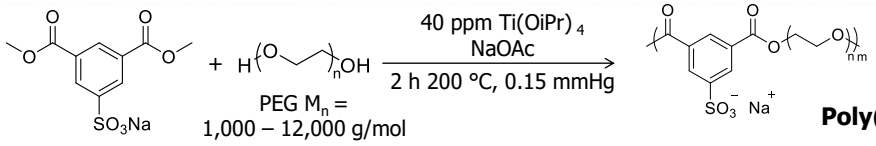
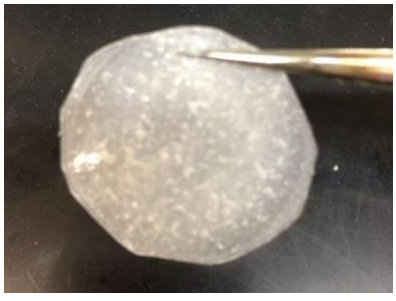
Melt transesterification enables melt processible, water-soluble AM polyesters on commercial scales



Advantages of sulfonates
- Potential to stabilize biologics
- Improved water dispersion times
- Lowered melting point
- Charge interactions for enhanced printing and mechanical properties
- Enhanced processability at lower molecular weight



Poly(PEG$_{4k}$-co-NaSIP)

Pekkanen, A. M.; Williams, C. B.; Long, T. E., et al. ACS Applied Materials & Interfaces **2017**, 9 (14), 12324-12331.

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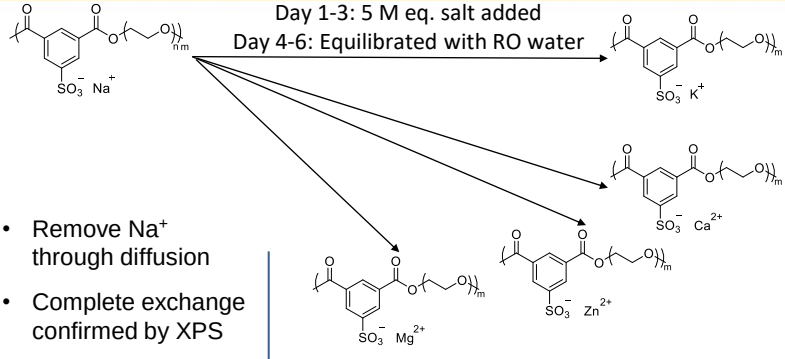
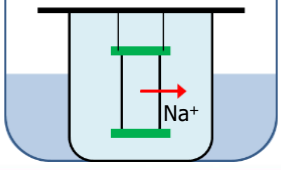
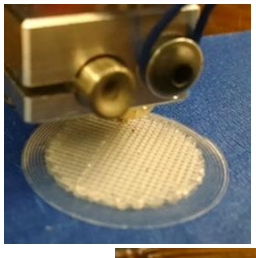
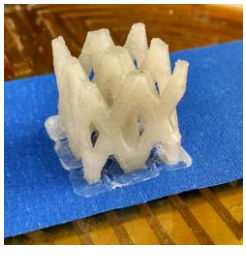
Poly(PEG$_{8k}$-co-NaSIP) can be exchanged to monovalent and divalent counterions



- Remove Na^+ through diffusion
- Complete exchange confirmed by XPS







- **Potential to introduce physical crosslinks between chains**
- **Potential to enhance interlayer adhesion**

Molecular weight (M_w) range of poly(PEG$_{8k}$-co-XSIP): 17,000 – 30,000 g/mol

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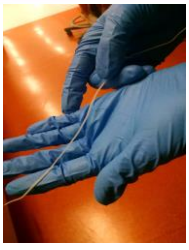
Extrusion AM Material Parameters

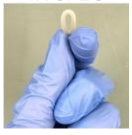


T_g & T_m

Viscosity as f(Shear rate, T)

