

SHAPE MEMORY POLYMER, FORMULATION FOR, METHOD OF FORMING AND DEVICE INCLUDING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10201603355Q filed on April 27, 2016, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various aspects of this disclosure relate to formulations for forming shape memory polymers. Various aspects of this disclosure relate to methods of forming shape memory polymers. Various aspects of this disclosure relate to shape memory polymers and/or devices including shape memory polymers.

BACKGROUND

[0003] Shape memory polymers (SMPs) belong to a class of polymeric smart materials that are responsive to stimuli or changes in conditions, such as varying temperatures, humidity, pH, light and/or magnetic fields. SMPs are first processed or polymerized into an original shape, then heated above a transition temperature (T_{trans}), which may be either a glass transition (T_g) temperature or a melting temperature (T_m), to switch from glassy state to rubbery state, which could be mechanically deformed and fixed into a temporary shape upon cooling. The SMP remains stable unless it is triggered by an appropriate external stimulus to return to the original “memorized” shape. This shape recovery phenomenon is also known as shape memory effect (SME). The reshaping capability may give rise to numerous applications, particularly in the biomedical field. Applications in the biomedical field may include sutures or stents for minimally invasive surgery, sensors, actuators, and even textiles.

[0004] However, the manufacturing and processing of SMPs still rely heavily on conventional methods such as resin transfer moulding (RTM) and solid state forming, which process either thermoset resins or thermoplastic resin in pellet form. The conventional manufacturing technologies require moulds to be fabricated, which delay the production lead time for the final products. Further, most moulds are of high geometrical complexity, resulting in the requirement for multi-machining steps, leading to cost-ineffective approaches.

Accordingly, there is a need for new processing methods to fabricate SMPs with high complexity.

[0005] Additive manufacturing (AM), also known as three dimensional (3D) printing or rapid prototyping, has advanced at remarkable speed, emerging as a robust technology to substitute existing manufacturing in increasingly complex tasks. The great design freedom enabled by AM capabilities has made possible the manufacturing of functional and aesthetically pleasing designs that were previously uneconomical or implausible. However, as the additive manufacturing matures, it comes to be realised that the printed parts are typically immobile and non-adaptive. Recently, there is a radical shift in additive manufacturing with an addition of a fourth dimension – the transformation over time. 4 dimensional (4D) printing is a scale up of 3D printing.

[0006] The convergence of 3D printing with the use of smart stimuli-responsive materials give rise to 4D printing which is now primarily based on polymer-based AM processes, where these printed SMPs offer greater flexibility and are able to withstand significantly larger recoverable strains for shape transformation as compared to metals. As of today, research and developments in 4D printing are largely based on the more widespread commercial systems in the market, which are the fused deposition modeling (FDM) printing or inkjet printing, such as Objet and PolyJet. The research interests in this field have been mainly focused on enabling the manufacture of designs that were previously unachievable or fabricating multi-material components using conventional smart materials. The development of SMPs for liquid based AM systems are scarce in literature, given that there are only very limited number or types of SMP materials being explored currently.

SUMMARY

[0007] Various embodiments may provide a formulation for forming a shape memory polymer. The formulation may include an acrylate monomer. The formulation may also include a cross-linker for forming one or more cross-links with the acrylate monomer to form the shape memory polymer. The formulation may further include a photoinitiator for initializing the formation of the one or more cross-links upon exposure to light. The formulation may additionally include a photoabsorber for controlling a rate of formation of the one or more cross-links. A concentration of the photoabsorber may be any one value selected from a range of 0.1 weight percent to 10 weight percent of the formulation.

[0008] Various embodiments may provide a method of shaping a shape memory polymer. The method may include mixing a formulation as provided herein. The method may also include exposing the mixture to light so that the cross-linker forms one or more cross-links with the acrylate monomer to form the shape memory polymer. The formation of the one or more cross-links upon exposure to light may be initialized by the photoinitiator. A rate of formation of the one or more cross-links may be controlled by the photoabsorber. A concentration of the photoabsorber may be any one value selected from a range of 0.1 weight percent to 10 weight percent of the formulation.

[0009] Various embodiments may provide a shape memory polymer formed by a method as described herein.

