Additive manufacturing of thermoset elastomers: A review of emerging technologies
Tóth Cs., Virág Á. D., Halász-Kutasi I. Z., Kovács N. K., Bárány T.

Engineering Science and Technology, an International Journal 69 (2025) 102143

Contents lists available at ScienceDirect

Engineering Science and Technology,
an International Journal

journal homepage: www.elsevier.com/locate/jestch

Additive manufacturing of thermoset elastomers: A review of emerging technologies

Csenge Tóth [a,b], Ábris Dávid Virág [a,*], István Halász-Kutasi [a], Norbert Krisztián Kovács [a,b], Tamás Bárány [a,b]

[a] *Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary*
[b] *MTA-BME Lendület Lightweight Polymer Composites Research Group, Műegyetem rkp. 3., H-1111 Budapest, Hungary*

ARTICLE INFO

Keywords:
3D printing
Rubber
Rapid prototyping
Crosslink
Photopolymerization
Sustainability

ABSTRACT

Thermoset elastomers (TSEs) are widely used in industries such as automotive, household appliances, healthcare, and fashion due to their flexibility and stability. However, these same properties make TSEs challenging to process using additive manufacturing (AM) techniques. This review categorizes AM technologies for producing TSEs into three main groups: photopolymerization-based, two-phase, and material extrusion–based techniques. Photopolymerization offers high resolution and material versatility but is constrained by build size and environmental impacts. Two-phase systems enable tunable properties but suffer from rheological and bonding issues, while material extrusion is more cost-effective yet less precise. Overall, current research primarily concentrates on technology and formulation development. Mechanical characterization of 3D-printed TSEs is typically limited to tensile properties. Comprehensive mechanical testing, including application-specific properties, is still rare and remains an essential area for future qualification of technological advances. The sustainability aspects of 3D printing TSEs are also addressed, with a focus on environmentally friendly raw material selection and the general environmental considerations of 3D printing methods. Emerging trends in this field include the development of smart materials, sustainable solutions, and integrated hybrid methods that incorporate artificial intelligence and machine learning.

1. Introduction

Thermoset elastomers are widely used in many fields, from tires and seals through gloves and medical devices to wearable electronics and footwear. The term elastomer refers to a polymeric material with highly elastic properties. As defined by ASTM D1566-21a, high elasticity refers to the material's ability to return to less than 1.5 times its original length within one minute after being stretched to twice its length at room temperature (18–29 °C) and held in that state for one minute prior to release. From the perspective of thermal reversibility (which is governed by molecular structure), elastomers can be divided into two categories: thermoplastic elastomers (TPEs), which are physically crosslinked and reprocessible upon heating, and thermoset elastomers (TSEs), which are chemically crosslinked and retain their structure permanently after curing. Both TPE and TSE materials can undergo large reversible strains even under relatively modest stresses, and they recover forcefully to almost their original dimensions and shape when the deforming force is removed [1]. The structural difference is the type of intermolecular bonding that holds the structure together. The molecular chains of TPEs are connected physically by only secondary bonds (mainly dipole and hydrogen bonds), while TSEs have primary covalent bonds between the molecular chains [2]. Due to their chemically crosslinked structure, TSEs usually have better reversibility than TPEs (usually well over 90 %) after large strains [3–5]. TPEs can be easily processed and recycled with standard thermoplastic methods, (re)melting and (re)shaping techniques, such as injection molding or extrusion. TSEs cannot undergo thermal (re)processing due to their permanent crosslinking [6]. However, now covalent adaptable networks (CAN) are developed through dynamic covalent cross-linking. These networks enable the exchange or dissociation of bonds in response to external stimuli, which allows for recyclability without loss in mechanical performance [7–9].

In this review, we focus on the additive manufacturing of conventional thermoset elastomers (Fig. 1). Currently, TSE parts are primarily produced by injection molding, compression molding, and transfer

---

* Corresponding author.
E-mail address: virag.abris.david@gpk.bme.hu (Á.D. Virág).

https://doi.org/10.1016/j.jestch.2025.102143
Received 29 April 2025; Received in revised form 20 June 2025; Accepted 14 July 2025

molding [10]. While the manufacturing processes of TPEs may vary, they share a common limitation: they require costly machinery and molds, which severely limits the possibilities for customization and individualization [11]. 3D printing cross-linked elastomer components could revolutionize product development by enabling functional prototyping at earlier stages [12]. It could speed up design, support greater customization, and significantly shorten development times. However, the technologies faces challenges [13] in terms of material limitations, scalability, and sustainability, the latter of which we discuss in detail in this article.

2. Crosslinking techniques for thermoset elastomers

According to the ASTM D1566 − 21a standard, cross-linking is the act of forming chemical bonds between polymer chains to create a network structure. It is a crucial part of manufacturing TSE products, enhancing mechanical strength, elasticity, and thermal stability. The method relies on specific triggers and material types, each with a unique molecular mechanism and required additives (Table 1). The most common method of producing TSE materials is the application of heat and sulfur-based systems with unsaturated rubbers such as natural rubber (NR), butadiene rubber (BR), styrene-butadiene rubber (SBR) and acrylonitrile-butadiene rubber [14–18]. Sulfur interacts with carbon–carbon double bonds (C=C) under heat, aided by accelerators (e.g., sulfenamides), activators like zinc oxide (ZnO), and other additives. Alternatively, organic peroxides can be used as vulcanizing agents for saturated or unsaturated rubbers, including ethylene-propylene-diene monomer rubber (EPDM) and silicone. When heated, these peroxides break down and produce radicals that initiate crosslinking [19].

Photopolymerization, initiated by ultraviolet (UV) or visible light, is commonly used for crosslinking photopolymer resins such as acrylates. In this case, the process needs photoinitiators, and covalent bonds are formed through free radical or cationic polymerization [20].

Ionizing radiation, such as electron beams or gamma rays, initiates crosslinking in radiation-sensitive polymers like EPDM [21]. This radiation generates free radicals that form covalent cross-links. Oxygen inhibitors, stabilizers, and other additives are also often used to tailor crosslink density and reduce degradation [22].

Moisture-induced crosslinking occurs in materials such as room-temperature vulcanizing (RTV) silicones [23,24]. The simplest uncrosslinked RTV silicones typically consist of poly(dimethyl siloxane) (PDMS) chains terminated with acetoxy groups. Crosslinking is a two-step reaction, initiated when the PDMS comes into contact with moisture [25]. The vulcanization of unsaturated elastomers with phenolic resins is a heat-activated reaction in which the phenolic resin interacts with the unsaturated sites of the elastomer chains and forms stable carbon–carbon and ether bonds via a carbocation mechanism [26]. Section 3 details the implementation of these crosslinking techniques in additive manufacturing to produce TSEs with customized geometries and functionalities.

3. Additive manufacturing of thermoset elastomers

Additive manufacturing or three-dimensional (3D) printing is a category of production technologies where three-dimensional objects are created through the sequential layer-by-layer deposition of material. Additive manufacturing has great benefits in rapid prototyping, product customization, and small-batch production, because complex and previously unachievable geometries can be produced directly from digital 3D models. There is no need for time-consuming and expensive tooling,

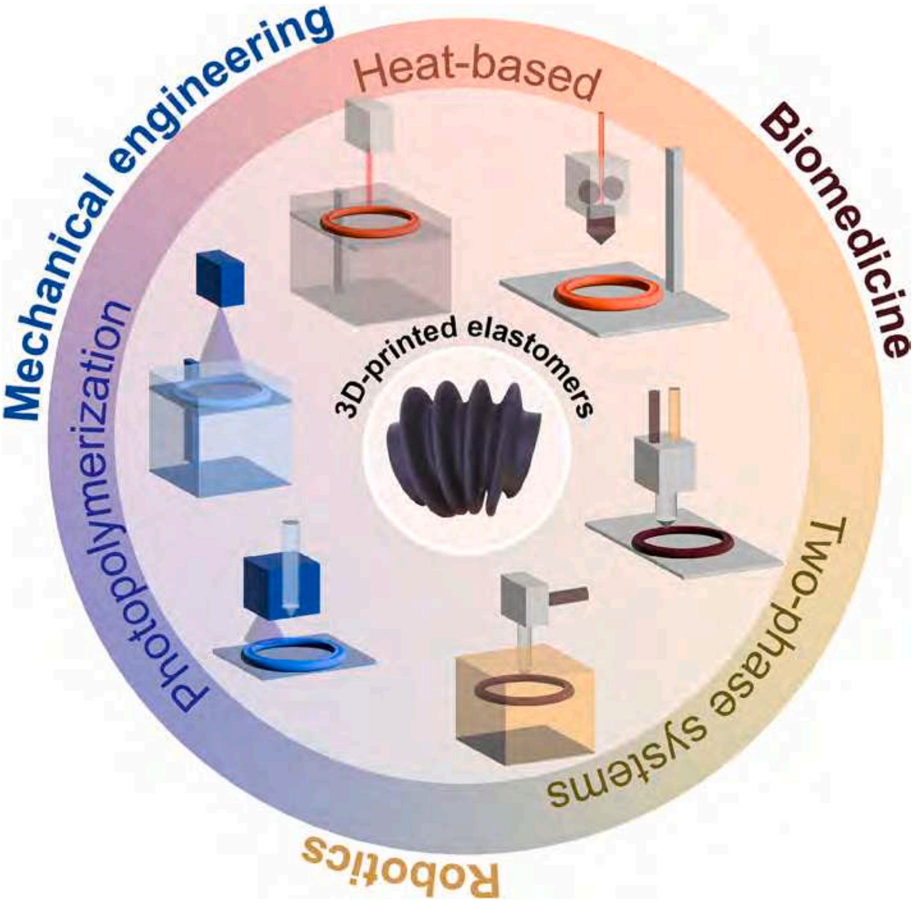


Fig. 1. Overview of 3D printing methods for thermosetting elastomers and their corresponding application fields.

Table 1
Classification of crosslinking techniques of thermosetting elastomers based on the trigger effect that drives the crosslinking process.

Trigger for Crosslinking	Material	Molecular Mechanism	Additives
UV or visible light	Photopolymer resins (e.g. acrylates)	Free radical or cationic polymerization forming covalent crosslinks	Requires photoinitiators, stabilizers may be used
Ionizing radiation (electron beam, gamma radiation)	Radiation-sensitive polymers (e.g. EPDM)	Radiation-induced free radicals initiate covalent crosslinking between chains	Oxygen inhibitors, stabilizers, and co-agents may be used to optimize crosslink density and prevent degradation
Moisture	Moisture-reactive materials (e.g. RTV silicones)	Hydrolysis and condensation (e.g. Si–OH to Si–O–Si) forming crosslinks	Catalysts (e.g. tin compounds) are often added to accelerate crosslinking
Heat + sulfur-based vulcanizing system (e.g. thiuram disulfides)	Unsaturated rubbers (e.g. NR, SBR, BR)	Heat activates accelerators and sulfur reactions. Sulfur crosslinks form at C=C bonds via radical and ionic intermediates	Sulphur donor (e.g. S_2Cl_2, DTDM, MBSS, etc.), accelerators (e.g. sulfenamides), activators (ZnO), and co-agents are usually added to tailor cure rate and crosslink type
Heat + organic peroxide as vulcanizing agent	Saturated or weakly unsaturated rubbers (e.g. EPDM, silicone)	Thermal decomposition of peroxides generates free radicals resulting in covalent crosslinks between polymer chains	Additives (e.g. triallyl cyanurate) may be used to increase efficiency and crosslink density
Meta- and *para*-substituted phenolic alcohols (phenolic resins)	Elastomers containing few unsaturated bonds (BR, ethylene propylene terpolymers)	Radical sites on the polymer backbone react with reactive benzylic or methylol groups of the resin	Halogen donors to generate reactive sites, metal oxides

such as molds and dies, which are commonly required in traditional manufacturing techniques. However, 3D printing TSEs is challenging. Unlike TPEs, TSEs undergo a chemical crosslinking reaction, which is irreversible, and the timing of curing during printing is difficult to control. If curing occurs too early, it can clog the nozzle, and if it occurs too late, the printed structure may collapse. These materials also often have high viscosity, which makes extrusion difficult and limits print resolution. In addition, many thermosetting systems have a short scorch time (the time during which an elastomer compound remains processable at a given temperature before crosslinking starts); once mixed, they begin to cure within a limited time, limiting print run times and increasing material waste. Because thermosetting elastomers remain soft or semi-liquid until cured, they may require support structures or a special printing environment [27], similarly to conventional thermosets used for 3D printing [28].

3D printing technologies to produce TSEs can be divided into three groups: photopolymerization-based, two-phase systems, and material extrusion–based technologies (Fig. 2). Photopolymerization technologies are methods that use photosensitive resins and where crosslinking is triggered by light. In some methods, the resin is held in a container, such as in vat photopolymerization, stereolithography (SLA), or digital light processing (DLP) (Fig. 2/**a**). In another form of photopolymerization technique, the resin is deposited directly from a print head onto the build surface, where it is cured by light, similar to inkjet-based 3D printing or direct ink writing (DIW) (Fig. 2/**b**). In photopolymerization-based techniques, thermosetting elastomers can be used, such as UV-curable polyurethanes [29], silicone-based resins like UV-curable polydimethylsiloxane [30,31], acrylate-modified rubbers [32] and thiol-ene systems [33].

The second group includes systems that initiate crosslinking via the chemical reaction of two components. These can be tank-based processes (Fig. 2/**c**), in which the mixture is prepared during deposition, and in-line mixing systems, where the components are combined within the print head during printing (Fig. 2/**d**). For two-phase 3D printing systems, suitable base materials are addition-cured silicones [34], two-part polyurethanes [35], natural rubber (NR) compounds [36], and epoxy-based elastomeric systems [37].

The third category includes material extrusion–based methods, where the raw material is typically a partially crosslinked or curable elastomer in filament form (Fig. 2/**e**). Crosslinking is initiated by heat. It is applied either during extrusion or in a post-processing thermal treatment. This group also includes processes in which a laser is the heat source, directly curing the material as it is extruded from the print head. Several thermosetting elastomers are suitable as base materials, such as natural and synthetic rubbers [38], latexes [39], EPDMs [40], and recycled rubber compounds [41].

3.1. Photopolymerization-based technologies

The photopolymerization of thermosetting elastomers requires light (typically UV or visible) to initiate crosslinking in photosensitive resin systems. The light transforms liquid precursors into solid elastomeric networks. In photopolymerization, the photoinitiator absorbs light and produces reactive species such as free radicals or cations. These initiate polymerization by reacting with unsaturated groups in the resin (e.g. acrylates), leading to chain growth. During the reaction, the monomers form covalent bonds, resulting in a cross-linked network. In some cases, a post-curing step is used, which completes or enhances crosslinking and improves the performance of the final part.

