ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

Have Questions?

Type them into questions box!

"Why am I muted?"
Don't worry. Everyone is muted except the presenter and host. Thank you and enjoy the show.

Contact ACS Webinars ® at acswebinars@acs.org

1

Check out the ACS Webinar Library!

An ACS member exclusive benefit

ACS Chemistry for Life®

Hundreds of presentations from the best and brightest minds that chemistry has to offer are available to you on-demand. The Library is divided into 6 different sections to help you more easily find what you are searching.

Professional Development

▶ View the Collection

Learn how to write better abstracts, deliver more engaging presentations, and network to your next dream job. Brush up on your soft skills and set a new career path by mastering what can not be taught in the lab.

Technology & Innovation

▶ View the Collection

From renewable fuels to creating the materials for the technology of tomorrow, chemistry plays a pivotal role in advancing our world. Meet the chemists that are building a better world and see how their science is making it happen.

Drug Design and Delivery

▶ View the Collection

The Drug Design Delivery Series has built a collection of the top minds in the field to explain the mechanics of drug discovery. Discover the latest research, receive an overview on different fields of study, and gain insight on how to possibily overcome your own med chem roadblocks.

Culinary Chemistry

▶ View the Collection

Why does food taste better when it is grilled or what molecular compounds make a great wine? Discover the delectable science of your favorite food and drink and don't forget to come back for a second helping.

Popular Chemistry

▶ View the Collection

Feeling burdened by all that molecular weight? Listen to experts expound on the amazing side of current hot science topics. Discover the chemistry of rockets, how viruses have affected human history, or the molecular breakdown of a hangover.

Business & Entrepreneurship

▶ View the Collection

How do ideas make it from the lab to the real world? Discover the ins and outs of the chemical industry whether you are looking to start a business or desire a priceless industry-wide perspective.

https://www.acs.org/content/acs/en/acs-webinars/videos.html

2

ACS Webinars®

CLICK • WATCH • LEARN • DISCUSS

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

Edited Recordings are an exclusive ACS member benefit and are made available once the recording has been edited and posted.

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.

www.acs.org/acswebinars

3

Advance YOUR CAREER

ChemIDP™

ChemIDP.org

Discover ACS PUBLICATIONS

Publishing Resources

ACS REVIEWER LAB™

ACS axial

ACS AUTHOR UNIVERSITY

ACS Authoring Services

publish.acs.org

Connect WITH CHEMISTS AND OTHER SCIENCE PROFESSIONALS

CAS SciFinder Future Leaders

171 alumni, 35 countries and over 120 institutions

acsoncampus.acs.org/resources

ACS Chemistry for Life®

CAS A DIVISION OF THE AMERICAN CHEMICAL SOCIETY

ACS Publications Most Trusted. Most Cited. Most Read.

4

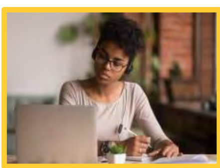
ACS ON CAMPUS

ACS Career Navigator: Your Home for Career Services

ACS Chemistry for Life®

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.

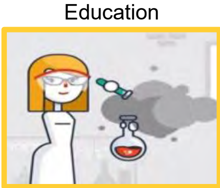
We have a collection of career resources to support you during this global pandemic:


Professional Education


Virtual Career Consultants

ACS Leadership Development System


Career Navigator LIVE!


ChemIDP


College to Career

ACS Webinars


Virtual Classrooms

Visit www.ACS.org/COVID19-Network to learn more!

6

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.

www.acs.org/donate

ACS Office of Philanthropy
Chemistry for Life®

7

ACS
Chemistry for Life®

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:
https://app.suggestionox.com/r/DI_R
Diversity@acs.org

@ACSDiversity

ACS Voices Diversity Podcast
acsvoices.podbean.com/

ACS Diversity

www.acs.org/diversity

8

"Being a member of POLY has helped me identify a network of colleagues and establish myself in the polymer chemistry community. For the small cost of a POLY membership, you can join a strong and passionate group of scientists that can assist you throughout your career, through discussions, networking, and guidance."

Diana Gerbi, 2018 POLY Chair
3M(retired)

"….the next generation of polymer scientists is where we put a lot of our focus and we've really established a tremendous network of scientists at all points in their career. …our more seasoned members are active in helping support and foster the growth of the next generation through mentoring and a very active awards program."

Marc Hillmyer, 2017 POLY Chair
University of Minnesota

"…. as the university relations manager, I knew I would need to connect with a wide variety of professors and students. The Division of Polymer Chemistry provided the perfect environment to build these connections."

Karl Haider, 2016 POLY Chair
Covestro

www.polyacs.org

ACS Chemistry for Life®

JOIN TODAY!

First-Year Free

Become a part of the ACS Division of Polymer Chemistry whose members are among legends in the field.

Benefits

- Networking Events
- Discounts on workshops
- POLY webinars and videos
- POLY LinkedIn and Facebook pages
- Access to job postings
- Polymer Preprints and Graphical Abstracts
- Newsletters and Books
- Many Award Opportunities

Visit:
http://bit.ly/JOINPOLY

ACS APPLIED POLYMER MATERIALS

ACS Publications
Most Trusted. Most Cited. Most Read.

The distributive manufacturing enabled by 3D printing has been on display in the response to shortages in critical medical resources for the response to the COVID-19 epidemic. In almost all cases, these 3D printed parts have been polymers and have been instrumental in providing a stopgap to logistical challenges in obtaining critical components.

These have included, amongst many other examples, engineered solutions to limited number of ventilators through 3D printing of valves for ventilators, parts to transform snorkeling masks into continuous positive airway pressure (CPAP) devices, and repurposing of existing medical equipment to meet demands for treating patients. The timely delivery of these 3D printed plastic components has been enabled by the advances in 3D printing over the past decades.

In light of their acute significance in this global health crisis, it is our pleasure to announce a **"virtual issue"** on the 3D printing of polymers for ***ACS Applied Polymer Materials.***

https://pubs.acs.org/page/aapmcd/vi/3d-printing-polymers

10

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

Date: Thursday, April 15, 2021 @ 2-3pm ET
Speaker: Jordan Harshman, Auburn University and Anne Kondo, Indiana University Pennsylvania
Moderator: Marian Gindy, Merck

Register for Free!

What You Will Learn:

- What collaborative work involves
- What collaborative and teamwork skills employers expect
- How these skills are acquired

Co-produced with: ACS Education

Date: Wednesday, April 21, 2021 @ 2-3pm ET
Speakers: Patricia Simpson, Game Changing Etiquette and the University of Illinois at Urbana-Champaign
Moderator: Matt Grandbois, DuPont Electronics & Industrial

Register for Free!

What You Will Learn:

- Why is business acumen important for all employees
- What are the core elements of a business acumen
- How to develop or enhance your business acumen

Co-produced with: ACS Division of Professional Relations

Date: Thursday, April 22, 2021 @ 2-3pm ET
Speakers: Rich Helling, Dow
Moderator: David Constable, American Chemical Society

Register for Free!

What You Will Learn:

- Why life cycle thinking and assessment is a good way to include environmental dimensions in decisions
- How life cycle thinking and assessment identifies potential hot spots and trade-offs
- Why simple calculations can be insightful and are a great way to include life cycle thinking in daily decisions

Co-produced with: ACS Green Chemistry Institute and the ACS Committee on Community Activities for the *Chemists Celebrate Earth Week* campaign

www.acs.org/acswebinars

11

FREE Webinar | TODAY at 2pm ET

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

THIS ACS WEBINAR WILL BEGIN SHORTLY...

12

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

Next Gen Additive Manufacturing: Predicting Polymer Printability and Performance

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

AMY PETERSON
Associate Professor, Associate Chair - Master's Studies, Department of Plastics Engineering, The University of Massachusetts Lowell

BRYAN VOGT
Professor, Chemical Engineering, Penn State University and Associate Editor for *ACS Applied Polymer Materials*

Presentation slides are available now! The edited recording will be made available as soon as possible.

www.acs.org/acswebinars

This ACS Webinar is co-produced with ACS Applied Polymer Materials and the ACS Division of Polymer Chemistry.

13

ASU Arizona State University
Ira A. Fulton Schools of Engineering

UMASS LOWELL
Learning with Purpose

TIMOTHY E. LONG

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

AMY M. PETERSON

Associate Professor,
Associate Chair - Master's Studies,
Department of Plastics Engineering,
The University of Massachusetts Lowell

14

Today, manufacturing accounts for 25% of U.S. energy consumption

SUSTAINABILITY, RECYCLING AND THE CONCEPT OF A CIRCULAR ECONOMY ARE ALL TOPICS VITALLY IMPORTANT IN TODAY'S CHANGING WORLD

"

REMADE is uniquely positioned to harness industry innovators, academic researchers and national labs that will ultimately enhance industrial competitiveness.

— Nabil Nasr, CEO, The REMADE Institute

REMADE INSTITUTE

ASU Biodesign Institute
Arizona State University

16

From Molecules to Manufacturing

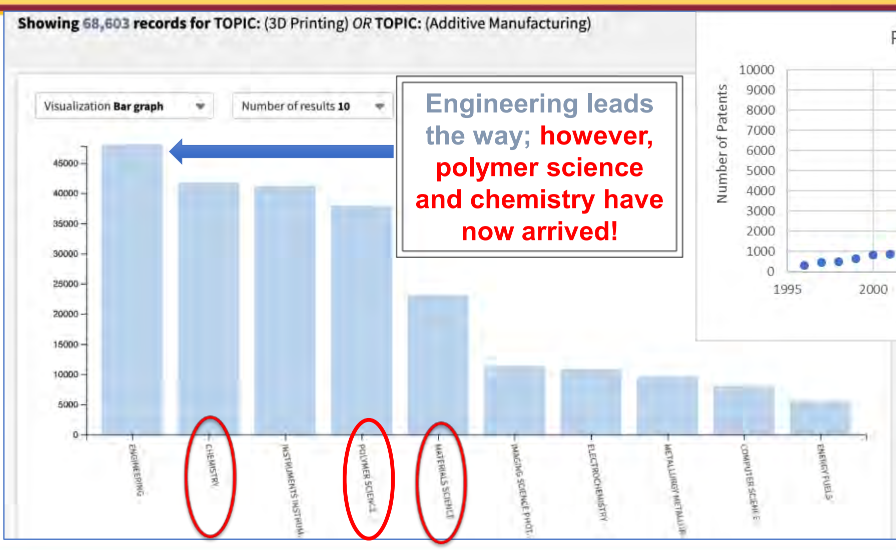
- The first 3D printer appeared in 1987 from Chuck Hull (3D Systems) employing a "stereolithography" (SLA) process.
- Advanced manufacturing now demands advanced materials design

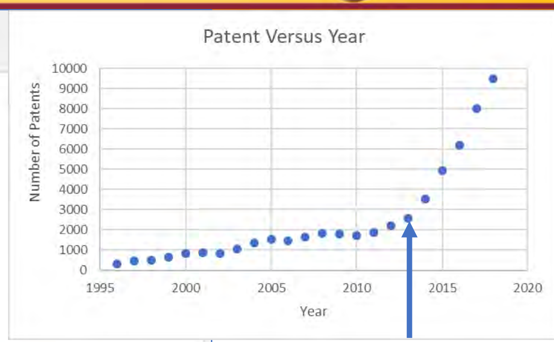
www.3dhubs.com/what-is-3d-printing#additive-manufacturing-infographic

Biodesign Institute
Arizona State University

17

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



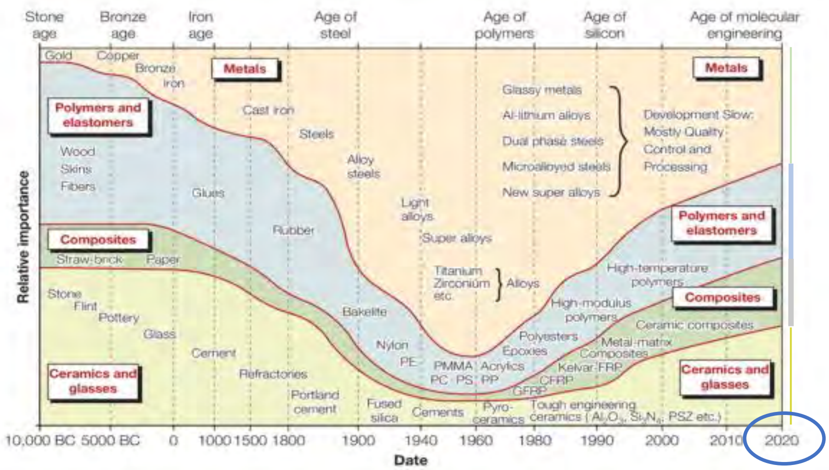


Biodesign Institute
Arizona State University

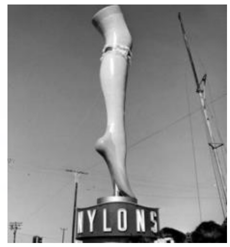
18

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

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

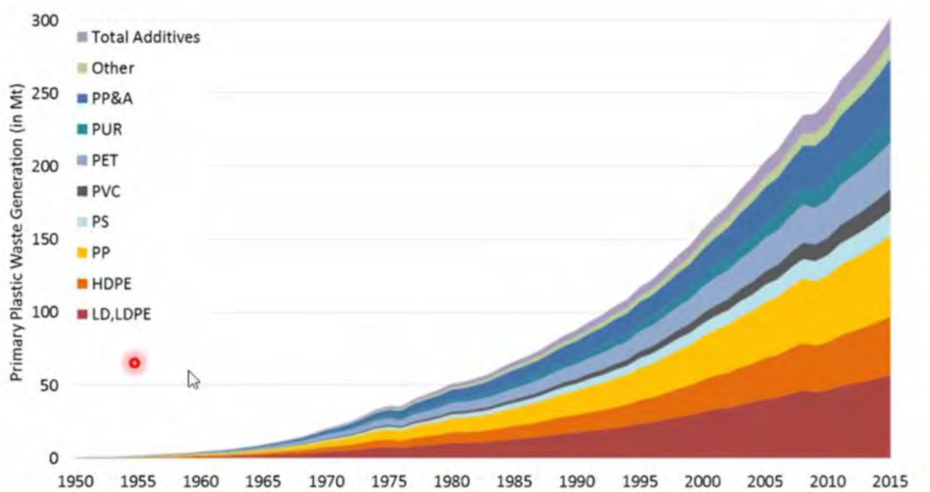


Polymer design from the 1950s are not tuned for the additive manufacturing of 2020



Biodesign Institute
Arizona State University

Literally tons of macromolecules continue to influence the quality of our lives



Geyer, Jambeck and Law, *Science Advances*, **2017**,

2.5 million
plastic bottles used in the US every hour

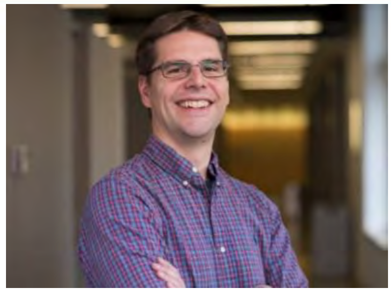
8 million metric tons
of plastic enter the ocean every year

9%
estimated percentage of plastic ever recycled

$86-125 billion
estimated value of annual global plastic packaging industry

Biodesign Institute
Arizona State University

Discoveries demand a convergence of chemistry and mechanical engineering!



