3D Printing of Elastomers

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Introduction

3D printing, also referred to as Additive Manufacturing (AM), has become a demanding technology in the world which can fabricate three-dimensional objects in a layer-by-layer fashion using computer-aided design (CAD) models. AM possesses the unique ability to create complex geometries not conducive for conventional manufacturing techniques such as injection moulding, forging, and machining. AM finds applications in myriad industrial and commercial sectors including biomedical engineering, medicine, dental, pharmaceutical, food, automotive, aerospace, military, electronics, and construction fields with a potential emerging $1 trillion market by 2030 via large capital investments over the next decade (Appuhamillage et al. 2019).

AM can process a spectrum of materials including polymers, composites, pastes, resins, ceramics, metals and alloys, powders, and living tissues via various techniques such as extrusion , jetting, vat photopolymerization (VP), powder bed fusion(PBF), directed energy deposition (DED), and sheet lamination. This commentary focuses on 3D printing of elastomers using the two extrusion based methods; fused filament fabrication (FFF) and direct-ink writing (DIW), inkjet printing/material jetting, and VP.

Elastomers are cross-linked polymer networks having a low cross-linking density and high molecular weight polymer strands between crosslinks. Upon applying of an external stress, long polymer strands change their chain conformation yielding a higher deformation while cross-links halt flow. Elastomers possess extremely high strain capacities (i.e. ≥ 400-1000%) and high resilience. These properties enable elastomers find applications in many industries including healthcare, automotive, aerospace, and textile (Herzberger et al. 2019).

FFF extrudes a thermoplastic filament through a heated print head on to a build platform where the extrudate solidifies yielding a 3D layered object. DIW uses pressure to extrude viscoelastic materials through a needle like nozzle at ambient temperature on to a print bed layer-by-layer fashion where the printed material usually undergoes post-curing solidification under UV. Inkjet printing deposits ink droplets on a substrate using pressure and subsequent solvent evaporation renders the layered solid architecture. Sometimes UV curing transforms the liquid into a solid. VP employs a photocurable resin in a vat which is cured under a UV laser that rasters the required pattern on the resin surface. Upon recoating a fresh layer of the photo-resin and patterning with the UV laser, subsequent solid layers will be formed building up the 3D object. Commonly used VP based AM systems for elastomer printing are stereolithography (SLA), digital light processing (DLP), and two-photon polymerization. These three methods basically utilize the printing mechanism mentioned under VP.

From here onwards, first, current trends in AM- based research efforts using different classes of elastomers are discussed. Then challenges of elastomer AM are briefly pointed out followed by elaborating on future outlook to develop the process addressing the challenges.

Current Trends in 3D Printing of Elastomers

Silicone Elastomers

These covalently crosslinked polysiloxane based networks generally possess extremely low glass transition temperatures (Tg), (ca. -127 °C for polydimethyl siloxane (PDMS)), low elastic moduli (several MPa max.), and extremely high strain capacities (i.e. ultimate strains > 300%). These are biocompatible, chemically and electrically inert. These properties make AM of silicone elastomers highly desirable for healthcare applications. Many DIW based AM approaches are found using silicone elastomers. Room temperature vulcanization (RTV) silicone and silver nanoparticle

infused silicone have been utilized to print a bionic ear while quick-curing acetoxy silicone (LOCTITE) for reaction-ware. Research have been reported utilizing DC SE 1700, a thermally curable PDMS-based resin having fumed silica nanoparticles, and its blends with unfilled PDMS to 3D print complex architectures, AM foams, vascularized tissue constructs, spider webs, and other structures for bioengineering applications via DIW. Studies using PDMS-co-polydiphenyl siloxane (PDPS) have rendered silicone elastomers processable at low temperatures due to suppression of undesired cold-crystallization of PDMS via bulkier PDPS segments. DPS blocks have also improved thermal and radiation resistance. Other reported strategies include efforts to tailor stiffness (i.e. using thiol-crosslinkers with vinyl terminated polysiloxanes), tune rheological properties via fumed silica fillers, paraffin wax etc., and utilize conductive inks to 3D print wearable electronics, soft robotics, and soft somatosensitive actuators (Shan et al. 2015; Schmalzer et al. 2017).

Two-photon microstereolithography (2PμSL) is another AM method successful in 3D printing PDMS-based elastomers. This method is an extremely precise route enabling printed features down to the size of 100 nm becoming suitable to yield optical waveguides or microfluidic devices. The first work to report 3D printing of PDMS-based elastomers (2004) had success with a radial photoinitiator that could improve photoimaging and feature sizes of 0.3-0.6 μm (Coenjarts and Ober 2004).

Since VP requires low viscosities, only silicone oligomers have appropriate printing properties. Recent research demonstrates use of oligomeric PDMS derivatives with methacrylate groups and acryloyl methacrylates etc. Long et al. (2018) came up with a strategy to employ two concurrent reactions; thiol-ene to lead chain extension while free-radical polymerization to yield the polymer network. Other efforts include adding reinforcing silica fillers to improve the toughness of PDMS-based resins and use of optically transparent PDMS elastomers for VP based AM of microfluidic devices.