Photosensitive resins are a class of materials that cross-link when exposed to light. Table 2 summarizes the main mechanical properties and part quality achieved with photopolymer-based 3D printing in the literature. Scott et al. [42] incorporated network precursors and a photoinitiator into the continuous aqueous phase of a latex emulsion. When exposed to UV light, these precursors undergo crosslinking and form a scaffold around the dispersed, high molecular weight latex particles, and create a free-standing "green body" hydrogel. As a result of subsequent drying and annealing, the latex particles diffuse and fuse together, producing a semi-interpenetrating polymer network (Fig. 3/**a**). Liu et al. [43] developed a concentrated pre-vulcanized natural rubber latex system through a multi-step process (Fig. 3/**b**). First, they produced the pre-vulcanized natural rubber latex by combining the concentrated natural rubber latex with a vulcanization system consisting of sulfur, an accelerator, and an activator. Then they added a stabilizer and a vulcanizing dispersant with mixing, and heated the system. After cooling, a stable pre-vulcanized latex with a solids content of 58 % was obtained. Superabsorbent polymer beads were gradually introduced and this way, a concentrated pre-vulcanized natural rubber latex was produced. This process allowed the precise control of the solids content of the latex. Wen et al. [44] invented a strategy to 3D print olefinic elastomers using light-curable latexes composed of potassium-neutralized sulfonated ethylene-propylene-diene monomer (K-sEPDM) particles. They used a formulation, in which they prepared a photocurable latex containing 20 wt% K-sEPDM particles by dissolving sodium dodecyl sulfate, N-vinylpyrrolidone (NVP), polyethylene glycol diacrylate (PEGDA575) and lithium cylphosphinate free radical photoinitiator (LAP) in water and then dispersing the K-sEPDM latex to form a homogeneous mixture. The reactive components, NVP and PEGDA575, served as scaffold precursors, while LAP initiated free radical photopolymerization under UV light (Fig. 3/**c**). Jin et al. [30] prepared UV-

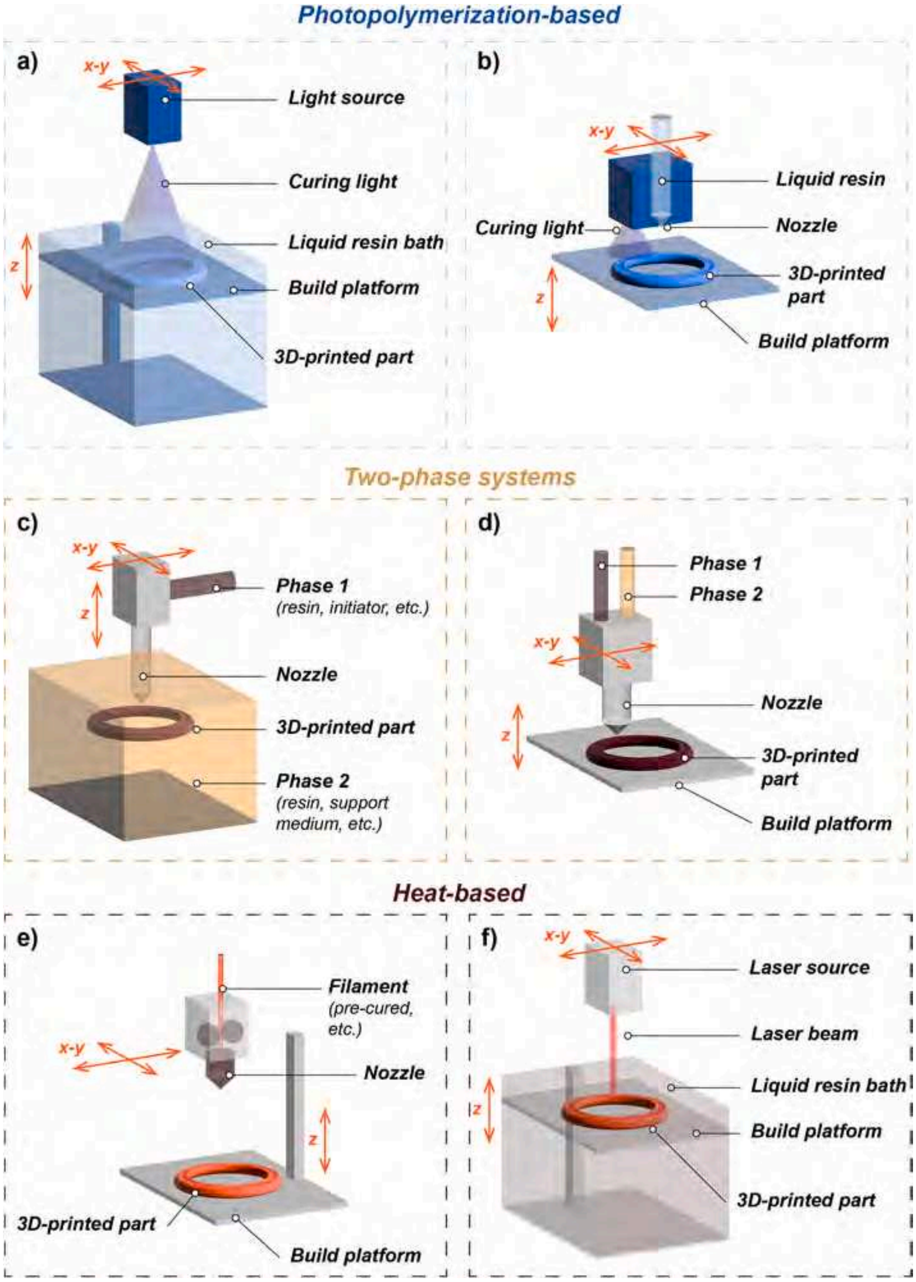


Fig. 2. Classification of 3D printing techniques for producing thermoset elastomers based on raw materials used and the crosslinking method applied: photopolymerization-based technologies (a) with liquid resin bath and (b) direct resin deposition; two-phase systems where (c) the mixture is prepared during deposition and (d) the mixture is combined in the print head, and heat-based technologies: (e) material extrusion, (f) laser-assisted curing techniques.

curable thermally conductive polysiloxane composites using mercaptopropyl-functionalized PDMS and tetravinyl cyclotetrasiloxane (V4) as reactive matrix. The use of V4 instead of conventional vinyl-terminated PDMS significantly reduced viscosity, allowing the use of high filler content (Fig. 3/**d**).

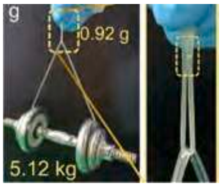
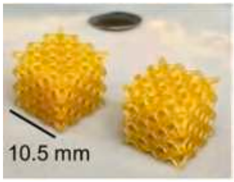
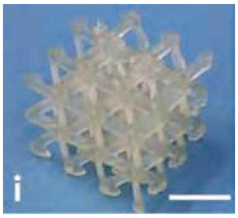
3.1.1. *Crosslinking in a liquid resin bath*

In resin bath or vat-based techniques, the liquid elastomer precursor is in a vat, and selective curing is initiated by targeted light exposure. Photopolymerization solidifies the material layer by layer to form the part. First, a photocurable elastomeric resin is produced, typically containing prepolymers/oligomers and photoinitiators, such as ethyl phenyl (2,4,6-trimethylbenzoyl)phosphinate (TPOL) or diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (BPO) [45]. A focused light source selectively illuminates specific areas of the resin. This triggers photo-initiated cross-linking and solidifies each layer. After each layer has solidified, the platform is gradually moved to allow fresh resin to flow over the previous layer, and the cycle is repeated until the entire part is formed. The finished part has to be rinsed to remove uncured resin. Additional post-curing can improve the mechanical properties of the final part.

Scott et al. [42] present an innovative approach to solve the problems of the vat photopolymerization (VP) of high molecular weight elastomers, particularly styrene-butadiene rubber (SBR) latex. The high viscosity of high molecular weight polymers limit their printability by VP. This study introduces a method that utilizes polymer lattices as colloidal dispersions, decoupling viscosity from molecular weight. This makes it possible to 3D print elastomers that were previously inaccessible to VP. The study also introduces a computer vision–based optimization system to compensate for light scattering during VP, which is a

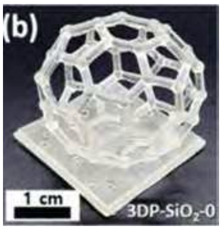
Table 2

Comparison of the mechanical (tensile) properties and the resolution for parts manufactured with photopolymer-based additive manufacturing (AM) technologies.

Base material	Technique	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Resolution / Sample	Ref.
Urethane-acrylate-based	Digital light processing	13.4 4.1 1.9	368 86.1 17.2	18 31 30		[45]
Styrene-butadiene rubber	Vat photopolymerization	2 4.5 5.1 5.2	– – – –	600 500 400 350		[42]
Polyurethane elastomer	Vat photopolymerization	4.23 5.42 8.94	– – –	259 409 450		[46]
Isoprene rubber	Digital light processing	0.9 0.78 0.32	2.1 1.5 0.8	42 54 42		[33]
Ethylene-propylene-diene monomer	Vat photopolymerization	4.3 7.6 7.8 8.2 10.5	2.6 6 6.3 8.3 16.2	534 453 365 315 100		[44]
UV curable elastomer	Digital light processing	7.5 7 6.3 3.5 1 1 0.5	7.5 4.5 3 2.5 2.5 2.5 2.5	1100 1000 950 870 520 430 240		[47]

(continued on next page)

Table 2 (*continued*)

Base material	Technique	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Resolution / Sample	Ref.
Polyether polyols	Digital light processing	6.5 5 4 4 3 2.9	– – – – – –	100 175 225 250 275 280		[48]
Natural rubber latex	Direct ink writing	24 24 26 25	– – – –	700 700 770 770		[43]
Polybutadiene rubber	Direct ink writing	0.5	–	390		[56]

common issue when colloidal systems are used (Fig. 4/**a**). By adjusting exposure times and projection intensities, the researchers were able to achieve highly accurate feature resolutions, demonstrating the successful fabrication of complex 3D geometries (Fig. 5/**a**). They produced tensile test specimens with elongation at break in excess of 500 % and a tensile strength of 9.7 MPa, making this method particularly suitable for creating elastomers with both high extensibility and mechanical strength. This study highlights the advantages of using latex-based VP to produce elastomeric materials. These materials have superior properties compared to traditional photopolymers, therefore functional elastomeric components can be produced for applications such as mold production, soft robotics, and wearable electronics.

Peng et al. [46] developed a vat photopolymerization printing method to fabricate self-healing stretchable elastomers (Fig. 4/**b**). They synthesized a photocurable oligomer containing dynamic hindered urea bonds to produce self-healing, and used nano-silica reinforcement to improve mechanical properties. Tensile strength and elongation at break increased by 73.7 % and 111.3 %, respectively. Scaffolds were successfully printed (Fig. 5/**b**), and after self-healing, the elastomer produced a tensile strength of 5.44 MPa and 372 % elongation, surpassing typical VP-printed self-healing materials. Strohmeier et al. [33] applied digital light processing (DLP) for the 3D printing of modified liquid isoprene rubber, utilizing thiol-click chemistry as a novel approach to crosslink diene rubbers (Fig. 4/**c**). Methacrylate-functionalized liquid isoprene rubber served as the base material, while divinyl ethers acted as reactive diluents to lower viscosity and enhance the photo-reactivity essential for DLP. Thiol-click chemistry was employed to crosslink the unsaturated carbon double bonds in the isoprene units. The addition of stabilizers, such as pyrogallol, helped prevent premature crosslinking, ensuring that the material was successfully printed without premature gelation. The authors were able to reduce the viscosity of the rubber formulations to a range between 1 and 6 Pa • s, which is suitable for DLP printing. Tensile tests showed reduced elongation at break and strength, which can be attributed to low molecular weight and lack of chain entanglements in the liquid rubber. Nevertheless, the printed objects demonstrated satisfactory flexibility and good structural precision, with high-resolution features as small as 0.5 mm (Fig. 5/**c**).

Wen et al. [44] developed a novel approach for 3D printing ethylene-propylene-diene monomer (EPDM) rubber using vat photopolymerization. By neutralizing sulfonated EPDM with potassium hydroxide, they created a stable latex (K-sEPDM), which allowed the formation of an interpenetrating polymer network (IPN) upon photopolymerization. Their elastomers had tunable elastomeric properties and excellent thermal recoverability, and high-resolution printing was possible with controllable isotropic shrinkage. The elongation at break and the tensile strength of the 3D-printed elastomers ranged from 304 to 490 %, and 7.1 to 8.5 MPa, respectively. Patel et al. [47] present a series of highly stretchable UV-curable elastomers tailored for DLP-based 3D printing. They produced these elastomers by blending aliphatic monofunctional acrylate (Ebecryl 113, Allnex, EAA) and radiation-curable resin oligomer (Ebecryl 8413, Allnex, AUD) in different proportions. The resulting materials had elongation at break of up to 1100 %, far exceeding that of commercially available UV-curable elastomers. Silver nanoparticle coating ensured electrical conductivity (Fig. 5/**d**). Jeong et al. [48] produced light-curable elastomers enhanced with crosslinking silicon dioxide (SiO_2) nanoparticles for 3D printing by DLP. The incorporation of well-dispersed, surface-modified SiO_2 nanoparticles up to 20 wt% significantly increased tensile strength and hardness. 20 wt% nanoparticles resulted in a tensile strength increase of 87 % and a hardness increase of 52 %, without any degradation in print quality. The resulting 3D-printed structures had excellent flexibility and mechanical durability.

3.1.2. *Direct resin deposition*

In direct resin deposition 3D printing, the elastomer resin is not held in a container but is fed directly from the print head to the print surface, where it is selectively cured by light. During the printing process, the resin is delivered by the print head to precisely defined locations, and the local light effect triggers photopolymerization. Once the entire geometry is deposited and cured, the printed part typically requires no post-processing, but additional UV or heat treatment may be applied to improve mechanical properties and the completeness of crosslinking [49,50].

Inkjet printing (IP) is a fluid-based technique that works by depositing tiny droplets of liquid onto a substrate. Once the droplets are in place, the solvent evaporates, leaving behind a solid pattern, or alter-

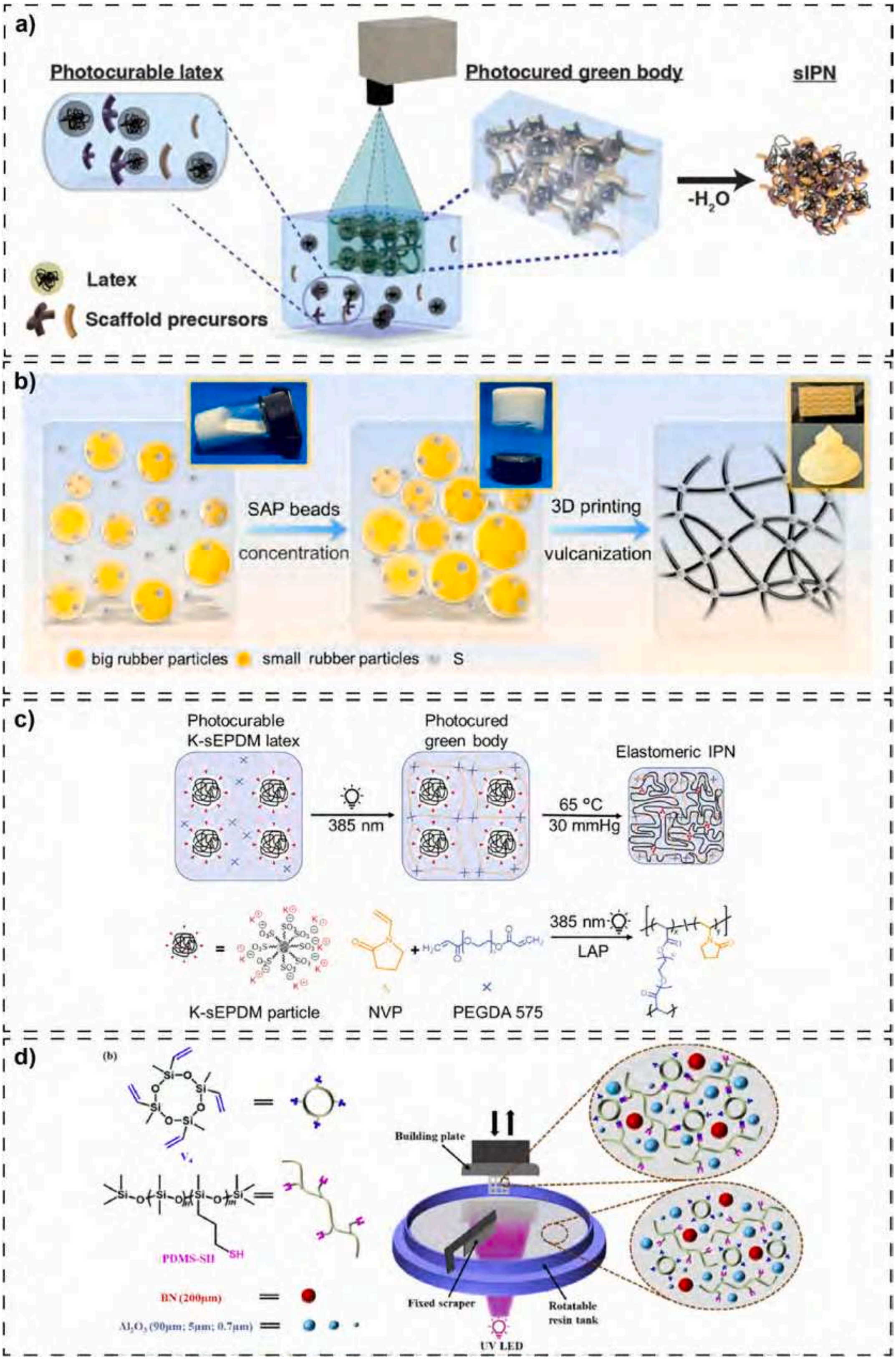


Fig. 3. Various mechanisms of photopolymerization on a molecular scale a) Crosslinking of molecules in the continuous phase of latex locks the polymer particles into a solid green body [42], b) Preparation of pre-vulcanized natural rubber latex [43], c) Chemical composition of light-curing latexes with water-soluble skeletal precursors [44], d) Schematic diagram of UV photopolymerization of polysiloxane composites [30]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