[0010] Various embodiments may provide a device including a shape memory polymer as described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

FIG. 1A is a schematic showing a formulation for forming a shape memory polymer according to various embodiments.

FIG. 1B shows an illustration of Sudan I according to various embodiments.

FIG. 1C shows an illustration of Sudan III according to various embodiments.

FIG. 1D shows an illustration of Rhodamine B according to various embodiments.

FIG. 2 is a schematic showing a method of forming a shape memory polymer according to various embodiments.

FIG. 3A shows a photograph of the permanent shape of a shape memory polymer (SMP) in the form of a bucky-ball according to various embodiments.

FIG. 3B is a photograph showing a deformed shape of the shape memory polymer in the form of a flat shape according to various embodiments, which is formed after the bucky-ball in FIG. 3A is heated to above the transition temperature (T_g), opened up by force and cooled down.

FIG. 3C is a photograph showing the restored bucky-ball shape recovered after the flattened shape shown in FIG. 3B according to various embodiments is placed in hot water.

FIG. 3D is a photograph showing another deformed shape of the shape memory polymer in the form of a flattened structure according to various embodiments, which is formed after the bucky-ball in FIG. 3A is heated to above the transition temperature (T_g), softened, and compressed.

FIG. 3E is a photograph showing the restored bucky-ball shape recovered after the flattened structure shown in FIG. 3D according to various embodiments is placed in hot water.

FIG. 4 is a schematic illustrating the chemical structure of the crosslinking between tert-butyl acrylate (tBA) monomer molecules and di(ethylene glycol) diacrylate (DEGDA) cross-linker molecules according to various embodiments.

FIG. 5 is a plot of excess width (millimeters or mm) as a function of laser scanning speed (millimeter per second or mm/s) showing the excess width of the cured specimens in x and y directions measured using digital caliper.

FIG. 6 is a plot of thickness (in micrometres or μm) as a function of length (in millimetres or mm) showing the curing depths of square laminates according to various embodiments with varying concentrations of photoinitiators.

FIG. 7A is a plot of weight percentage (in percent or %) of the original weight and the derivative of the weight percentage (in weight percent per degree Celsius or $\text{wt}\% / ^\circ\text{C}$) of the printed shape memory polymer (SMP) according to various embodiments as a function of temperature (in degrees Celsius or $^\circ\text{C}$).

FIG. 7B is a plot of storage modulus (in mega Pascals or MPa), tan delta ($\tan \delta$), and loss modulus (in mega Pascals or MPa) as a function of temperature (in degree Celsius or $^\circ\text{C}$) showing the dynamic mechanical analysis (DMA) curves of the shape memory polymers according to various embodiments in which the glass transition temperature (T_g) and viscoelasticity of the shape memory polymers may be determined.

FIG. 7C is a plot of dimension change (in micrometres or μm) as a function of temperature (in degrees Celsius or $^\circ\text{C}$) indicating the softening temperature of the shape memory polymer (SMP) according to various embodiments.

FIG. 8A is a table showing tensile properties of printed shape memory polymers according to various embodiments at room temperature (r.t.p) and at glass transition temperature (T_g).

FIG. 8B shows a plot of stress (mega-Pascals or MPa) as a function of strain (in percent or %) showing stress-strain curves of the shape memory polymers according to various embodiments at room temperature (r.t.p) and at glass transition temperature (T_g).

FIG. 8C is a table comparing properties of stereo-lithography (SLA) printed shape memory polymers according to various embodiments and properties of a commercial thermoset Veriflex shape memory polymer.

FIG. 9 shows a plot of fixity (in percent or %) as a function of cycles of a printed shape memory polymer (SMP) according to various embodiments.

FIG. 10 is a plot of recovery percentage (in percent or %) as a function of cycles showing the shape recovery properties of the shape memory polymers (SMPs) according to various embodiments over several cycles until the shape memory polymers fail to recover.

FIG. 11A is a three-dimensional (3D) plot of strain (in percent or %) as a function of temperature (in degrees Celsius or °C) and stress (in mega-Pascals or MPa) showing a thermomechanical cyclic test of a shape memory polymer (SMP) according to various embodiments under 0.3N deformation force.