Stiffness & Strength

4K SPEG

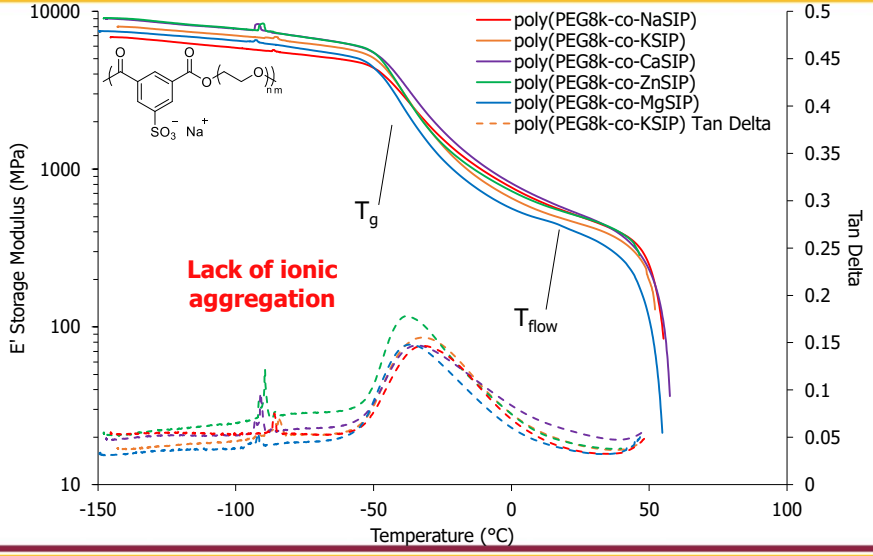


8K SPEG

Thermal Diffusivity & Expansion

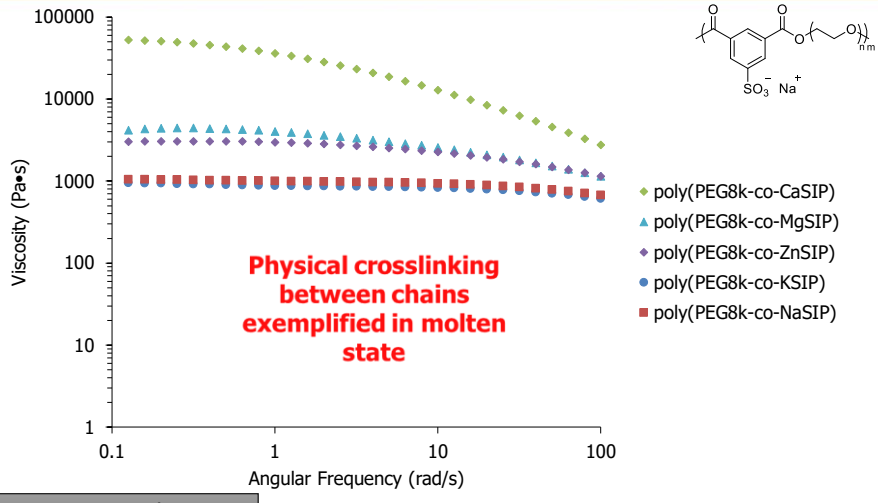
Surface Tension & Hydrophilicity

Dynamic mechanical analysis reveals similarity between samples below T_m



TA Q800, Tension mode, 3 °C/min, 1 Hz

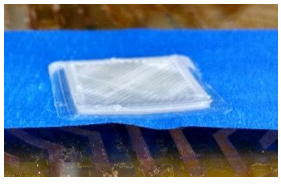
Rheological studies show an increase in viscosity with divalent counterion



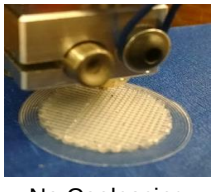
US Patent App 15/667,654

Ares G2 rheometer, 1 % strain, 78 °C, 25 mm parallel plate

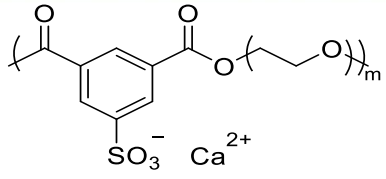
Poly(PEG_{8k}-co-CaSIP) exhibits favorable viscosity for extrusion 3D printing

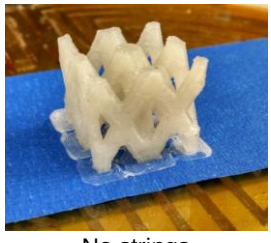


Minimal shrinkage

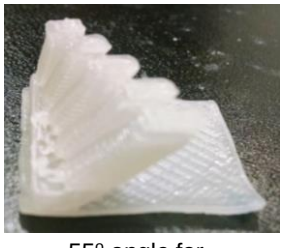


No Coalescing

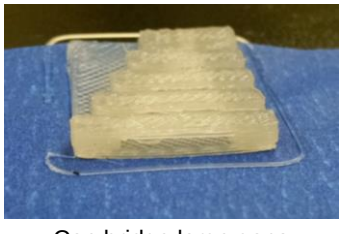




No strings between gaps



~55° angle for 0 Support

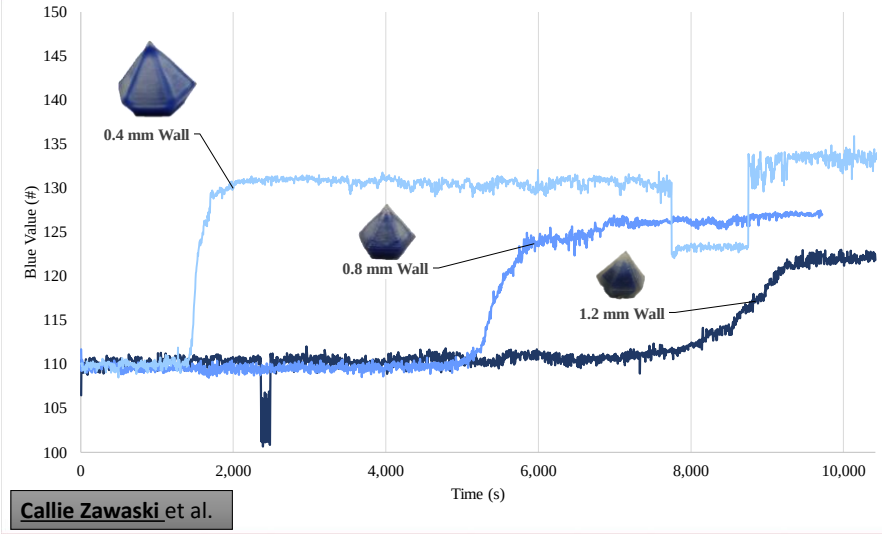


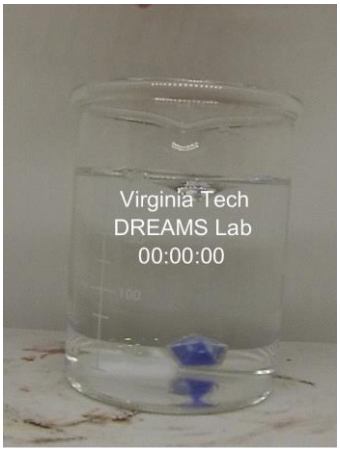
Can bridge large gaps
10 mm gap shown

70 °C hot end, 5 mm/sec, 0.4 mm nozzle diameter

See distribution statement on the title page

Controlling dissolution and release as a function of time for an embedded liquid





Callie Zawaski et al.