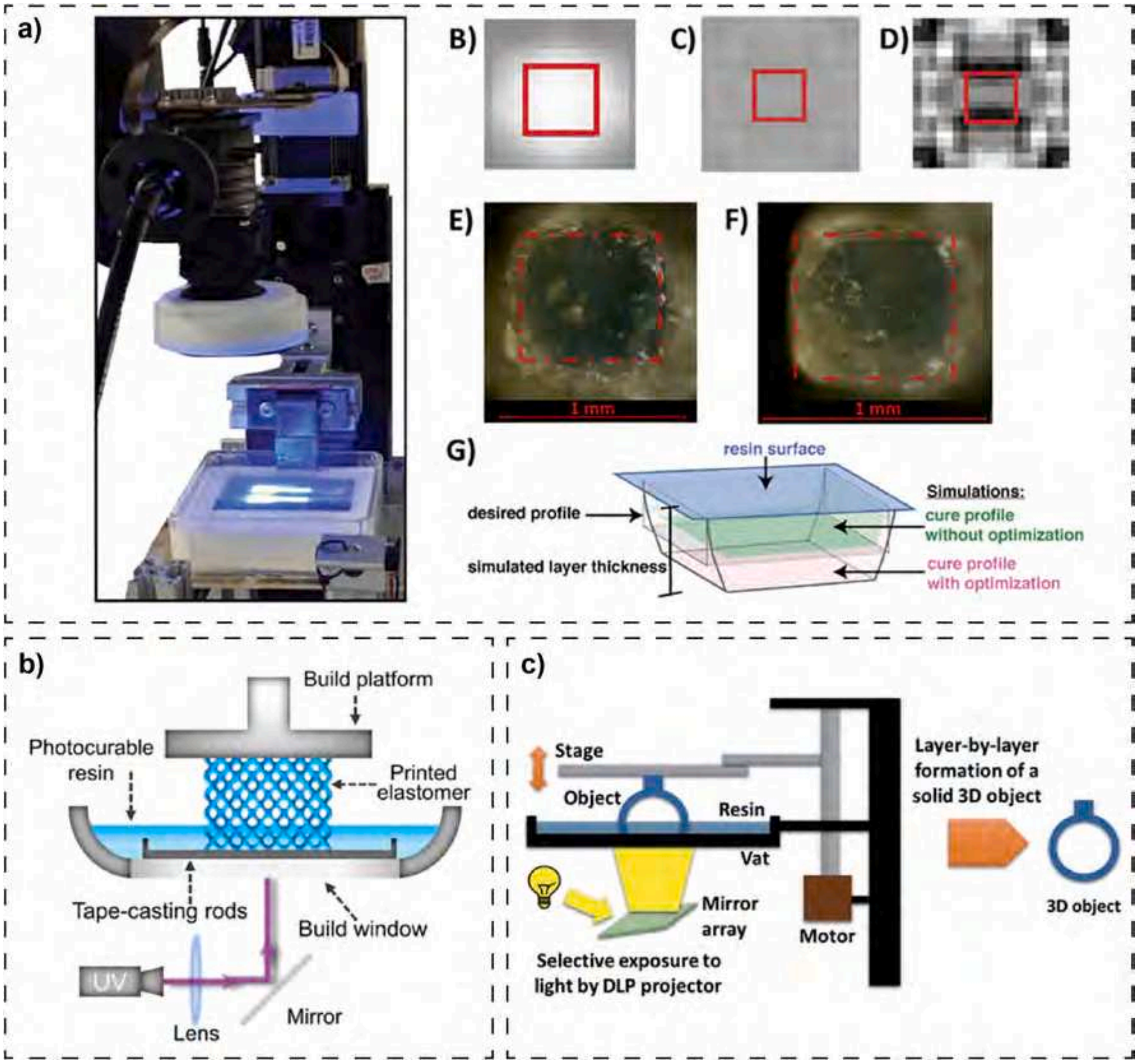


Fig. 4. Photopolymerization-based technologies a) Scanning mask projection vat photopolymerization: clear resin scatters less UV light while heterogeneous resins scatter more UV light; dimensional accuracy [42], b) Schematics of bottom-up vat photopolymerization where the crosslinking is initiated with focused UV light [46], c) Schematics of digital light processing (DLP) 3D printing method where the photocurable resin is exposed selectively to light by a DLP projector [33].

natively, UV curing is used to solidify the liquid [51]. For traditional inkjet printers to function effectively, the inks must have low viscosity, typically ranging from 0.5 to 40 mPa • s, and surface tension between 20 and 70 mN/m. These factors ensure stable droplet formation. The lateral resolution of inkjet printing typically ranges from 20 μm to 70 μm, with layer thicknesses between 100 nm and 1 μm [52]. Recent advancements in jetting printheads have made it possible to print with high-viscosity inks (up to 100,000 mPa • s). This improvement significantly broadens the range of materials that can be printed and enhances the potential applications of inkjet technology in various industries [53]. Tu and Sodano [54] studied direct ink writing, where they developed a UV–thermal dual-curing DIW method to process vinyl ester (Fig. 6/**a**).

Liu and Ma [55] successfully formulated a fast-curing liquid silicone rubber using polydimethylsiloxanes with a thiol-ene click reaction for DIW 3D printing (Fig. 6/**b**). Polytetrafluoroethylene (PTFE) was also added to tailor the yield strength of the inks. Their direct ink writing method enabled in-situ curing, which significantly improved formability and dimensional stability compared to post-print curing (Fig. 7/**b**).

Liu et al. [43] developed a concentrated pre-vulcanized natural rubber latex ink with a high solid content of 73 % using superabsorbent polymer (SAP) beads to enhance its rheological properties for Direct Ink Writing (DIW) 3D printing. This approach improved colloidal stability and printability (Fig. 7/**a**). Their findings showed that the mechanical properties of printed specimens were highly dependent on the printing angle, with 90°-oriented samples achieving a tensile strength of 26 MPa and a strain of approximately 800 %, outperforming most 3D-printed rubber latex materials.

Bragaglia et al. [56] developed a photo-induced thiol-ene crosslinking method for the 3D printing of polybutadiene rubber, with the goal of reproducing the high elasticity and elongation of vulcanized diene rubber. By using trimethylolpropane tris(3-mercaptopropionate) as a crosslinking agent, they achieved rapid, solvent-free vulcanization with low energy consumption. A unique UV curing system allowed layer-by-layer deposition with partial curing, followed by post-curing. The printed samples showed strong interlayer adhesion, and mechanical properties similar to traditionally vulcanized elastomers.

3.2. Two-phase systems

In two-phase system–based 3D printing, crosslinking is triggered by the chemical reaction of two reactive components. Depending on the arrangement, the components are either mixed in a tank immediately at deposition or mixed directly in the print head (in-line mixing systems) during the printing process. After mixing, the reactive ink is extruded layer by layer onto the building platform and crosslinking begins on site during the chemical reaction. After deposition, the part may be post-

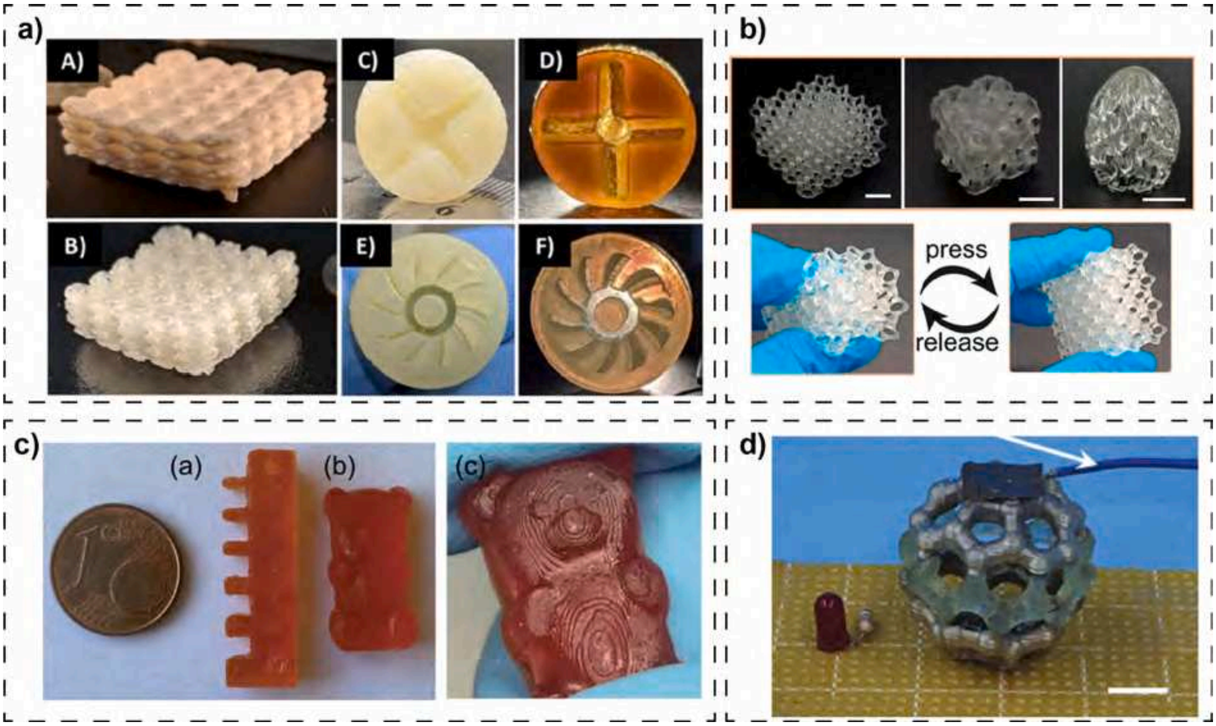


Fig. 5. Parts manufactured with photopolymerization-based methods: a) latex lattices and molds: A) shows a green body, B) shows the part after curing, and C-F) shows 3D-printed casting molds [42], b) polyurethane elastomer scaffolds: different geometries (up) and the parts ability to reversible deformation (down) [46], c) small 3D-printed parts made with tri(ethylene glycol) divinylether (comb and bear) [33], d) stretchable UV-curable elastomer ball coated with silver nanoparticles [47]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cured, typically with heat. The elastomer reaches complete cross-linking and its final mechanical and thermal properties during post-curing. Table 3 presents the main mechanical properties of parts manufactured with two-phase systems.

3.2.1. *Phases mixed after deposition*

Chansoda et al. [36] developed a support medium for the 3D printing of natural rubber (NR) latex using direct ink writing (DIW) within a support bath (Fig. 8). Traditional extrusion-based 3D printing of natural rubber is limited by the lack of structural support during printing. To overcome this, the authors developed a support medium to preserve the shape and stability of NR latex throughout the process. The study introduces a blend of triethanolamine (TEA), alcohol, water, and Carbopol 940, a crosslinked polyacrylic acid polymer, as the support medium. The results proved that the support medium effectively supported the natural rubber during printing, preventing sagging and ensuring dimensional accuracy. However, the mechanical properties of 3D-printed NR were found to be inferior to those of molded rubber due to differences in layer-by-layer curing versus simultaneous curing in molding. The research highlights that vulcanization and layer integrity remain critical to producing high-quality 3D-printed rubber products. Davoodi et al. [57] developed a template-based 3D printing approach for the fabrication of porous silicon structures. Using extrusion-printed sacrificial molds based on triple periodic minimum surface areas, they molded and cured silicone prepolymers capable of controlled volumetric shrinkage (~70 %) when treated with a solvent, reaching pore sizes of 500–600 μm. The resulting scaffolds exhibited excellent compressive stress recovery.

3.2.2. *Phases mixed in the print head*

Direct Ink Writing (DIW) is a flexible additive manufacturing method that extrudes materials through a nozzle. DIW is especially promising for printing elastomeric materials. Recent advancements have focused on the DIW printing of silicone-based elastomers [58]. Silicone elastomers are frequently used due to their biocompatibility, flexibility, and stability. The use of fast-curing room temperature–vulcanizing (RTV) silicone elastomers in DIW allows for the creation of highly stretchable and durable structures. Fast-curing materials not only ensure strong layer adhesion but also maintain structural integrity during printing, avoiding collapse or deformation before the material fully solidifies [59,60].

Additionally, recent advancements in multi-material DIW systems have enabled the creation of complex, graded elastomeric structures. These systems enable the printing of objects with varying mechanical properties within a single structure, which is beneficial for applications such as soft actuators and flexible electronics. Multi-material DIW systems can integrate active mixers or voxelated printing heads to combine different elastomeric inks in a single print, producing structures with tailored elasticity and functionality [58,61].

Li et al. [61] produced silicone parts with by DIW. Printing parameters were optimized for layer height and print speed according to the shear-thinning behavior of the material. The authors produced bionic artificial muscle actuators (Fig. 9**/a**) and soft robotic grippers with the method.

Kamath and Choi [62] have demonstrated the feasibility of using synthetic rubber inks by DIW as a cost-effective alternative to conventional high-pressure, high-temperature rubber processing. Their study demonstrates that properly setting printing parameters and incorporating additives such as carbon black or ground tire rubber can improve the mechanical properties of printed parts to match those of commercial tire treads (Fig. 9**/b**).

Shen et al. [63] 3D printed butyl rubber (BR). Neat BR has low green strength—the material’s ability to hold its shape before curing—so it is unsuitable for DIW or other common additive manufacturing techniques. To overcome these challenges, the authors developed a solvent-assisted DIW method to print BR (Fig. 9**/c**) successfully. The ink formulation had BR dispersed in toluene and nano clay to improve rheological properties. The used post-printing crosslinking with sulfur monochloride, which effectively crosslinked the isoprene units in BR

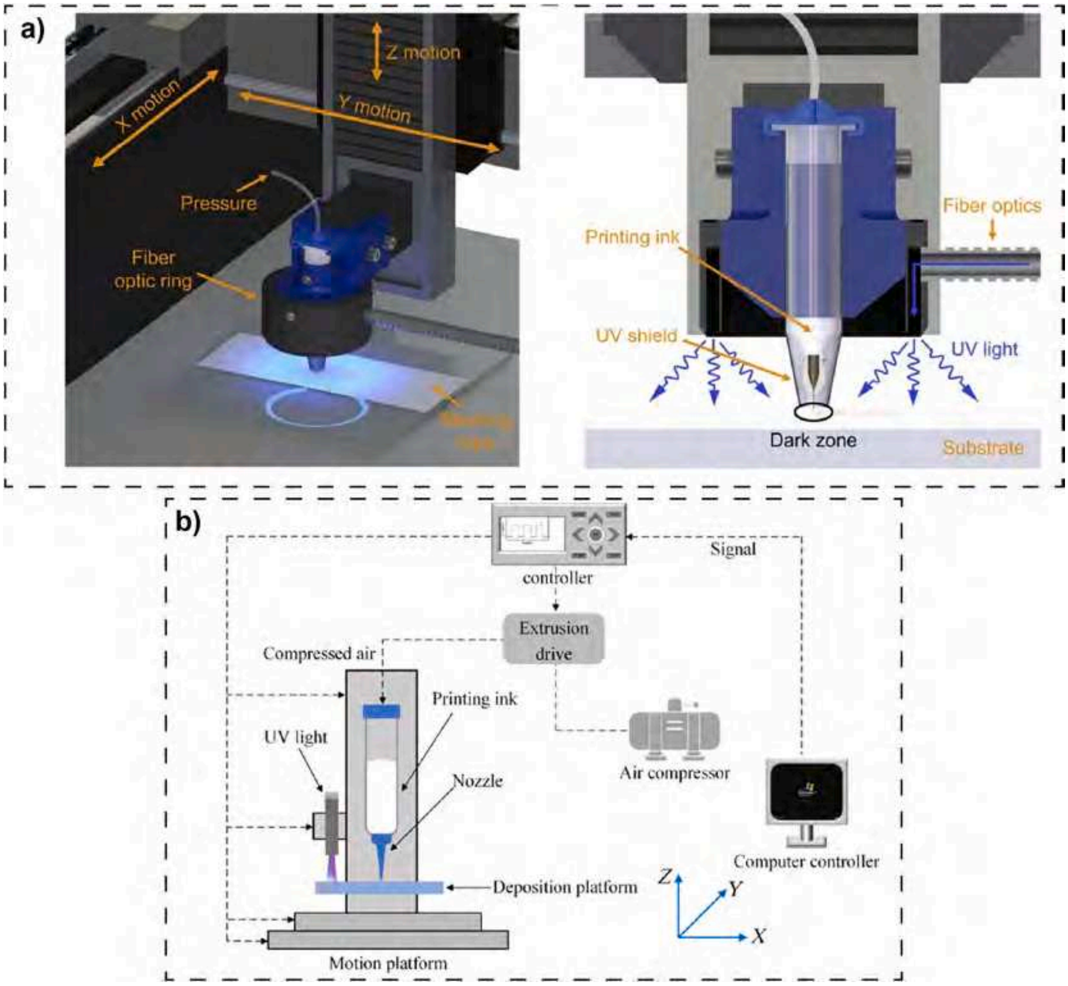


Fig. 6. Photopolymerization-based methods using direct resin deposition a) equipment (left) and print head (right) of the UV-assisted direct ink writing (DIW) method, where resin is dispensed from a syringe in a pressure-controlled manner and cross-linking is achieved by local UV exposure. In order to avoid cross-linking in the nozzle, the nozzle is insulated with a UV protective shield. [54], b) Schematics of a complete UV-follow curing DIW system, where the material flow is controlled with compressed air. [55].

