3D printing of shape memory polymers

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Abstract
Shape memory polymers (SMPs) are polymers which "remember" their original shape and can return to it after deformation, if an external stimulus—often an increased temperature— is applied. Some SMPs can be 3D printed, typically by fused deposition modeling (FDM). The most well-known SMP is poly(lactic acid), which belongs to the most often used materials in FDM 3D printing. There are; however, many more SMPs which can be 3D printed to combine the possibilities to prepare new, sophisticated shapes with the opportunity to restore these shapes after undesirable or intentional deformation. This review gives an overview of several 3D printable SMPs, their mechanical characteristics and their possible applications.

KEYWORDS
blends, mechanical properties, photopolymerization, sensors and actuators, thermal properties

1 | INTRODUCTION

Shape memory polymers (SMPs) have attracted the interest of researchers and industry for decades, resulting in the development of new polymers and polymer blends with shape memory properties.1 They are applied in diverse areas, such as, smart textiles,2,3 spacecraft,4,5 or biomedicine.6–8

Shape memory polymers can return to their original shapes after a deformation, if a stimulus is applied. Typical stimuli are heat, light, a magnetic field, the pH value of a surrounding liquid, and so on.9 Depending on the polymer, diverse molecular mechanisms can be made responsible for shape memory properties. Polymer networks with covalently and physically cross-linked amorphous or crystalline copolymers typically work due to a phase separation between hard, droplet-like segments working as cross-links and a soft matrix phase, working as switch.10,11 In polymer blends from an elastomer and a crystalline switch polymer with immiscible materials, stretching and recovery are provided by the elastomer, while the switch polymer defines the performance of fixing and recovering.12

SMPs can occur in diverse forms, such as films,13 foams14 or as bulk materials.15 Another possibility to prepare diverse shapes is nowadays given by 3D printing, resulting in the so-called 4D printing, meaning that an object is printed flat and afterwards given a three-dimensional shape, for example, by heat treatment.16 This technique can be used, for example, for controlled sequential folding,17 enabling easier printing of certain structures or even making unprintable shapes available,18 or even producing soft robotics.19–21 There are even attempts using this method in bioprinting22,23 or as the microscale.24,25

Several 3D printing technologies exist, amongst them stereolithography (SLA), selective laser sintering (SLS), selective laser melting (SLM), and the nowadays very often used fused deposition modeling (FDM).26 These 3D printing techniques are typically based on slicing the CAD model into a number of layers which are subsequently printed. In this way, diverse new shapes can be
created which would not be hard or impossible to create with injection molding, thus also allowing for using 3D printed parts for new applications.

During the last years, increasing research and development was performed on combining both techniques, that is, 3D printing SMPs. Figure 1 shows the numbers of results found in the Web of Science, searching “3d print* shape memory” or “shape memory polymer*”. On the one hand, the number of papers dealing with shape memory polymers is still steadily increasing, although first reports have been published 30 years ago. On the other hand, an even higher increase in research of 3D printed shape memory polymers can be recognized, underlining the importance of this emerging field of research.

The aim of this review is to give an overview of the relatively young field of 3D printing shape memory polymers. The paper is structured as follows: Section 2 gives a brief overview of possible physical mechanisms of temperature-stimulated shape memory polymers. Section 3 concentrates on the most often used SMP for 3D printing via the FDM technology, poly(lactic acid) (PLA), in pure form, composites and blends. Section 4 gives an overview of other SMPs used in FDM printing. Finally, Section 5 shows SLA printable photopolymers and gives a brief outlook on the view SMPs available for other 3D printing techniques.

2 | MECHANISMS OF SHAPE MEMORY PROPERTIES

As mentioned before, SMPs typically work due to an interaction of shape-fixing and shape-switching parts. Typically, for low temperatures, such a material is in a solid or glass-like region, while for high temperatures, an elastic or rubbery state is reached. Between these regions, there is a transition range. For some materials, researchers investigated this mechanism more in detail.

Beloshenko et al. describe this effect from a physical perspective as the system's desire to reach thermodynamic equilibrium, that is, minimizing the difference between internal energy and entropy. They mention that increasing polymer chain orientation decreases the entropy, while the internal energy has to decrease on deformation to compensate this decrease in entropy, in order to realize a stable structure. This can be found in crystallizing polymers with strong enough bonding between polymer chains.