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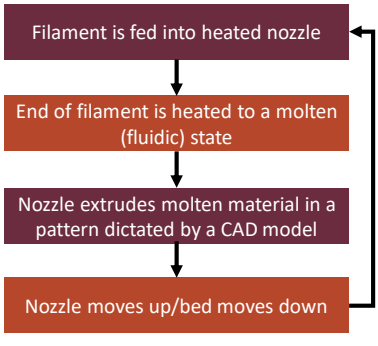
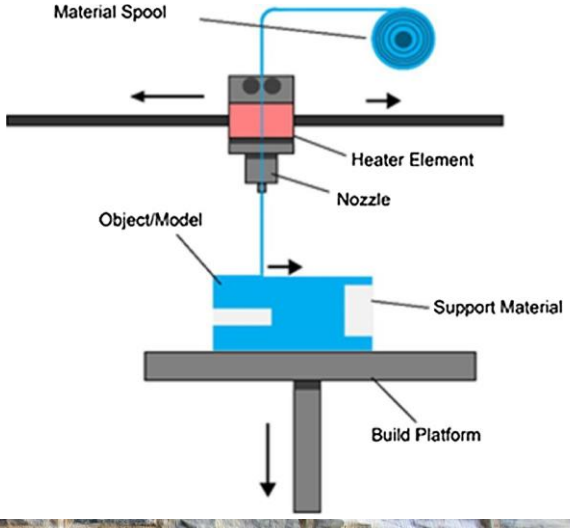
PCML

Fused Filament Fabrication (FFF)

- Material extrusion AM
- Filament feedstock
- Continuous process





VIRGINIA TECH

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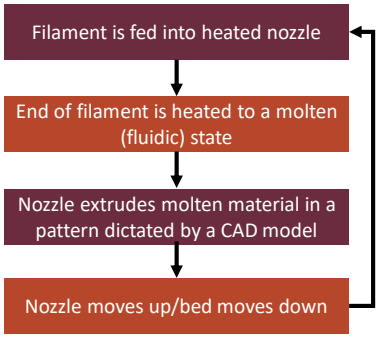
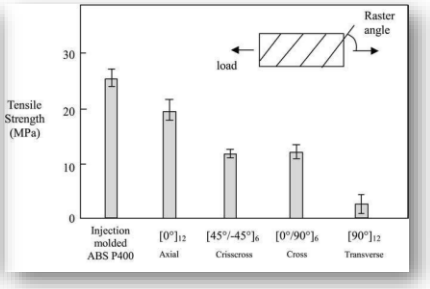
Fused Filament Fabrication (FFF)

- Material extrusion AM
- Filament feedstock
- Continuous process



FFF Fundamental Challenges Where Rheology can Guide Process Design

- Interface provides point of weakness
- Bulk properties are regained when interface fully heals



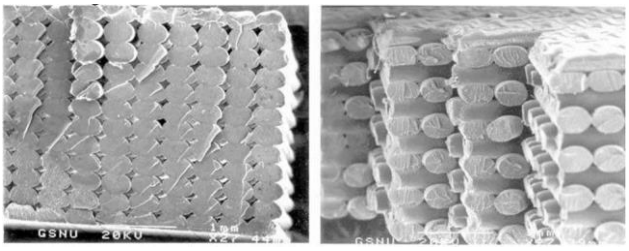
- Anisotropic mechanical properties
- Short time above T_g

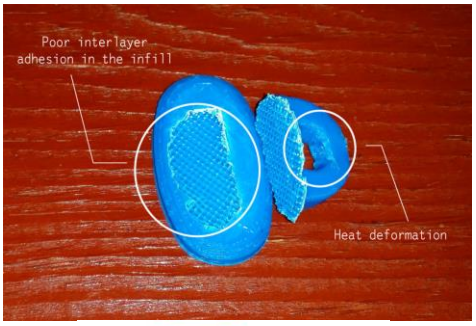
- Material limitation (1950s materials, 2020s process!) especially compared to traditional manufacturing

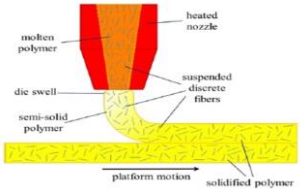
Jiang, D. Thesis. Baylor University, 2017.