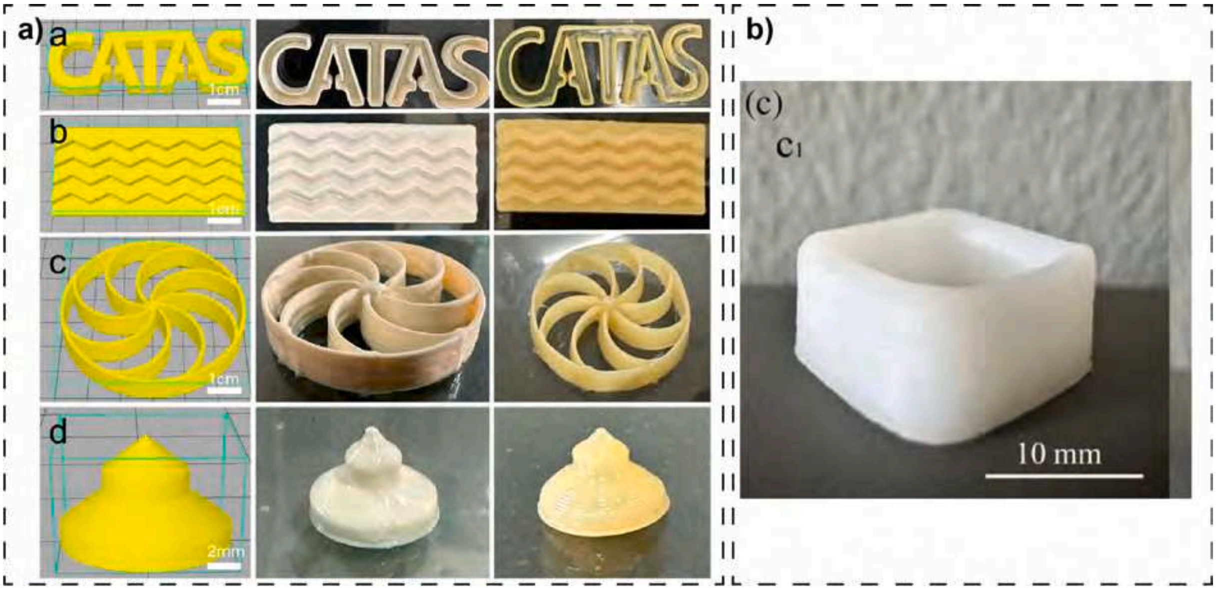
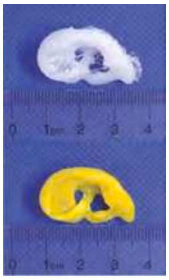
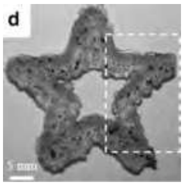


Fig. 7. Parts manufactured with photopolymerization-based direct resin deposition methods a) pre-vulcanized natural rubber latex parts before (left) and after (right) vulcanization [43], b) cured silicone + 30 w% polytetrafluoroethylene box [55].

Table 3
Comparison of the mechanical (tensile) properties and the resolution for parts manufactured with two-phase system AM technologies.

Base material	Technique	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Resolution / Sample	Ref.
Natural rubber latex	Direct ink writing	1.5 4 4.1	– – –	290 750 990		[36]
Butyl rubber	Direct ink writing	0.1 4 4.5	– – –	900 850 750		[63]
Silicone elastomer	Direct ink writing	0.57	0.017	1859		[60]
Biodegradable elastomer	Material extrusion Vat photopolymerization	0.4 0.25	– –	45 40		[65]
Liquid latex Liquid latex and end of life rubber	Direct ink writing Direct ink writing	7.9 7.5 7.7 5.4	2.7 2.1 2.4 2.5	75.1 51.5 48.5 48.1		[66]

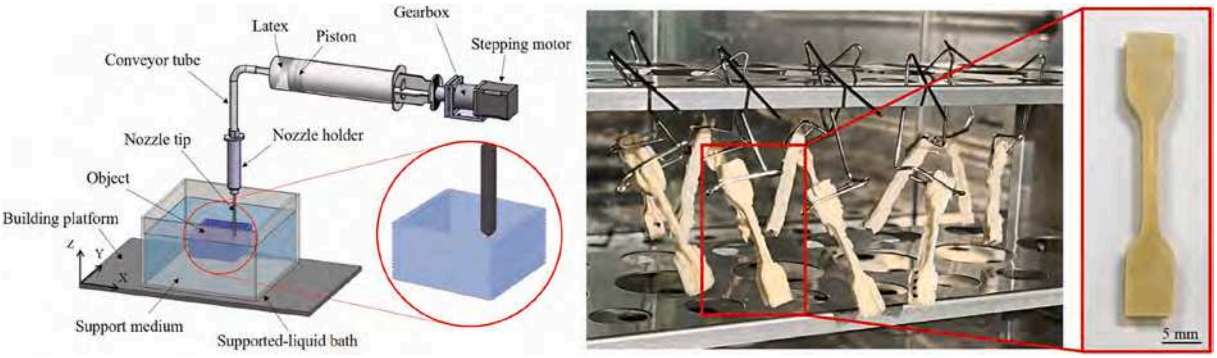


Fig. 8. Two-phase method where the phases mix after deposition: schematics of liquid-supported 3D printing (left) and natural rubber latex samples (right) [36].

without distorting the printed structure. This crosslinking technique made the high temperatures usually needed in the vulcanization of traditional BR unnecessary. The results showed that 10 wt% nano clay significantly improved the storage modulus of the BR ink, enabling stable 3D printing. Moreover, the study showed that the printed structures maintained their integrity after crosslinking, and the crosslinked objects had minimal shrinkage and improved thermal stability. Gharaie et al. [60] developed custom static mixers for the DIW 3D printing of two-component silicones. Compared to molded samples, the 3D-printed silicone showed higher elongation at break. The authors successfully used the method for soft actuators and showed that it can be used to print complex structures with cavities, such as a model of a human heart (Fig. 9/**d**).

Luis et al. [64] presented a study on a directly 3D-printable silicone

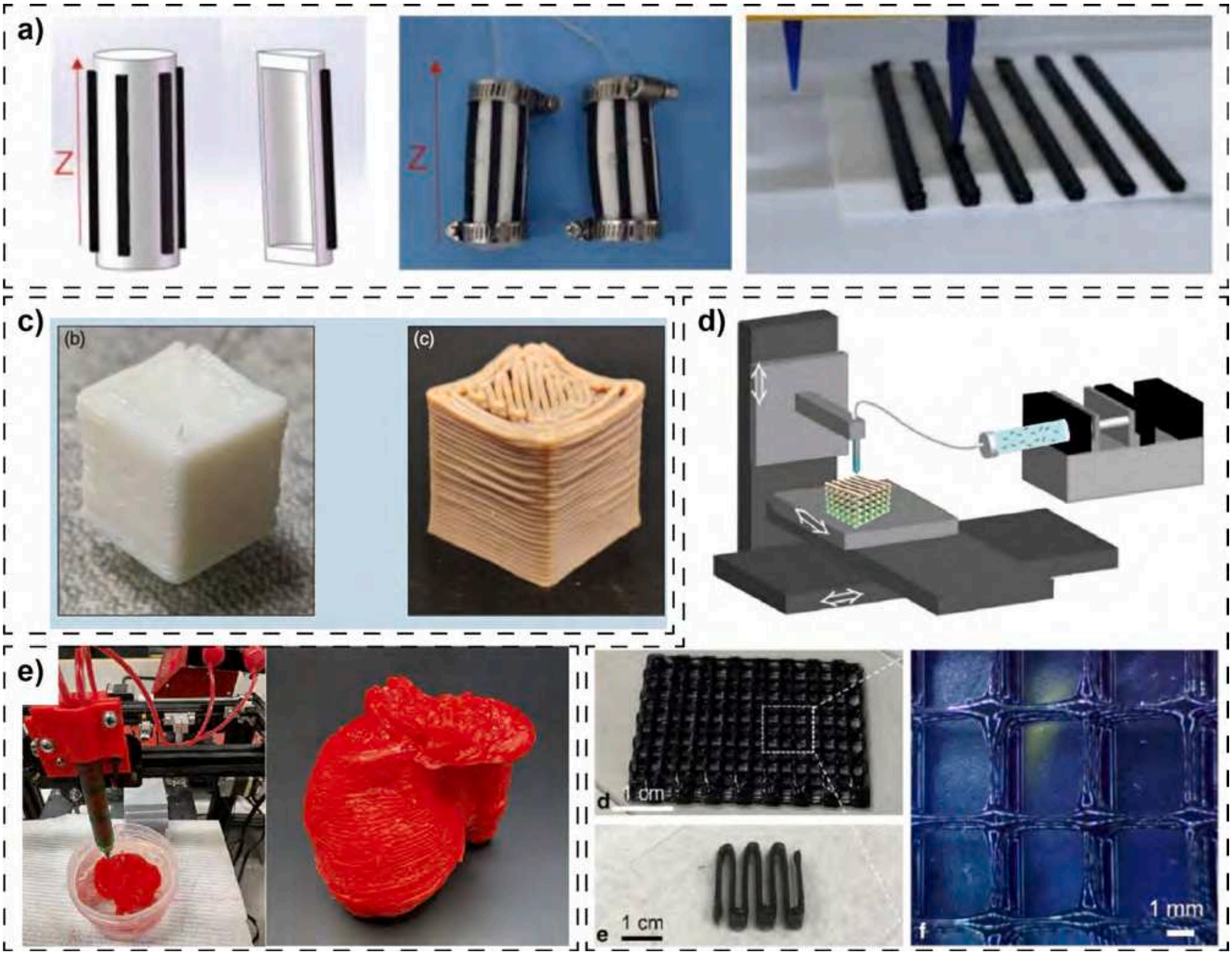


Fig. 9. In-line mixing equipment and parts a) silicone artificial muscle virtual model, printed parts and the 3D-printing process (from left to right) [61] b) styrene-butadiene rubber cube before (left) and after (right) vulcanization [62] c) schematic for solvent-assisted 3D printing of butyl rubber (up) and butyl rubber + 10 wt% nanoclay composite scaffold [63], d) static mixer 3D printer head (left) and silicone human heart-shaped part (right) [60].

meniscus implant that is cytocompatible, mechanically robust and resistant to cyclic loading. Using a custom 3D printer, they demonstrated that the printing process does not alter the chemical, thermal or mechanical properties of the silicone material. Akman et al. [65] presented the first report on the 3D printing of acrylated poly(glycerol-dodecanedioate) (APGD), a biodegradable shape memory polymer designed for minimally invasive biomedical implants. APGD resins were tailored for both material extrusion (MEX) and vat photopolymerization (VP) printing, with results showing that VP produced higher quality, more complex structures with superior mechanical properties and shape fixity compared to MEX.

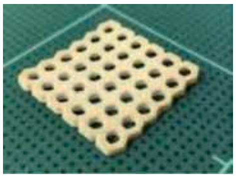
Quetzeri-Santiago et al. [66] introduced a novel approach to additive manufacturing of liquid latex and recycled micronized rubber powder (MRP) derived from end-of-life tires. They applied drop-on-demand inkjet printing and successfully printed multilayer objects. The inclusion of MRP in the latex formulations, at concentrations up to 10 wt%, did not significantly alter the stiffness of the cured latex. However, the addition of MRP reduced the maximum elongation of the material from 750 % to 430 %. Challenges such as nozzle clogging due to particle aggregation and slow drying times were noted.

3.3. Heat-based systems

Heat-based systems are processes where cross-linking is induced by thermal energy, including laser-assisted methods and extrusion-based techniques. Material extrusion-based systems work by depositing the building polymer (and optionally a support material) directly to a tray from a nozzle after a pretreatment process, such as heating it to a liquid state [67]. Due to its simplicity and low cost, MEX has become the most popular 3D printing method for TPEs. For a TPE material, the model and support materials are heated to a molten state before they are extruded through a nozzle. Once deposited, the material cools and solidifies, forming a firm layer that is stacked on top of the previous one according to the design. MEX processing of TSE materials usually uses a liquid phase and crosslinking at different points in the process. The main question for MEX-based processing of TSE materials is at which stage of the process crosslinking occurs. Table 4 shows a summary of the mechanical properties of parts manufactured with heat-based systems.

Chansoda et al. [39] modified a Cartesian MEX 3D printer by placing a syringe and a laser beam on the print head (Fig. 10/**a**). They dispensed a natural rubber latex compound (containing a sulfur-based vulcanization system) through the syringe nozzle while using the laser beam for real-time crosslinking. As a case study, they manufactured a shoe insole with the 3D printing method they developed. But in this case, they also applied a post-processing heat treatment at 80 °C in a hot air oven for 4 h. Wittek et al. [68] presented a process based on material extrusion printing of a conventional rubber compound. The printed, not yet cross-linked rubber compound was supported by a simultaneously printed thermoplastic polymeric supporting material (Fig. 10/**b**). The printed product was crosslinked in an autoclave, and then the support material

Table 4
Comparison of the mechanical (tensile) properties and the resolution for parts manufactured with heat-based AM technologies.

Base material	Technique	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Resolution / Sample	Ref.
Natural rubber latex	Laser	14 9.5 7	– – –	1600 1450 1400	 10 mm	[39]
Natural rubber latex	Laser	17.1	0.69	757		[69]
Fluoro-elastomer rubber	Material extrusion	1.4 1.4 2.1 1.6 1.9 1.6	– – – – – –	167 155 216 209 183 154	 10 mm 20°	[38]

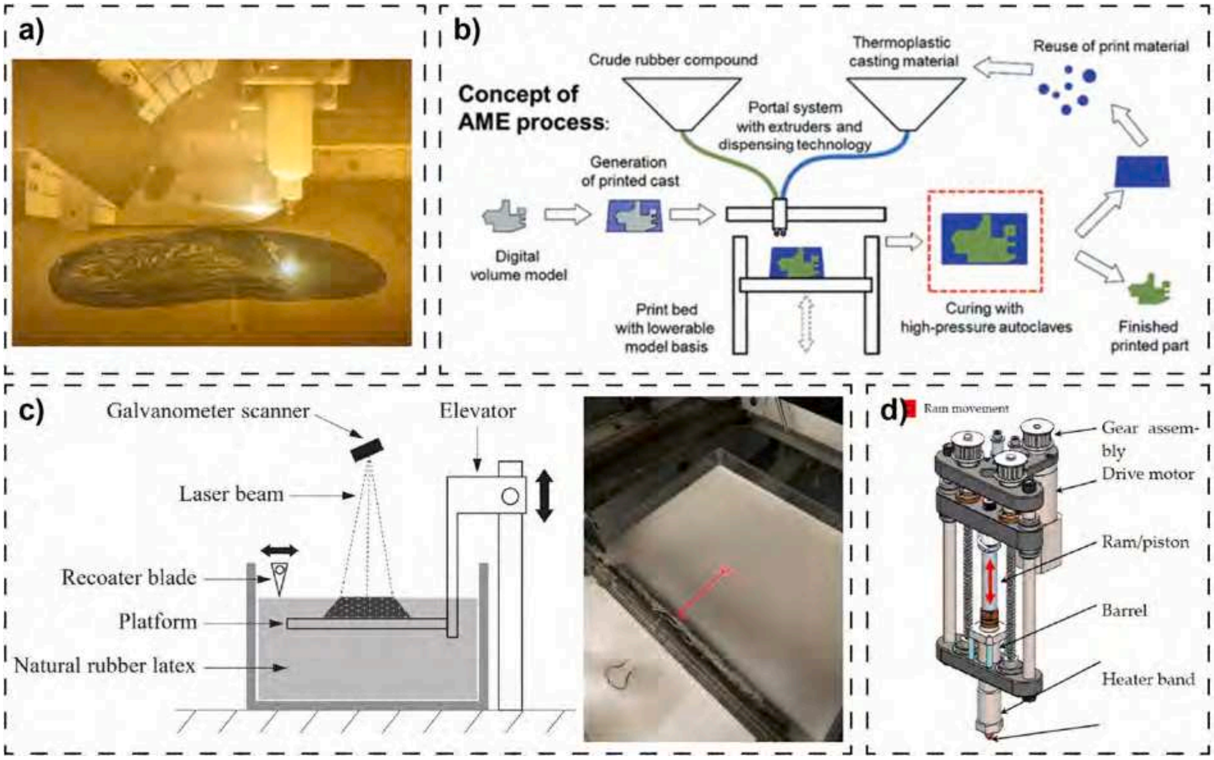


Fig. 10. Methods for heat-based 3D printing a) laser-assisted material extrusion equipment during the manufacture of a shoe sole [39] b) schematic for dual material extrusion where the crude rubber and a thermoplastic casting material are dispersed selectively, then the part is cured under high pressure in autoclave, which is followed by the removal of the reusable casting material [68] c) schematic of the laser-assisted vat method (left) and during the process (right) where natural rubber latex is selectively exposed to laser beam to locally induce crosslinking [69] d) schematic of ram extruder head which applies pressure to extrude the high-viscosity printing material [38].