For glassy (amorphous) polymers, full recovery can be expected, described by different models based on one or more energy barriers which have to be overcome.

For amorphous-crystalline homopolymers, more complicated effects have to be taken into account, for example, transition from a paracrystalline into a crystalline phase, packing or originally extended chains in crystallites and crystallite melting, and so on.

For copolymers, on the other hand, the aforementioned segmentation into hard and soft segments (or frozen and reversible phases) results in the shape memory effect. Kim et al. examined the shape memory effect of polyurethanes as a typical example of a copolymer. They attributed shape recovery to the elastic strain generated during deformation, either above or below the shape recovery temperature. They also mentioned the importance of the tensile modulus in the glassy state, resulting in high shape fixity for a high glassy state modulus, and of the tensile modulus in the rubbery state which provides high elastic recovery.

Since most 3D printable shape memory polymers are based on thermal stimuli, the more complicated mechanisms of chemo-responsive or light-responsive polymers are not described here in detail.

3 | PLA AS A SHAPE MEMORY POLYMER

PLA belong to the most often used polymers in 3D printing by FDM. This is not only based on its ease of use, relatively low printing temperature, and due to the fact that it shows much lower warping than several other polymers, but also on its low toxicity, especially in comparison with acrylonitrile butadiene styrene (ABS) which is also relatively often used. Nevertheless, its shape memory properties are often unknown. Here, an overview is given on recent research on shape memory properties of 3D printed objects from pure PLA and PLA blends.
3.1 | Pure PLA

PLA contains, as described above, shape-fixing and shape-switching parts. The shape memory properties are ascribed to physical cross-links as well as crystallization. However, pure PLA cannot be extended by more than approximately 10% without breaks. This is why it is necessary for many applications of PLA as a shape memory polymer to design sophisticated structures to overcome these limitations, as they can be prepared by 3D printing.

Most recently, Langford et al. used origami structures to solve this problem. The idea of such origami structures is that they enable folding and unfolding, in this way expanding from a small to a large volume or vice versa. This property is advantageous, e.g., for minimally invasive introduction of biomedical scaffolds into the human body. Comparing a waterbomb and a herringbone tessellation, they found that the first deformed in an unreliable way, while herringbone tessellated tubes could be used to strongly compress them and afterwards restore them mostly, as visible in Figure 2. They found that the PLA filament showed a constant shape recovery of approx. 61%, independent from the applied deformation, while the recovery rate of the herringbone tessellated origami tube was increased to approx. 96% in spite of some cracks visible after compression (Figure 2(c)). The recovery rate remained unaltered after adding a porous bone-mimicking infill structure.

PLA printed cubes with different infills were investigated by our group. On the one hand, the 3D honeycomb structures was found to show lower recovery in a hot water bath since this structure is fully closed, and thus the inner parts of the cubes were less heated than the borders. The gyroid infill structure was examined with different infill degrees, showing strongly different forces necessary to reach the planned deformation and also strongly different recovery properties. To enable a quantitative comparison of the recovery properties of samples with different infill degrees under partial indentation from different sides, diverse new mathematical descriptions were suggested, based on the force necessary for a defined impact or on the residual strain after each test cycle. Mehrpouya et al. used an open honeycomb structure in the form of an irregular hexagon with outermost closed sheets, with the open combs being oriented parallel to the long direction of a test sample which was bent perpendicular to the long axis. They modified printing speed, nozzle temperature and recovery temperature and found the highest recovery ratio for an activation temperature of 85°C, a nozzle temperature of 230°C, and a printing speed of 30 mm/s. The unfolding angle of the bent samples was measured optically and showed also clear time dependencies for different activation temperatures and printing speeds, while the different nozzle temperatures did not significantly influence the start of the unfolding process.