Moreover, inkjet based AM of silicone elastomers reported successful in fabricating stretchable electronics/microfluidics, and dielectric or stacked elastomer actuators (McCoul et al. 2017).

Polyurethanes (PUs)

These highly versatile class of polymers find AM related applications including biomedical engineering, soft robotics, and bio-photonics etc. PUs can either be segmented/blocked or non-segmented. Segmented ones contain soft and hard blocks in their backbone. Most of these are printed from solution while some are from melt. DIW, FFF, and inkjet methods have been reported successful in 3D printing PUs. Segmented PUs with chain extenders have been 3D printed via DIW and subsequent freeze-drying resulted 3D vasculature models. DIW co-extrusion of cell-laden hydrogel precursor and PU- tetraglycol solution has yielded layered, flexible PU-collagen conduits. In another effort, biocompatible poly(ester urethane)s (PEUs) have been 3D printed to form scaffold structures (via DIW) and sponges (via salt-leaching). DIW based scaffolds have shown improved viability towards rat bone marrow stem cells with high proliferation rates. Voit et al. (2018) investigated AM of relatively untouched family of thiourethanes via FFF. Several thermal inkjet based 3D printing have also been reported for PUs resulting structures as tissue engineering scaffolds and elastomeric optical waveguides for soft robotics and biophotonics applications. Furthermore, waterborne polyurethane dispersions (PUDs), a greener approach for conventional organic solvent based PUs, have been 3D printed via DIW and inkjet based approaches (Hsu et al. 2015).

Thermoplastic elastomers (TPEs) that derived from PUs have been utilized for AM mainly via FFF. These possess tunable mechanical properties owing to the content and composition of hard and soft segments in their backbone. Various shapes of cell/tissue scaffolds and vasculature models have been 3D printed using TPEs.

Liquid Crystalline Elastomers (LCEs)

LCEs are flexible polymers yet slightly crosslinked and bear liquid crystalline mesogenic groups in side or main chains. According to literature, LCEs have been 3D printed mainly via DIW. Past research evidence DIW based 3D printing of several geometries with varying curvatures, ring- shaped LCE in a PDMS slab where latter could be utilized as a variable focusing

lens. In another DIW based approach, LCE strips were 3D printed and subjected for weight bearing tests. Results showed that these 3D printed LCE actuators (1 mm thickness) lifted 1000 times of their own weight confirming promising approach towards 3D printed artificial muscles and actuators (Kotikian et al. 2018).

Commercial Elastomers

A plethora of commercially available elastomers are being utilized for AM based applications via various methods. Many of these are synthetic photopolymers, photopolymers of PUs, thermoplastic polyurethanes (TPUs), few TPEs and UV curable silicones. Related AM methods include VP based methods (i.e. SLA, DLP, Continuous liquid interface printing (CLIP)), extrusion (FFF, DIW), jetting (polyjet, multijet), and selective laser sintering (SLS). Main AM based applications include biomedical engineering, wearable electronics, and soft robotics (Herzberger et al. 2019).

Figure 1 summarizes current trends in 3D printing of elastomeric materials for the various applications as discussed above.