FFF Fundamental Challenges Where Rheology can Guide Process Design

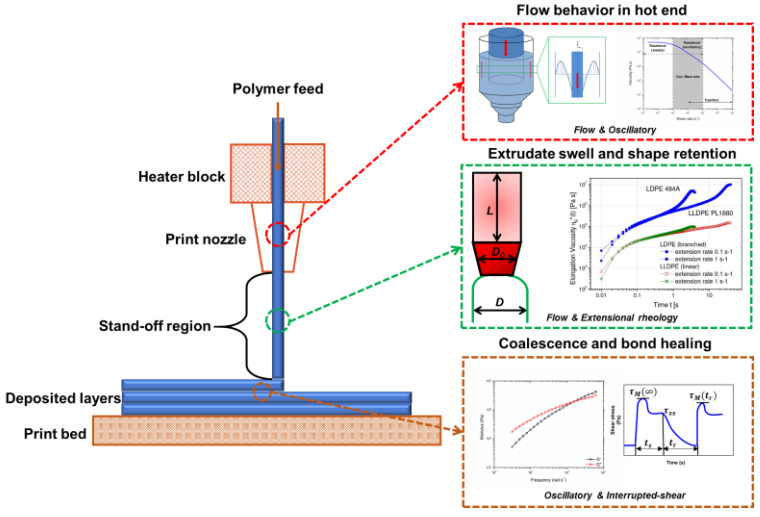
Bed Adhesion (stress buildup)
Poor interlayer (z-axis) adhesion







Modeling and Rheology of the FFF process



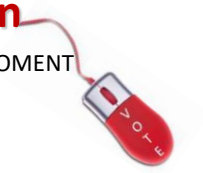
- Will a material extrude?
- What happens when it exits the nozzle?
- What are the dynamics driving interlayer adhesion?
- How do all of these couple to final part properties?

http://blog.capinc.com/2014/12/design-for-3d-printing-success/

A. Das, E.L. Gilmer, S. Biria, and M.J. Bortner, "Importance of Polymer Rheology on Material Extrusion Additive Manufacturing: Correlating Process Physics to Print Properties", *ACS Applied Polymer Materials*, (2021)

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



Indicate whether the following statement is True or False.

Polymer melts are generally non-Newtonian in behavior.

- True
- False

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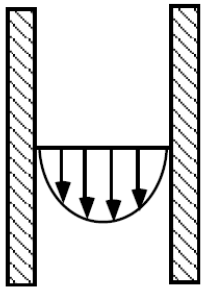
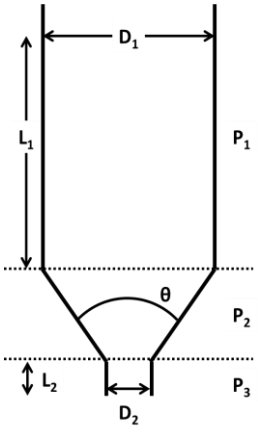
General MatEx Considerations: Will it Extrude?

General design equations for capillary flow – stress and shear rate

$$\sigma_w = \frac{R}{2}\frac{p_c}{L}$$

$$\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3}$$





A. Bellini, S. Güçeri, M. Bertoldi, Liquefier Dynamics in Fused Deposition, J. Manuf. Sci. Eng. 126 (2004) 237.

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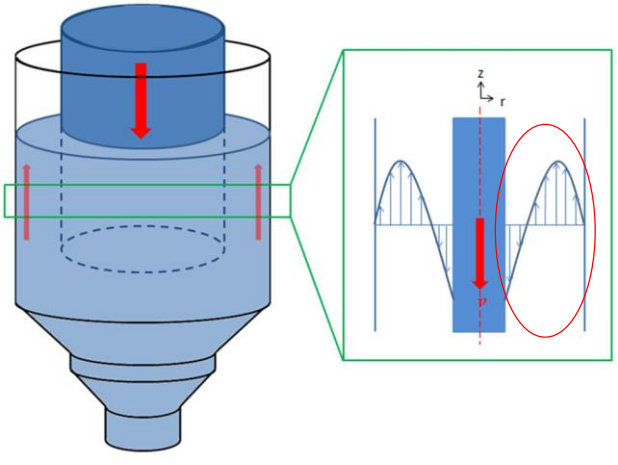
Failure Modes to Accelerate Materials Discovery!

Apply first principles flow models: describe the complex flow field in FFF nozzles

Common failure modes

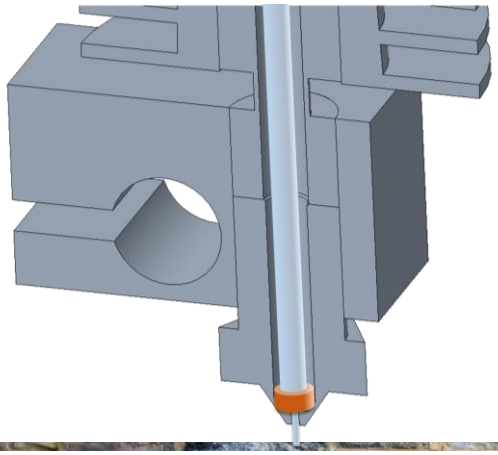
1. Inconsistent filament diameter
   - Processing concern
2. Filament buckling
   - Model exists in literature predicting this phenomenon
3. Annular backflow
   - Little work exists describing this behavior

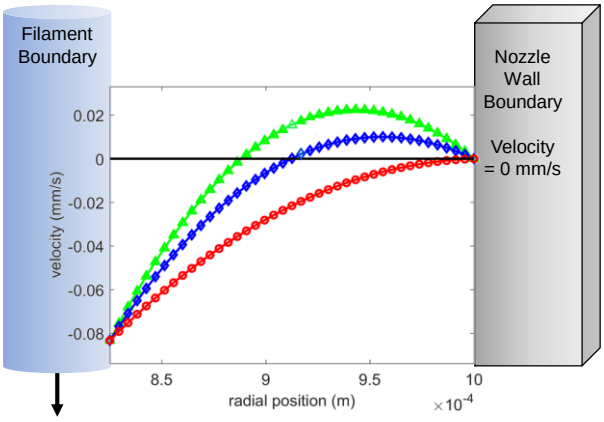
Flow Field and First Principles Modeling