The same group also investigated flat origami structures 3D printed from PLA, foldable to a pyramid with square base at a temperature near the glass transition temperature. The idea behind this structure is an application to release an encapsulated material, grasp an

![Herringbone tessellated tube](image-url)
object or block a gap. By varying different geometrical and printing parameters, the authors found that recovery was highest for the highest activation temperature of 75°C, for a layer height of 0.3 mm, for the highest examined nozzle temperature of 225°C, and the smallest overall thickness. In another parameter optimization study, Wu et al. found maximum recovery for a deformation temperature of 55°C, a recovery temperature of 70°C, a raster angle during printing of 45°, and a layer thickness of 0.15 mm.45

Jia et al. investigated self-expanding vascular stents printed from PLA.46 A hexagon nested tubular structure was designed and FDM printed with diameter 4 mm, length 40 mm, and wall thickness 0.4 mm. Recovery was performed at 70°C in a water bath after compression at the same temperature and subsequent fast cooling. While the quenched temporary shape was retained for a week at room temperature without visible modifications, the initial shape was recovered after 5 s at 70°C. Shape recovery rates were measured for elongated samples and found to be approximately 87% after the first cycle and 96% after the second one, which was attributed to a better molecular orientation after the first test. Another shape of stents was suggested by Wu et al. who combined shape memory properties of PLA with auxetic properties, that is, a negative Poisson’s ratio, of an arrowhead structure, as depicted in Figure 3.47 Such auxetic structures allow for decreasing radial and longitudinal dimensions at the same time and have been reported before in different 3D printing applications.48 Here, different geometries were investigated to prepare vascular stents, compressed and recovered in a water bath of 65°C. These geometries strongly influenced the forces necessary for compression (Figure 3(b)). Recovery rates between 95% and 98% were found for diameter and length recovery, showing that such auxetic structures may be highly suitable for stent preparation.

Besides these basic research studies and few other studies aiming at biomedical applications,49,50 other authors suggest applications of pure PLA as 3D printed shape memory polymer for deployable antennas51 or smart textiles.52 Many research groups, however, add fibers, nanoparticles etc. to PLA or blend it with other polymers. Both these ways of increasing the shape memory properties of PLA will be discussed in the next subsections.

3.2 | PLA composites

Diverse materials in different shapes are reported to be mixed with PLA to improve the recovery properties. Most recently, Zhao et al suggested PLA/Fe₃O₄ as shape memory polymer which can be recovered in an external magnetic field.53 Such stimuli alternative to heat treatment are especially important for in vivo applications where high temperatures cannot be used. The structures used in this study mimicked porous lotus rhizomes and bone trabecular structures with porosities of 50%–60%, with one of the latter being similar to the aforementioned gyroid structure.40–42 Filaments for the FDM printer were prepared by mixing 80% PLA with 20% Fe₂O₄ (magnetite) to form a solid mixture which was shredded and then extruded in a twin-screw extruder.53 By applying a magnetic field alternating with 30 kHz, shape recovery of more than 95% was reached after only 14–24 s. Besides, good biocompatibility and cell adhesion and proliferation were found, with differences between the structures due to the different pore size distributions.53

Good biocompatibility can also be reached by adding a biomedical agent like hydroxyapatite (HA) to PLA. This is why several studies concentrate on PLA/HA composites, for example, as an alternative of implants for small bone defects.54,55 Singh et al added different amounts of HA powder (4–8 wt%) to PLA granules, milled the mixture and prepared a filament in a twin-screw extruder.56 Different infill percentages, numbers of outer perimeters and post-heating steps to improve the mechanical strength were compared. By this, the authors found recovery rates between approx. 72% and 96% for

![Figure 3](https://wileyonlinelibrary.com)
regeneration temperatures between 60 and 70°C. Sui et al. used synchrotron X-ray scattering to investigate the thermo-mechanical properties of PLA/HA composites, finding a nearly full strain recovery in this way, which underlined that 15 wt% HA did not significantly decrease the recovery.

Another composite was prepared by Zeng et al who added continuous carbon fibers to a PLA filament during 3D printing. Using a modified FDM printer, they fed a special PLA with good shape memory properties and continuous carbon filaments simultaneously through a single nozzle. In this way, different nozzle temperatures, printing speeds and infill angles were investigated in terms of their influence on the mechanical sample properties. The conductive carbon filaments allowed for electrical actuation by resistive heating, leading to recovery above 95% in approx. 75 s. Carbon nanotubes (CNTs) were introduced in PLA instead by Liu et al. They found a dependency of the volume resistivity on the raster angle as well as the temperature, especially above approx. 70°C. Resistive heating thus resulted in different time-dependencies of the temperatures reached in the samples. Shape recovery values near 100% were reached during 100–350 s, depending on the voltage and the printing parameters. CNT reinforced PLA filaments were also used to prepare different braid-mimicking printed shapes. Recovery was performed for a temperature of 90°C, approached with a heat rate of 5 K/min, and found to start earlier for CNT/PLA specimens than for pure PLA samples and to depend on the printed shapes. Besides, samples infused with a silicone elastomer matrix were tested which always showed higher shape recovery near 97%.