was removed. Srisawadi et al. [69] investigated the application of stereolithography (SLA) to the 3D printing of NR (Fig. 10/**c**). Sulfur and other additives were added to the pre-vulcanized latex, followed by dilution, which set total solid content to 50 %. They used laser irradiation to selectively solidify layers of latex to form 3D parts. They claim that the parts processed (Fig. 11/**d**) with their technique have strength flexibility comparable to TSE manufactured with conventional processes. Periyasamamy et al. [38] investigated the use of a perfluoropolyether plasticizer to modify the viscosity and improve the 3D printability of fluoroelastomer rubber compounds. The authors used a custom ram extruder head to achieve high pressure for material deposition (Fig. 10/**d**). The plasticizer reduced viscosity and post-print

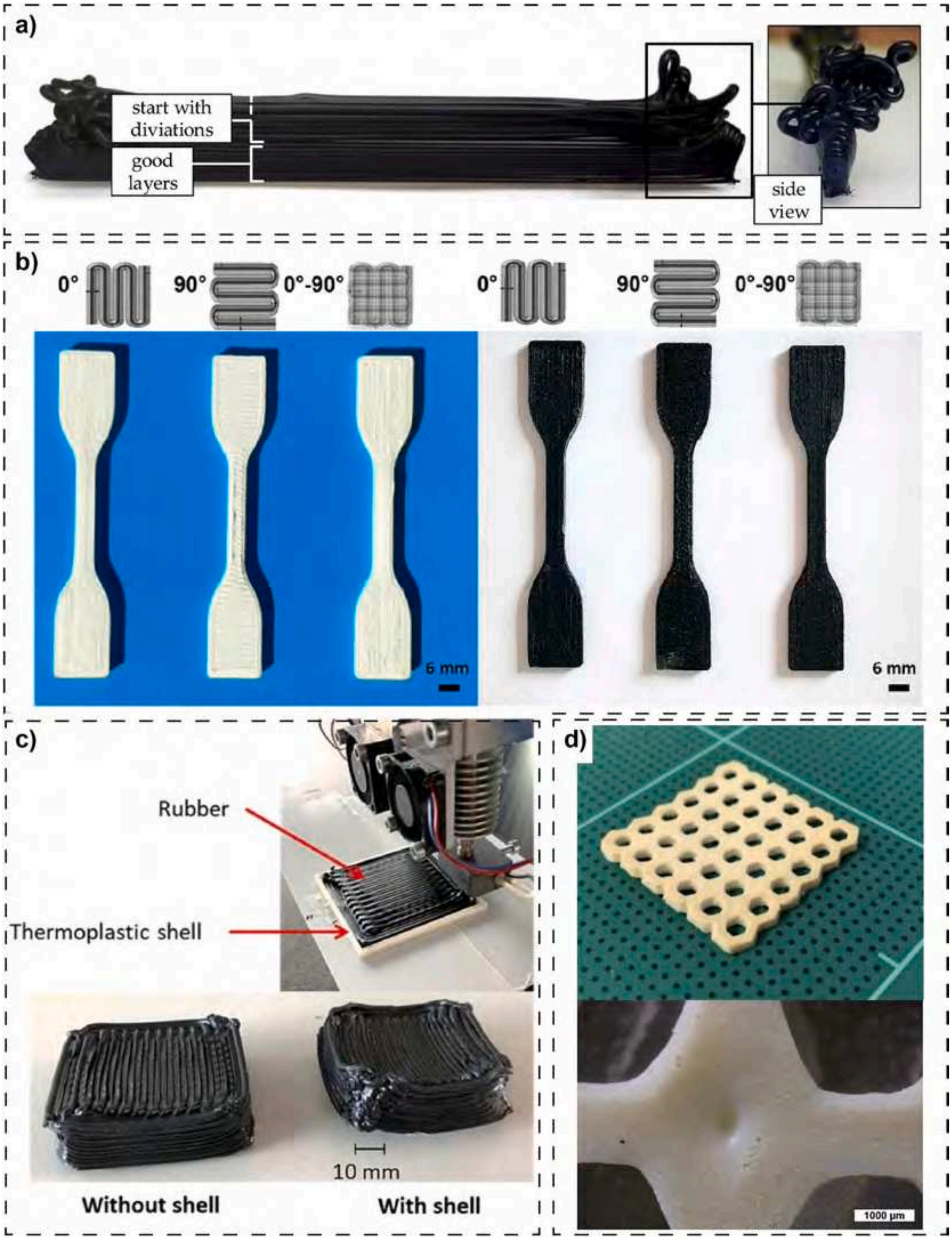


Fig. 11. Parts manufactured with heat-based methods a) layer adhesion problems in nitrile-butadiene rubber (NBR) samples prepared by material extrusion [71], b) thermoplastic polyurethane (left) and thermoplastic polyurethane–waste tire rubber composite parts (right) [41] c) carbon black–filled natural rubber parts [72], d) natural rubber latex scaffold [69].

shrinkage while it improved interlayer adhesion, although it slightly reduced overall modulus. The study also investigated various additive manufacturing strategies for prototyping seals. They found that thermoplastic mounts and a hybrid AM–soft tooling approach significantly improved part quality and dimensional control.

Sundermann [70] further developed the concept and used a unidirectional rotating twin-screw extruder to feed the rubber compound, which made the rubber compound more stable. A major limitation of this technique was that the movement of the extruder head was difficult to control, mainly due to its relatively high mass.

Drossel et al. [71] modified a MEX 3D printer with a screw extruder to process natural rubber (NR), nitrile-butadiene rubber (NBR), and ethylene propylene diene monomer (EPDM). One of the major problems with the method was the printing quality at the reversal point of the double strands (Fig. 11/**a**). Badini et al. [41] studied the mechanical properties, printing parameters of material extrusion, and potential applications of filaments of thermoplastic polyurethane (TPU) and 20 wt % ground tire rubber (GTR) TPU/GTR. They studied the effect of GTR on printability and mechanical properties: dogbone specimens were printed at three different raster angles and at three different nozzle temperatures (Fig. 11/**b**). The GTR content improved mechanical properties and reduced the hysteresis slightly compared to the virgin TPU. However, raster angles and nozzle temperature did not significantly influence the obtained results.

Leineweber et al. [72] printed NR-based rubber plates with an extruder temperature of 100 °C and a distance of 0.9 mm between the nozzle and the printing bed, and then vulcanized them in an autoclave at 150 °C and 7 bar for 15 min. They concluded that the additively produced samples can have similar mechanical properties to the conventionally produced samples (Fig. 11/**c**).

4. Applications and challenges

Due to their exceptional flexibility, elongation at break, and durability, 3D-printed crosslinked elastomers can be used in a wide range of industries. Table 5 compares the 3D printing methods (photopolymerisation-based, two-phase systems and material extrusion-based) in terms of strengths, challenges and overall mechanical properties based on the average of the literature data presented earlier. The two main strengths of photopolymerization-based processes are the wide range of materials, and good resolution. Its ability to produce intricate details makes it ideal for prototypes and small-scale production, though it faces challenges related to limited build size and the necessity of post-processing due to the support structures required. In addition, concerns about potentially harmful materials further limit its wider application.

Two-phase systems, especially silicon-based 3D printing, are gaining increasing attention in applications requiring soft, flexible parts. These systems allow tunable hardness and multi-material printing, but problems such as poor interfacial bonding, limited print speed and difficulties in achieving optimal rheological behaviour are significant obstacles. In addition, support structures are still required for complex designs.

3D printing based on material extrusion is cost-effective and easy to scale compared to other methods. However, its shortcomings include poor interfacial bonding, low dimensional accuracy and high viscosity challenges that affect printability. Post-processing steps such as vulcanisation are often required to achieve the desired mechanical properties.

Table 5
Comparative analysis of the 3D printing methods for crosslinked elastomers. The mechanical properties are derived from data presented in Section 3.

3D printing method	Strengths	Challenges/ limitations	Mechanical performance
Photopolymerization-based	*• High resolution* *• Material versatility*	*• Post-processing is required due to the support system for complex geometries* *• Limited build size* *• Possibly harmful materials*	*• Tensile strength: 0.3–26 MPa* *• Elongation at break: 100–1000 %*
Two-phase systems	*• Silicone-based materials* *• Tunable hardness* *• Multi-material 3D printing*	*• Achieving optimal rheological behavior* *• Need of support for complex geometries* *• Limited printing speed* *• Poor interfacial bonding*	*• Tensile strength: 0.1–8 MPa* *• Elongation at break: 50–1000 %*
Material extrusion-based	*• Cost-effective equipment* *• Possibility of integration with other manufacturing techniques* *• Possibility to use recycled materials*	*• Poor interfacial bonding* *• Poor printability due to high viscosity* *• Low dimensional accuracy* *• Post-processing is required for vulcanization*	*• Tensile strength: 1–17 MPa* *• Elongation at break: 150–1500 %*

4.1. *Implants and biomedical devices*

If produced from biocompatible materials, 3D-printed elastomers can be ideal for biomedical applications, including prostheses, implants, and tissue engineering scaffolds. Their flexibility closely mimics the mechanical behavior of soft biological tissues, making them particularly suitable for use in artificial ligaments and wearable medical devices. The customization capabilities of additive manufacturing also allow the creation of patient-specific designs, significantly improving the fit, comfort, and functionality of medical wearables and prostheses. Peng et al. [46] produced wearable sensors from transparent, self-healing polyurethane using vat photopolymerization technique (Fig. 12/**a**). The 3D-printed material was found to be applicable as a substrate for strain/pressure sensors, and the resin was formulated for conventional photopolymerization-based 3D printing platforms, therefore it can be integrated into existing systems without specialized hardware. Bachtiar et al. [73] investigated the mechanical behavior of 3D-printed thermoplastic polyurethane (TPU) for potential use in biomedical devices. The study highlights that, with proper optimization, TPU structures exhibit flexibility and strength suitable for applications like prosthetics, soft tissue implants, and wearable medical devices (Fig. 12/**b**). Abdollahi et al. [74] fabricated patient-specific polydimethylsiloxane (PDMS) elastomer cuffs for wearable pulse oximeters (Fig. 12/**c**). By printing liquid PDMS within a sacrificial hydrogel bath, they achieved anatomically tailored geometries with high dimensional accuracy. The resulting wearable device effectively measured heart rate, blood oxygenation, and pressure signals in real time, performing on par with commercial pulse oximeters. Guo et al. [75] developed a conductive, recyclable composite based on dynamic covalently cross-linked elastomers and hierarchical hybrid nanofillers for use in wearable electronics. The material demonstrated excellent mechanical strength, environmental stability, and recyclability, retaining high toughness after multiple recycling cycles. Using direct 3D printing, the authors successfully fabricated functional devices, including a triboelectric nanogenerator and a capacitive pressure sensor (Fig. 12/**d**).

4.2. *Soft robotics*

Due to their durability and fatigue resistance, crosslinked elastomers are suited for long-term use in dynamic environments. In the field of robotics, 3D-printed elastomers are particularly valuable due to their high flexibility and elastic recovery, therefore they can function as soft actuators, robot skins, and grippers that can undergo repeated deformation without permanent damage [76,77]. The successful manufacture and testing of robot grippers has been featured in several articles including Patel et al. [47] (Fig. 13/**a**), Yirmibesoglu et al. [78] (Fig. 13/**b**) and Gomez et al. [76] (Fig. 13/**c**). These grippers exploit the flexibility and adaptability of elastomers to securely grip and move objects of various shapes, sizes and fragility. Zhu et al. [79] developed an insect-scale ultrafast soft robot capable of moving at ~4 body lengths per second, fabricated by multimaterial coaxial 3D printing (Fig. 13/**d**). The authors used a coil dielectric elastomer actuator made from a highly elastic silicone elastomer and conductive materials, fabricated via multimaterial coaxial 3D printing. The printed actuator achieves high-frequency operation (760 Hz), long durability (>1 million cycles), and combines lightweight design with mechanical performance. Cai et al. [80] developed ultra-tough, transparent conductive elastomers with self-healing properties, using a novel 3D printing strategy based on photopolymerization. The dynamic hydrogen bonding network imparts efficient self-healing capabilities, extending the functional lifespan of printed components. A case study was presented for the application of 3D printed transparent conductive elastomeric sensors in intelligent

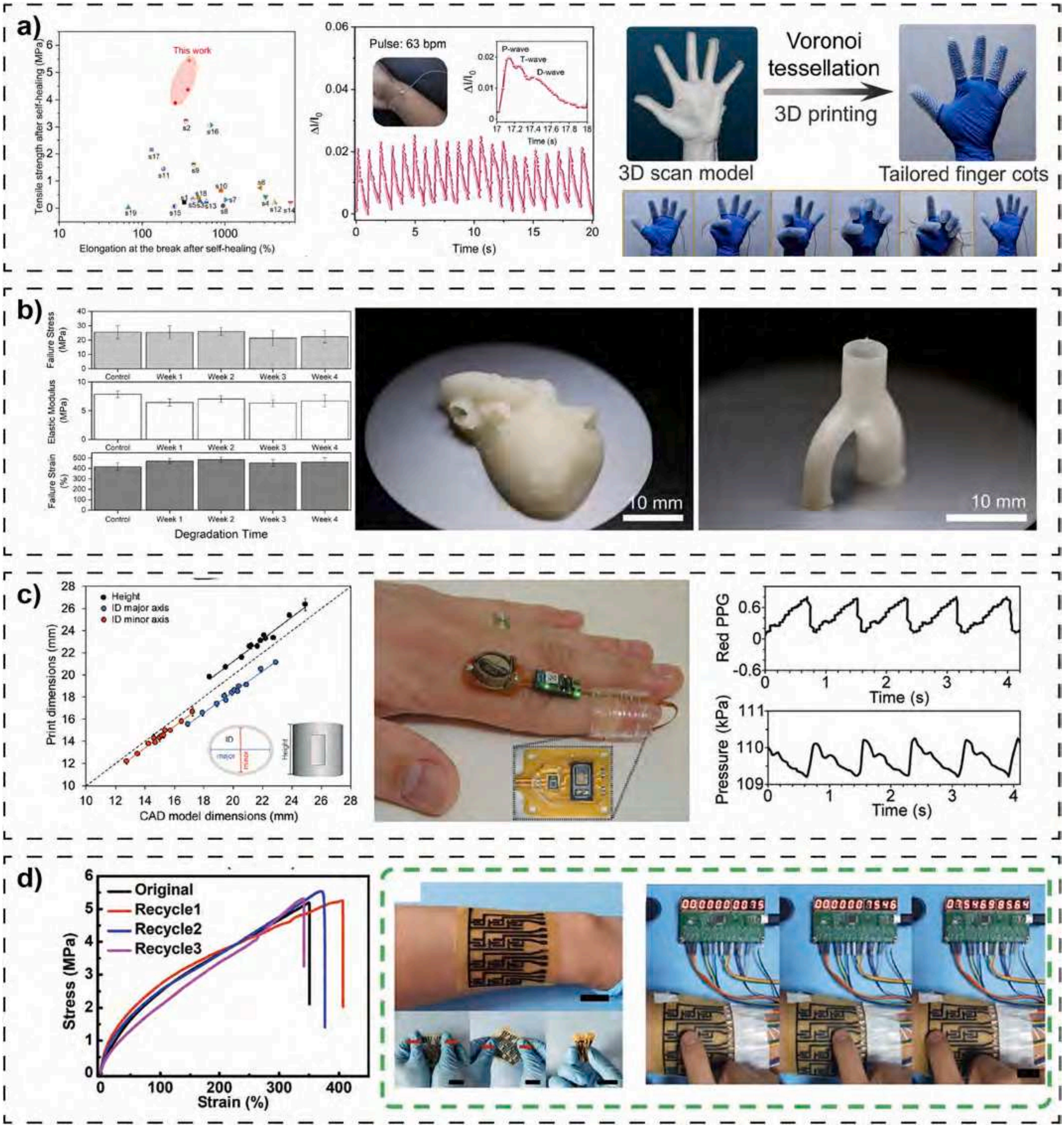


Fig. 12. Application examples of 3D-printed thermoset elastomers (TSEs) for medical devices a) Tailored finger cots prepared with vat photopolymerization: mechanical properties, applications of the 3D-printed sensors for human motion monitoring and tailored finger cots [46] b) Biomedical applications: mechanical properties as a function of degradation, a patient-specific heart model and a thin-wall tubular structure [73] c) polydimethylsiloxane elastomer finger cuffs: dimensional accuracy, patient-specific wearable pulse oximeter and raw signal outputs [74] d) Dynamic thermoset elastomer wearable sensor: mechanical properties as a function of recycling cycles, the wearable sensor during use [75].

detection of road roughness (Fig. 13/**e**).