Arizona State University

Tim Long
The Long Group
http://www.tlong.chem.vt.edu

Virginia Tech

Chris Williams
DREAMS Lab
http://www.me.vt.edu/dreams

And now at the intersection of multiple universities together with national laboratories and industry

Biodesign Institute
Arizona State University 21

Polymer additive manufacturing offers much promise, many challenges

Advantages
- Capable of creating parts with complex geometries – "complexity for free"
- Customization
- Short runs
- Less energy and less waste

Challenges
- Reliability, reproducibility
- Scale/speed
- Need for advanced material reactivity and rheology to achieve optimum resolution
- Imposing a lens of sustainability

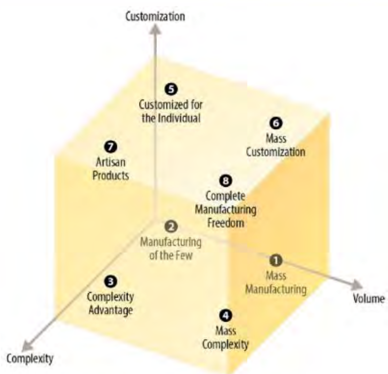
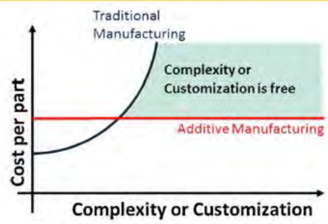
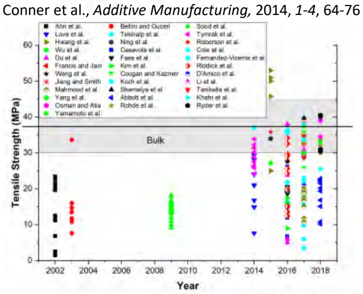


Fig. 2. Three axis model of manufactured products.
Conner et al., *Additive Manufacturing,* 2014, *1-4*, 64-76



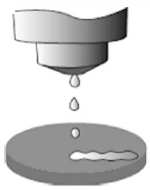
Conner et al., *Additive Manufacturing,* 2014, *1-4*, 64-76



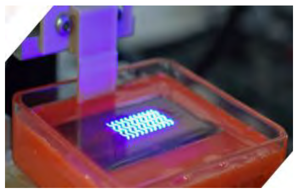
Peterson, *Additive Manufacturing,* 2019, *27*, 363-371

Biodesign Institute
Arizona State University 22

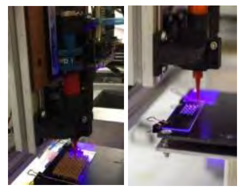
Understanding viscosity ranges for commercial 3D printing platforms



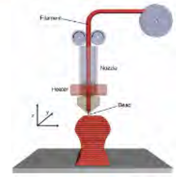
Ink-jetting



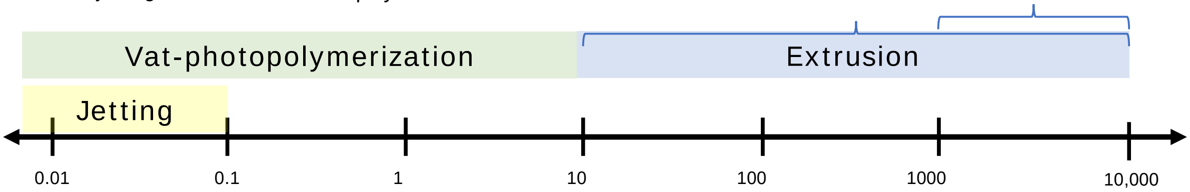
Vat Photopolymerization



Direct-ink-write



Fused-filament fabrication (melt viscosity)

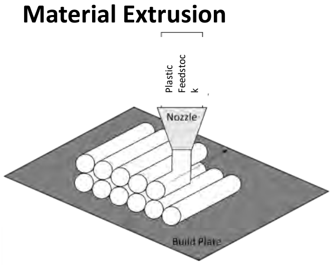


- Melt viscosity dictates particle coalescence and layer bonding in selective laser sintering (SLS) (also called powder bed fusion)
- SLS-grade-nylon-12 reports 60 Pa·s (melt viscosity)

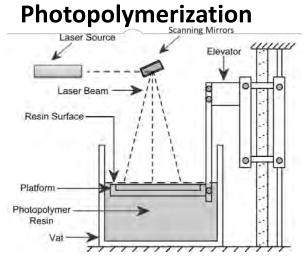
Gibson, I., David, W. R., Brent, S. *Additive manufacturing technologies*; Springer: New York, 2014; Vol. 17.

In this webinar, we will highlight processing-structure-property relationships in polymer AM

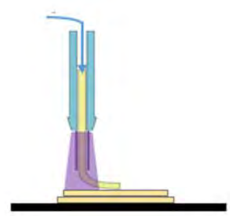
Thermally-Driven Material Extrusion



Vat Photopolymerization

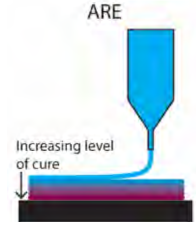


UV-Assisted Direct Ink Writing



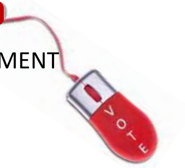
Ambient Reactive Extrusion

ARE



Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

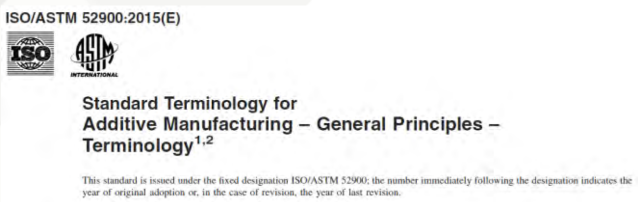


What is the most commonly 3D printed polymer?

- Nylon
- Acrylate
- ABS (Acrylonitrile butadiene styrene)
- PLA (Polylactic Acid)
- Other (Let us know in the chat)

** If your answer differs greatly from the choices above tell us in the chat!*

Material extrusion (MatEx) is the most common form of polymer AM

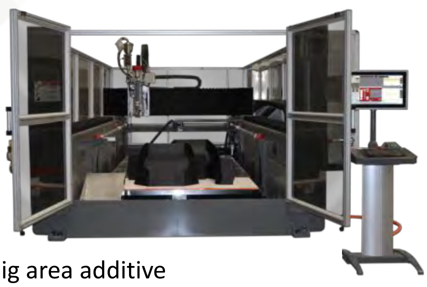


ISO/ASTM 52900:2015(E)

Standard Terminology for Additive Manufacturing – General Principles – Terminology[1,2]

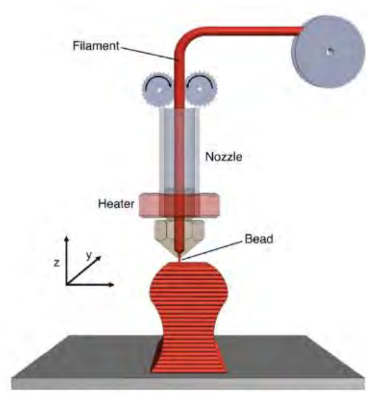
This standard is issued under the fixed designation ISO/ASTM 52900; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision.

"Additive manufacturing process in which material is selectively dispensed through a nozzle or orifice"



Big area additive manufacturing (BAAM)

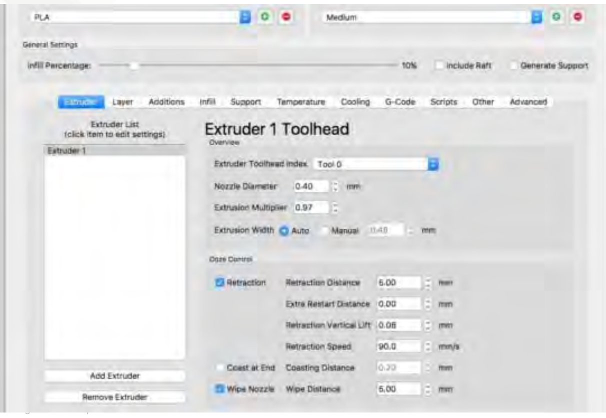
Fused filament fabrication (FFF)

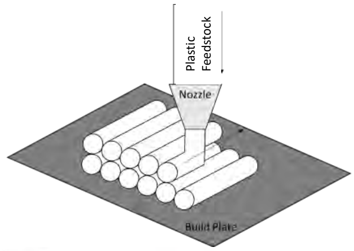


Osswald et al. *Additive Manufacturing*, 2018, *22*

MatEx - even benchtop, commercial systems – is incredibly complex

- >100 adjustable parameters
- Toolpath based on proprietary algorithms
- Feedstocks – polymer choice, grade, fillers

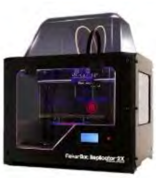




We printed the same parts with three different printers using the same material

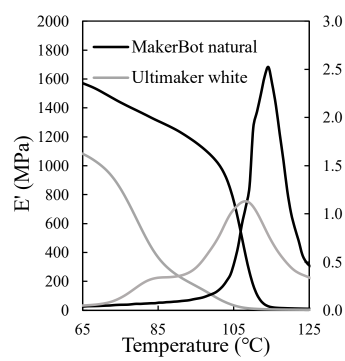
- 3 printer round robin
- Selected four commonly adjusted print parameters (speed, extruder temperature, layer thickness, print bed temperature) at two levels
- ASTM D638 Type V dog bones
- Screening DOE (18 conditions)
- Zortrax and Makerbot used same spool of natural ABS (1.75 mm), Ultimaker used spool of natural ABS (2.85 mm)

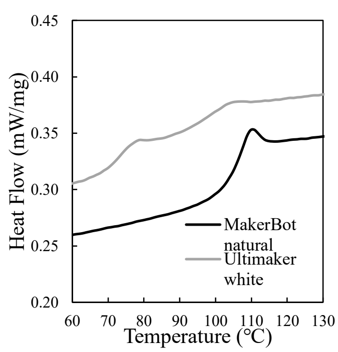
Print ID	Printer Type	ET (°C)	LT (µm)	PBT (°C)	PS (mm/sec)
M2211	MakerBot Replicator 2X	255	290	80	10
M2212	MakerBot Replicator 2X	255	290	80	35
M1212	MakerBot Replicator 2X	210	290	80	35
M1121	MakerBot Replicator 2X	210	140	100	10
M1122	MakerBot Replicator 2X	210	140	100	35
M2121	MakerBot Replicator 2X	255	140	100	10
U2222	Ultimaker 3	255	290	100	35
U2111	Ultimaker 3	255	140	80	10
U2222	Ultimaker 3	255	290	100	35
U1111	Ultimaker 3	210	140	80	10
U1222	Ultimaker 3	210	290	100	35
U1111	Ultimaker 3	210	140	80	10
Z1211	Zortrax M200	210	290	80	10
Z1221	Zortrax M200	210	290	100	10
Z2221	Zortrax M200	255	290	100	10
Z2112	Zortrax M200	255	140	80	35
Z2122	Zortrax M200	255	140	100	35
Z1112	Zortrax M200	210	140	80	35



Braconnier, Jensen, AMP, *Additive Manufacturing*, 2020, 31, 100924

Thermal analysis indicates that the ABS formulations used are quite different



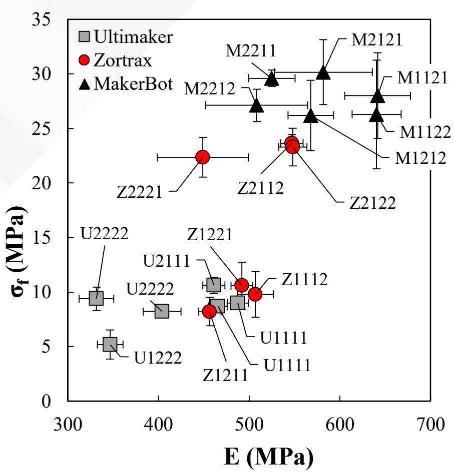


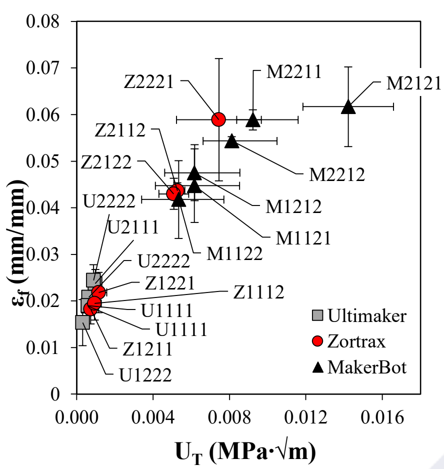
What is ABS?