FIG. 11B is another three-dimensional (3D) plot of strain (in percent or %) as a function of temperature (in degrees Celsius or °C) and stress (in mega-Pascals or MPa) showing a thermomechanical cyclic test of a shape memory polymer (SMP) according to various embodiments under 0.7N deformation force.

FIG. 12A is a plot of exotherm (in arbitrary units or a.u.) as a function of temperature (in degree Celsius or °C) showing the digital scanning calorimetry (DSC) results of shape memory polymers formed with different concentration of the cross linkers according to various embodiments.

FIG. 12B is a plot of tangent delta ($\tan \delta$) as a function of temperature (in degree Celsius or °C) showing the tangent delta ($\tan \delta$) ratios shape memory polymers according to various embodiments with different concentrations of cross-linker molecules.

FIG. 13A is a plot of fixity ratio R_f (in percent or %) as a function of number of cycles illustrating the effect of increasing concentrations of cross-linkers on shape fixity of the shape memory polymers according to various embodiments.

FIG. 13B is a plot of recovery ratio R_r (in percent or %) as a function of number of cycles illustrating the effect of increasing concentrations of cross-linkers on shape recovery properties of the shape memory polymers according to various embodiments.

FIG. 14 is a plot of recovery ratio (in percent or %) as a function of strain (in percent or %) comparing the shape recovery properties between the developed stereo-lithography shape memory polymers (SLA SMPs) according to various embodiments and other thermoset shape

memory polymers (SMPs) fabricated using conventional methods such as injection molding and casting.

FIG. 15A is an image of a stereo-lithography (SLA) printed part including a shape memory polymer (SMP) without addition of silicon oxide (SiO_2) particles according to various embodiments.

FIG. 15B is an image of another stereo-lithography (SLA) printed part including a shape memory polymer (SMP) without addition of silicon oxide (SiO_2) particles according to various embodiments.

FIG. 15C is an image of a stereo-lithography (SLA) printed part including a shape memory polymer (SMP) including silicon oxide (SiO_2) particles according to various embodiments.

FIG. 15D is an image of another stereo-lithography (SLA) printed part including a shape memory polymer (SMP) including silicon oxide (SiO_2) particles according to various embodiments.

FIG. 16 is a plot of reflectance (in percent or %) as a function of wavenumbers (in per centimetres or cm^{-1}) showing the Fourier Transform Infra-red (FTIR) spectra of shape memory polymers with different amounts of silicon oxide (SiO_2) nanoparticles according to various embodiments.

FIG. 17 is a plot of stress (in mega Pascals or MPa) as a function of strain (in percent or %) showing the stress-strain curves of shape memory polymers with different concentrations of silicon oxide (SiO_2) nanoparticles according to various embodiments.

FIG. 18A is an image showing the agglomeration of the nanoparticles after a few print jobs to form large clusters which may affect the printed parts according to various embodiments.

FIG. 18B is a plot of intensity (percent or %) as a function of size (in nanometres or nm) showing the particle size distribution in the mixture or formulation according to various embodiments.

FIG. 19 is a schematic showing an experimental setup for determining curing depth.

FIG. 20A shows an image of a dental aligner including the shape memory polymer (SMP) according to various embodiments.

FIG. 20B shows another image of the dental aligner including the shape memory polymer (SMP) according to various embodiments.

DETAILED DESCRIPTION

[0012] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0013] Embodiments described in the context of one of the methods or formulation/polymer/device is analogously valid for the other methods or formulation/polymer/device. Similarly, embodiments described in the context of a method are analogously valid for formulation/polymer/device, and vice versa.

[0014] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0015] The word "over" used with regards to a deposited material formed "over" a side or surface, may be used herein to mean that the deposited material may be formed "directly on", e.g. in direct contact with, the implied side or surface. The word "over" used with regards to a deposited material formed "over" a side or surface, may also be used herein to mean that the deposited material may be formed "indirectly on" the implied side or surface with one or more additional layers being arranged between the implied side or surface and the deposited material. In other words, a first layer "over" a second layer may refer to the first layer directly on the second layer, or that the first layer and the second layer are separated by one or more intervening layers.

[0016] In the context of various embodiments, the articles "a", "an" and "the" as used with regard to a feature or element include a reference to one or more of the features or elements.

