New Materials Utilized in Filaments for 3-D Printing

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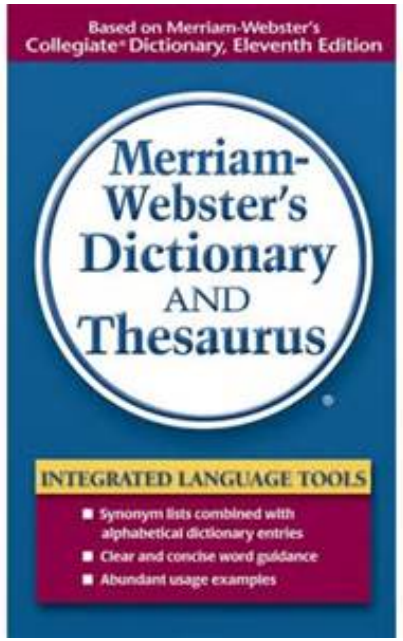
Outline

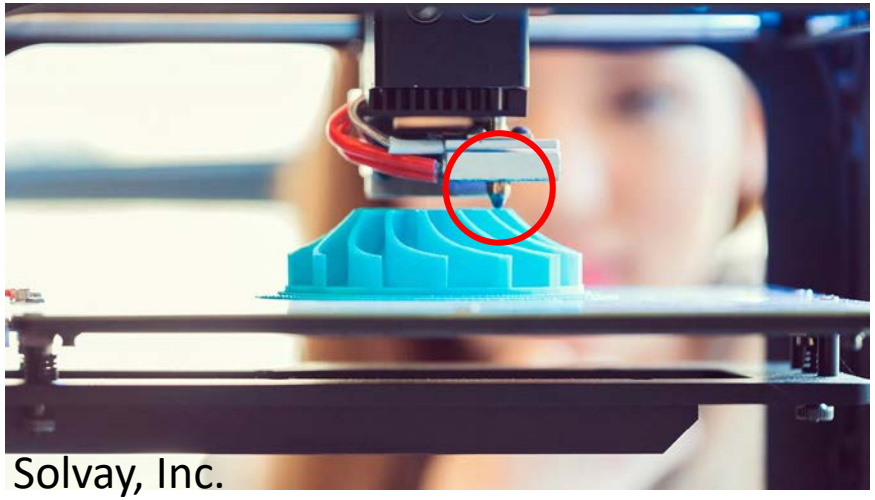
- Fused filament fabrication (FFF) 3-D printing with advanced materials
  - Polymer fillers
- FFF 4-D printing with smart materials
  - Shape memory effects
- Standards development

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



Polymer Additives

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

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Review

Human exposure to metals in consumer-focused fused filament fabrication (FFF)/ 3D printing processes

Getachew Tedla [a], Annie M. Jarabek [b], Peter Byrley [b], William Boyes [c], Kim Rogers [a,*]