- ABS is used to describe many blends and polymers of acrylonitrile, butadiene, and styrene
- Today, this is typically SAN + lightly cross-linked polybutadiene particles grafted with SAN
- (Some) Variables:
  - SAN:polybutadiene
  - Styrene:acrylonitrile in SAN
  - Amount of grafted SAN
  - Polybutadiene particle size and distribution
  - Polybutadiene cross-link density
  - Additives

Braconnier, Jensen, AMP, *Additive Manufacturing*, 2020, 31, 100924

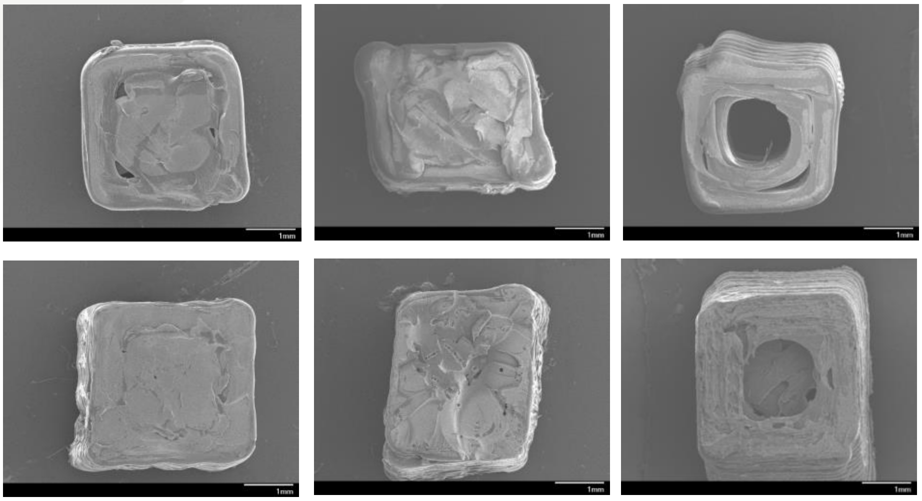
Initial comparison indicates significant differences between printers, even with same material, same .stl file





Braconnier, Jensen, AMP, *Additive Manufacturing*, 2020, 31, 100924

Each printer interprets gcode differently

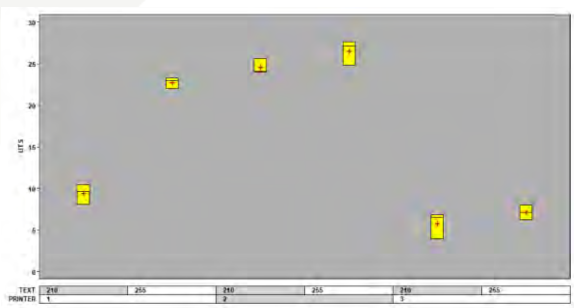


Zortrax Makerbot Ultimaker

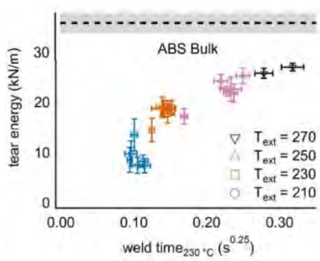
(Top row = lowest tensile strength, bottom row = highest tensile strength)

Braconnier, Jensen, AMP, *Additive Manufacturing*, 2020, 31, 100924

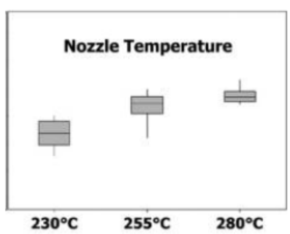
Extruder temperature is very important for the Zortrax, less so for Makerbot, Ultimaker



Zortrax Makerbot Ultimaker



Seppala et al., *Soft Matter* 2018 13(38)



Coogan and Kazmer, *Rapid Prototyping J.*, 2017 23(2)

Principal component analysis was used to correlate processing and performance variables

MakerBot Replicator 2X				
	ET	LT	PBT	PS
σ_f	Positive	N/A	N/A	Negative
ε_f	Positive	N/A	N/A	N/A
E	N/A	Negative	Positive	N/A
Ultimaker 3				
	ET	LT	PBT	PS
σ_f	Positive	N/A	N/A	N/A
ε_f	Positive	N/A	N/A	N/A
E	N/A	Negative	Negative	Negative
Zortrax M200				
	ET	LT	PBT	PS
σ_f	Positive	N/A	Positive	N/A
ε_f	Positive	N/A	Positive	N/A
E	N/A	Negative	N/A	Positive

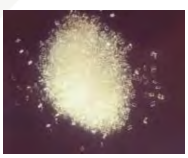
Recommendations based on correlations:

- Increase extrusion temperature
- Decrease layer thickness
- Print speed, print bed temperature need further investigation

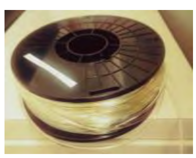
Braconnier, Jensen, AMP, *Additive Manufacturing*, 2020, 31, 100924

Hot melt adhesives are interesting candidates for MatEx

- **Properties**
  - Designed to cool and reach bond strength rapidly, good adhesion
  - Technomelt PA 6910: Semi-crystalline polymer with sub-ambient T_g and high T_m, gives rise to a transparent, tough, strong material
- **Science**
  - How does strength evolve during MatEx of semi-crystalline polymer?
  - What are the roles of the crystalline vs. amorphous phases?
  - How do we treat systems with sub-ambient T_g?

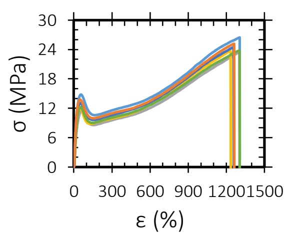


As-received Pellets



Filament Extrusion

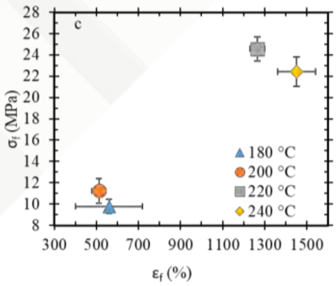
FFF



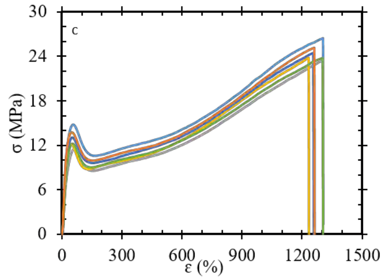
Characterization of printed structures

Technomelt PA 6910 can be printed at a range of temperatures

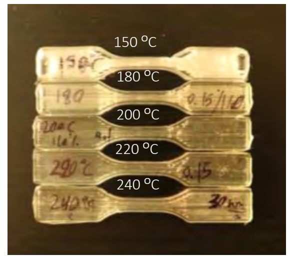
- Incomplete printing and opaque at low temperatures
- Tensile properties comparable to bulk at T_{ext} = 220°C



90° raster angle, 0.15 mm layer height



T_{ext} = 220°C



T_{ext} = 160°C

T_{ext} = 200°C

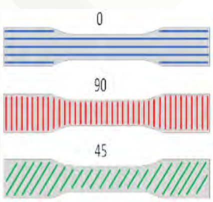
Compression Molded Samples

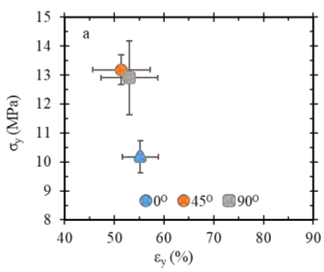
σ_y (MPa)	σ_f (MPa)	ε_f (%)
11	26	534

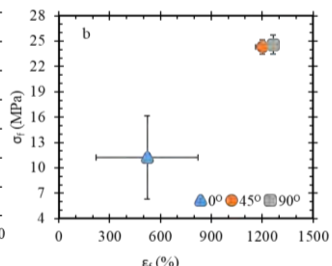
Pourali and AMP, *Submitted*

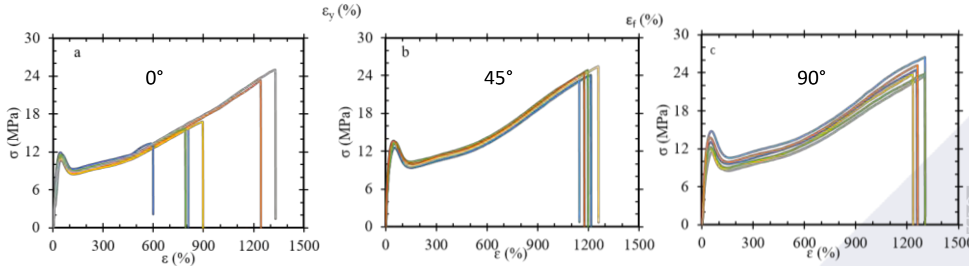
The highest tensile properties were observed at a 90° raster angle

- Typically, this is the weakest orientation
- May be due to toolpath-related differences in cooling, cooling rate





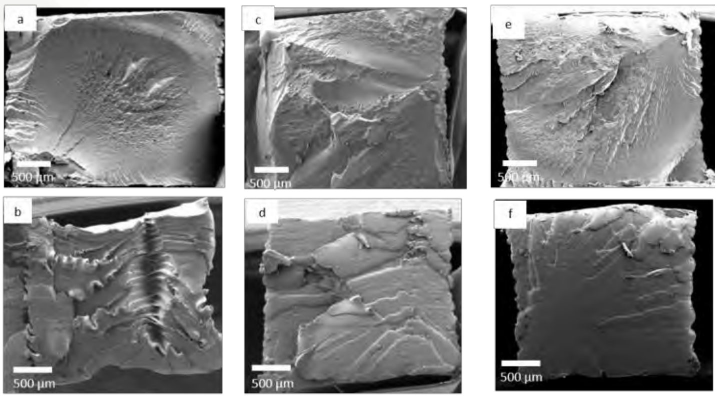


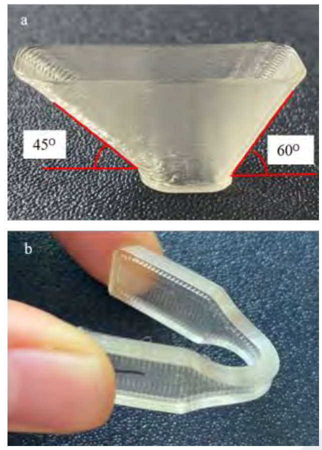


Pourali and AMP, *Submitted*

Printed hot melt adhesives have properties that match compression molded, with ability to fabricate complex structures

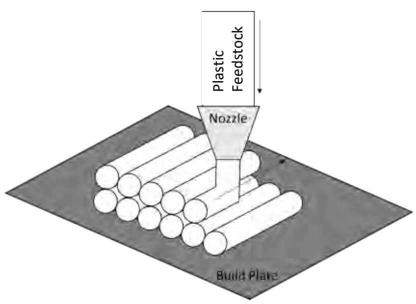
- Flexible, strong, and void-free prints
- Printed structures are transparent/translucent, indicating small crystalline regimes
- Motivates ongoing work in FEA of semi-crystalline polymers





Pourali and AMP, *Submitted*

Principles of MatEx are the same, from FFF to BAAM



However, scale affects the dominating physics

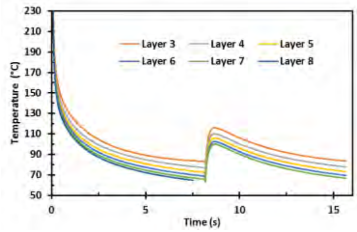
	FFF	BAAM
Build Space (m^3)	~10^{-2}	25
Nozzle Diameter (mm)	0.4	5-13
Layer Thickness (mm)	0.02-0.4	2.5-5
Deposition Rate (kg/hr)	0.07	36

http://web.ornl.gov/sci/manufacturing/media/news/detroit-show/

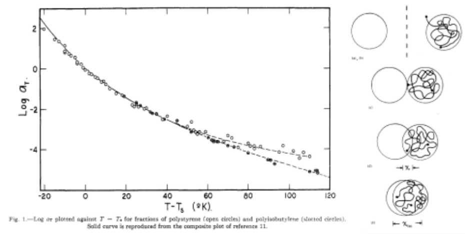
Using thermal modeling, we investigate material-processing-property relationships in MatEx

Thermal Modeling

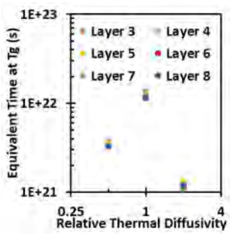
Temperature Profiles



TTS and Weld Theory

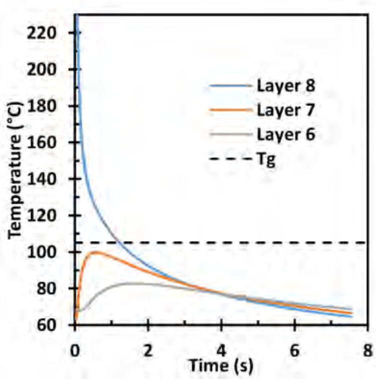


Bead Parameterization

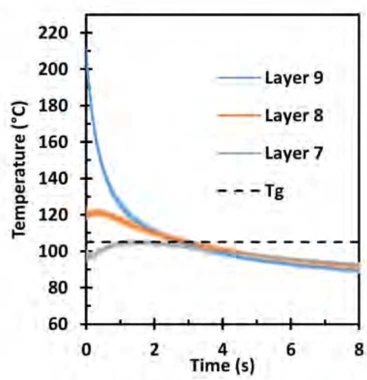


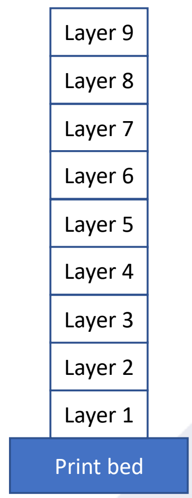
Direct comparison of FFF simulation and experiment – same geometry (wall) and other print parameters

Simulation



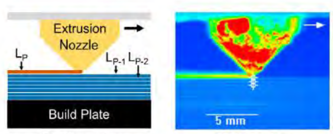
Experiment





Notes:

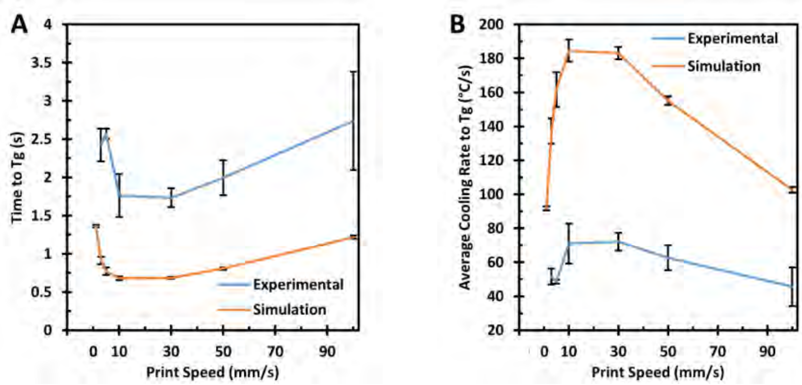
- Simulation values measured at center of bead vs. layer surface for experiment
- Both graphs contain error bars representing 95% confidence interval



(a) Illustration (b) Extrusion

D'Amico and AMP, *Additive Manufacturing*, 2018, *21*, 422-430
Seppala, J. E.; Migler, K. D. *Additive Manufacturing*, 2016, *12*, 71–76

Simulation overestimates heat transfer, but captures trends



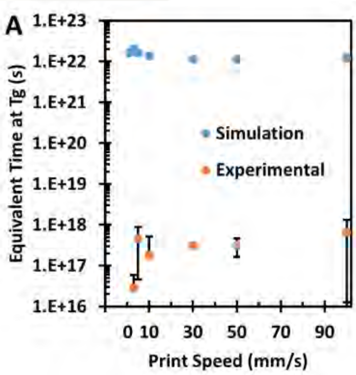
- Assumes full contact between roads
- Room temperature ABS values used
- Assumes no thermal resistance between build plate/extruder tip and print
- Temperatures captured at different locations

Learning with Purpose

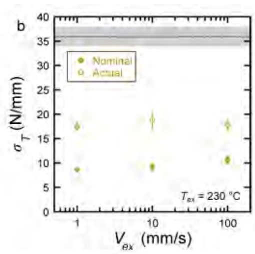
D'Amico and AMP, *Additive Manufacturing*, 2018, *21*, 422-430