4.3. Sealing and protective equipment

Their ability to absorb energy and dampen vibrations also makes 3D-printed TSEs ideal for impact-resistant components. Furthermore, their inherent chemical stability and resistance to harsh environmental conditions mean they can perform reliably in demanding industrial applications. Therefore, the use of 3D-printed TSEs is expanding to sealing applications and protective equipment. Periyasamy et al. [38] prepared specialized seals using specialized fluoroelastomer compounds and laser-assisted 3D-printing method (Fig. 14/**a**), while Sundermann et al. [81] presented NBR-based rod seals made with material extrusion-based 3D printing (Fig. 14/**b**). Korger et al. [82] explored the use of a

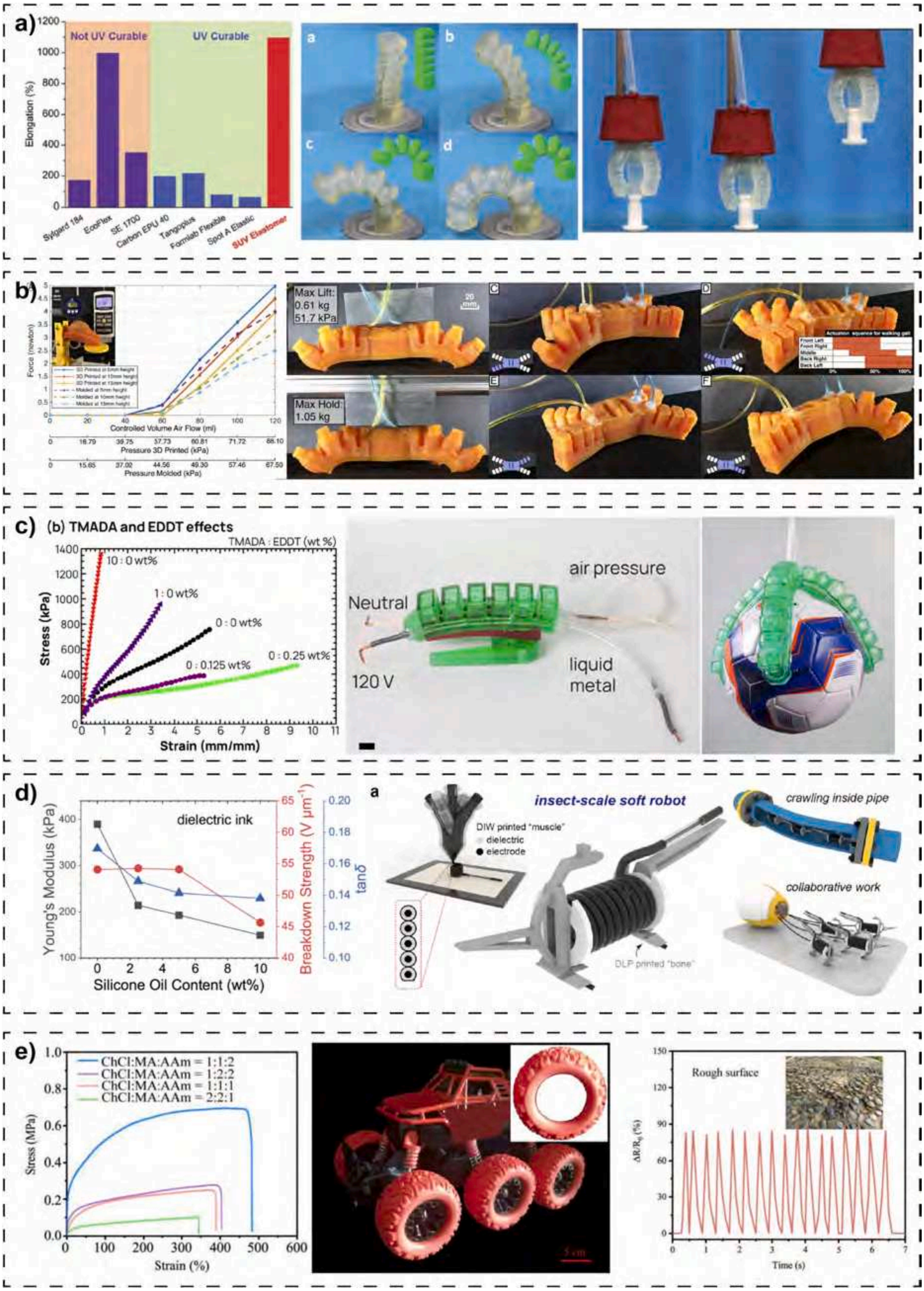


Fig. 13. Application examples a) Photopolymer gripper mechanical properties and during use [47], b) Silicone elastomer gripper mechanical performance and during use [78], c) Self-healing elastomer gripper stress–strain curves and during application [76], d) Insect-scale soft robot prepared with dielectric elastomer actuator: mechanical properties of the dielectric ink and application examples [79], e) Transparent conductive elastomeric sensors in intelligent detection of road roughness [80].

Fig. 14. a) Specialized seals using fluoroelastomer compounds and laser-assisted 3D-printing method: ultimate strain of the compounds, manufacture and the seal [38], b) nitrile-butadiene rubber (NBR)-based rod seals made with material extrusion-based 3D printing: stress at 50% strain, the seal and friction force as a function of pressure [81], c) Elastomer 3D-printed directly onto textile for personal protective equipment: adhesion force, virtual model and 3D-printed prototype [82], d) Self-healing polyurethane elastomer pull-link: tensile stress as a function of restoration temperature, case study and testing of the link [83] e) Foot orthopedics with orthotic insole: anatomy-based design, 3D model and printed prototypes [84].

material extrusion-based method to 3D print flexible thermoplastic elastomers directly onto textiles for applications in personal protective equipment, sportswear, and technical fabrics (Fig. 14/**c**). They demonstrated that the equipment exhibited excellent adhesion, abrasion resistance, and wash durability on a range of woven and knitted textile substrates. Zhang et al. [83] developed a 3D-printable self-healing polyurethane elastomer with excellent mechanical properties and rapid healing capability, achieving 95.86 % recovery after thermal treatment at 50 °C for 6 h. To demonstrate practical applicability, the team fabricated and tested post-healing elastomer components capable of towing a vehicle over a distance of 5 m, highlighting the material's mechanical recovery (Fig. 14/**d**). Li et al. [84] developed a series of poly (urethane-urea-amide) elastomers with integrated self-healing, one-way/two-way, and multiple shape memory capabilities for 4D printing applications. They demonstrated that the filaments can be successfully processed via material extrusion-based 3D printing. The printed structures retained good mechanical properties, including a tensile strength of 9.6 MPa and 402.3 % elongation, while achieving a healing efficiency of 69 %. A case study was presented with the successful preparation of foot orthopedics with an orthotic insole (Fig. 14/**e**).

5. Sustainability and environmental considerations

Thermoset elastomers present a considerable sustainability challenge. Their irreversible covalent crosslinking gives them outstanding mechanical strength, thermal stability, and chemical resistance. However, this structural design also makes them inherently difficult to repair, recycle, or reprocess once they reach the end of their life cycle [85]. To tackle this problem, a comprehensive strategy is necessary, which includes innovations in material design, waste valorization, and the implementation of safe, energy-efficient manufacturing methods. An outline of material selection and technological aspects is shown in Fig. 15.

5.1. Sustainable material design and raw material selection

A highly promising approach is the shift towards bio-based matrix materials. Bio-based elastomers are renewable and are progressively engineered to match or surpass the mechanical performance of traditional synthetic rubbers [86,87], therefore they can present effective alternatives to petroleum-derived polymers. In addition to the polymer matrix, the use of sustainable additives also plays an important role. For example, carbon black has long been the primary reinforcing filler in rubber composites. Yet, the production of carbon-black is energy-intensive and poses considerable environmental and health risks, including carbon dioxide (CO$_2$) emissions and particulate pollution. Biochar, a carbon-rich material derived from biomass pyrolysis, is gaining attention as a greener alternative. Biochar not only presents a reduced carbon footprint and lower costs but also allows for the recycling of agricultural or forestry waste, aligning with circular economy principles [88].

Another way to reduce raw material demand is to incorporate recycled materials, such as devulcanized ground tire rubber (GTR), into new elastomer compounds [89]. This sustainable approach enables the reuse of end-of-life tires, which are otherwise difficult to recycle. Devulcanization partially breaks sulfur bonds in vulcanized rubber, restoring its plasticity and allowing it to be reprocessed. As a circular economy solution, it diverts tire waste from landfills, reduces reliance on virgin materials, and lowers the carbon footprint of rubber production [90].

To address the irreversibility of conventional crosslinked networks, recyclable thermosets based on dynamic molecular architectures are being developed [85,91,92]. One promising approach involves the use of dynamic covalent bonds, such as those incorporated in elastic vitrimer systems [93], which enable the polymer network to undergo rearrangement when exposed to heat or specific chemical triggers. Another strategy relies on noncovalent interactions [94], including hydrogen bonding and π–π stacking, which facilitate reversible bonding and allow for mechanical reuse without the need for complete network degradation. Additionally, covalent adaptive networks (CANs) [95] and depolymerizable systems [96] are being designed to break down into their original or modified monomers under controlled conditions, paving the way for closed-loop recycling. Beyond recyclability, these dynamic material systems often exhibit valuable functional properties such as self-healing, which can extend the service life of components and reduce the frequency of replacement, further enhancing their sustainability profile [97–99].

5.2. Environmental aspects of additive manufacturing

From a technological perspective, AM offers a promising route to sustainable production. AM naturally facilitates low-waste manufacturing, accurate material placement, and automated fabrication, all of which can enhance resource efficiency and enable on-demand production [100]. Despite the advantages, limited scalability and energy consumption pose a significant environmental challenge for 3D printing technologies. AM usually demands more energy per unit of material than conventional techniques, particularly in small-scale or batch production [101]. However, this energy demand can be compensated by creating lightweight, intricate geometries that enhance product performance and minimize material waste throughout the product's life cycle [102]. Additionally, the decentralized manufacturing capability provided by AM allows for cutting transportation costs by as much as 25 times, greatly decreasing the CO$_2$ emissions commonly linked to long-distance logistics [103].

Another key environmental and health challenge in AM processes is the release of fine particles and volatile organic compounds (VOCs), which can be hazardous, especially in indoor printing environments

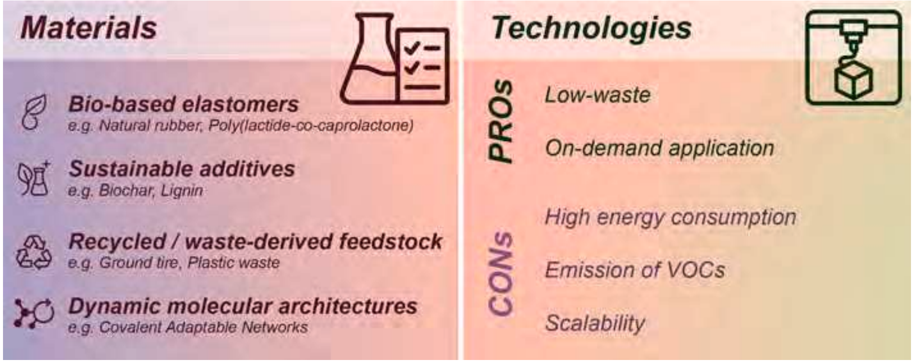


Fig. 15. Main sustainability aspects of 3D-printing thermosetting elastomers: potential environmentally friendly considerations for raw material selection (left) and general advantages and disadvantages of 3D printing technologies from an environmental perspective (right).

[104]. To mitigate these risks, stricter safety regulations, effective ventilation systems, and low-VOC resin formulations are essential [105,106]. Ensuring the safe handling of photoinitiators and reactive chemicals, through proper storage, protective equipment, and waste management protocols, is also critical for minimizing occupational and environmental hazards.

6. Summary

Our review presents the advancements in 3D printing of thermoset elastomer (TSE) materials, focusing on the challenges and possibilities of various technologies. 3D printing eliminates the need for time-consuming and costly tooling, such as molds and dies, typically required in conventional manufacturing. It can also produce customized parts efficiently and is particularly cost-effective for low-volume or one-off items. However, 3D printing TSEs is a challenge. Unlike thermoplastic elastomers (TPEs), TSEs undergo an irreversible chemical cross-linking reaction. Therefore, controlling the timing of curing during printing is of paramount importance. If curing happens too early, it can clog the nozzle; if it occurs too late, the printed structure may collapse. The materials used typically have high viscosity, making extrusion difficult and limiting print resolution. State-of-the-art 3D printing technologies for producing TSEs can be categorized into three groups: photopolymerization-based, two-phase systems, and material extrusion–based technologies. Each method has distinct strengths and limitations. Photopolymerization-based methods offer excellent resolution and material versatility, making them ideal for biomedical and microfluidic applications. However, they can be harmful to the environment, and the build size is limited. Two-phase systems are especially suitable for silicone-based materials; they allow tunable mechanical properties and multi-material printing, but face challenges related to rheology, speed, and layer adhesion. Material extrusion-based methods are cost-effective and compatible with recycled materials, although they cannot use high-viscosity inks and are less precise than some other methods. All methods require post-processing, such as removal of support materials, post-irradiation for a complete cross-linked structure or vulcanisation.. Overall, the current focus of research is on technology and formulation development. For the qualification of 3D printed prototypes, tensile properties are typically presented, with a few cases of frequency dependent properties and hardness. Extensive mechanical characterisation is rare and application specific properties are less investigated. This could include tests related to typical applications of rubber products, such as sealing force, wear resistance or biocompatibility. These will be essential in the future to qualify technological developments.

7. Emerging trends and future outlook

A recent trend in the field of AM of TSEs is the integration of smart materials. Self-healing and shape-memory TSEs expand applications in soft robotics, biomedical devices, and adaptive systems, as these materials enable components to respond to stimuli, autonomously repair damage, or recover their shape [46,107]. Sustainability goals are also shaping the field, with research advancing green manufacturing strategies such as recyclable [83] and bio-based thermosets [86,87], and devulcanized fillers [108]. These innovations aim to align with environmental and circular economic priorities, such as minimizing the ecological footprint. Additionally, multi-material [109], and hybrid AM technologies [110] are emerging, permitting the combination of TSEs with other polymers, conductive inks, or reinforcement phases in a single build. This supports the fabrication of devices with varying properties, paving the way for advanced soft electronics, actuators, and custom implants. The integration of digital design and simulation tools, including finite element modeling and rheology-based printability simulations, is optimizing AM processes, predicting outcomes, and tailoring material behavior. Furthermore, artificial intelligence (AI) and machine learning (ML) approaches are increasingly influencing AM, aiding in real-time process monitoring, defect detection, and adaptive control of print conditions [13]. AI-driven discovery in materials science is identifying new formulations with desired properties more efficiently than traditional methods. Collectively, these trends suggest a future for thermoset elastomer additive manufacturing that is smarter, more capable, sustainable, adaptive, and digitally integrated—positioning it at the forefront of next-generation materials engineering and manufacturing.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author(s) used ChatGPT in order to assist with writing, phrasing, and language editing. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

CRediT authorship contribution statement

Csenge Tóth: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Ábris Dávid Virág:** Writing – original draft. **István Halász-Kutasi:** Writing – original draft. **Norbert Krisztián Kovács:** Writing – original draft. **Tamás Bárány:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Research, Development and Innovation Office, Hungary (K146085). Project no. TKP-6-6/PALY-2021 has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme.

References

[1] R.A. Shanks, I. Kong, General Purpose Elastomers: Structure, Chemistry, Physics and Performance, in: P.M. Visakh, S. Thomas, A.K. Chandra, Aji.P. Mathew (Eds.), Advances in Elastomers I: Blends and Interpenetrating Networks, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013: pp. 11–45. doi: 10.1007/978-3-642-20925-3_2.