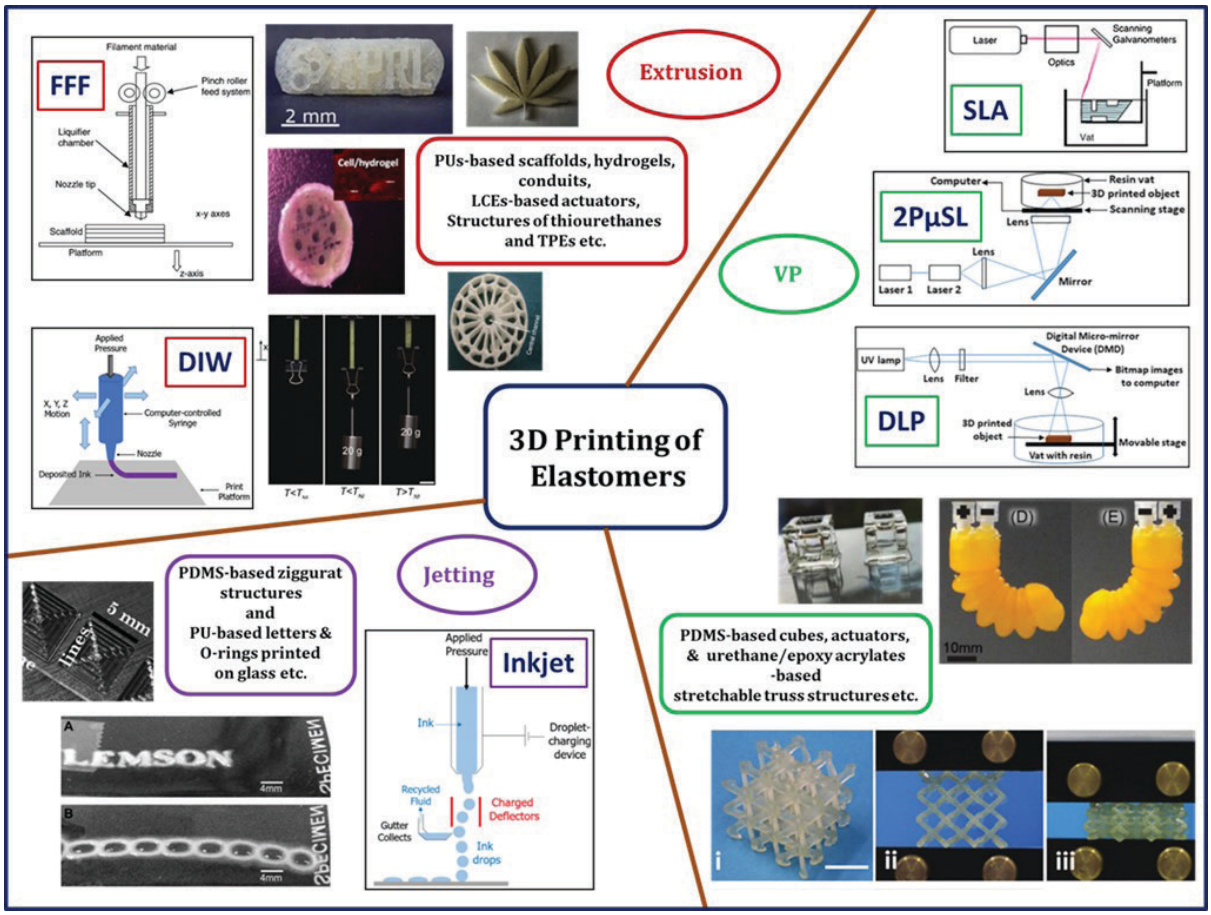

Figure 1. Current trends in 3D printing of elastomeric materials for various applications.

Challenges

AM of elastomers meet several challenges. These are summarized for VP, inkjet, FFF, DIW, and PBF AM techniques. Polymer viscosity is crucial in VP. Too high viscosities result slower prints and even warping of printed parts. A practical upper viscosity limit is 5 Pa.s. When recoating blades are employed, cured networks with low storage moduli cannot withstand shear forces from them resulting structural collapse. Volatility and toxicity needs to be concerned when using reactive or non-reactive diluents/monomers/or solvents. Potential thermoplymerization (e.g. (meth)acrylates) could occur when a heating vat is employed. Printing elastomers with low moduli needs support scaffolds that need to be removed after printing along with any solvent(s) used. Silicone elastomers possess high oxygen permeability

which affects UV curing of acrylates and methacrylates. During inkjet 3D printing, both viscosity and surface tension matter. Printing of high molecular weight (Mw) polymers becomes a challenge above 1 wt% loading and complicates fluid line drying. High dilutions lead to non-uniform print patterns. Use of polymer emulsions and multi-material printing are some possible solutions to diminish these hurdles. Challenges during FFF are of two classes; specific to the AM technology and specific to elastomers used. Technological barriers include inter-layer adhesion, object-bed adhesion, overhangs, extrusion failures (filament buckling, backflow etc.), and clogging. Elastomeric issues include low filament moduli, slow refilling of nozzle after filament retraction, and void formation in prints due to hygroscopic nature (e.g. PUs). DIW based AM of elastomers with low storage moduli finds collapsing of printed material under own bodyweight. Use of fillers and support bath are solutions. Removal of supporting medium is often challenging. Powder flow needs to be maintained optimized in PBF. High toughness (e.g. TPUs) challenges powder formation and low powder modulus leads to tackiness issues (Ligon et al. 2017; Gilmer et al. 2017).

Future Outlook

Since elastomers play highly important roles in many fields as discussed above, their AM based developments would be crucial in future. AM possesses the huge advantage of customized design freedom. Coupled with computed tomography/3D surface scanning, AM of elastomers could yield customized implants and prostheses faster with high accuracy that would save millions of lives in future. Combined efforts of polymer chemists, materials scientists, and engineers would be crucial for novel elastomeric formulations and simultaneous printer designs (i.e. hybrid AM techniques for high viscosity materials). This would also address many of the aforementioned challenges by setting proper rheology that broadens processability of elastomers under the particular AM technology. Developing novel analytical and screening techniques is crucial to optimize printing parameters for novel materials. Developing methods to detect network inhomogeneities is useful to evaluate VP based printed objects. Other factors such as thorough evaluations of impact of fillers, additives on elastomer biocompatibility, reports on elastomeric recovery and hysteresis of 3D printed objects would be important. Research and developments on stretchable mechanical metamaterials would also become attractive in future.

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