41

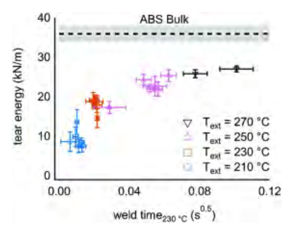
Equivalent time at T_g is insensitive to print speed, which is consistent with literature z-strength results



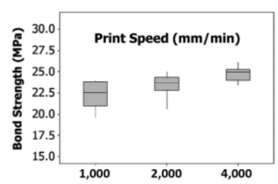
D'Amico and AMP, *Additive Manufacturing*, 2018, *21*, 422-430



Davis et al. *Additive Manufacturing*, 2017, *16*, 162–166



Seppala et al. *Soft Matter*, 2017, *13*, 6761-6769



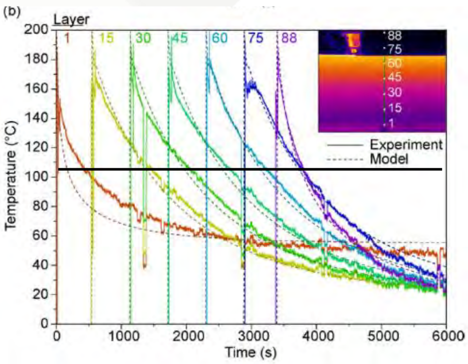
Coogan and Kazmer, *Rapid Prototyp. J.* 2017, *23*, 414–422

Learning with Purpose

42

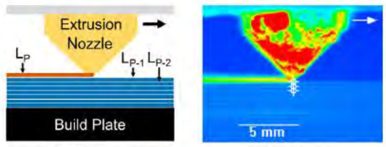
BAAM structures cool more slowly than FFF

BAAM

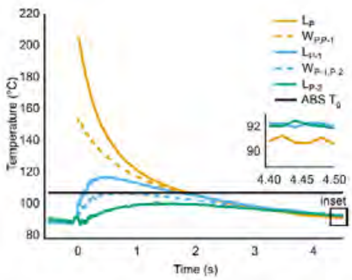


Dinwiddie et al., *SPIE* 9105 (2014)

FFF



(a) Illustration (b) Extrusion

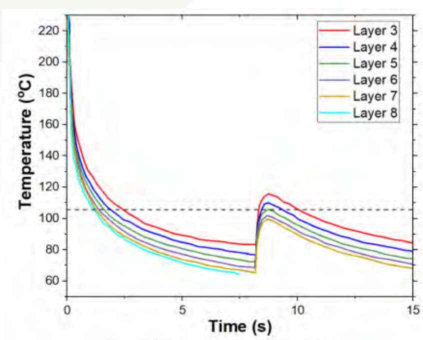


Seppala and Migler, *Additive Manufacturing* 12 (2016)

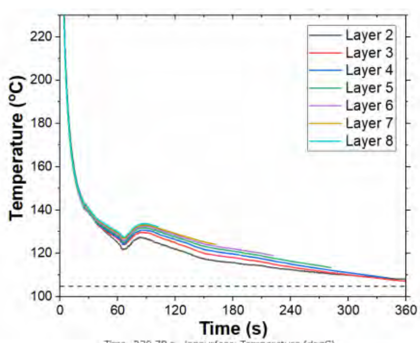
	BAAM	FFF
Build Space (m^3)	25	~10^{-2}
Nozzle Diameter (mm)	5-13	0.4
Layer Thickness (mm)	2.5-5	0.02-0.4
Deposition Rate (kg/hr)	36	0.07

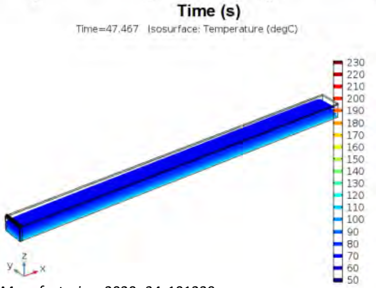
Temperatures are higher in BAAM with the same material (ABS)

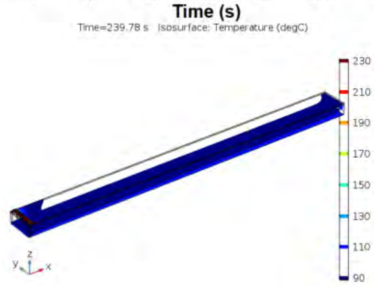
Desktop Scale, FFF



Room Scale, BAAM





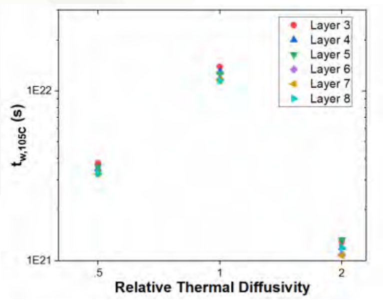


Temperatures on the surface and within a BAAM bead differ by at least 10°C

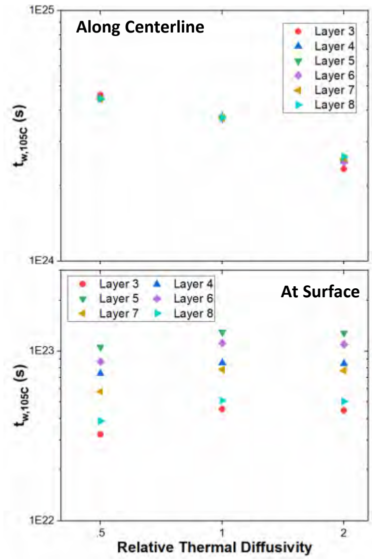
D'Amico and AMP, *Additive Manufacturing*, 2020, *34*, 101239

Thermal/physical properties of ABS make it inappropriate for use in BAAM when unreinforced

FFF



BAAM



Love et al., *J. Mater. Res.,* 2014, 1893-1898

$$\alpha = \frac{k}{\rho C_p}$$

Relative thermal diffusivity normalized to α for ABS as RT

Learning with Purpose

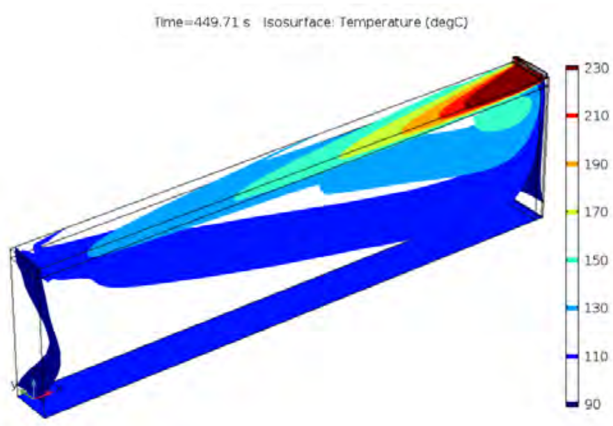
D'Amico and AMP, *Additive Manufacturing*, 2020, *34*, 101239

45

Principles of MatEx are the same, from FFF to BAAM

However, scale affects the dominating physics

- Radiation
- Optimal thermal diffusivity
- Cooling
- Temperature variations across a bead



Learning with Purpose

46

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

What range of wavelengths is used in MOST commercial vat photopolymerization?

- 380-420 nm
- 630-660 nm
- 800-850 nm
- 10.2-10.6 µm

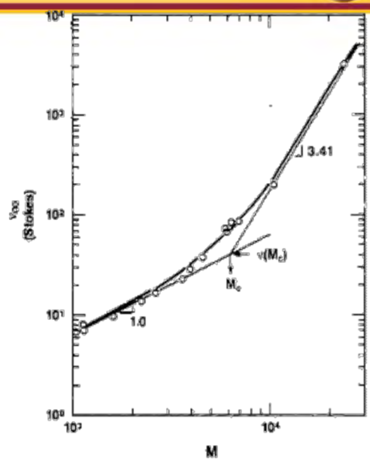
** If your answer differs greatly from the choices above tell us in the chat!*

47

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.

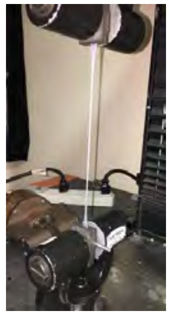
Biodesign Institute
Arizona State University

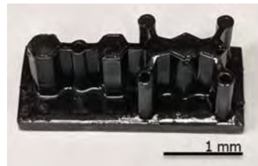
48

"A tale of two printers"

- Latexes and colloids for **vat photopolymerization**
  - Styrene-butadiene elastomers
  - Semi-interpenetrating networks
  - Silica-filled nanocomposites

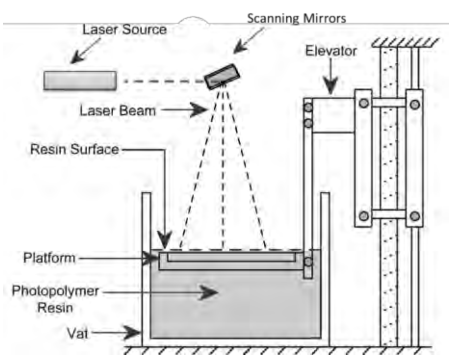
- Printing high performance engineering polymers with **UV assisted direct-ink-write (DIW) and scanning mask projection vat photopolymerization**
  - Fully aromatic polyimides
  - Printed organogels as reactors





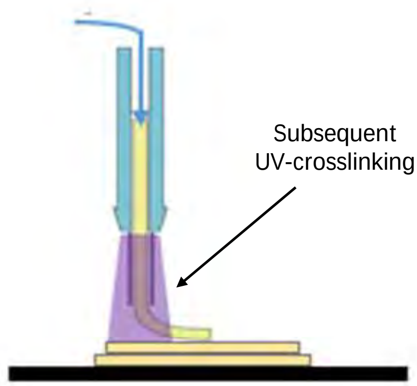
Additive manufacturing techniques utilized for polyimide 3D printing

Vat photopolymerization (VP)



Schultz *et al.*, *ACS Macro Lett.* 2014, *3* (11), 1205–1209.
Sirrine *et al.*, *Aust. J. Chem.* 2015, *68* (9), 1409.
Sirrine *et al.*, *Polymer (Guildf).* 2018, *152*, 25–34.
Wilts *et al.*, *Polym. Chem.* 2019, *10* (12), 1442–1451.

UV-assisted direct ink write (DIW)



Aduba *et al.*, *Mater. Today Commun.* 2019, *19*, 204–211.
Sirrine *et al.*, *Macromol. Chem. Phys.* 2019, *220* (4), 1800425.
Mondschein *et al.*, *Biomaterials* 2017, *140*, 170–188.

3D printing functionalized hydrogels as reactors for unprecedented metallic nanoparticles

3D PRINTING

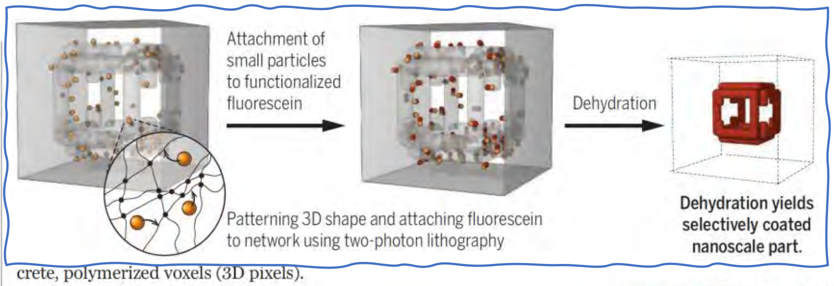
Printing nanomaterials in shrinking gels

Photopatterning of reactive sites in gels enables arbitrary patterning of nanoparticles

By **Timothy E. Long** *and* **Christopher B. Williams**

The creation of nanoscale electronics, photonics, plasmonics, and mechanically robust metamaterials will benefit from nanofabrication processes that allow a designer full control in manipulating nanomaterial precursors in a programmable and volumetric manner. Despite decades of research, it remains

Printing nanomaterials in shrinking gels.
Long, Timothy. *Science* Volume: 362 Issue 6420 (2018)
ISSN: 0036-8075 Online ISSN: 1095-9203



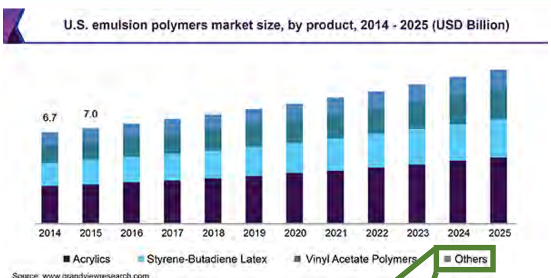
crete, polymerized voxels (3D pixels).

D. Oran *et al.*, *Science* **362**, 1281(2018).

ASU Biodesign Institute Arizona State University

51

A world of **aqueous latex** is waiting to be printed!

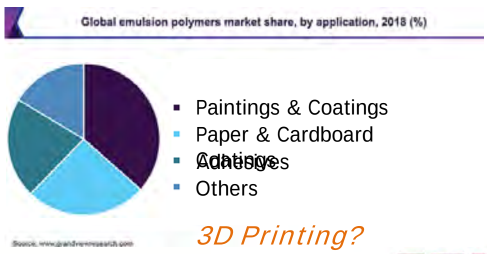


Polyisoprene (natural rubber)?
Polyacrylonitrile?
Polyethylene?
Polyurethane?
Polyvinyl chloride?
PTFE?

Global synthetic latex polymers market in 2017: $27.02 billion

By 2024, global synthetic latex polymers market forecasted to reach:

- $37.52 billion†
- 21.88 million tons‡



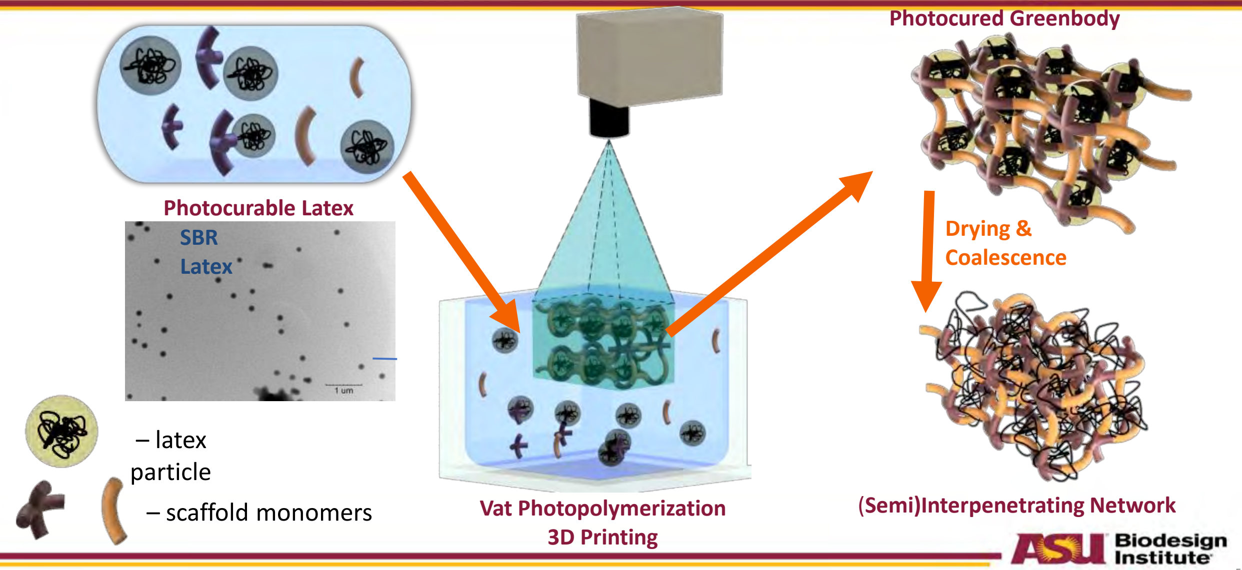
3D Printing?