[2] M.A.S.N. Weerasinghe, O.J. Dodo, C.W.H. Rajapawasam, I.O. Raji, S. V. Wanasinghe, D. Konkolewicz, N., De Alwis Watuthanthrige, Educational series: turning monomers into crosslinked polymer networks, Polym. Chem. 14 (2023) 4503–4514, https://doi.org/10.1039/D3PY00912B.

[3] A.N. Gent, Relaxation processes in vulcanized rubber. I. Relation among stress relaxation, creep, recovery, and hysteresis, J Appl Polym Sci 6 (1962) 433–441, https://doi.org/10.1002/app.1962.070062207.

[4] L. Wang, F. Lang, S. Li, Du. Fanglin, Z. Wang, Thermoplastic elastomers based on high-density polyethylene and waste ground rubber tire composites compatibilized by styrene–butadiene block copolymer, J. Thermoplast. Compos. Mater. 27 (2013) 1479–1492, https://doi.org/10.1177/0892705712473628.

[5] K. Yamaguchi, A.G. Thomas, J.J.C. Busfield, Stress relaxation, creep and set recovery of elastomers, Int. J. Non Linear Mech. 68 (2015) 66–70, https://doi.org/10.1016/J.IJNONLINMEC.2014.07.004.

[6] C.W.H. Rajawasam, O.J. Dodo, M.A.S.N. Weerasinghe, I.O. Raji, S. V. Wanasinghe, D. Konkolewicz, N., De Alwis Watuthanthrige, Educational series: characterizing crosslinked polymer networks, Polym. Chem. 15 (2024) 219–247, https://doi.org/10.1039/D3PY00914A.

[7] C. Ma, W. Liu, X. Zhou, J. He, Z. Wang, Z. Wang, Dynamic Chemical Cross-linking and Mechanical Training of Bio-based Polyamides Fabricate strong and Recyclable Elastomers, ACS Sustain. Chem. Eng. 10 (2022) 6775–6783, https://doi.org/10.1021/acssuschemeng.2c01145.

[8] G.M. Scheutz, J.J. Lessard, M.B. Sims, B.S. Sumerlin, Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets, J. Am. Chem. Soc. 141 (2019) 16181–16196, https://doi.org/10.1021/jacs.9b07922.

[9] S. Maes, N. Badi, J.M. Winne, F.E. Du Prez, Taking dynamic covalent chemistry out of the lab and into reprocessable industrial thermosets, Nat. Rev. Chem. 9 (2025) 144–158, https://doi.org/10.1038/s41570-025-00686-7.

[10] Global Market Insights, Rubber molding market size, growth trends & forecast, 2024–2032, 2023.

[11] E. Princi, 8. Manufacturing and transformation technologies, in: In, De Gruyter, Science and Technology, 2019, pp. 147–164, https://doi.org/10.1515/9783110640328-008.

[12] D. Kazmer, Three-Dimensional Printing of Plastics, Applied Plastics Engineering Handbook: Processing, Materials, and Applications: Second Edition (2017) 617–634, https://doi.org/10.1016/B978-0-323-39040-8.00029-8.

[13] K. Kanishka, B. Acherjee, Revolutionizing manufacturing: a comprehensive overview of additive manufacturing processes, materials, developments, and challenges, J. Manuf. Process. 107 (2023) 574–619, https://doi.org/10.1016/J.JMAPRO.2023.10.024.

[14] H.L. Fisher, VULCANIZATION OF RUBBER Vulcanization of Rubber, Ind. Eng. Chem. 31 (1939) 1381–1389, https://doi.org/10.1021/ie50359a015.

[15] M. Pöschl, R. Stoček, P. Zádrapa, M. Stěnička, G. Heinrich, How is cut and chip wear influenced by the variation of the cross-link density within the conventional vulcanization system of natural rubber? Express Polym Lett 18 (2024) 1178–1190, https://doi.org/10.3144/expresspolymlett.2024.90.

[16] A. Rodak, J. Haponiuk, S. Wang, K. Formela, Investigating the combined effects of devulcanization level and carbon black grade on the SBR/GTR composites, Express Polym Lett 18 (2024) 1191–1208, https://doi.org/10.3144/expresspolymlett.2024.91.

[17] X. Colom, M.R. Saeb, J. Cañavate, Microstructural phenomena in ground tire rubber (GTR) devulcanized via combined thermochemomechanical and microwave processes monitored by FTIR and DTGA assisted by other techniques, Express Polym Lett 18 (2024) 950–961, https://doi.org/10.3144/expresspolymlett.2024.72.

[18] A. Chelli, H. Mechakra, A. Chellil, D.E. Tria, W. Bessa, K. Ikkache, B. Safi, Evaluation of Viscoelastic Performance and Molecular Structures of Natural Rubber/NBR Blends Reinforced by Carbon Black and Nano-Silica, Periodica Polytechnica, Mech. Eng. 68 (2024) 162–171, https://doi.org/10.3311/PPme.28792.

[19] J. Kruželák, R. Sýkora, I. Hudec, Sulphur and Peroxide Vulcanisation of Rubber Compounds – Overview 70 (2016) 1533–1555, https://doi.org/10.1515/chempap-2016-0093.

[20] S.C. Ligon-Auer, M. Schwentenwein, C. Gorsche, J. Stampfl, R. Liska, Toughening of photo-curable polymer networks: a review, Polym. Chem. 7 (2016) 257–286, https://doi.org/10.1039/C5PY01631B.

[21] A. Shoushtari Zadeh Naseri, A. Jalali-Arani, Study on the morphology, static and dynamic mechanical properties of (styrene butadiene rubber/ethylene propylene diene monomer/organoclay) nanocomposites vulcanized by the gamma radiation, J Appl Polym Sci 133 (2016), https://doi.org/10.1002/app.43581.

[22] S.K. Ghosh, N.C. Das, Application of Radiation Curing on Properties and Performance of Polymers and Polymer Composites, in: S.R. Chowdhury (Ed.), Applications of High Energy Radiations: Synthesis and Processing of Polymeric Materials, Springer Nature Singapore, Singapore, 2023: pp. 1–39. doi: 10.1007/978-981-19-9048-9_1.

[23] D. Chen, S. Yi, W. Wu, Y. Zhong, J. Liao, C. Huang, W. Shi, Synthesis and characterization of novel room temperature vulcanized (RTV) silicone rubbers using Vinyl-POSS derivatives as cross linking agents, Polymer (guildf) 51 (2010) 3867–3878, https://doi.org/10.1016/J.POLYMER.2010.06.028.

[24] T. Arends, H.P. Huinink, L. Pel, Dynamics of heterogeneous crosslinking in room temperature vulcanizing poly(dimethyl siloxane) and its dependence on moisture supply, Polymer (guildf) 164 (2019) 8–16, https://doi.org/10.1016/J.POLYMER.2018.12.059.

[25] F. De Buyl, Silicone sealants and structural adhesives, Int. J. Adhes. Adhes. 21 (2001) 411–422, https://doi.org/10.1016/S0143-7496(01)00018-5.

[26] R.P. Lattimer, R.A. Kinsey, R.W. Layer, C.K. Rhee, The Mechanism of Phenolic Resin Vulcanization of Unsaturated Elastomers, Rubber Chem. Technol. 62 (1989) 107–123, https://doi.org/10.5254/1.3536228.

[27] A. Dasgupta, P. Dutta, Printability of elastomer as a 3D printing material for additive manufacturing, Journal of Rubber Research 27 (2024) 137–157, https://doi.org/10.1007/s42464-024-00241-x.

[28] R. Mahshid, M.N. Isfahani, M. Heidari-Rarani, M. Mirkhalaf, Recent advances in development of additively manufactured thermosets and fiber reinforced thermosetting composites: Technologies, materials, and mechanical properties, Compos. Part A Appl. Sci. Manuf. 171 (2023) 107584, https://doi.org/10.1016/J.COMPOSITESA.2023.107584.

[29] D. Mohan, M.S. Sajab, H. Kaco, S.B. Bakarudin, A. Mohamed Noor, 3D Printing of UV-Curable polyurethane Incorporated with Surface-Grafted Nanocellulose, Nanomaterials 9 (2019), https://doi.org/10.3390/nano9121726.

[30] H. Jin, X. Zhong, C. Zhong, W. Dai, H. Xiang, L. Zhang, UV-curable, 3D printable, thermally conductive polysiloxane composites for thermal interface devices, Addit. Manuf. 99 (2025) 104658, https://doi.org/10.1016/J.ADDMA.2025.104658.

[31] J. Holländer, R. Hakala, J. Suominen, N. Moritz, J. Yliruusi, N. Sandler, 3D printed UV light cured polydimethylsiloxane devices for drug delivery, Int. J. Pharm. 544 (2018) 433–442, https://doi.org/10.1016/J.IJPHARM.2017.11.016.

[32] Y. Hu, G. Zhu, J. Zhang, J. Huang, X. Yu, Q. Shang, R. An, C. Liu, L. Hu, Y. Zhou, Rubber seed Oil-based UV-Curable polyurethane Acrylate Resins for Digital Light Processing (DLP) 3D Printing, Molecules 26 (2021), https://doi.org/10.3390/molecules26185455.

[33] L. Strohmeier, H. Frommwald, S. Schlögl, Digital light processing 3D printing of modified liquid isoprene rubber using thiol-click chemistry, RSC Adv. 10 (2020) 23607–23614, https://doi.org/10.1039/D0RA04186F.

[34] J. Stieghorst, T. Doll, Rheological behavior of PDMS silicone rubber for 3D printing of medical implants, Addit. Manuf. 24 (2018) 217–223, https://doi.org/10.1016/J.ADDMA.2018.10.004.

[35] K. Hajash, B. Sparrman, C. Guberan, J. Laucks, S. Tibbits, Large-Scale Rapid Liquid Printing, 3D Print Addit Manuf 4 (2017) 123–132. doi: 10.1089/3dp.2017.0037.

[36] K. Chansoda, C. Suvanjumrat, P. Wiroonpochit, T. Kaewprakob, W. Chookaew, Support medium development for 3D printing natural rubber latex via direct ink writing in the support bath technique, Cleaner Mater. 13 (2024) 100257, https://doi.org/10.1016/J.CLEMA.2024.100257.

[37] A. Fantoni, J. Ecker, M. Ahmadi, T. Koch, J. Stampfl, R. Liska, S. Baudis, Green Monomers for 3D Printing: Epoxy-Methacrylate Interpenetrating Polymer Networks as a Versatile Alternative for Toughness Enhancement in Additive Manufacturing, ACS Sustain. Chem. Eng. 11 (2023) 12004–12013, https://doi.org/10.1021/acssuschemeng.3c02194.

[38] M. Periyasamy, A.A. Mubasshir, S. Kodra, S. Chandramouli, R. Campbell, D. O. Kazmer, J.L. Mead, From Formulation to Application: Effects of Plasticizer on the Printability of Fluoro Elastomer Compounds and Additive Manufacturing of Specialized Seals, Micromachines (basel) 15 (2024), https://doi.org/10.3390/mi15050622.

[39] K. Chansoda, W. Chookaew, C. Suvanjumrat, Optimizing laser 3D printing parameters for customized rubber latex health shoe insoles, Prog. Addit. Manuf. (2024), https://doi.org/10.1007/s40964-024-00870-z.

[40] J.R. Innes, B. Shriky, D. Nocita, G. Thompson, P. Coates, B. Whiteside, A. Kelly, M. Hebda, Development of thermoplastic vulcanizates based on polypropylene/ethylene propylene diene monomer for prototyping by Fused Filament Fabrication, Polymer (guildf) 273 (2023) 125839, https://doi.org/10.1016/J.POLYMER.2023.125839.

[41] S. Badini, S. Graziosi, M. Carboni, S. Regondi, R. Pugliese, Sustainable 3D printing with recycled tire rubber-based filaments: an investigation of process parameters and mechanical behaviour, Rapid Prototyp. J. 30 (2024) 571–587, https://doi.org/10.1108/RPJ-08-2023-0309.

[42] P.J. Scott, V. Meenakshisundaram, M. Hegde, C.R. Kasprzak, C.R. Winkler, K. D. Feller, C.B. Williams, T.E. Long, 3D Printing Latex: a Route to complex Geometries of High Molecular Weight Polymers, ACS Appl. Mater. Interfaces 12 (2020) 10918–10928, https://doi.org/10.1021/acsami.9b19986.

[43] L. Liu, J. Zhang, Z. Luo, N. Kong, X. Zhao, X. Ji, J. Li, S. Huang, P. Zhao, S. Li, Y. Shao, J. Tao, Concentrated Pre-Vulcanized Natural Rubber Latex without Additives for Fabricating High Mechanical Performance Rubber Specimens via Direct Ink Write 3D Printing, Polymers (basel) 17 (2025), https://doi.org/10.3390/polym17030351.

[44] J. Wen, G. Nayyar, E.R. Crater, R.H. Bean, R. Zhang, R.B. Moore, T.E. Long, Vat photopolymerization of olefinic elastomers from sulfonated ethylene-propylene-diene monomer (EPDM) latexes, Addit. Manuf. 91 (2024) 104359, https://doi.org/10.1016/J.ADDMA.2024.104359.

[45] G. Kuang, H. Bakhshi, W. Meyer, Urethane-acrylate-based photo-inks for digital light processing of flexible materials, J. Polym. Res. 30 (2023) 141, https://doi.org/10.1007/s10965-023-03519-7.

[46] S. Peng, N. Thirunavukkarasu, J. Chen, X. Zheng, C. Long, X. Huang, Z. Weng, L. Zheng, H. Wang, X. Peng, L. Wu, Vat photopolymerization 3D printing of transparent, mechanically robust, and self-healing polyurethane elastomers for tailored wearable sensors, Chem. Eng. J. 463 (2023) 142312, https://doi.org/10.1016/J.CEJ.2023.142312.

[47] D.K. Patel, A.H. Sakhaei, M. Layani, B. Zhang, Q. Ge, S. Magdassi, Highly Stretchable and UV Curable Elastomers for Digital Light Processing based 3D Printing, Adv. Mater. 29 (2017) 1606000, https://doi.org/10.1002/adma.201606000.

[48] G. Jeong, C.H. Park, B.-Y. Kim, J. Kim, S.-D. Park, H. Yang, W.S. Lee, Photocurable Elastomer Composites with SiO2-Mediated Cross-Links for Mechanically durable 3D Printing Materials, ACS Appl. Polym. Mater. 2 (2020) 5228–5237, https://doi.org/10.1021/acsapm.0c00966.

[49] A. Bagheri, J. Jin, Photopolymerization in 3D Printing, ACS Appl. Polym. Mater. 1 (2019) 593–611, https://doi.org/10.1021/acsapm.8b00165.

[50] S. Subedi, S. Liu, W. Wang, S.M.A. Naser Shovon, X. Chen, H.O.T. Ware, Multi-material vat photopolymerization 3D printing: a review of mechanisms and applications, Npj Advanced Manufacturing 1 (2024) 9, https://doi.org/10.1038/s44334-024-00005-w.

[51] M. Vatani, J.-W. Choi, Direct-print photopolymerization for 3D printing, Rapid Prototyp. J. 23 (2017) 337–343, https://doi.org/10.1108/RPJ-11-2015-0172.

[52] J.A. Lewis, G.M. Gratson, Direct writing in three dimensions, Mater. Today 7 (2004) 32–39, https://doi.org/10.1016/S1369-7021(04)00344-X.

[53] F. Liravi, E. Toyserkani, A hybrid additive manufacturing method for the fabrication of silicone bio-structures: 3D printing optimization and surface characterization, Mater. Des. 138 (2018) 46–61, https://doi.org/10.1016/J.MATDES.2017.10.051.

[54] R. Tu, H.A. Sodano, Additive manufacturing of high-performance vinyl ester resin via direct ink writing with UV-thermal dual curing, Addit. Manuf. 46 (2021) 102180, https://doi.org/10.1016/J.ADDMA.2021.102180.

[55] B. Liu, B. Ma, 3D printing molding of UV-curing liquid silicone rubber by UV follow curing, J. Appl. Polym. Sci. 142 (2025) e56453, https://doi.org/10.1002/app.56453.

[56] M. Bragaglia, F.R. Lamastra, V. Cherubini, F. Nanni, 3D printing of polybutadiene rubber cured by photo-induced thiol-ene chemistry: a proof of concept, Express

Polym Lett 14 (2020) 576–582, https://doi.org/10.3144/expresspolymlett.2020.47.

[57] E. Davoodi, H. Montazerian, A. Khademhosseini, E. Toyserkani, Sacrificial 3D printing of shrinkable silicone elastomers for enhanced feature resolution in flexible tissue scaffolds, Acta Biomater. 117 (2020) 261–272, https://doi.org/10.1016/J.ACTBIO.2020.10.001.