Liu et al. filled PLA filaments not only with graphite powder, but also with silicon carbide (SiC). In the samples without or with 20 wt% SiC, shape recovery after stretching resulted in a residual compressive strain, that is, an effect opposite to the training strain. A similar behavior was also observed in Ref.42. Oppositely, introducing 50 wt% SiC into PLA led to a small residual elongation after recovery. The recovery forces were increase with increasing amount of SiC.

Bodkhe and Ermanni combined barium titanate, a piezoelectric material, with a blend of PLA and polyether-esteramide (PEA), another shape memory polymer. Opposite to most other studies dealing with PLA, here no filaments for FDM printing were prepared, but a shape memory ink by dissolving 20% PLA in dichloromethane and adding 0–6 wt% PEA as well as 0–30 wt% barium titanate nanoparticles. These shape memory inks were printed by extrusion from syringes onto a movable platform, applying an electric field between nozzle and substrate, in this way poling the piezoelectric material. After applying small forces on the samples, nearly full recovery could be reached, with slightly smaller values for larger amounts of PEA. The piezoelectric output was measured by adding painted silver electrodes, with an increasing force leading to an increasing voltage. This combination of multiple functions has the advantage of piezoelectric sensing by a self-powered sensor. Another multi-function approach was chosen by Wang et al. who combined shape memory properties with thermochromics properties. They found an influence of the printing parameters, namely nozzle temperature and layer thickness, as well as of geometry and excitation temperature on the recovery ratios. The most critical parameter to define was the ratio of recovery and color conversion speed, which was enabled by fitting the aforementioned parameters, in this way allowing for preparing blooming, color-changing flowers etc. as proofs-of-principle (Figure 4).

Similar flower-petals were also designed by Hua et al who printed PLA with multi-walled CNTs on paper substrates. By adding CNTs, the 3D printed layer could be heated up photothermally by NIR irradiation, so that the bilayer could deform triggered by NIR irradiation. Such flexible actuators were suggested for possible use in soft robotics. A similar idea was proposed by Wang et al. who used a single layer PLA on a sheet of copy paper and mentioned also interactive arts, entertainment and home environment as possible areas of application.

Similarly, combining sheet of paper and a 3D printed bionic leaf, Hu et al prepared a soft gripper. They applied a voltage of 220 V/50 Hz to heat polyimide electrothermal films which again heat the bionic leaves. In this way, opening the leaves by heating and grasping little objects by cooling down, closing the leaves again, was enabled. A similar approach was chosen by Shin and So who investigated the raster angle dependency of actuating the PLA/paper bilayer composite. Instead of paper as the substrate, Yang et al used two layers of carbon fiber reinforced PLA and polyether-ether-ketone (PEEK) which bent due to a strain mismatch between both layers if temperature was applied directly or by an electric current. These double-layer smart materials were suggested for a possible use in biomimetic sensors and actuators as well as artificial muscles.

As these examples showed, introducing nanoparticles or fibers into PLA or forming double-layer sandwiches can be used to increase recovery properties, broaden the possible areas of application and can even be used to add a second functionality, triggered by the same stimulus. Besides these possibilities, PLA can also be blended with other polymers to create objects with other mechanical or recovery properties.
3.3 | PLA blends

PLA can be blended with diverse materials to improve recovery or to introduce additional properties. Liu et al., for example, prepared PLA/poly(ε-caprolactone) (PCL) blends in which they found PCL to be the reversible phase and PLA to be the fixed phase. Depending on the PCL content between 10% and 60%, different shape recovery ratios between ~59% and 84% were reached, while the shape fixity was more than 95%. Testing different printing parameters, layer thickness and raster angle showed large impact on the shape memory properties, while the infill density left the shape memory effect nearly unaltered.