- Assumptions
  - Steady state (!)
  - One dimensional velocity
  - Radially symmetric about the center of the filament
- Area under the curve (net flow magnitude) provides insight into backflow potential

Approach for modeling annular backflow



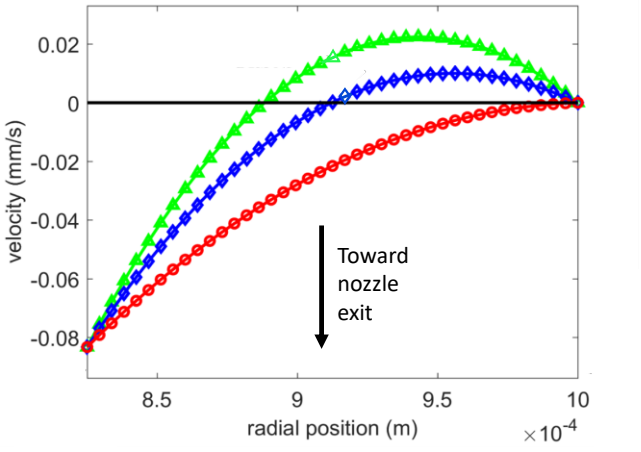


E.L. Gilmer, D. Miller, C.A. Chatham, C. Zawaski, J.J. Fallon, A. Pekkanen, T.E. Long, C.B. Williams, M.J. Bortner, "Model analysis of feedstock behavior in fused filament fabrication: Enabling rapid materials screening", Polymer, 152, 51-61 (2018)

Magnitude of Annular Backflow

Normalized Net Flow Magnitude

No Backflow: < 0.5
Transition: 0.5 – 0.75
Backflow: > 0.75



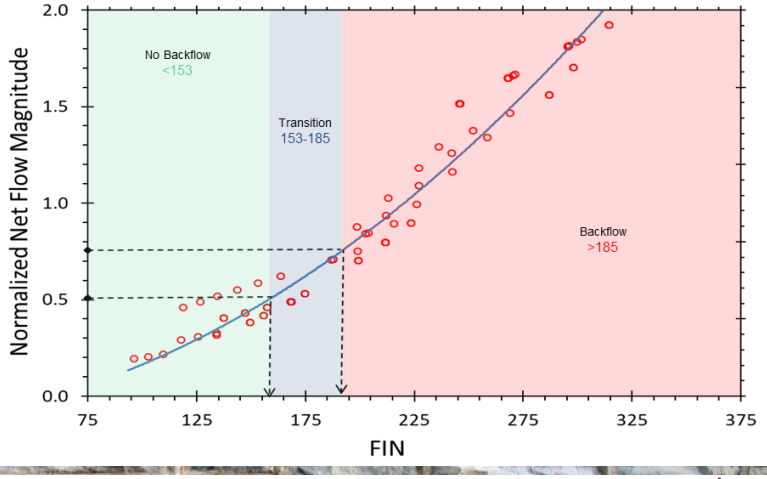
E.L. Gilmer, D. Miller, C.A. Chatham, C. Zawaski, J.J. Fallon, A. Pekkanen, T.E. Long, C.B. Williams, M.J. Bortner, "Model analysis of feedstock behavior in fused filament fabrication: Enabling rapid materials screening", Polymer, 152, 51-61 (2018)

Determining the Flow Identification Number

Dimensionless number to correspond to normalized net magnitude of flow predict backflow

$$FIN = \frac{\Delta P/L}{\eta * v} * \pi(D_B^2 - D_F^2)$$

- No backflow: < 153
- Transition: 153 – 185
- Backflow: > 185



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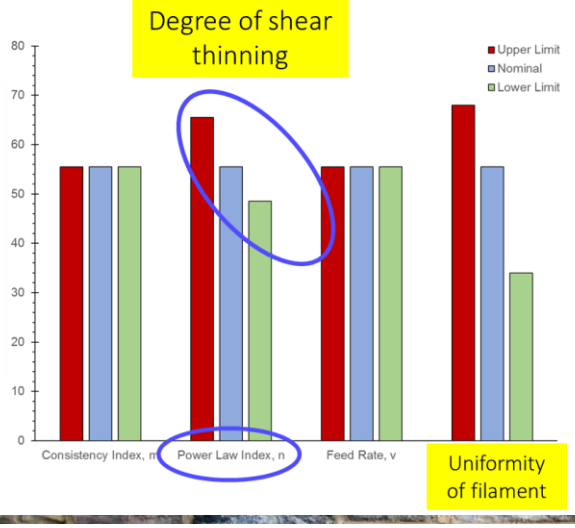
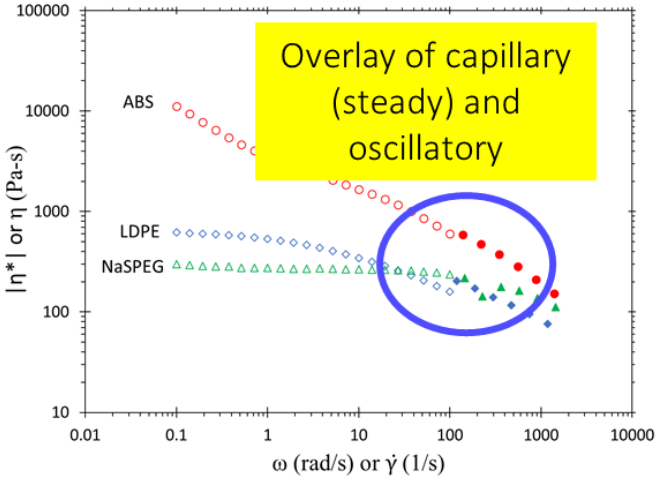
Sensitivity Analysis and Screening Materials