[0017] In the context of various embodiments, the term "about" or "approximately" as applied to a numeric value encompasses the exact value and a reasonable variance.

[0018] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0019] FIG. 1A is a schematic showing a formulation 100 for forming a shape memory polymer according to various embodiments. The formulation 100 may include an acrylate monomer 102. The formulation 100 may also include a cross-linker 104 for forming one or more cross-links with the acrylate monomer 102 to form the shape memory polymer. The formulation 100 may further include a photoinitiator 106 for initializing the formation of the one or more cross-links upon exposure to light. The formulation 100 may additionally include a photoabsorber 108 for controlling a rate of formation of the one or more cross-links. A concentration of the photoabsorber 108 may be any one value selected from a range of 0.1 weight percent (wt %) to 10 weight percent (wt %) of the formulation.

[0020] In other words, the formulation 100 may include an acrylate monomer 102, a cross-linker 104, a photoinitiator 106 and the photoabsorber 108.

[0021] Various embodiments may provide a formulation that is more suitable for printing shape memory polymers (SMPs). Various embodiments may provide a formulation that forms a shape memory polymer that has improved properties or advantages over conventional shape memory materials. The shape memory polymer formed may be of a higher quality with fewer surface defects due to better surface finish compared to conventional shape memory polymers. Various embodiments may provide an enabling formulation for printing shape memory polymers using resin based three-dimensional (3D) or four-dimensional (4D) printing techniques.

[0022] The formulation may be a mixture or a resin, i.e. a photopolymer resin.

[0023] The photoinitiator and the photoabsorber may lead to fast polymerization, which satisfies the criteria for 3D printing techniques. Polymerization may alternatively be referred to as curing, and may include formation of the one or more cross-links.

[0024] The photoabsorber may provide for controlled curing so that any complex or thin features can be printed precisely and accurately with no excess width. The photoabsorber may help to prevent unwanted polymerization under ambient light by increasing the threshold curing intensity.

[0025] In various embodiments the light may be ultraviolet (UV) light. The photoinitiator may be configured to initialize the formation of the one or more cross-links upon exposure to UV light. The photoabsorber may be configured to absorb UV light.

[0026] Various embodiments may address or demonstrate the possibility of regulating material compositions and types of materials to fabricate ultraviolet (UV) curable shape memory polymers (SMPs) of tunable properties for specific applications with prototype available and/or widen the spectrum of available materials for 4D printing.

[0027] The acrylate monomer may be a monomer including an acrylate functional group and/or a methacrylate functional group. The acrylate monomer may be tert-butyl acrylate (tBA) monomer, or tert-butyl methacrylate monomer.

[0028] The cross-linker may be a compound including two or more functional groups, such as acrylates or methacrylates. In various embodiments, the cross-linker may be di(ethylene glycol) diacrylate (DEGDA).

[0029] In various embodiments, the molar ratio of the acrylate monomer to the cross-linker may be approximately 15 : 1 according to molecular weight. In various embodiments, the acrylate monomer have a molecular weight of about 142.2.

[0030] The photoinitiator may be phenyl bis (2, 4, 6-trimethylbenzoyl) phosphine oxide (BAPO).

[0031] The photoabsorber may be any one selected from a group consisting of 1-phenylazo-2-naphthol (Sudan I), 1-[4-(phenylazo)phenylazo]-2-naphthol (Sudan III), and $C_{28}H_{31}ClN_2O_3$ (Rhodamine B). FIG. 1B shows an illustration of Sudan I according to various embodiments. FIG. 1C shows an illustration of Sudan III according to various embodiments. FIG. 1D shows an illustration of Rhodamine B according to various embodiments. Sudan III and Rhodamine B may have higher absorptions of light wavelengths ($> 500\text{nm}$) due to more aromatic rings, but Sudan I may only allow light absorption up to a maximum of 418 nm. This may ensure the effectiveness of Sudan I in controlling curing within the shape memory network. In various embodiments, the photoabsorber may preferably be Sudan I.

[0032] In various embodiments, the phrase “acrylate monomer” may refer to a type of monomer. The formulation may include one or more acrylate monomers. The formulation may include a plurality of monomer molecules including acrylate or methacrylate. The plurality of monomer molecules may have structures similar to one another, or may have structures different from one another.