[58] V.G. Rocha, E. Saiz, I.S. Tirichenko, E. García-Tuñón, Direct ink writing advances in multi-material structures for a sustainable future, J Mater Chem A Mater 8 (2020) 15646–15657, https://doi.org/10.1039/D0TA04181E.

[59] K. Yamagishi, R. Karyappa, T. Ching, M. Hashimoto, Direct ink writing of silicone elastomers to fabricate microfluidic devices and soft robots, MRS Commun. 14 (2024) 846–861, https://doi.org/10.1557/s43579-024-00631-7.

[60] S. Gharaie, A. Zolfagharian, A.A.A. Moghadam, N. Shukur, M. Bodaghi, B. Mosadegh, A. Kouzani, Direct 3D printing of a two-part silicone resin to fabricate highly stretchable structures, Prog. Addit. Manuf. 8 (2023) 1555–1571, https://doi.org/10.1007/s40964-023-00421-y.

[61] J. Li, S. Wu, W. Zhang, K. Ma, G. Jin, 3D Printing of Silicone Elastomers for Soft Actuators, Actuators 11 (2022), https://doi.org/10.3390/act11070200.

[62] S.S. Kamath, J.-W. Choi, 3D Printing of Synthetic Rubber Ink via the Direct Ink writing Process, Rubber World 263 (2021) 28–33.

[63] N. Shen, L. Duan, M. Yang, S. Liu, W. Xu, Solvent-assisted 3D printing of butyl rubber and its hybrid materials, MRS Commun. 12 (2022) 597–602, https://doi.org/10.1557/s43579-022-00205-5.

[64] E. Luis, H.M. Pan, A.K. Bastola, R. Bajpai, S.L. Sing, J. Song, W.Y. Yeong, 3D Printed Silicone Meniscus Implants: Influence of the 3D Printing Process on Properties of Silicone Implants, Polymers (basel) 12 (2020), https://doi.org/10.3390/polym12092136.

[65] R. Akman, H. Ramaraju, A. Verga, S.J. Hollister, Multimodal 3D printing of biodegradable shape memory elastomer resins for patient specific soft tissue repair, Appl. Mater. Today 29 (2022) 101666, https://doi.org/10.1016/J.APMT.2022.101666.

[66] M.A. Quetzeri-Santiago, C.L. Hedegaard, J.R. Castrejón-Pita, Additive Manufacturing with Liquid Latex and Recycled End-of-Life Rubber, 3D Print Addit Manuf 6 (2019) 149–157. doi: 10.1089/3dp.2018.0062.

[67] I. Gibson, D. Rosen, B. Stucker, Extrusion-Based Systems, in: I. Gibson, D. Rosen, B. Stucker (Eds.), Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, Springer New York, New York, NY, 2015: pp. 147–173. doi: 10.1007/978-1-4939-2113-3_6.

[68] H. Wittek, B. Klie, U. Giese, S. Kleinert, L. Bindszus, L. Overmeyer, Approach for Additive Manufacturing of High-Viscosity, Curable Rubbers by AME Processing (Additive Manufacturing of Elastomers) – Rubber 3D, KGK-Kautschuk Gummi, Kunststoffe 72 (2019) 53–56.

[69] S. Srisawadi, S. Lapapong, S. Dokkhan, P. Wiroonpochit, Stereolithography of Natural Rubber Latex, a Highly Elastic Material, in: Proceedings of the 30th Annual International Solid Freeform Fabrication Symposium, 2019, pp. 864–874.

[70] L. Sundermann, B. Klie, U. Giese, S. Leineweber, L. Overmeyer, Development, Construction and Testing of a 3D-printing-system for Additive Manufacturing of Carbon Black Filled Rubber Compounds, KGK-Kautschuk Gummi, Kunststoffe 73 (2020) 30–35.

[71] W.-G. Drossel, J. Ihlemann, R. Landgraf, E. Oelsch, M. Schmidt, Basic Research for Additive Manufacturing of Rubber, Polymers (basel) 12 (2020), https://doi.org/10.3390/polym12102266.

[72] S. Leineweber, L. Sundermann, L. Bindszus, L. Overmeyer, B. Klie, H. Wittek, U. Giese, ADDITIVE MANUFACTURING AND VULCANIZATION OF CARBON BLACK–FILLED NATURAL RUBBER–BASED COMPONENTS, Rubber Chem. Technol. 95 (2021) 46–57, https://doi.org/10.5254/rct.21.79906.

[73] E.O. Bachtiar, O. Erol, M. Millrod, R. Tao, D.H. Gracias, L.H. Romer, S.H. Kang, 3D printing and characterization of a soft and biostable elastomer with high flexibility and strength for biomedical applications, J. Mech. Behav. Biomed. Mater. 104 (2020) 103649, https://doi.org/10.1016/J.JMBBM.2020.103649.

[74] S. Abdollahi, E.J. Markvicka, C. Majidi, A.W. Feinberg, 3D Printing Silicone Elastomer for Patient-specific Wearable Pulse Oximeter, Adv. Healthc. Mater. 9 (2020) 1901735, https://doi.org/10.1002/adhm.201901735.

[75] Y. Guo, S. Chen, L. Sun, L. Yang, L. Zhang, J. Lou, Z. You, Degradable and fully Recyclable Dynamic Thermoset Elastomer for 3D-printed Wearable Electronics, Adv. Funct. Mater. 31 (2021) 2009799, https://doi.org/10.1002/adfm.202009799.

[76] E.F. Gomez, S.V. Wanasinghe, A.E. Flynn, O.J. Dodo, J.L. Sparks, L.A. Baldwin, C. E. Tabor, M.F. Durstock, D. Konkolewicz, C.J. Thrasher, 3D-printed Self-Healing Elastomers for Modular Soft Robotics, ACS Appl. Mater. Interfaces 13 (2021) 28870–28877, https://doi.org/10.1021/acsami.1c06419.

[77] E. Sachyani Keneth, A. Kamyshny, M. Totaro, L. Beccai, S. Magdassi, 3D Printing Materials for Soft Robotics, Adv. Mater. 33 (2021) 2003387, https://doi.org/10.1002/adma.202003387.

[78] O.D. Yirmibesoglu, J. Morrow, S. Walker, W. Gosrich, R. Cañizares, H. Kim, U. Daalkhaijav, C. Fleming, C. Branyan, Y. Menguc, Direct 3D printing of silicone elastomer soft robots and their performance comparison with molded counterparts, in, IEEE International Conference on Soft Robotics (RoboSoft) 2018 (2018) 295–302, https://doi.org/10.1109/ROBOSOFT.2018.8404935.

[79] Y. Zhu, N. Liu, Z. Chen, H. He, Z. Wang, Z. Gu, Y. Chen, J. Mao, Y. Luo, Y. He, 3D-printed High-Frequency Dielectric Elastomer Actuator toward Insect-Scale Ultrafast Soft Robot, ACS Mater. Lett. 5 (2023) 704–714, https://doi.org/10.1021/acsmaterialslett.2c00991.

[80] L. Cai, G. Chen, B. Su, M. He, 3D printing of ultra-tough, self-healing transparent conductive elastomeric sensors, Chem. Eng. J. 426 (2021) 130545, https://doi.org/10.1016/J.CEJ.2021.130545.

[81] L. Sundermann, S. Leineweber, B. Klie, H. Wittek, T. Ebel, B. Reitz, K. Ottink, M. Graf, T. Lankenau, L. Overmeyer, U. Giese, Tailoring the Curing Kinetics of NBR-Based Rubber Compounds for Additive Manufacturing of Rod Seals, Adv. Polym. Tech. 2023 (2023) 7343194, https://doi.org/10.1155/2023/7343194.

[82] M. Korger, A. Glogowsky, S. Sanduloff, C. Steinem, S. Huysman, B. Horn, M. Ernst, M. Rabe, Testing thermoplastic elastomers selected as flexible three-dimensional printing materials for functional garment and technical textile applications, J Eng Fiber Fabr 15 (2020) 1558925020924599, https://doi.org/10.1177/1558925020924599.

[83] H. Zhang, Y. Shang, N. Li, X. Hu, Z. Ye, X. Zhang, L. Qu, X. Song, Y. He, K. Fu, B. Shi, Dynamic bond-enhanced, recyclable polyurethane elastomer with high strength and self-healing properties for advanced 3D printing, Compos. B Eng. 304 (2025) 112500, https://doi.org/10.1016/J.COMPOSITESB.2025.112500.

[84] Z. Li, Z. Cao, Q. Zhao, S. Mei, Y. Zhang, W. Zhao, X. Li, X. Zhang, Z. Cui, P. Fu, X. Pang, M. Liu, Self-Healing and shape memory reconfigurable Poly(urethane-urea-amide) elastomers containing multiple dynamic bonds for improving performance of 4D printout, Chem. Eng. J. 485 (2024) 149933, https://doi.org/10.1016/J.CEJ.2024.149933.

[85] K. Cerdan, M. Thys, A. Costa Cornellà, F. Demir, S. Norvez, R. Vendamme, N. Van den Brande, P. Van Puyvelde, J. Brancart, Sustainability of self-healing polymers: a holistic perspective towards circularity in polymer networks, Prog Polym Sci 152 (2024) 101816, https://doi.org/10.1016/J.PROGPOLYMSCI.2024.101816.

[86] Q. Liu, P. Lou, Z. Sun, D. Li, H. Ji, Z. Xu, L. Li, J. Xue, R. Wang, Z. Wang, L. Zhang, Bio-based Elastomers: Design, Properties, and Biomedical applications, Adv. Mater. 37 (2025) 2417193, https://doi.org/10.1002/adma.202417193.

[87] S. Tang, J. Li, R. Wang, J. Zhang, Y. Lu, G.-H. Hu, Z. Wang, L. Zhang, Current trends in bio-based elastomer materials, SusMat 2 (2022) 2–33, https://doi.org/10.1002/sus2.45.

[88] L. Karunanayake, T. Etampawala, D.J. de Silva, J. Bandara, A.U. Rajapaksha, M. Vithanage, Role and potential of biochar as a sustainable alternative reinforcing filler to carbon black in rubber composites, Biochar 7 (2025) 60, https://doi.org/10.1007/s42773-025-00429-3.

[89] Á. Görbe, A. Kohári, T. Bárány, Rubber Compounds from Devulcanized Ground Tire Rubber: Recipe Formulation and Characterization, Polymers (basel) 16 (2024), https://doi.org/10.3390/polym16040455.

[90] Z.U. Haq, T. Ren, X. Yue, K. Formela, D. Rodrigue, X.C. Fajula, T. McNally, D. Dawei, Y. Zhang, S. Wang, Progress in devulcanization of waste tire rubber: Upcycling towards a circular economy, Express Polym Lett 19 (2025) 258–293, https://doi.org/10.3144/expresspolymlett.2025.20.

[91] S. Sarkar, A. S., S. Salaeh, V. Hirschberg, S.S. Banerjee, Self-healing and shape memory functions in elastomers: recent advances and future prospectives, Polym. Eng. Sci. 65 (2025) 1620–1654, https://doi.org/10.1002/pen.27092.

[92] C. Liu, F. Wenhang, C. Qianqian, Q. Biwei, S. Yonggang, J. and Shi, Revolutionizing Elastomer Technology: Advances in Reversible Crosslinking, Reprocessing, and Self-Healing Applications, Polymer Reviews 65 (2025) 483–526. doi: 10.1080/15583724.2024.2405904.

[93] J. Luo, Z. Demchuk, X. Zhao, T. Saito, M. Tian, A.P. Sokolov, P.F. Cao, Elastic vitrimers: beyond thermoplastic and thermoset elastomers, Matter 5 (2022) 1391–1422, https://doi.org/10.1016/J.MATT.2022.04.007.

[94] Y. Li, M. Zhou, R. Wang, H. Han, Z. Huang, J. Wang, Self-healing polyurethane elastomers: an essential review and prospects for future research, Eur. Polym. J. 214 (2024) 113159, https://doi.org/10.1016/J.EURPOLYMJ.2024.113159.

[95] Y. Zhu, Z. Xu, F. Wu, M. Wang, L. Chen, Liquid-crystal elastomers based on covalent adaptable networks: from molecular design to applications, Sci. China Mater. 66 (2023) 3004–3021, https://doi.org/10.1007/s40843-023-2474-8.

[96] Z. Cao, X. Xu, F. Sun, H. Yao, J. Zhang, Y. Li, Y. Cheng, G. Chen, Y. Jia, B. Yao, J. Xu, J. Fu, Depolymerizable Thermosetting Dielectric Elastomers Toughened by Sacrificial Hydrogen Bonds for Sustainable Capacitive Strain-Sensor, Adv Funct Mater n/a (2025) 2505979. doi: doi: 10.1002/adfm.202505979.

[97] S. Aiswarya, P. Awasthi, S.S. Banerjee, Self-healing thermoplastic elastomeric materials: challenges, opportunities and new approaches, Eur. Polym. J. 181 (2022) 111658, https://doi.org/10.1016/J.EURPOLYMJ.2022.111658.

[98] S. Utrera-Barrios, R. Verdejo, M.Á. López-Manchado, M. Hernández Santana, Self-Healing Elastomers: a sustainable solution for automotive applications, Eur. Polym. J. (2023) 112023, https://doi.org/10.1016/J.EURPOLYMJ.2023.112023.

[99] S. Utrera-Barrios, R. Verdejo, M.A. López-Manchado, M. Hernández Santana, Evolution of self-healing elastomers, from extrinsic to combined intrinsic mechanisms: a review, Mater. Horiz. 7 (2020) 2882–2902, https://doi.org/10.1039/D0MH00535E.

[100] J. Su, N. Wei Long, A. Jia, Y. Wai Yee, C. Chee Kai, S.L. Sing, Achieving sustainability by additive manufacturing: a state-of-the-art review and perspectives, Virtual Phys Prototyp 19 (2024) e2438899, https://doi.org/10.1080/17452759.2024.2438899.

[101] D. Rejeski, F. Zhao, Y. Huang, Research needs and recommendations on environmental implications of additive manufacturing, Addit. Manuf. 19 (2018) 21–28, https://doi.org/10.1016/J.ADDMA.2017.10.019.

[102] S. Zakaria, P. Mativenga, A scientific base for optimising energy consumption and performance in 3D printing, J. Clean. Prod. 482 (2024) 144227, https://doi.org/10.1016/J.JCLEPRO.2024.144227.

[103] I. Fidan, V. Naikwadi, S. Alkunte, R. Mishra, K. Tantawi, Energy Efficiency in Additive Manufacturing: Condensed Review, Technologies (basel) 12 (2024), https://doi.org/10.3390/technologies12020021.

[104] K. Min, Y. Li, D. Wang, B. Chen, M. Ma, L. Hu, Q. Liu, G. Jiang, 3D Printing-Induced Fine Particle and Volatile Organic compound Emission: an Emerging Health Risk, Environ. Sci. Technol. Lett. 8 (2021) 616–625, https://doi.org/10.1021/acs.estlett.1c00311.

[105] D.A. Baguley, G.S. Evans, D. Bard, P.S. Monks, R.L. Cordell, Review of volatile organic compound (VOC) emissions from desktop 3D printers and associated health implications, J. Expo. Sci. Environ. Epidemiol. (2025), https://doi.org/10.1038/s41370-025-00778-y.

[106] J.P. Miller-Schulze, N.D. Williams, Volatile Organic Chemical Emissions from Standard and "Eco" Resins for Vat Photopolymerization Additive Manufacturing ("3D") Printers and potential Mitigation strategies, ACS Chemical Health & Safety 32 (2025) 175–185, https://doi.org/10.1021/acs.chas.4c00087.

[107] C. Luo, X. Luo, D. Liu, G. Ma, L. Zhang, J. Fu, Y. Li, F. Guo, M. Zhang, Y. Long, Self-healing, photoluminescent elastomers for 3D printing fabrication of flexible sensors, Chem. Eng. J. 501 (2024) 157761, https://doi.org/10.1016/J.CEJ.2024.157761.

[108] A. Toncheva, L. Brison, P. Dubois, F. Laoutid, Recycled Tire Rubber in Additive Manufacturing: Selective Laser Sintering for Polymer-Ground Rubber Composites, Appl. Sci. 11 (2021), https://doi.org/10.3390/app11188778.

[109] R. Setter, K. Wudy, Additive manufacturing and mechanical analysis of multi-material polymer parts combining thermosets and thermoplastics, Adv. Compos. Hybrid Mater. 7 (2024) 122, https://doi.org/10.1007/s42114-024-00935-1.

[110] U.M. Dilberoglu, B. Gharehpapagh, U. Yaman, M. Dolen, Current trends and research opportunities in hybrid additive manufacturing, Int. J. Adv. Manuf. Technol. 113 (2021) 623–648, https://doi.org/10.1007/s00170-021-06688-1.