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Testing the Screening Process - Results

Applied model to print parameters*

Material	Feed Rate	BGM Value
ABS	5 mm/s	151
LDPE		175
NaSPEG		204

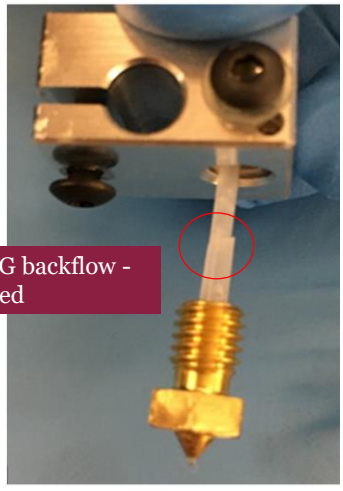
*Model assumes constant filament diameter

FIN Limits

No Backflow: < 153

Transition: 153 - 185

Backflow: > 185



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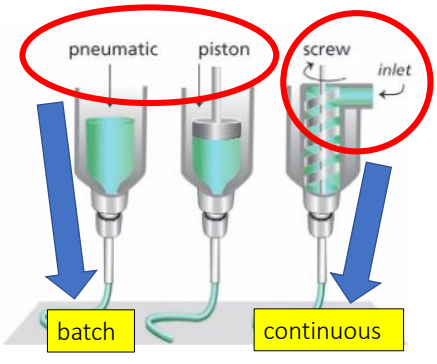
Rheology to describe laydown process: nozzle outlet, standoff region, layer adhesion

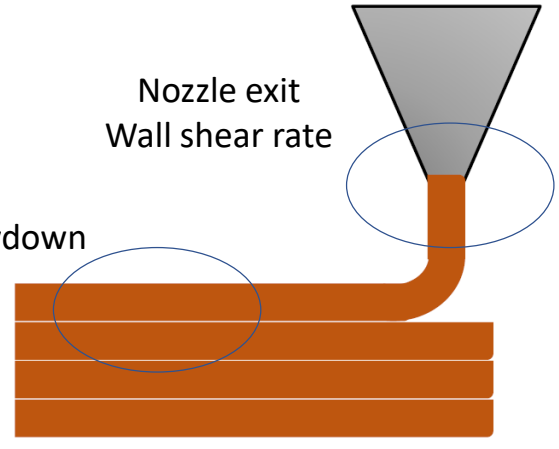
Any Matex process:

DIW, FFF, BAAM



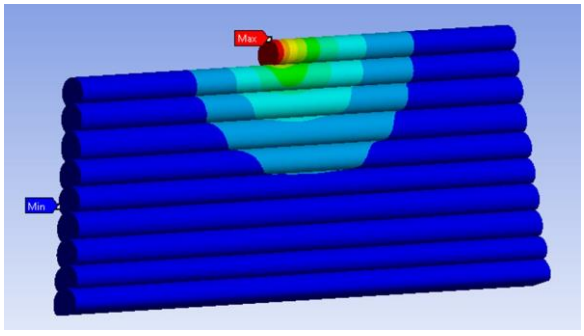
Nozzle exit
Wall shear rate

"Road" laydown



Malda, Jos, et al. "25th anniversary article: engineering hydrogels for biofabrication." *Advanced materials* 25.36 (2013): 5011-5028.

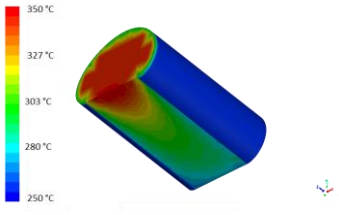
Thermal Models to Capture Nonisothermal Diffusion for Interlayer Adhesion

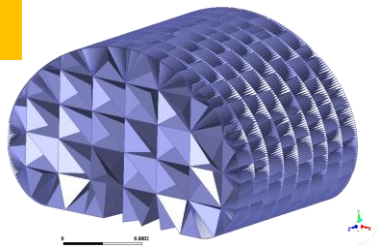


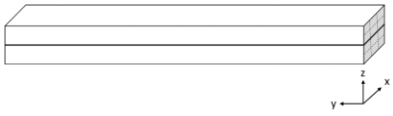
Highly transient nonisothermal profile

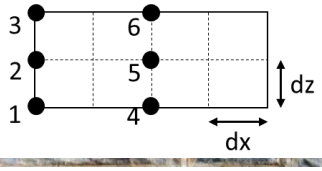
2D vs. 3D analysis

Computational complexity









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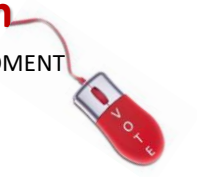
Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



Why are nonisothermal transient models important in fused filament fabrication?