†www.researchandmarkets.com
‡www.prnewswire.com

ASU Biodesign Institute Arizona State University

52

Photocurable **aqueous latex** cures into a free-standing green interpenetrating network

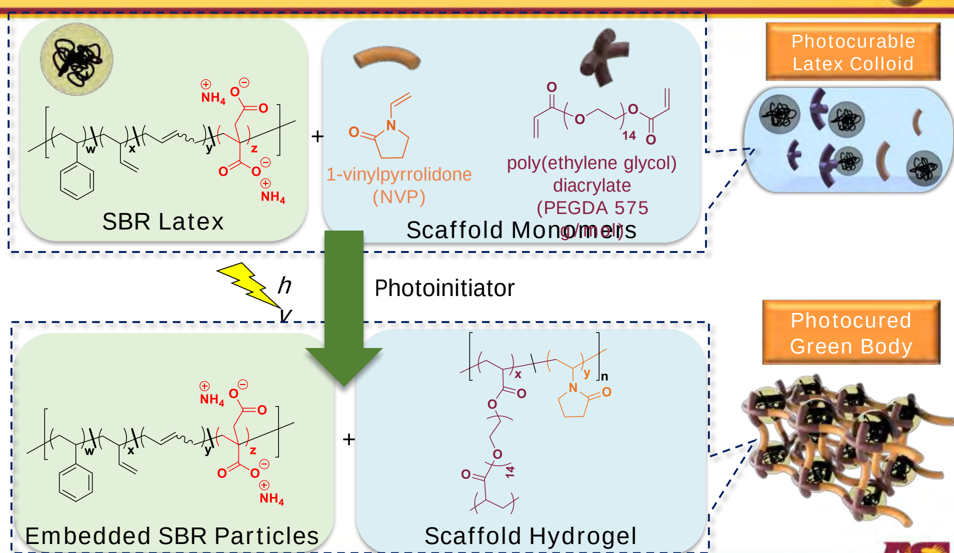


Scott, P. J.; Meenakshisundaram, V.; Hegde, M.; Kasprzak, C.; Winkler, C.; Feller, K.; Williams, C. B.; Long, T. E. *ACS Appl. Mater. Interfaces* **2020**.

ASU Biodesign Institute
Arizona State University

53

Water-soluble monomers provide photocurable precursors for tunable, supportive scaffold

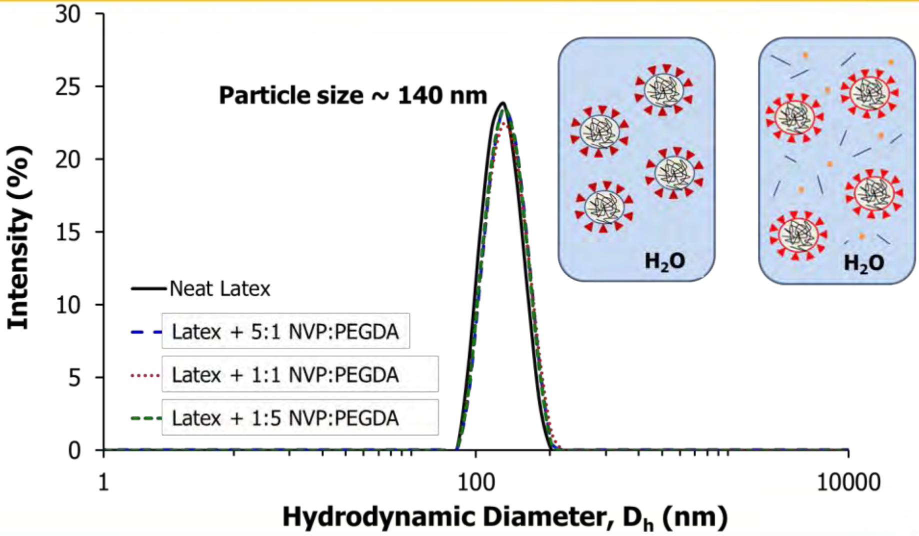


Carboxylated SBR Latex = Mallard Creek Rovene® 4176

ASU Biodesign Institute
Arizona State University

54

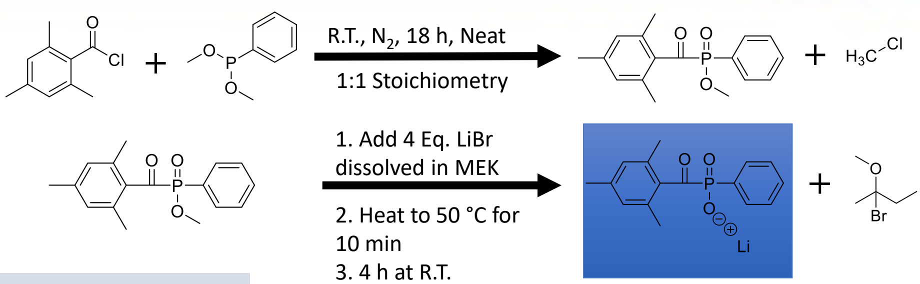
Monomer addition to latex does not significantly impact particle size



DLS: 30 scans/sample, intensity distribution, 1 wt% dilution, wt:wt ratios

ASU Biodesign Institute Arizona State University

Synthesis of Lithium Acylphosphinate (LAP) Provides a **Water Soluble** TPO Analog



- Absorption maximum ~370 nm
- Radicals formed effectively initiate olefinic and styrenic compounds
- **Water soluble**

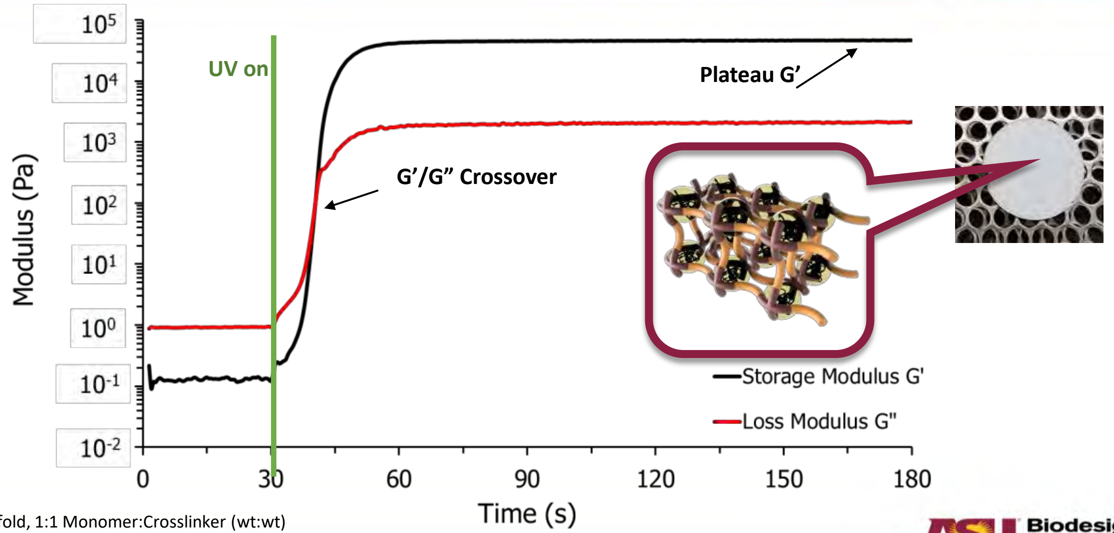
Water-soluble LAP photo-initiator overcomes the complications of colloidal instability observed with TOPO

Fairbanks, B. D., *et. al. Biomaterials* **2009**, *30*, 6702–6707.

ASU Biodesign Institute Arizona State University

56

Photocurable polymer colloids rapidly photocure to yield free-standing green bodies

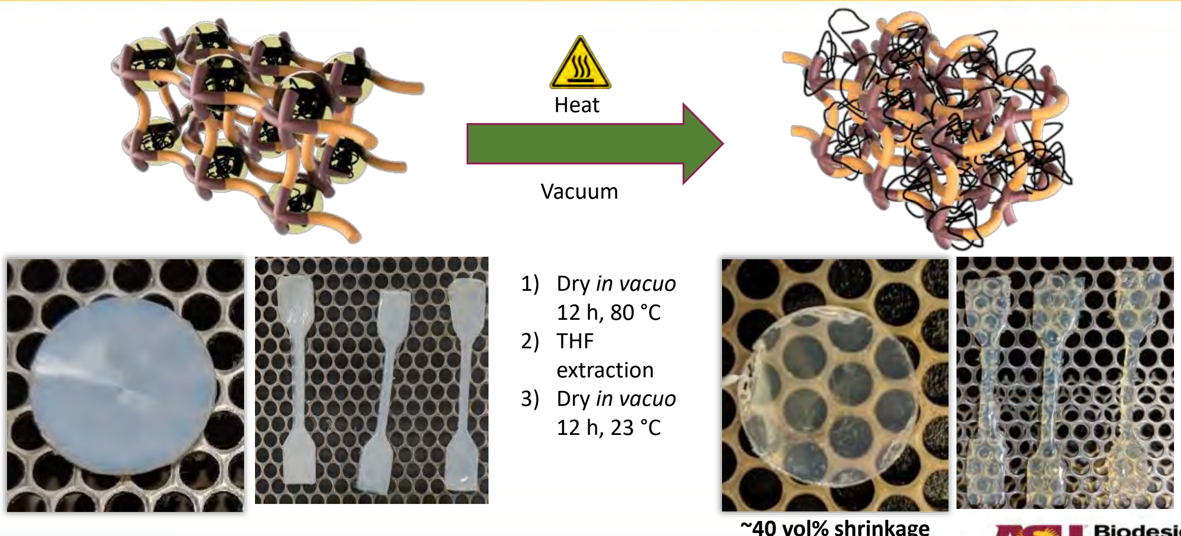


4:1 SBR:Scaffold, 1:1 Monomer:Crosslinker (wt:wt)

Photorheology: 0.2% strain, 20 mm parallel plate, 1 Hz, 200 mW/cm²

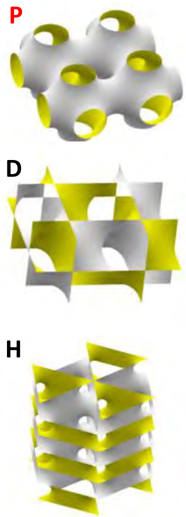
ASU Biodesign Institute Arizona State University 57

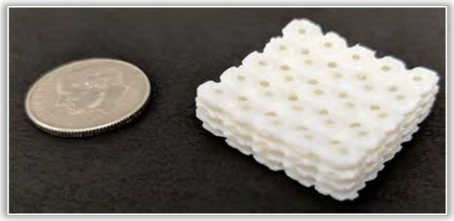
Heat and vacuum remove water and enable SBR particles to interpenetrate the scaffold

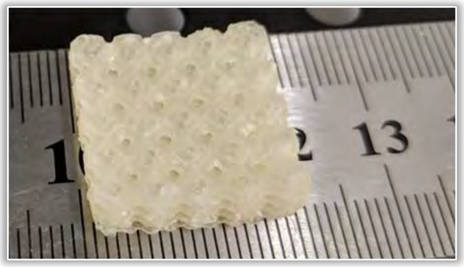


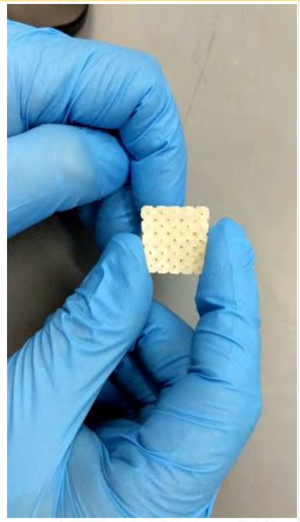
ASU Biodesign Institute Arizona State University 58

Schwarz lattices of sIPN elastomers demonstrates excellent durability









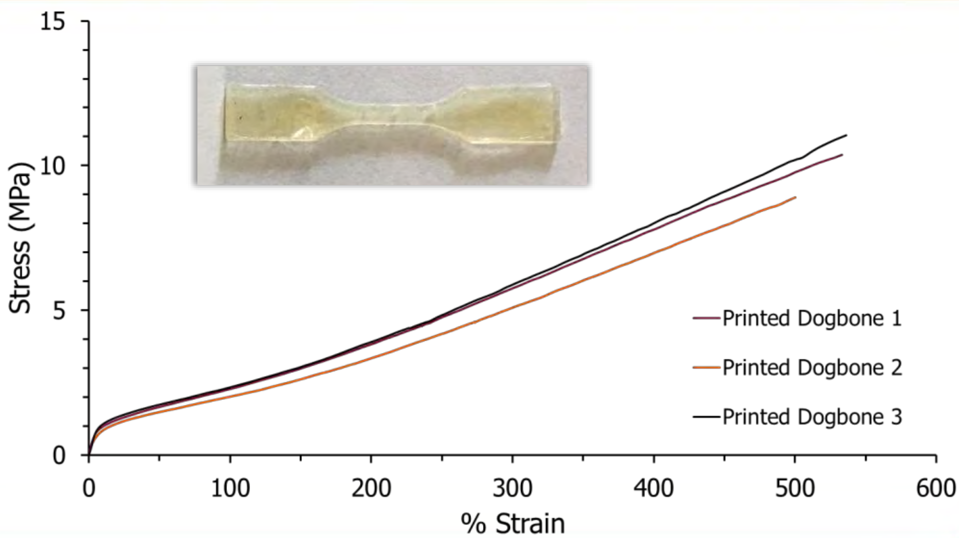
Printed with 125 µm layers with 12 s exposure/pixel

https://en.wikipedia.org/wiki/Schwarz_minimal_surface

Biodesign Institute
Arizona State University

59

3D printed latex dogbones exhibited consistent tensile performance with strain at break >500%