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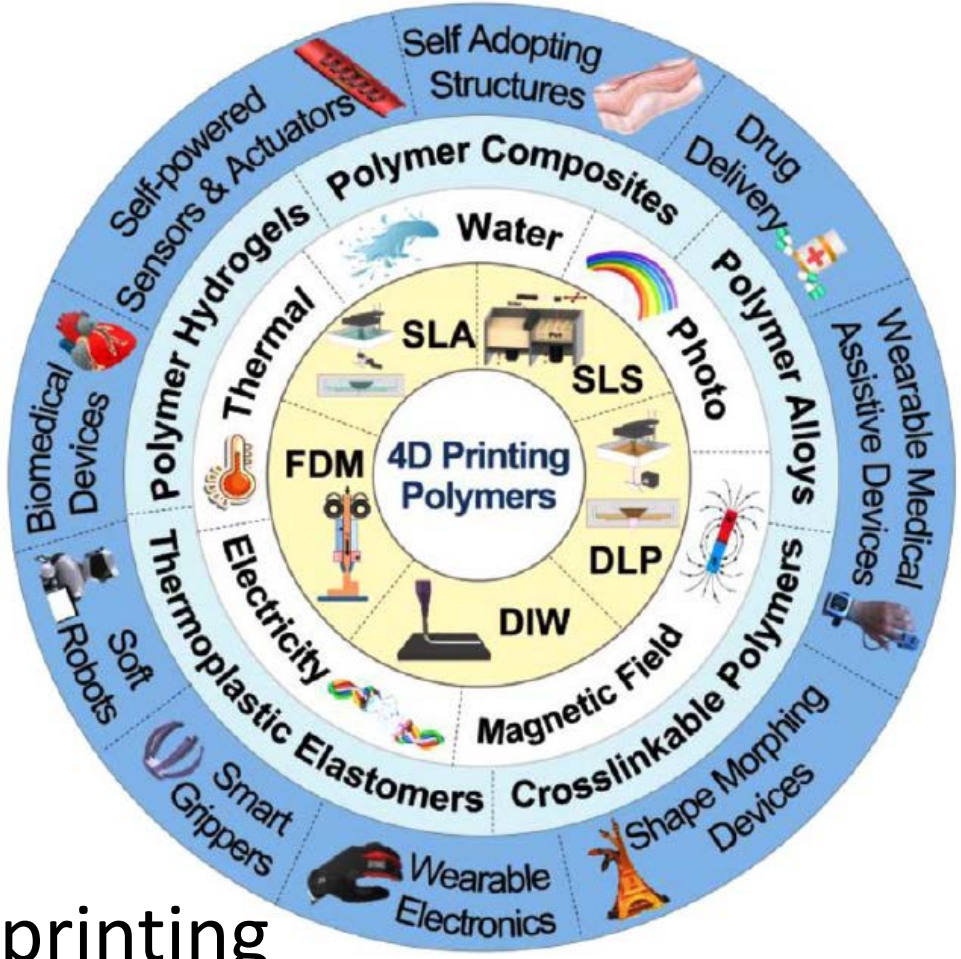
4-D Printing

- 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



Fu et al. Prog Polymer Sci. (2022)

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

Imrie and Jin. J Polymer Sci. 60:149-174 (2022)
Carrell et al. Rap Proto J. 26:855-869 (2020)

4-D Printing

- Many potential applications
  - Research phase
  - Smart materials

- Intricate shape changes

Alshebly et al. Eur J Polym. 159 Article 110708. (2021)

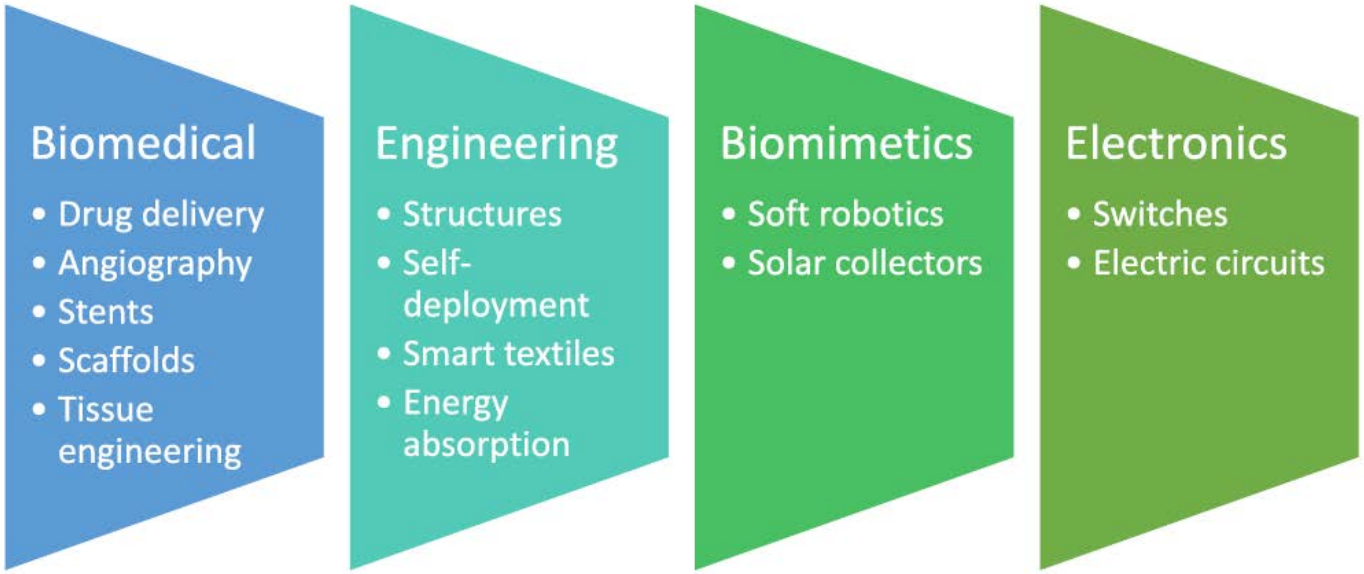


Fig. 14. Application fields that are popular in 4D printing.