Blending PLA with chitosan, which is known to have antimicrobial properties advantageous for scaffolds and other biomedical applications, Pandey et al. prepared doggy-bone-shaped samples which were pre-elongated and annealed, and length recovery was measured. Shape memory was found to be strongly reduced with increasing amount of chitosan. On the other hand, it was possible to improve the hydrophilic properties of the samples by subjecting it to a higher range of stimulating temperature, which increased the adhesive properties of the surface and thus adhesion and proliferation of liver cells tested on these scaffolds. Carlson and Li blended PLA with thermoplastic polyurethane (TPU) in different weight ratios between 9:1 and 6:4 to reduce the brittleness of PLA at room temperature and thus the aforementioned problem of cracks which reduce the shape memory properties. They printed L-shaped specimens and analyzed recovery after deformation to flat shapes. Recovery ratios of 65%–78%, averaged over 11 deformation and recovery cycles, were found. It must be mentioned that here a strong deformation, that is, bending by 90°, was tested, opposite to other studies using compression by 10% or less. Sun et al. modified the PLA filament by melt-blending it with 10 or 30 wt% of poly(ethylene glycol) (PEG). In this way, actuation temperatures of different parts of a sample could be tuned, here with a recovery temperature of pure PLA above 60°C, while the PEG-blended samples had recovery temperatures of 55°C and below. Objects with position-dependent recovery temperature could be used to define the order of actions of a thermomechanic actuator etc.

Besides these few examples of PLA blends, there is a broad range of other FDM printable shape memory polymers which will be discussed in the next section.

4 | OTHER FDM PRINTABLE SHAPE MEMORY POLYMERS

At first glance, it may be unexpected that many FDM printable polymers exhibit shape memory properties, amongst them quite well-known materials and also more unusual ones, such as bisphenol A epoxy with benzoxazine, (meth)acrylate systems with dynamic imine bonds, polycyclooctene (PCO) or a zinc-neutralized poly(ethylene-co-methacrylic acid).

One of the more often used materials is polyurethane (PU). Nguyen and Kim, for example, added single-walled CNTs to polyurethane by dispersing the CNTs in dimethylformamide (DMF) and afterwards melting PU pellets in the same solvent, stirring for 2 days and preparing a composite film, which was shredded to receive an

![Image](https://example.com/image.png)
FDM filament. This was used to print a triple-layer system with two shape memory layers sandwiches a conductive silver paste layer, added by Polyjet printing, or the aforementioned conductive PU/CNT layer. They found that higher ratios of CNTs led to reduced and slower recovery, while the silver paste showed lower resistance, but higher heterogeneity. Kabir and Lee printed a sinusoidal mesh on a nylon woven fabric and investigated recovery of this sandwich at 70°C after changing the shape from flat to L-shape at 70°C. They found shape recovery ratios near 100% for all samples even after 50 deformation and recovery cycles. Recovery durations were higher for higher sample thicknesses and also increased with the number of test cycles. The authors suggested using these composites as three-dimensional protective clothing which can be individually fitted to knee, elbow or other curvy body parts.

Vitola et al. embedded 0%–2% CuS nanoparticles, stabilized by polyvinylpyrrolidone (PVP), in PU by solvent casting. CuS nanoparticles show photothermal response in UV and NIR and offer thus different possibilities to stimulate recovery. The 3D printed stripes were programmed by bending them at 40°C to reach a stable temporary shape. Recovery was performed by irradiation with a Xe lamp at a temperature below 30°C. For 0.5% CuS nanoparticles, recovery was reached in 1 min. Carbon black was used as a photothermal conversion material by Bi et al. in PU/PCL blends. Highest thermally stimulated recovery rates were found for a PCL content of 30 wt%, while carbon black enabled also light-triggered recovery.

Commercial SMP polyurethane was printed by Cersoli et al. using a pellet extruder mounted on an FDM printer, in this way enabling direct printing from pellets. They found a shape recovery higher than 96%, using either a heat gun or hot water. The authors suggested this material for a possible application in authentication and electronics and underlined this idea by preparing a QR code which was not readable in the deformed state, but detectable after applying a thermal stimulus (Figure 5). Besides, by combining this SMP with a shape memory allow, they produced a hybrid actuator working as a thermal switch.

By embedding cellulose nanocrystals (CNCs) in polyurethane, Chen et al. prepared cardiovascular stents which could be programmed at 45°C and recovered at 40°C. This was enabled by the glass transition temperature dropping from 39.7 to 34.2°C due to the addition of CNCs. In addition, the recovery force was improved by the added CNCs.