[0033] The term “cross-linker” may refer to a type of molecule. The formulation may include one or more cross-linkers. The formulation may include a plurality of cross-linker molecules present in the formulation. The plurality of cross-linker molecules may have

structures similar to one another, or may have structures different from one another. Each of the plurality of cross-linker molecules may form one or more cross-links with a monomer molecule. Each of the plurality of cross-linker molecules may form cross-links with one, two, or more monomer molecules.

[0034] The term “photoinitiator” may refer to a species or a substance that initialize the formation of crosslinks. The formulation may include one or more photoinitiators. The formulation may include a plurality of photoinitiator molecules, which may have structures similar to one another, or may have structures different from one another.

[0035] The term “photoabsorber” may refer to a species or a substance that control a rate of formation of the cross-links. The formulation may include one or more photoabsorbers. The formulation may include a plurality of photoabsorber molecules, which may have structures similar to one another, or may have structures different from one another.

[0036] The formulation may further include one or more nanostructures. In various embodiments, the nanostructures may include nanoparticles, nanowires, nanorods, or nanosheets etc., or a combination as such. The one or more nanostructures may be or may include one or more silicon oxide nanoparticles.

[0037] In various embodiments, the concentration of the cross-linker may be any one value selected from a range of 5 weight percent to 50 weight percent of the formulation, e.g. 9 weight percent to 50 weight percent, e.g. 10 weight percent to 30 weight percent.

[0038] The concentration of the photoinitiator may be any one value selected from a range of 1 weight percent to 10 weight percent of the formulation, e.g. 2 weight percent to 10 weight percent of the formulation, e.g. 2 weight percent to 5 weight percent of the formulation.

[0039] Three dimensional (3D) printing or four dimensional (4D) printing may require rapid polymerization or curing, i.e. formation of the polymer. The percentage composition or relative ratio of photoinitiator and photoabsorber may be required to initiate the fast polymerization, i.e. by forming one or more cross-links, which may satisfy the criteria for resin based three dimensional (3D) printing or four dimensional (4D) printing.

[0040] The photoabsorber may ensure controlled curing so that complex or thin features may be printed precisely and accurately with no excess width. The relative compositions may be selected so that the shape memory polymer formed is not too soft or that the printing process fails halfway.

[0041] FIG. 2 is a schematic 200 showing a method of forming a shape memory polymer according to various embodiments. The method may include, in 202, mixing a formulation as described herein. The method may also include, in 204, exposing the mixture to light so that the cross-linker forms one or more cross-links with the acrylate monomer to form the shape memory polymer. The formation of the one or more cross-links upon exposure to light may be initialized by the photoinitiator. A rate of formation of the one or more cross-links may be controlled by the photoabsorber.

[0042] In other words, the method may include mixing an acrylate monomer, a cross-linker, a photoinitiator, and a photoabsorber to form a mixture. The mixture may then be exposed to light so that polymerization between the acrylate monomer and the cross-linker may occur. The photoinitiator may be required to commence the polymerization reaction, while the photoabsorber may decrease the rate of formation of the formation of the cross-link(s).

[0043] In various embodiments, the method may further include depositing the mixture over a substrate layer by layer. The method may include printing the mixture over a substrate layer by layer. A first layer including the mixture may be formed on or over the substrate, and the first layer may be exposed to light. The method may further include forming a second layer on the first layer, and exposing the second layer to light. The method may further include forming a third layer on the second layer, and exposing the third layer to light. In such a manner, a layer may be formed over the substrate and cured, before a subsequent layer is formed and cured.

[0044] In various embodiments, the light may be ultraviolet light.

[0045] The photoinitiators and photoabsorbers may be added after mixing the acrylate monomer and the cross-linker.

[0046] In various embodiments, the mixture may be exposed to light within a predetermined duration, e.g. within 5 seconds, e.g. within 4 seconds, e.g. within 3 seconds.

[0047] In various embodiments, parameters such as surface power density of the light, duration of light exposure etc. may be set so that curing, formation of the one or more cross-links, may be carried out within a desired duration of time for three-dimensional (3D) or four-dimensional (4D) printing. The photoabsorber may be included so that the mixture does not cure easily under ambient light. However, rapid curing may be achievable during the printing process, i.e. when the mixture is exposed to light such as an ultraviolet laser beam or

ultraviolet light from a projection system, provided that process parameters or windows are met.