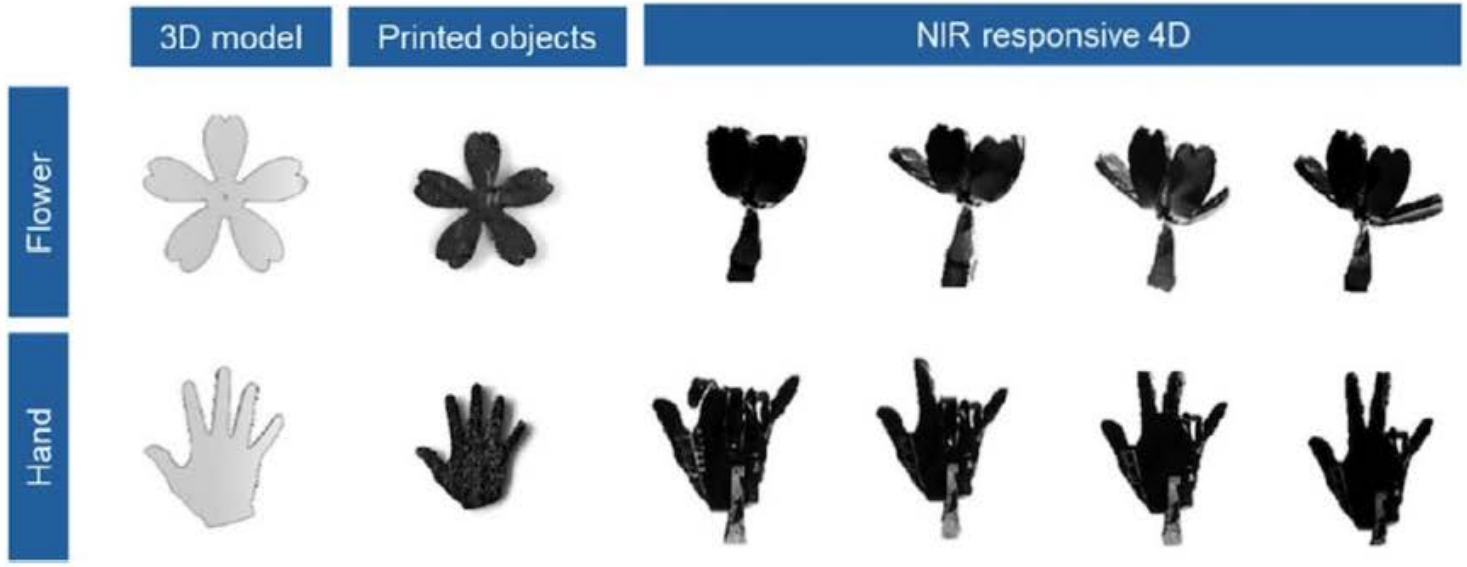


FIGURE 4 Dynamically controllable transformation of 4D printed constructs built from SMP/graphene composite material. NIR sensitive 4D transformation behavior of the nanocomposite models, including a blooming flower and a hand gesture. The shape of these models could be dynamically and precisely controlled under NIR exposure[148]

Imrie and Jin. J Polymer Sci. 60:149-174 (2022)

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 → 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

Carrell et al. Rap Proto J. 26:855-869 (2020)
Ahmed et al. Polymer. 228 Article 123926 (2021)
Imrie and Jin. J Polymer Sci. 60:149-174 (2022)