Damanpack et al. investigated the shape memory effect after large deformations due to contact or impact loading in 3D printed beams from polyurethane. They found nearly full recovery by heating the samples and

**Figure 5** (a) 3D printed SMP with printed QR code (red square); (b) after deformation; (c) after recovery. From Ref.85, originally published under a CC-BY license [Color figure can be viewed at wileyonlinelibrary.com]
suggested using similar beam-like SMP structures for applications exposed to impact loadings.

While polyurethane-based 3D printing materials are often investigated in terms of their shape memory properties, nylon is only scarcely mentioned in the literature. Peng et al. developed a polypropylene (PP)/nylon 6 (PA6) blend with PA6 contents between 0 and 30 wt.%.

They found good shape recovery properties after setting a temporary shape at 175°C, followed by reheating to 175°C, after approx. 3 min.

Kang et al. who combined a shape memory polymer with a shape memory alloy (SMA). By preparing a composite from nylon as a shape memory polymer in which a Nitinol wire as a shape memory alloy was embedded, they reached reversible actuation since depending on the temperature, one of the shape memory effects was dominant. This effect is illustrated in Figure 6. In most other studies, nylon is not used as a shape memory polymer.

Poly(vinyl alcohol) (PVA) also shows shape memory properties. While often used as a water-soluble support material in 3D printing, the slow dissolution in water can also be utilized for drug delivery, as Melocchi et al. showed. They plasticized PVA by blending it with glycerol before adding drug-containing materials. Spiral original shapes were compressed to enable easier oral administration and were found to recover their original shape after approx. 3 h in 0.1 M hydrochloric solution at 37°C. Drug release was slowed down by coating the FDM printed samples.

Other typical FDM printing materials, such as ABS, polyethylene terephthalate glycol (PETG) or PEEK, are not reported to show shape memory properties. A few studies can be found dealing with unknown commercially available SMPs which will not be described here in more detail. However, besides these materials suitable for FDM printing, other materials can even be processed by SLA or other 3D printing techniques. They will be described in the next sections.

5 SLA PRINTABLE SHAPE MEMORY POLYMERS

One of the materials developed for 3D printing by the SLA technique was suggested by Radchenko et al. They prepared cycloaliphatic epoxy-functionalized ionic liquids with one or two imidazolium units, which could be cured using SLA printing. A thermoacid generator, diazidonium hexafluoroantimonate, was used to increase the crosslinking rate, leading to a poly-ionic liquid network showing a rubbery state. Interestingly, all networks produced from the cycloaliphatic epoxy-functionalized ionic liquids showed shape memory properties with good shape retention in the temporary state and good recovery properties. Seo et al prepared an SLA printable material to mimic 3D artificial tissue. They firstly produced hydroxybutyl methacrylated chitosan and compounded this material with poly(ethylene glycol) dimethacrylate, cellulose nanofibrils and a photo-initiator. As a reference, a resin without the hydroxybutyl methacrylated chitosan was prepared. Both materials were printed in a commercial SLA printer. Interestingly, the samples including the hydroxybutyl methacrylated chitosan showed reversible pore structure formation, depending on the temperature, which could be translated into reversal bending and unbending of a sample during few minutes, while these effects did not occur in the resin without chitosan.

Chooong et al combined a monomer and a crosslinker, with the monomer being the soft (switching) component which enables large plastic deformation, while the crosslinker delivers the net-points with strong, thermally stable bonds defining the permanent shape. More exactly, they combined a tert-butyl acrylate monomer with a di(ethylene glycol) diacrylate crosslinker in different mass ratios. To test shape memory properties, the samples were heated above the glass transition temperature, deformed up to 10% strain, cooled the sample down, took the force away, and heated the sample up again to measure shape recovery ratio. This cycle was repeated until the samples were fractured. Depending on the mass ratio of both components, recovery rate between nearly 100% (for 10% crosslinker) even after 22 test cycles and approx. 90% during 6–8 test cycles were found. On the other hand, larger amounts of crosslinkers could increase the shape fixity, that is, the ability to retain the temporary shape.

