New Materials Utilized in Filaments for 3-D Printing

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Outline

• Fused filament fabrication (FFF) 3-D printing with advanced materials
  • Polymer fillers

• FFF 4-D printing with smart materials
  • Shape memory effects

• Standards development
Advanced Materials and FFF 3-D Printing

• Advanced materials
  • Enhanced or novel materials
  • Polymers → advanced materials

• FFF 3-D printing
  • Polymer filament extrusion process
  • Powerful tool for making complex objects
  • Popular platform for research on advanced materials
For more information on polymer additives, see Allen and Edge. J Vinyl & Additive Tech. (2021)
Fillers in Commercially Available Filaments

- Engineered nanomaterials
  - Carbon nanotubes/fibers
  - Diamond
  - Graphene
  - Hexagonal boron nitride
  - Hydroxyapatite

- Woods
  - Bamboo
  - Pine
  - Beech

- Metals (generally micronscale)
  - Bismuth
  - Brass
  - Bronze
  - Copper
  - Iron
  - Stainless steels
  - Tungsten

- Other compounds
  - Calcium carbonate

Amount can range from a few percent to 90% or more depending on product and material
Sources of Metals in Filaments

- Fillers
- Pigments
- Dyes
- Flame retardants
- Antioxidants
- Heat stabilizers
- Catalysts
- Processing aids
4-D Printing

- Existing AM technique
- Stimuli-responsive shape-altering polymers
- Apply controlled external stimuli
  - Increase polymer temperature
  - “Programming” → induce *predictable* change
  - “Recovery” → return to original state
- Time dimension to create final object = 4-D printing

- Definition shifting to account for non-shape changes over time
  - “Smart materials” or “active materials”

Fu et al. Prog Polymer Sci. (2022)
Imrie and Jin. J Polymer Sci. 60:149-174 (2022)
4-D Printing

- Many potential applications
  - Research phase
  - Smart materials

- Intricate shape changes

**FIGURE 4** Dynamically controllable transformation of 4D printed constructs built from SMP/graphene composite material. NIR sensitive 4D transformation behavior of the nanocomposite models, including a blooming flower and a hand gesture. The shape of these models could be dynamically and precisely controlled under NIR exposure^148^
Smart Materials – Shape Memory Polymers (SMPs)

• Filament used with FFF 3-D printers
• Possess glassy-to-rubbery transition capacity
  • Amorphous or semi-crystalline polymers
  • Application of external stimuli heats polymer \( \rightarrow \) shape changes
    • Cooling polymer restricts polymer chain movement and preserves shape
    • Reheating releases stored strain and object returns to its as-printed shape
• Most common polymer feedstocks
  • PLA
  • Polyurethane (PU)
  • Thermoplastic urethane (TPU)
  • Nylon

Ahmed et al. Polymer. 228 Article 123926 (2021)  
Imrie and Jin. J Polymer Sci. 60:149-174 (2022)
Smart Materials – SMPs

• TPU “robotic” gripper

1. “Open” configuration
2. Lowered over object
3. External stimuli (heat)
4. Closed configuration
5. Raising object

Smart Materials – SMP Composites

• Combine benefits of two or more SMPs
  • Polymer-polymer systems
    • Poly (2-vinylpyridine) + ABS
    • Polypropylene + Nylon-6
    • PLA + TPU
    • TPU + polycaprolactone (PCL)

![Figure 13] Shape recovery of PU/PCL composite

Notes: (a) Original shape; (b) Shape at room following deformation at transition temperature of TPU scaffold; (c) Shape after heating back up to PCL melting point; (d) Shape after deformation at PCL transition temperature; (e) Recovery to the new memorized shape after reheating; (f) Recovered initial shape after heating back up to the TPU scaffold transition temperature

Source: Estelle et al. (2017)

Valvez et al. Polymers. 13 Article 701 (2021)
Smart Materials – SMP-Particle Composites

• Polymer + particle mixture
  • Particles provide smart functionality

• ENMs
  • Nylon-12 + stainless steel
  • TPU + CNTs
  • Polycyclooctene (PCO) + MWCNTs
  • PLA + CNTs (or graphene, Ag nanowires, iron oxide, HA, or silicon carbide)

• Micronscale particles
  • Poly(vinylidene fluoride) + BaTiO$_3$
  • Nylon-11 + BaTiO$_3$
  • PCO + h-BN

Ahmed et al. Polymer. 228 Article 123926 (2021)
Valvez et al. Polymers. 13 Article 701 (2021)
Imrie and Jin. J Polymer Sci. 60:149-174 (2022)
Smart Materials – SMP-Particle Composites

- TPU + carbon black

**Notes:** (a) Shape recovery based on light source 87 mWcm\(^{-2}\); (b) shape recovery based on light source 76 mWcm\(^{-2}\)

**Source:** Yang et al. (2017b)
Standards

• How can standards help with commercialization and acceptance?
  • Terminology/vocabulary
  • Material specifications/classifications
  • Test methods

• Engaging relevant SDOs
  • ISO TC229 (Nanotechnologies), TC261 (additive manufacturing), others?
  • ASTM E56 (Nanotechnology), F42 (additive manufacturing), others?
  • Underwriters Laboratory
  • Others?

• Engaging relevant scientific disciplines
Summary

• FFF 3-D and 4-D printing
  • Polymer filament feedstocks

• Polymer feedstocks
  • Advanced materials
  • Smart materials

• Active and growing research
  • Opportunities for standards