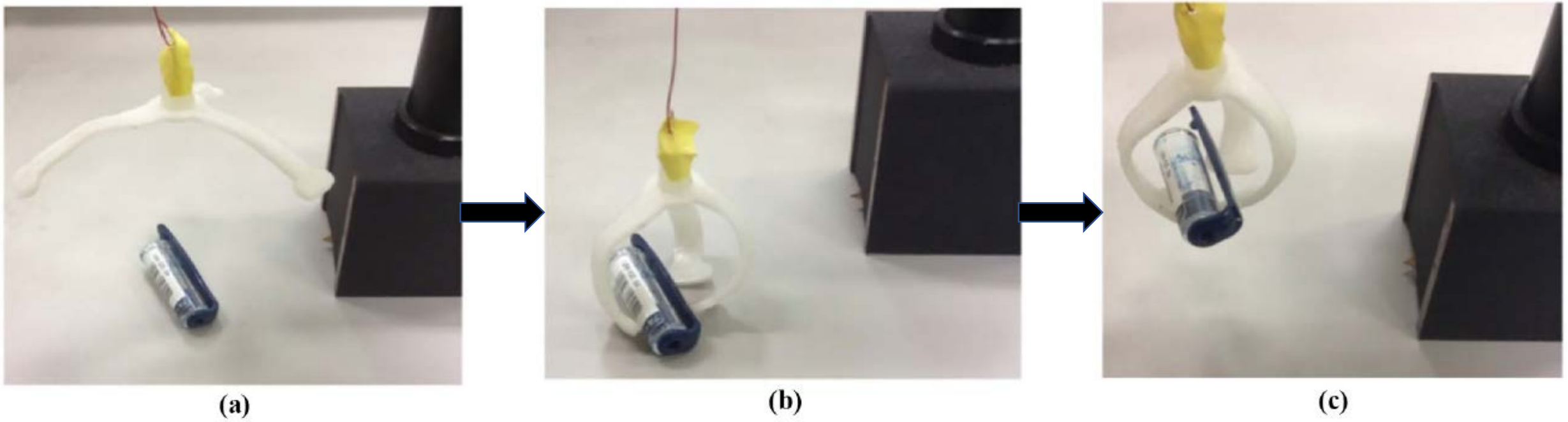
Smart Materials – SMPs

- TPU “robotic” gripper

1. “Open” configuration

2. Lowered over object
3. External stimuli (heat)
4. Closed configuration

5. Raising object



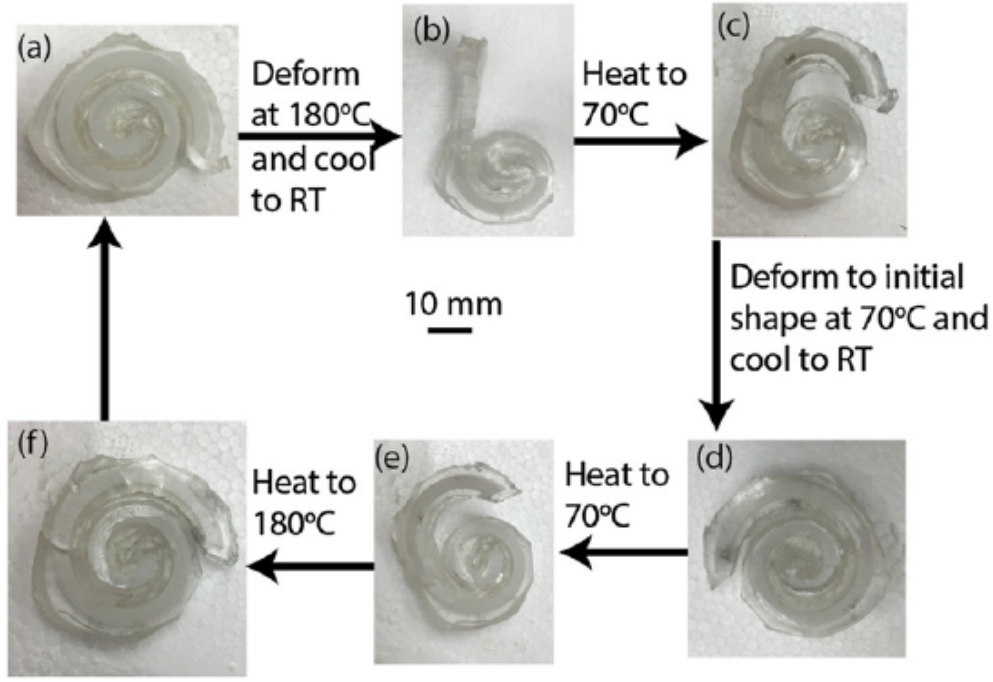
(a) (b) (c)