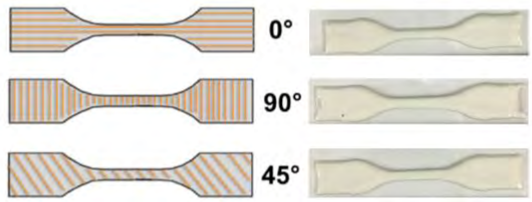


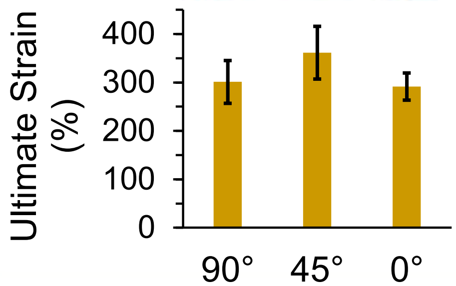
Tensile: 5 mm/min, 2.5:1 NVP:PEGDA printed dogbones

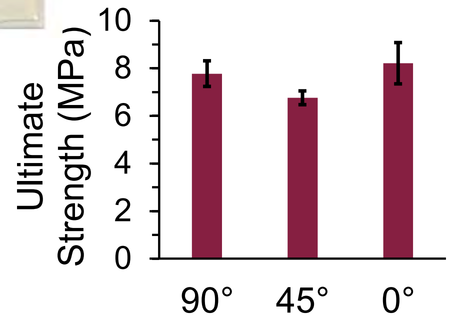
Biodesign Institute
Arizona State University

60

Printed sIPN nanocomposite dogbones exhibit minimal tensile anisotropy with layer direction







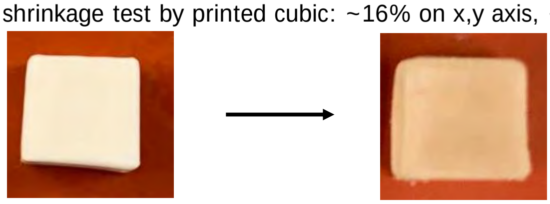
Tensile testing: 50 mm/min, 30:70 silica:SBR

Biodesign Institute Arizona State University 61

Honeycomb prints showed promise for natural rubber latex printing

❖ NR latex with 16.7 wt% scaffold precursors enabled VP printing

Linear shrinkage test by printed cubic: ~16% on x,y axis, ~21% on z



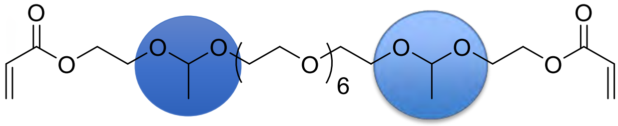
Hexagon grid printed by VP

Collaborated with Keyton Feller from DREAMS lab in Virginia Tech

Biodesign Institute Arizona State University 62

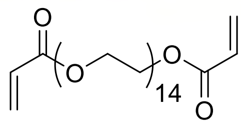
Acetal-containing PEG crosslinkers provide **pH-triggered degradability**

PEGdAdAc



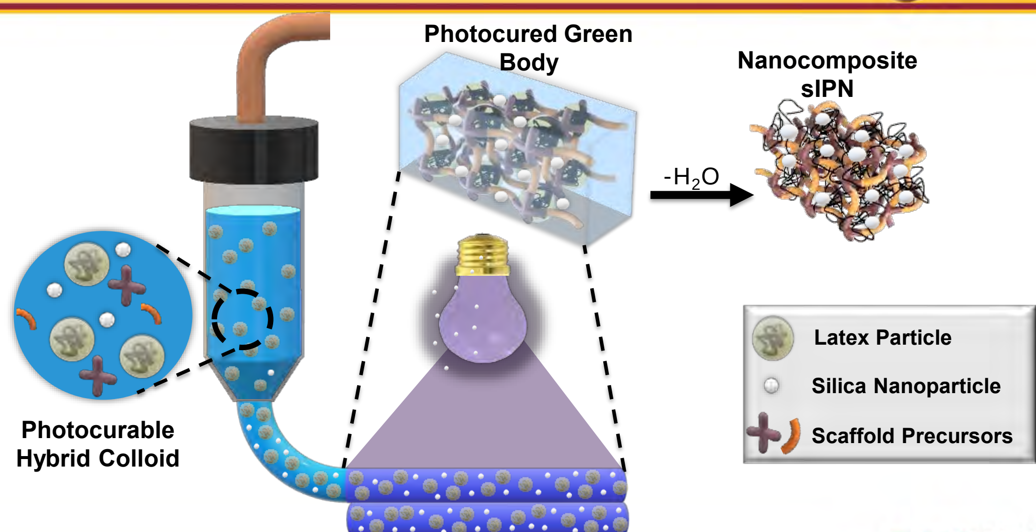
- Water soluble crosslinker
- MW = 586 g/mol
- **Acetal linkages provide increased degradability**
- Efficient polymerization process with versatility for scale-up

PEGDA

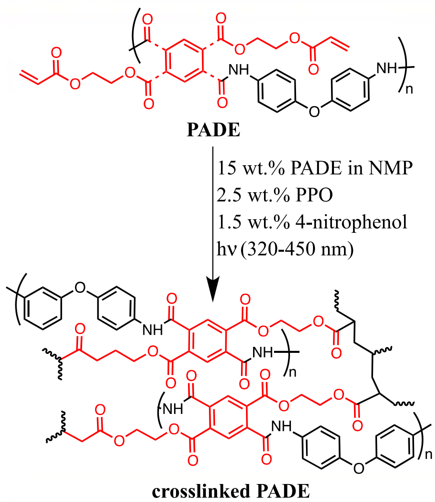


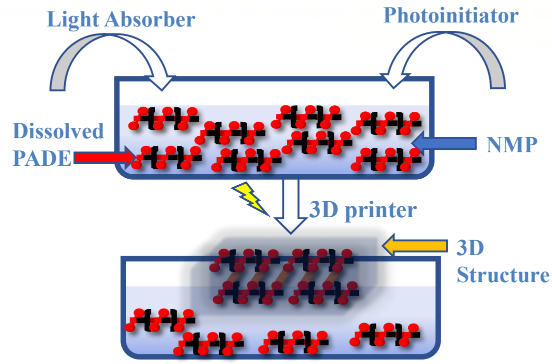
- Water soluble crosslinker
- MW = 575 g/mol
- **Only contains ester linkages as sites for degradation**
- Commercially available

Direct ink writing enables 3D printing of **SBR-Silica photocurable hybrid colloids**



Acrylate-containing poly(amic acid)s allow for printing **organogels**





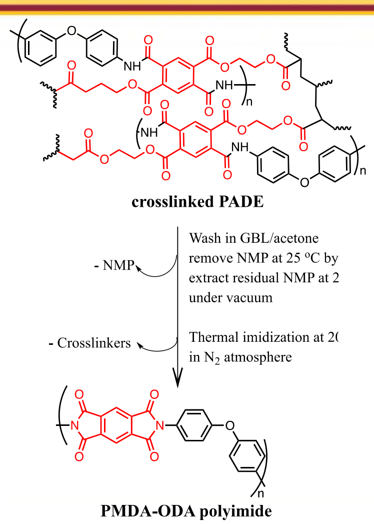
- Photo-crosslinking of high MW polymer precursor instead of low molecular weight oligomers. Viscosity tuned by wt % of PADE
  - Loading of PADE alters green body modulus and dictates accessible geometries

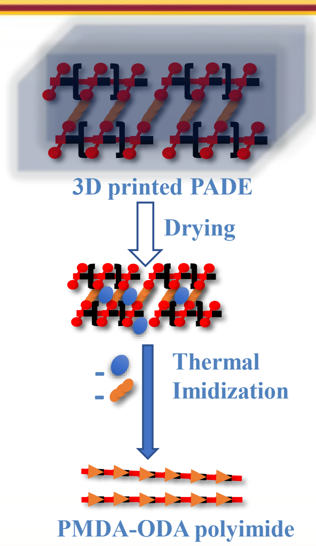
Hegde, M.; Tafti, D.; Williams, C. B.; Long, T. E. *et al., Adv. Mater*. **2017**, 29 (31), 1701240.

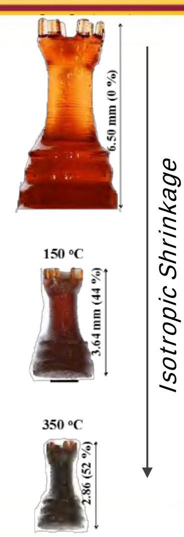
ASU Biodesign Institute Arizona State University

65

Imidization and solvent removal provide PMDA-ODA polyimide isotropic parts





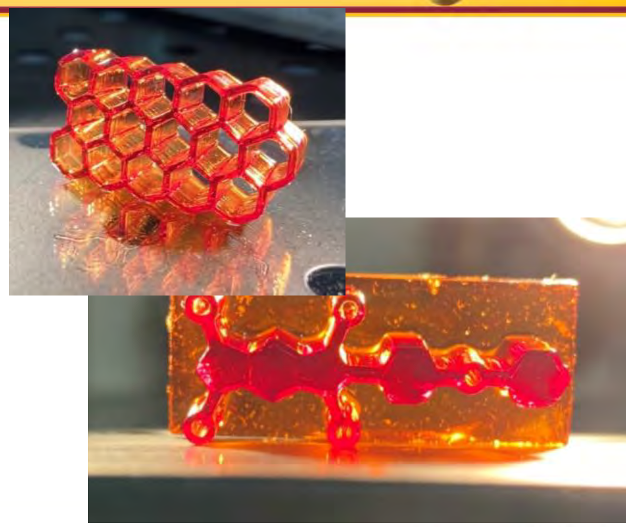


Modulus: 2.2 GPa
Strain at failure: 9.5 %
Tensile strength: 79 MPa
Modulus at 300 °C: 1 GPa
Decomposition: 600 °C

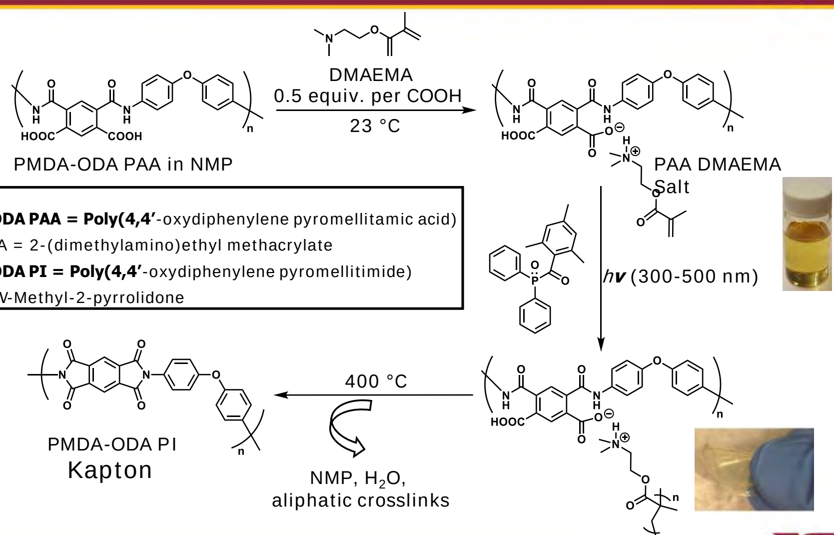
ASU Biodesign Institute Arizona State University

66

Continued advancements in synthesis and printing improve printed part accuracy



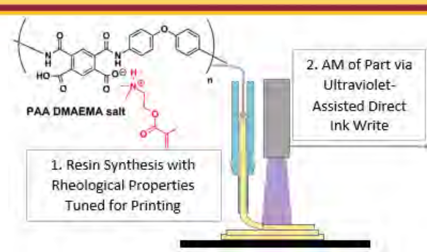
Attaching the crosslinking site using a supramolecular interaction

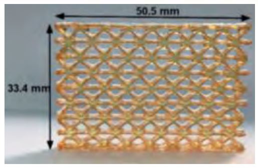


- PMDA-**ODA PAA = Poly(4,4′**-oxydiphenylene pyromellitamic acid)
- DMAEMA = 2-(dimethylamino)ethyl methacrylate
- PMDA-**ODA PI = Poly(4,4′**-oxydiphenylene pyromellitimide)
- NMP = *N*-Methyl-2-pyrrolidone

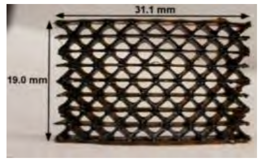
ACS Macro Lett. 2018, *7*, 493−497

UV-DIW and VP enable facile AM PAA salt solutions

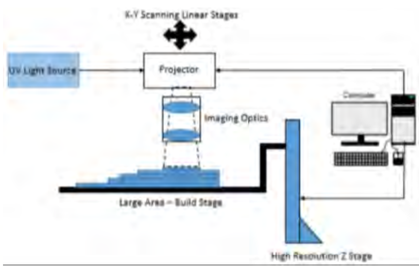


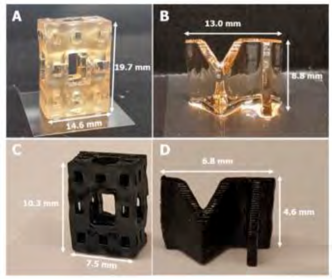


As Printed



Fully Imidized





As Printed

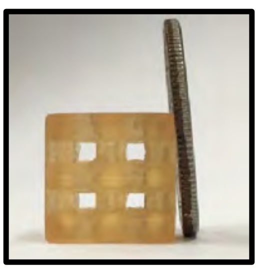
Fully Imidized

U.S. Patent Application No: 62/650,370

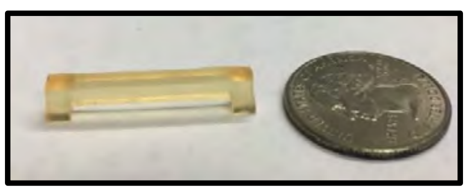
Continued advancement of UV+DIW process yields improved part quality