(Select all that apply)

- The rheology of the polymers is highly temperature dependent
- Tim is worried about his ice cream melting in Phoenix while he is busy 3D printing new polymers
- As each layer is deposited, thermal effects are often felt in multiple layers beneath it

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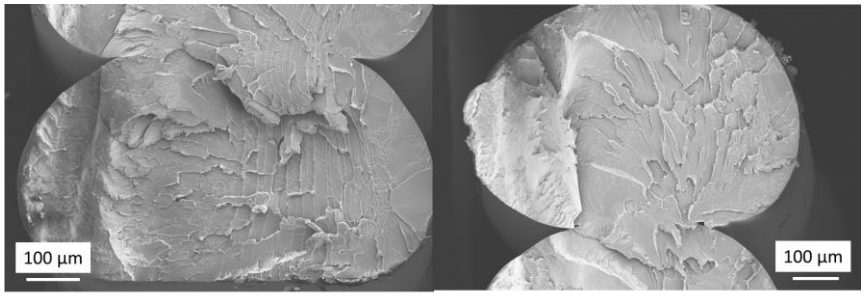
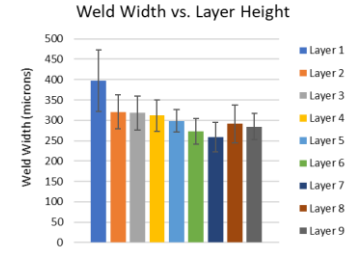
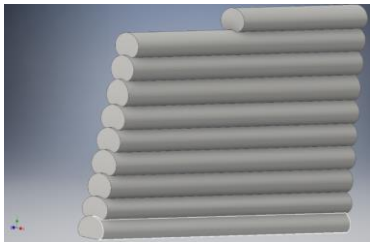
Dynamics of Layer Deposition: Geometry, Thermal and Viscoelastic Response







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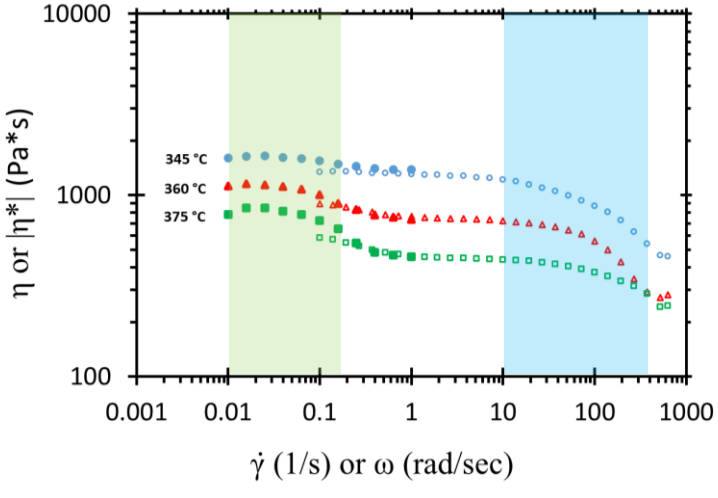
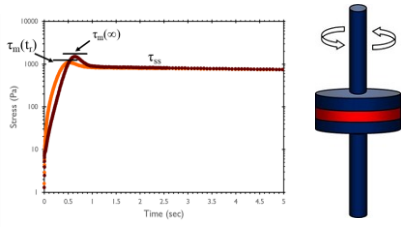
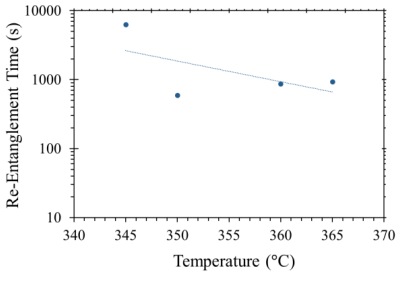
Rheology – Diffusion Dynamics, Extrudate Properties







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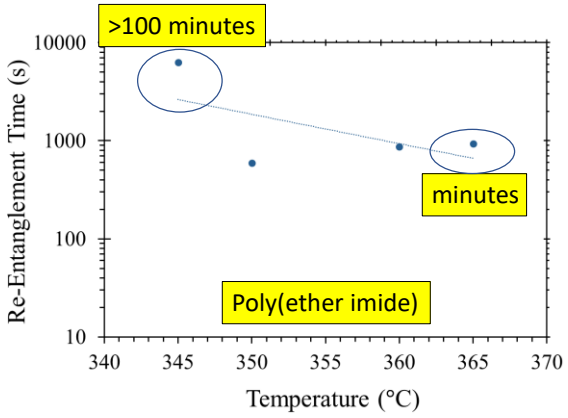
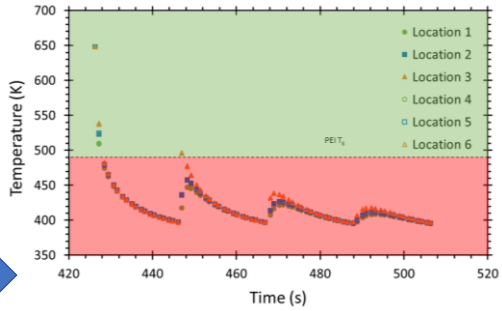
Re-Entanglement Times can be Long!