Carrell et al. Rap Proto J. 26:855-869 (2020)

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)
Carrell et al. Rap Proto J. 26:855-869 (2020)

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

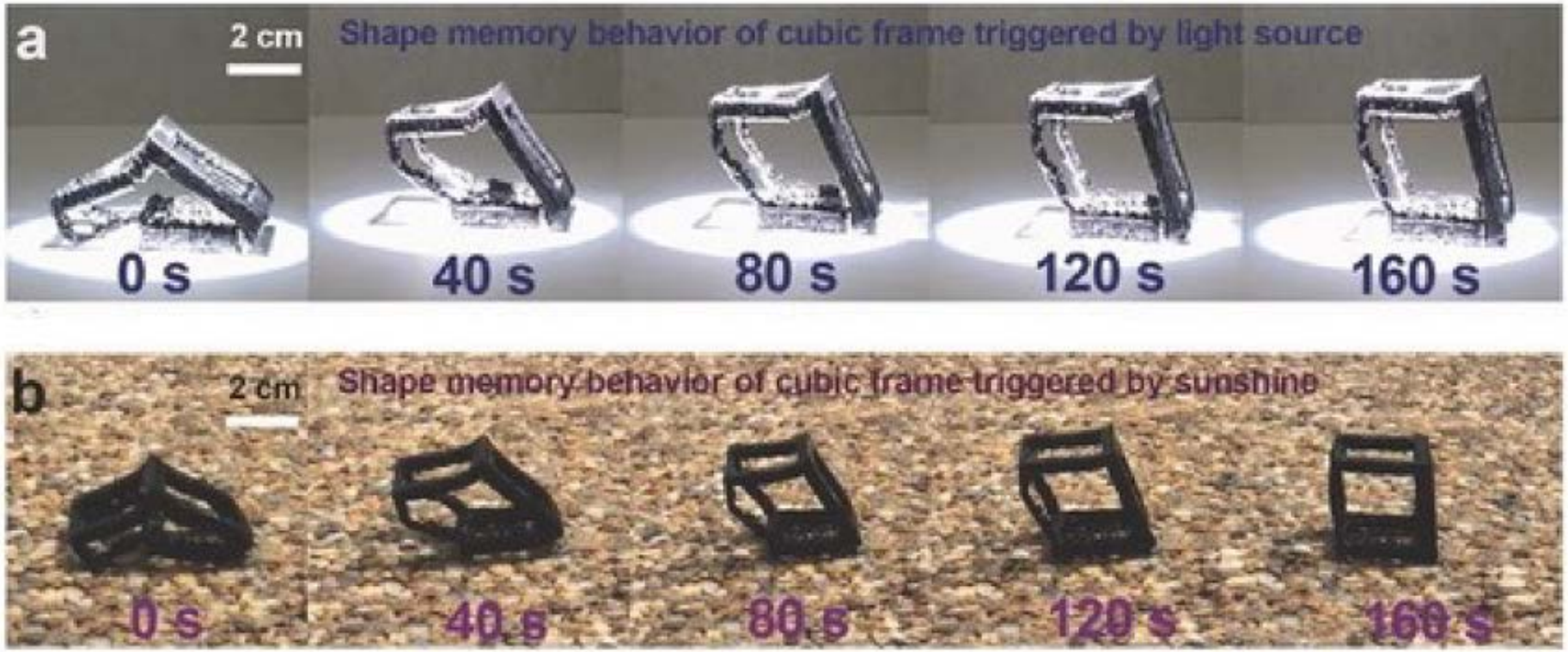
Carrell et al. Rap Proto J. 26:855-869 (2020)
Ahmed et al. Polymer. 228 Article 123926 (2021)
Valvez et al. Polymers. 13 Article 701 (2021)
Imrie and Jin. J Polymer Sci. 60:149-174 (2022)

Smart Materials – SMP-Particle Composites

- TPU + carbon black

Bulb light

Sunshine



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)

Carrell et al. Rap Proto J. 26:855-869 (2020)

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

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