Excellent resolution lattices

Preserving resolution/tolerances upon imidization

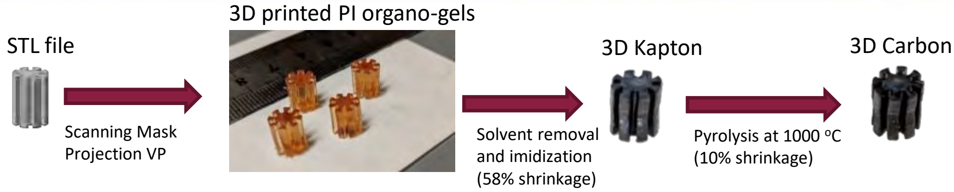


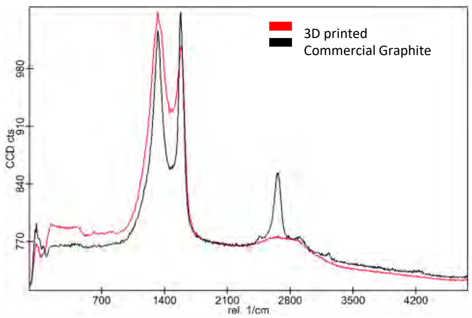
Organogels of 10^5 Pa Modulus



Printing over air

AM of Carbonaceous Objects via Polyimide Pyrolysis

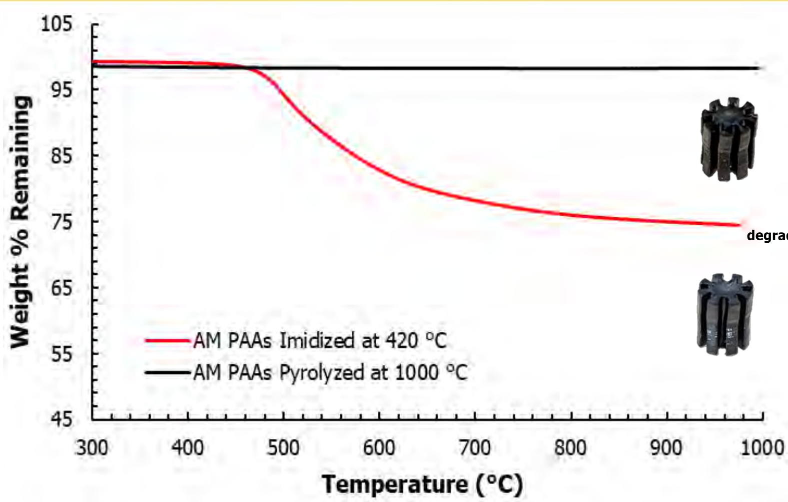


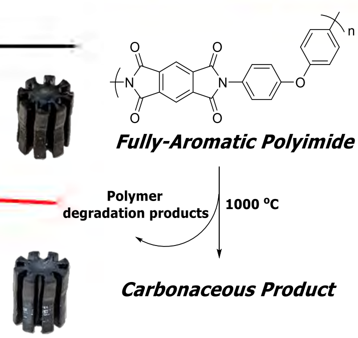


- Preliminary analysis via Raman spectroscopy shows reduced graphene oxide with a broad D-band
- Printed parts do not show presence of amorphous carbon

Biodesign Institute Arizona State University

TGA indicated extreme weight retention for post-pyrolyzed samples



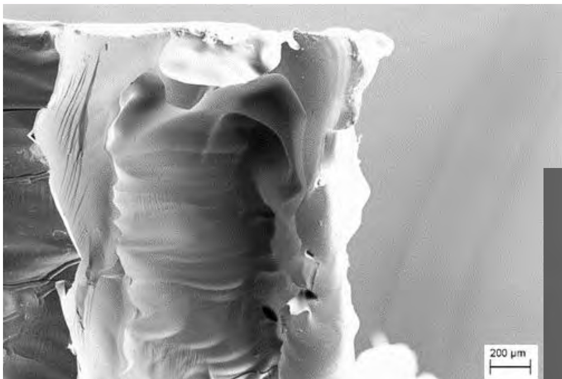


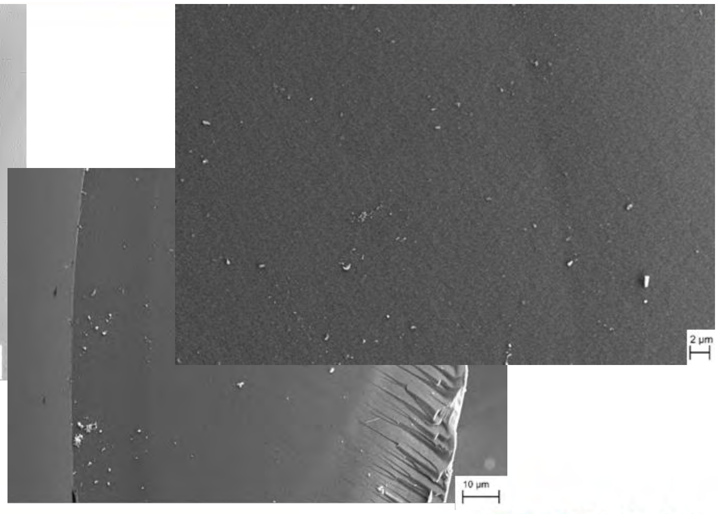
➢ TGA samples retain shape even when ramped at 10 °C/min!

TGA-Q50, RT- 1000°C, 10°C/min, N_2 Fill gas *ACS Macro Lett.* 2021, *16*, 412–418.

Biodesign Institute Arizona State University

Scanning electron microscopy examined cross-sections and surfaces of pyrolyzed parts



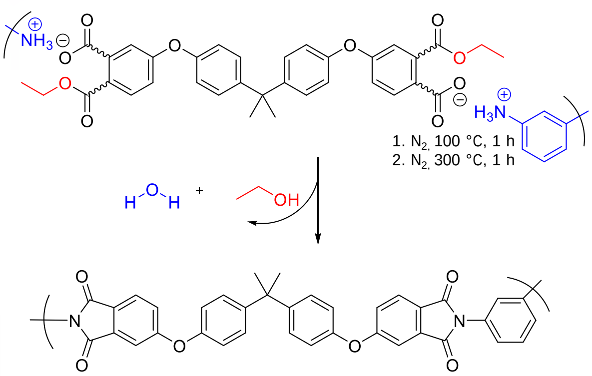


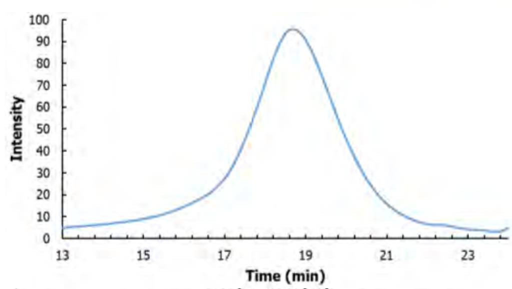
- Fracture prior to analysis
  - No cracks seen outside of large cracks induced by fracture!
  - Non-porous internal structure!

ACS Macro Lett. 2021, *16*, 412–418.

Biodesign Institute
Arizona State University
73

Ethyl ester control probed achievable molecular weight polysalt synthetic route





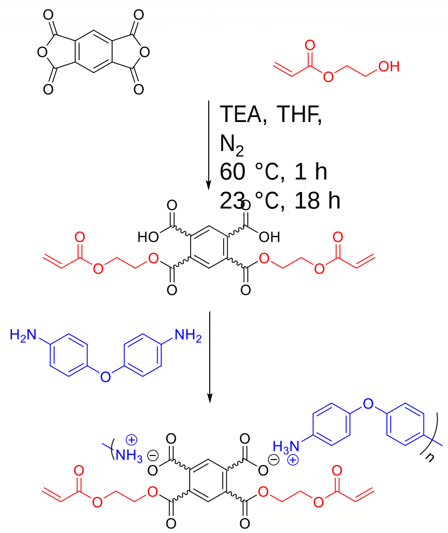
Re-casted film

- >150 °C induces polymerization
- Simple solid state polymerizaiton
- Mn = 34,000 g/mol, PDI = 1.7

Waters e2695, chloroform, 35 °C, 1 ml/min, Wyatt TREOS II, dn/dc =0.2173

Biodesign Institute
Arizona State University
74

Facile acid-base reaction of the dicarboxylic acid and diamine enables polysalt formation of a fully-aromatic PI



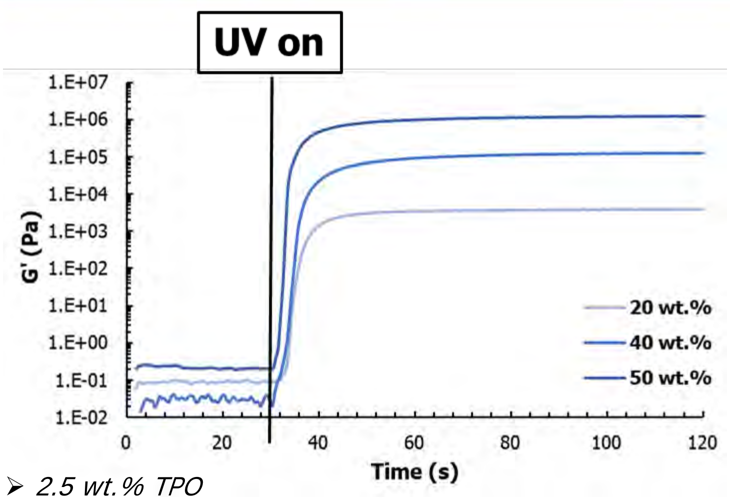
40 wt.% polysalt

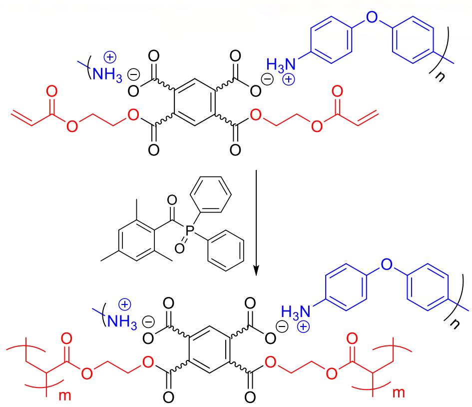
- Mixture of isomers utilized
- Displays solubility in host of solvents
- Readily crosslinks to organo-gel

Biodesign Institute
Arizona State University

75

Polysalt NMP solutions exhibit rapid crosslinking and high plateau modulus





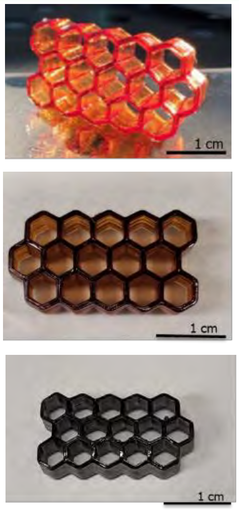
- *2.5 wt.% TPO*
- Cross-over times ~ 2 s

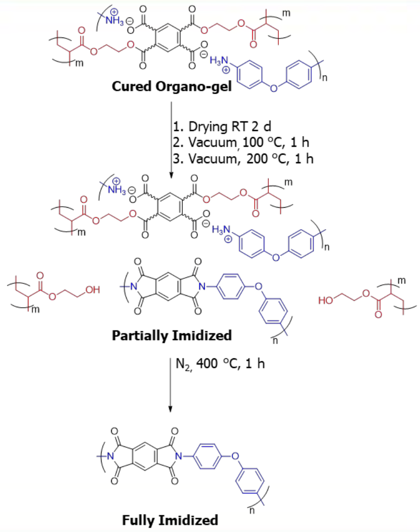
TA DHR-2, 20 mm parallel plate, 0.3 % strain, 4 Hz, 250 mW/cm², 25 °C

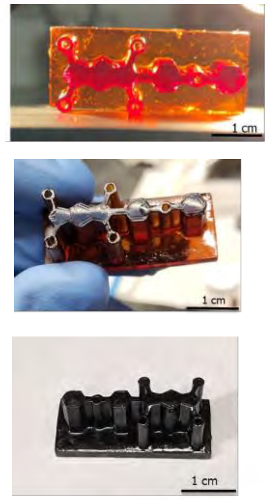
Biodesign Institute
Arizona State University

76

Polysalt parts displayed isotropic shrinkage and allowed for imidization and scaffold removal

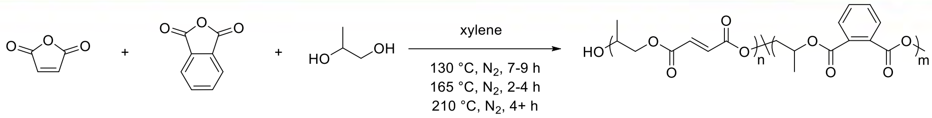






24% shrinkage on linear basis

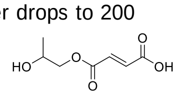
Utilizing a temperature ramp results in an unsaturated polyester with controlled acid number



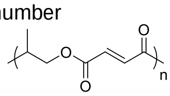
Acid Number = [(A-B)N x 56.1)/ W
A = KOH required for sample N= KOH Normality
B = KOH required for blank W= sample mass

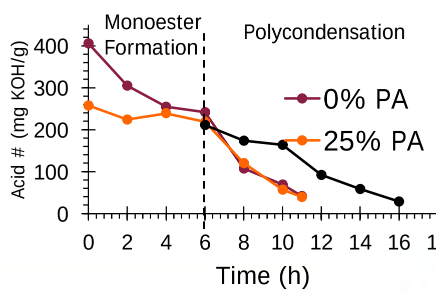
- Monitor reaction progress with titration (ASTM D4662)

1. Monoester formation: Mix monomers at 130 °C until acid number drops to 200 mg KOH/g



2. Polycondensation: Add 6 wt% xylene and ramp to 210 °C until acid number drops to ~30 mg KOH/g



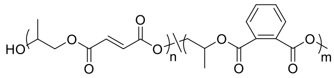


White, B. T.; Long, T. E., et al., *Polymer* 2021, 123727.

Incorporation of an appropriate UV blocker improves resolution of 3D printed parts

70 wt% solids in diglyme

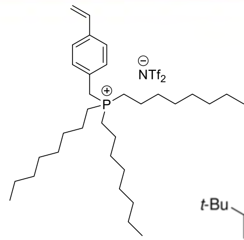
60 wt%

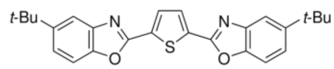


UPE 25 mol% PA

\+

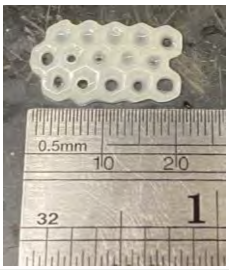
40 wt%





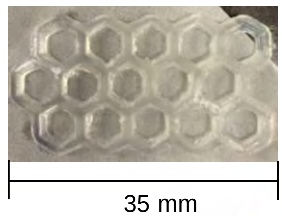
UV Blocker:

0 wt% UV Blocker



0.5 wt% Avobenzone

0.1 wt% BBOT



35 mm

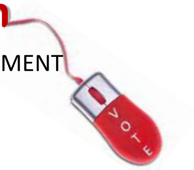
- VP Printing: 1.5 wt% TPO, 30 mW/cm², 405 nm wavelength, 13 s/layer exposure, 100 μm layer thickness

Biodesign Institute
na State University

79

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



Which AM method allows for printing with the HIGHEST viscosity?