SLA-printable shape memory gels with high transparency and high strength were firstly described by Kumagai et al. They found that the refractive index depended on the monomer concentration, but was independent from...
crosslinker and photoinitiator. Both the latter, however, influenced the gelation progression rate. In this way, shape memory gels with different refractive indices were produced which were suggested for the use as gel intraocular-lens replica. Zhang et al. used a liquid resin, mainly consisting of an acrylic resin monomer, for SLA printing. They produced hollow tubes, arranged in an octet lattice similar to an FCC lattice, which were evacuated and then filled with gallium (Ga). Shape recovery of this metamaterial at 90°C was actually performed by the core rather than by the potentially damaged polymer shell. Mixing poly(D,L-lactide)dimethacrylate (PDLLA-2MA) macromonomers with diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO), 2,5-bis(5-tert-butyl-benzoxazo1-2-yl) thiophene (BBOT) UV-absorber and hydroquinone (HQ) inhibitor, Di Bartolo and Melchels produced an SLA printable liquid. They reached average shape recovery ratios of up to approx. 90%, depending on the recovery temperature, and a broad range of recovery durations between minutes and weeks, combined with a high retention of the temporary state below the glass transition temperature. Such shape memory polymer networks were suggested for novel applications in the medical field.

Instead of preparing own resins, Inverardi et al. used a commercially available photoreactive resin (FLGPCL02), based on methacrylic acid esters and photoinitiator. SLA printed cubes from this resin were compressed by 40% at different temperatures between room temperature and 120°C, cooled down and afterwards recovered well above the glass transition temperature. For all tests, full recovery was reached. Since the material has a broad glass transition temperature range, the recovery temperature was found to be related to the deformation temperature. The authors thus suggested such a material to obtain sequential motion by printing only a single material. Compounding polyurethane acrylate with epoxy acrylate and isobornyl acrylate and a radical photoinitiator, Zhao et al. prepared an SLA printable photopolymer. In this way, not only high strength and toughness of the printed materials were found, but also a recovery rate near to 100% within less than 20 s in a hot water bath.

A combination of stereolithography and photolithography was used by Miao et al. to produce hierarchical micro-patterns from smart soybean oil epoxidized acrylic inks for bone marrow mesenchymal stem cell growth and alignment. The printed thin-film scaffolds could be triggered to self-assemble into rolling structures by immersion in ethanol which was attributed to a cross-link density gradient due to the photolithographic process.

Since the last mentioned study already combined two different printing processes, it is obvious to search for shape memory polymers produced by other 3D printing processes. However, only few reports can be found dealing with digital light processing (DLP) of shape memory polymers, while no reports were found on selective laser sintering (SLS), selective laser melting (SLM) or Polyjet printing. Apparently, the idea of 3D printing shape memory polymers is still too new to be transferred into the whole range of 3D printing technologies.

6 CONCLUSION

3D printing shape memory polymers gained increasing interest in research and development during the last years. While most research groups work with pure PLA as the most common 3D printing polymer for the FDM technique, several studies were found reporting on adding diverse fillers to PLA or blending it with other polymers. Amongst the other FDM printable polymers, especially polyurethane is prominently investigated by different researchers.

Besides FDM, there are also diverse approaches to prepare SLA printable shape memory polymers. However, only a small amount of studies was found dealing with the DLP technique, and no reports on shape memory polymers for SLS, SLM, or Polyjet were found.

This short overview shows the broad range of shape memory polymers already available, but also the spaces which are still open for new developments. We hope that our review stimulates more researchers to enter the increasing field of 3D printable shape memory polymer.

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REFERENCES

[1] P. T. Mather, X. F. Luo, I. A. Rousseau, Annual Rev. Mater. Res. 2009, 39, 445.
[2] Q. H. Meng, J. L. Hu, L. Y. Yeung, Smart Mater. Struct. 2007, 16, 830.
[3] Q. H. Meng, J. L. Hu, Y. Zhu, J. Lu, Y. Liu, Smart Mater. Struct. 2007, 16, 1192.
[4] J. S. Flanagan, R. C. Strutzenberg, R. B. Myers, J. E. Rodrian, 48th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, And Materials Conference, Honolulu, Hawaii, pp. 1–3. 2007
[5] T. Blachowicz, K. Pajak, P. Recha, A. Ehrmann, AIMS Mater. Sci. 2020, 7, 926.
[6] A. Metcalfe, A.-C. Desfaits, I. Salazkin, L. Yahiaib, W. M. Sokolowskic, J. Raymonda, Biomaterials 2003, 24, 491.
[7] H. M. Wache, D. J. Tartakowska, A. Hentrich, M. H. Wagner, J. Mater. Sci. Mater. Med. 2004, 14, 109.
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