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<td>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.</td>
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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
Engineering leads the way; however, polymer science and chemistry have now arrived!

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

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

Polymer design from the 1950s are not tuned for the additive manufacturing of 2020
The challenge to “print every molecule in our laboratory“

Understanding viscosity ranges for commercial 3D printing platforms

- 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)
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?


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)

Staying on the “road”
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

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
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)

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
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
Water-soluble polymers for materials extrusion AM remain limited

Poly(vinyl alcohol)  Eudragit EPO

Printing parameters:

190 °C, 90 mm/s

Printing parameters:

135 °C, 90 mm/s

Tailored dissolution of extrusion printed polymers with temperature-sensitive biologics

Product Requirements

- Water soluble (<10 min)
- Incorporation of actives (Max temp 80 °C)
- 3D printable via desktop material extrusion

Molecular Design & Synthesis

Product Geometric Design

Manufacturing Process Design

Product Performance Analysis

Material, Process, & Product
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

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

\[
\begin{align*}
\text{SO}_3\text{Na} + \text{H}_2\text{O} \rightarrow \text{SO}_3\text{Na} \quad &\text{PEG} \quad \text{n} = 1,000 - 12,000 \text{ g/mol} \quad \text{NaOAc} \\
40 \text{ ppm Ti(OiPr)}_4 &\text{ 2 h 200 K, 0.15 mmHg} \\
&\text{Poly(PEG\text{n=k}-co-NaSIP)}
\end{align*}
\]

**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\text{n=k}-co-NaSIP)


**Poly(PEG\text{n=k}-co-NaSIP) can be exchanged to monovalent and divalent counterions**

Day 1-3: 5 M eq. salt added
Day 4-6: Equilibrated with RO water

- 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\text{n=k}-co-XSIP):
17,000 – 30,000 g/mol
Extrusion AM Material Parameters

- $T_g$ & $T_m$
- Viscosity as $f$(Shear rate, $T$)
- Stiffness & Strength
- Thermal Diffusivity & Expansion
- Surface Tension & Hydrophilicity

Dynamic mechanical analysis reveals similarity between samples below $T_m$

![Dynamic mechanical analysis graph](image)

- TA Q800, Tension mode, 3 °C/min, 1 Hz
- Lack of ionic aggregation
Rheological studies show an increase in viscosity with divalent counterion.

Physical crosslinking between chains exemplified in molten state.

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

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


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

Callie Zawaski et al.

Fused Filament Fabrication (FFF)

- Material extrusion AM
- Filament feedstock
- Continuous process

- Filament is fed into heated nozzle
- End of filament is heated to a molten (fluidic) state
- Nozzle extrudes molten material in a pattern dictated by a CAD model
- Nozzle moves up/bed moves down
**Fused Filament Fabrication (FFF)**

- Material extrusion AM
- Filament feedstock
- Continuous process

![Diagram of FFF 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

---

**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/

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

General MatEx Considerations: Will it Extrude?

General design equations for capillary flow – stress and shear rate

\[ \sigma_w = \frac{R \, p_c \, R}{2 \, L} \]

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

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

Magnitude of Annular Backflow

Normalized Net Flow Magnitude

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

Determining the Flow Identification Number

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

\[ \text{FIN} = \frac{\Delta P/L}{\eta \cdot v} \cdot \pi (D_B^2 - D_F^2) \]

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

Sensitivity Analysis and Screening Materials

Degree of shear thinning

Overlay of capillary (steady) and oscillatory
Testing the Screening Process - Results

Applied model to print parameters*

<table>
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<tr>
<th>Material</th>
<th>Feed Rate</th>
<th>BGM Value</th>
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<tbody>
<tr>
<td>ABS</td>
<td>5 mm/s</td>
<td>151</td>
</tr>
<tr>
<td>LDPE</td>
<td></td>
<td>175</td>
</tr>
<tr>
<td>NaSPEG</td>
<td></td>
<td>204</td>
</tr>
</tbody>
</table>

*Model assumes constant filament diameter

FIN Limits
No Backflow: < 153
Transition: 153 - 185
Backflow: > 185

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

Any Matex process: DIW, FFF, BAAM

Nozzle exit
Wall shear rate

“Road” laydown
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
Dynamics of Layer Deposition: Geometry, Thermal and Viscoelastic Response


Rheology - Diffusion Dynamics, Extrudate Properties

Re-Entanglement Times can be Long!

How much re-entanglement is required for strong bonds?

Thermal model - only ~1-2 seconds above $T_g$

Poly(ether imide)

>100 minutes

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

Do not lose track of the “big picture”
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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LA MARAVILLA DE LA BIODIVERSIDAD
A TRAVÉS DEL PRISMA DE LA CHROMATOGRAFÍA

Fecha: Miércoles, 26 de Septiembre @ 2-3pm ET (1-2pm CT)
Fonenta: Diana Stashenko, Universidad Industrial de Santander
Moderadora: Troy Rottier, Universidad de Puerto Rico, Recinto de Río Piedras y American Chemical Society

Lo Que El Público Aprenderá:
- Juntos con la biodiversidad biológica existe una diversidad molecular bastantes amplia para su estudio, lo que demuestra la diversidad de las técnicas de cromatografía y espectrometría de masas.
- Los sistemas moleculares de los fosfatos desempeñan papel importante en la comunicación, la adaptación y la supervivencia de las plantas.
- El color de algunas flores está asociado con la capacidad antioxidante de sus volatilizadores.
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

Fecha: Lunes, 30 de Septiembre @ 2-3pm ET
Huesped: Angela Zhou, ACS / Andrea Confino, University of North Texas /
Rogberto Hernández, Johns Hopkins University / Frank Laipple, University of North Carolina
Moderado: Laura Horwitz, Chemical & Engineering News

What You Will Learn:
- Who are the frontrunners for this year’s Nobel Prize in Chemistry?
- Big ideas in chemistry that we think should someday win the prize.
- Nobel trivia, different division techniques, and much more

Catalyze the Vote!
2022 ACS President-Elect Candidates

Fecha: Viernes, 1 de Octubre @ 2-3pm ET
Huesped: Judith Granier, woodMC and the Chemical Angel Network and Juan C. Warner, Zymergen
Moderador: Amber Wilson, Green Analytics, LLC

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
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