How much re-entanglement is required for strong bonds?

Thermal model - only ~1-2 seconds above T_g



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Do not lose track of the "big picture"

Intrinsic properties

For example, chemical composition, stereochemistry, topology, and molecular weight

Processing Properties

For example, orientation and effects on crystallinity

Product Performance

For example, optics, tensile, barrier properties, thermal and chemical stability

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Perhaps you are running out of energy!

Polymer Design Parameters for Additive Manufacturing: Concluding Remarks

- ✓Polymers must be designed for additive manufacturing modalities
- ✓Printing modalities must be designed for polymer reactivity and processibility
- ✓Polymer design parameters guide innovation with attention to fundamental structure-property-relationships
- ✓Chemists, chemical engineers, and mechanical engineers working together to advance the AM field

Sharing your ideas is critical for nurturing partnerships!

“The best way to have a good idea is to have a lot of ideas.”

- Linus Pauling

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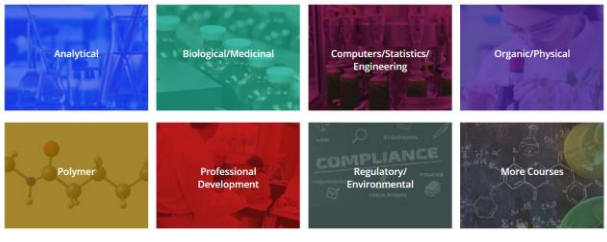

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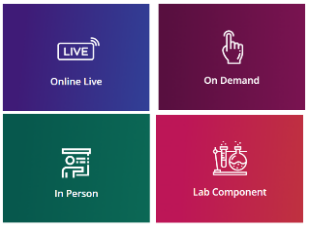

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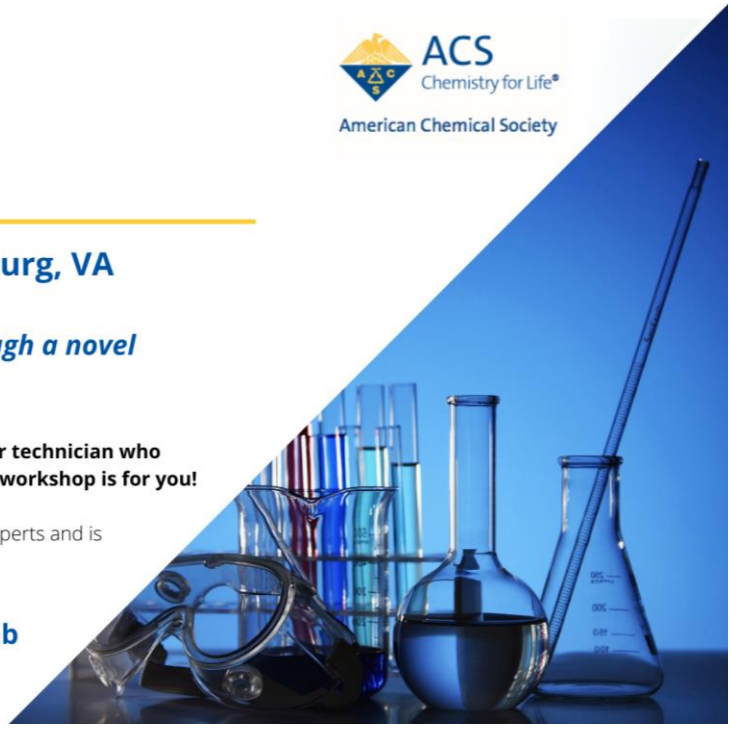

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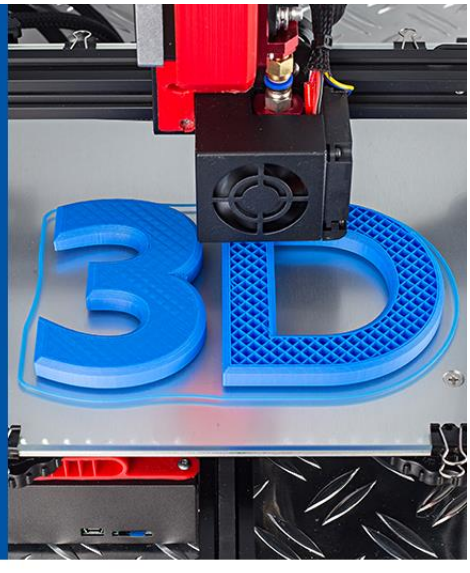

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Senior Portfolio Manager, Learning and Career Development, American Chemical Society

TIMOTHY LONG
Center Director & Professor, Biodesign Center for Sustainable Macromolecular Material and Manufacturing (SM3), Arizona State University

MICHAEL BORTNER
Associate Professor and College of Engineering Faculty Fellow, Department of Chemical Engineering, Virginia Tech

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Moderadora: Ingrid Montes, Universidad de Puerto Rico, Recinto de Río Piedras y American Chemical Society

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- Junto con la biodiversidad biológica existe una diversidad molecular bastante amplia para cuyo estudio son indispensables las técnicas de cromatografía y espectrometría de masas
- Los llamados metabolitos secundarios desempeñan papeles importantes para la comunicación, la adaptación, y la supervivencia de las plantas
- El color de algunas flores está asociado con la capacidad antioxidante de sus colorantes

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