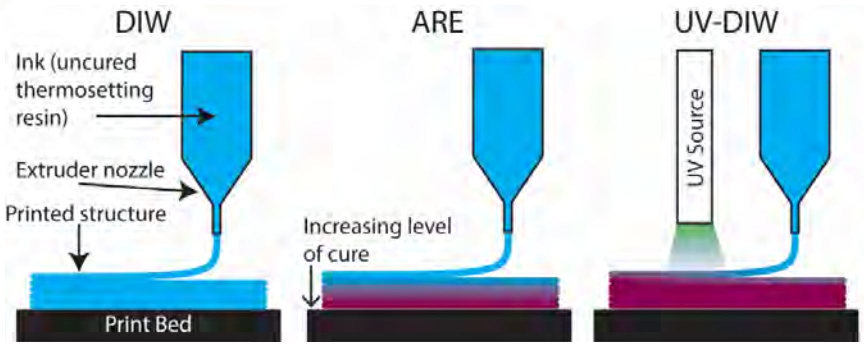
- Vat photopolymerization
- Direct-Ink-Writing
- Material jetting
- They all produce the same viscosity

** If your answer differs greatly from the choices above tell us in the chat!*

80

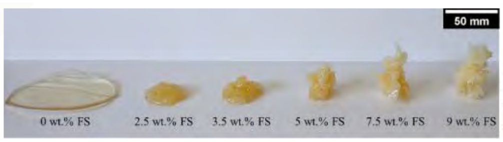
Ambient reactive extrusion (ARE) is a form of DIW

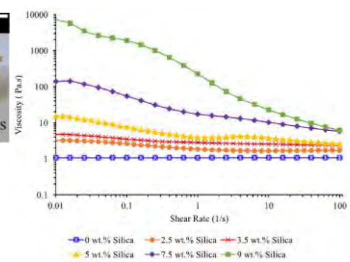
- Ink cures under ambient conditions
- Enables larger structures, new materials



Hansen, AMP, Park, in *Handbook of Thermoset Plastics*, Dodiuk ed., 2021

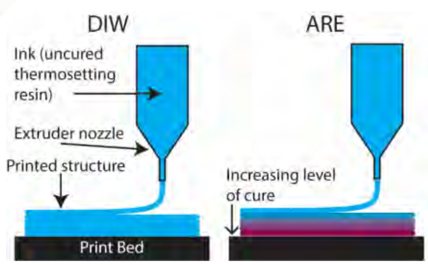
Ink design



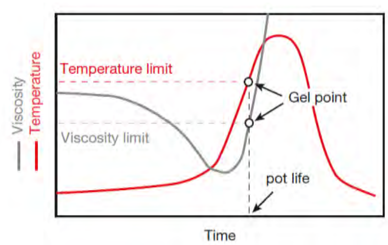


Uitz et al., *Addit. Manuf.*, 2021, *41*, 101919

- Shear thinning – processing
- Behave as a liquid (G”>G’) under extrusion conditions
- Rapidly recover solid-like behavior (G”<G’) under zero shear conditions
- Curing during printing, enables larger scale structures
- Challenge of balancing reaction kinetics with processability



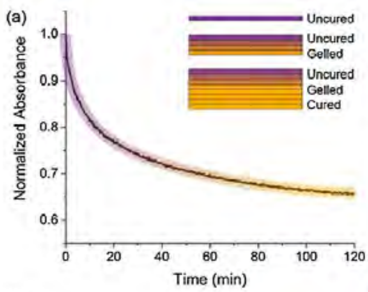
Hansen, AMP, Park, in *Handbook of Thermoset Plastics*, Dodiuk ed., 2021

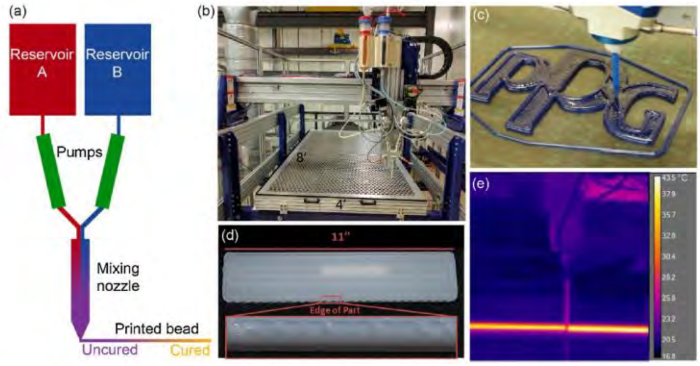


Rudolph and Osswald, *Polymer Rheology*

ARE is capable of printing two-part chemistries at small and large scales

- Isocyanate + amine
- Recommendations:
  - Initial G”/G’ < 1.5
  - Initial G’ > 2MPa
  - G’ > 1,000 MPa six minutes after extrusion
  - G” > 600 MPa six minutes after extrusion



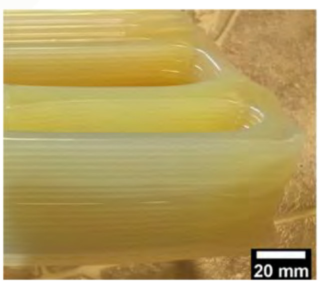


Rios et al., *Mater. Today Comm.*, 2018, *15*, 333-336

ARE is an emerging method of polymer AM

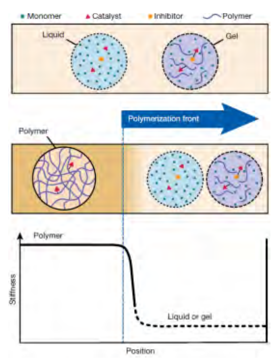
- Thermosetting extrusion
- Can allow for use of common resin classes, although viscosity may need to be modified
- Capable of printing with high viscosity feedstocks
- Balancing print speed with curing rate essential – to do otherwise leads to a big mess

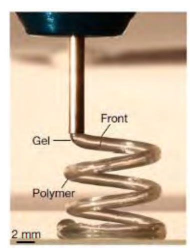
EPON 8111 and EPIKURE 3271



Uitz et al., *Addit. Manuf.*, 2021, *41*, 101919

Frontal polymerization – polymerization proceeds along a reaction front at a controlled rate



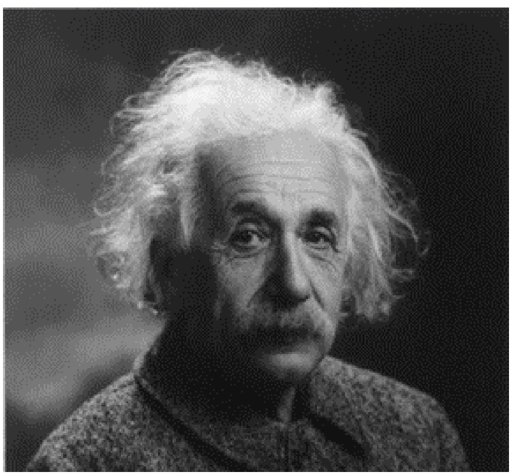


Robertson et al., *Nature*, 2018, *557*, 223-227

Rethink the process and tools for discovery of future AM materials

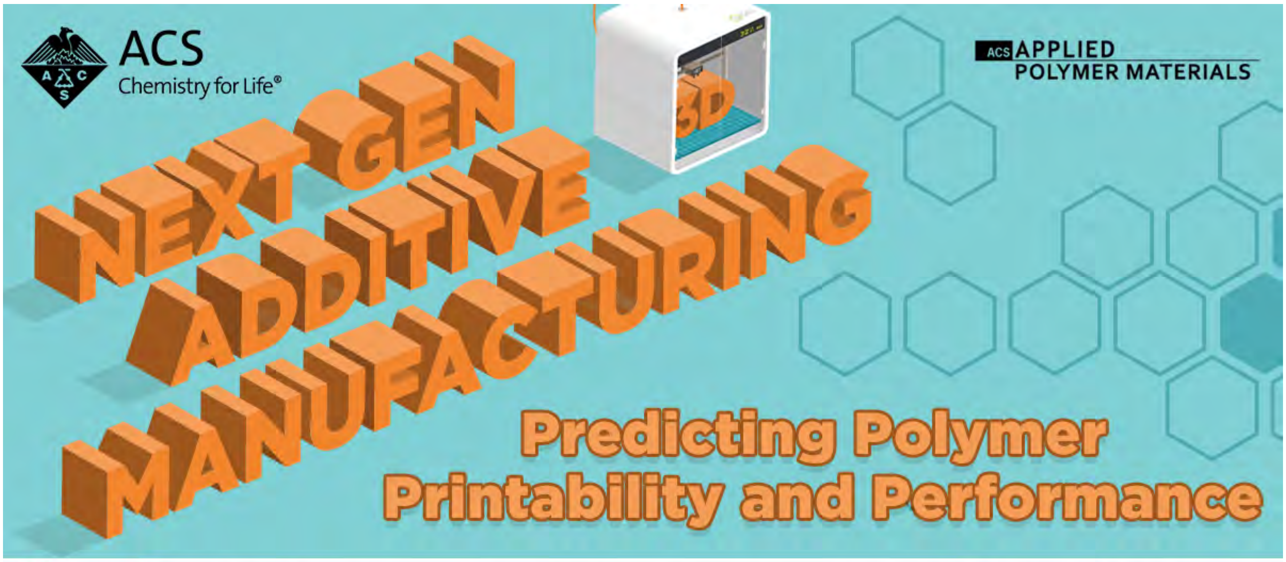
- **Nurture the intersection of mechanical engineering and polymer science**
  - Design printers to accommodate emerging materials design
  - Design chemistry with processing in mind
  - Educate the next generation workforce at this intersection
- **Seek analytical tools that provide predictive data to accelerate discovery**
  - Partner with physical characterization tool providers
  - Envision hyphenating conventional tools with photochemistry
- **Establish a foundation in structure-property-processing relationships**
  - Design materials with attention to rheological constraints
  - Understand how material design meets part design
  - Predict how resolution and geometry will lead to new part design

Thank you for the invitation to participate!



"If you always do what you always did, you will always get **what you always got."**

- Albert Einstein



FREE Webinar | TODAY at 2pm ET

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ASK YOUR QUESTIONS AND MAKE YOUR COMMENTS IN THE QUESTIONS PANEL NOW! 87

ACS APPLIED POLYMER MATERIALS

ACS Publications
Most Trusted. Most Cited. Most Read.

The distributive manufacturing enabled by 3D printing has been on display in the response to shortages in critical medical resources for the response to the COVID-19 epidemic. In almost all cases, these 3D printed parts have been polymers and have been instrumental in providing a stopgap to logistical challenges in obtaining critical components.

These have included, amongst many other examples, engineered solutions to limited number of ventilators through 3D printing of valves for ventilators, parts to transform snorkeling masks into continuous positive airway pressure (CPAP) devices, and repurposing of existing medical equipment to meet demands for treating patients. The timely delivery of these 3D printed plastic components has been enabled by the advances in 3D printing over the past decades.

In light of their acute significance in this global health crisis, it is our pleasure to announce a **"virtual issue"** on the 3D printing of polymers for ***ACS Applied Polymer Materials.***

https://pubs.acs.org/page/aapmcd/vi/3d-printing-polymers

88

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

Next Gen Additive Manufacturing: Predicting Polymer Printability and Performance

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

AMY PETERSON
Associate Professor, Associate Chair - Master's Studies, Department of Plastics Engineering, The University of Massachusetts Lowell

BRYAN VOGT
Professor, Chemical Engineering, Penn State University and Associate Editor for *ACS Applied Polymer Materials*

Presentation slides are available now! The edited recording will be made available as soon as possible.

www.acs.org/acswebinars

This ACS Webinar is co-produced with ACS Applied Polymer Materials and the ACS Division of Polymer Chemistry.

89

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

Date: Thursday, April 15, 2021 @ 2-3pm ET
Speaker: Jordan Harshman, Auburn University and Anne Kondo, Indiana University Pennsylvania
Moderator: Marian Gindy, Merck

Register for Free!

What You Will Learn:

- What collaborative work involves
- What collaborative and teamwork skills employers expect
- How these skills are acquired

Co-produced with: ACS Education

Date: Wednesday, April 21, 2021 @ 2-3pm ET
Speakers: Patricia Simpson, Game Changing Etiquette and the University of Illinois at Urbana-Champaign
Moderator: Matt Grandbois, DuPont Electronics & Industrial

Register for Free!

What You Will Learn:

- Why is business acumen important for all employees
- What are the core elements of a business acumen
- How to develop or enhance your business acumen

Co-produced with: ACS Division of Professional Relations

Date: Thursday, April 22, 2021 @ 2-3pm ET
Speakers: Rich Helling, Dow
Moderator: David Constable, American Chemical Society

Register for Free!

What You Will Learn:

- Why life cycle thinking and assessment is a good way to include environmental dimensions in decisions
- How life cycle thinking and assessment identifies potential hot spots and trade-offs
- Why simple calculations can be insightful and are a great way to include life cycle thinking in daily decisions

Co-produced with: ACS Green Chemistry Institute and the ACS Committee on Community Activities for the *Chemists Celebrate Earth Week* campaign

www.acs.org/acswebinars

90

ACS Webinars®

CLICK • WATCH • LEARN • DISCUSS

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

Edited Recordings are an exclusive ACS member benefit and are made available once the recording has been edited and posted.

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.

www.acs.org/acswebinars

91

ACS Webinars® CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

ACS Webinars® does not endorse any products or services. The views expressed in this presentation are those of the presenter and do not necessarily reflect the views or policies of the American Chemical Society.

Contact ACS Webinars ® at acswebinars@acs.org

92

ACS Webinars
CLICK • WATCH • LEARN • DISCUSS

ACS Chemistry for Life®

Date: Thursday, April 15, 2021 @ 2-3pm ET
Speaker: Jordan Harshman, Auburn University and Anne Kondo, Indiana University Pennsylvania
Moderator: Marian Gindy, Merck

Register for Free!

What You Will Learn:

- What collaborative work involves
- What collaborative and teamwork skills employers expect
- How these skills are acquired

Co-produced with: ACS Education

Date: Wednesday, April 21, 2021 @ 2-3pm ET
Speakers: Patricia Simpson, Game Changing Etiquette and the University of Illinois at Urbana-Champaign
Moderator: Matt Grandbois, DuPont Electronics & Industrial

Register for Free!

What You Will Learn:

- Why is business acumen important for all employees
- What are the core elements of a business acumen
- How to develop or enhance your business acumen

Co-produced with: ACS Division of Professional Relations

Date: Thursday, April 22, 2021 @ 2-3pm ET
Speakers: Rich Helling, Dow
Moderator: David Constable, American Chemical Society

Register for Free!

What You Will Learn:

- Why life cycle thinking and assessment is a good way to include environmental dimensions in decisions
- How life cycle thinking and assessment identifies potential hot spots and trade-offs
- Why simple calculations can be insightful and are a great way to include life cycle thinking in daily decisions

Co-produced with: ACS Green Chemistry Institute and the ACS Committee on Community Activities for the *Chemists Celebrate Earth Week* campaign

www.acs.org/acswebinars

93