[0048] In various embodiments, stereo-lithography (SLA) may be used. In various embodiments, exposing the mixture to light may include using a laser scanning system to provide an ultraviolet laser beam to form the shape memory polymer. The ultraviolet laser beam may be moved across the mixture at a speed of at least 700 mms^{-1} . The ultraviolet laser beam may have a surface power density of a value in the range of 40 mWcm^{-2} to 80 mWcm^{-2} .

[0049] In various embodiments, digital light processing (DLP) may be used. In various embodiments, exposing the mixture to light may include using a projection system to project the ultraviolet light to form the shape memory polymer. The ultraviolet light may be projected for a duration of any value less than 3 seconds. The projected ultraviolet light may have a surface power density of a value in the range of 10 mWcm^{-2} to 40 mWcm^{-2} .

[0050] In various embodiments, the shape memory polymer formed may have a thickness of $25 \text{ }\mu\text{m}$ or less. The shape memory polymer may be a layer. The thickness of the layer may be less than a curing depth of the shape memory polymer. A thinner layer may reduce the likelihood of voids in the polymer, and/or may reduce the risk of delamination.

[0051] In various embodiments, the method may include introducing one or more nanostructures. In various embodiments, the one or more nanostructures may include one or more silicon oxide nanoparticles. The one or more nanostructures may be chemically bonded to a polymer chain including the acrylate monomer and the cross-linker upon exposing the formulation to light. In various embodiments, the nanostructures may have to be carefully processed before adding into the resin mixture of the acrylate monomer and the cross-linker (e.g. tBA + DEGDA). The photoinitiators and photoabsorbers may be added to the resin mixture of the acrylate monomer and the cross-linker after adding the nanostructures to the resin mixture of the acrylate monomer and the cross-linker. The nanostructures may be coupled or treated with surfactants first to prevent agglomeration and to ensure homogenous dispersion within the resin mixture.

[0052] Various embodiments may provide a shape memory polymer formed by a method as described herein. In various embodiments, the shape memory polymer may be tert-butyl acrylate (tBA) – co – di(ethylene glycol) (DEGDA). In various embodiments, the monomer may be tert-butyl acrylate (tBA). The cross-linker may be di(ethylene glycol) (DEGDA).

[0053] The shape memory polymer may be a thermoset polymer.

[0054] The shape memory polymer may be configured to switch from a first shape (which may alternatively be referred to as permanent shape) to a second shape (which may alternatively be referred to as deformed shape or temporary shape) upon the shape memory polymer being heated to a temperature above a predetermined temperature. The shape memory polymer may be configured to switch from the second shape to the first shape upon application of an external stimulus. The external stimulus may be heat. The external stimulus may alternatively or additionally be electric field, magnetic field, light and/or solution.

[0055] The predetermined temperature may be any value selected from a range of 30 °C to 90 °C.

[0056] The shape memory polymer may further include one or more nanostructures. The one or more nanostructures may be chemically bonded to a polymer chain including the acrylate monomer and the cross-linker. The one or more nanostructures may include one or more silicon oxide nanoparticles.

[0057] Various embodiments may include mixing a formulation including one or more acrylate monomers, one or more cross-linkers, one or more photoinitiators, and one or more photoabsorbers. The method may also include exposing the mixture to light so that the one or more cross-linkers form cross-link(s) with the one or more acrylate monomers to form the shape memory polymer. The formation of the cross-link(s) upon exposure to light may be initialized by the one or more photoinitiators. A rate of formation of the one or more cross-links may be controlled by the one or more photoabsorbers.

[0058] For avoidance of doubt, a polymer with a specific weight percent of a constituent (e.g. cross-linker) as described herein may mean that the polymer may be formed from a formulation having the specific weight percent of the constituent.

[0059] Various embodiments may provide a device or an article including a shape memory polymer. The device or article may be any one of a suture, a stent, and a dental aligner. The device or article may include a single polymer formed from a single resin or a single formulation as described herein.

[0060] Various embodiments may relate to developing a photo-sensitive shape memory polymer (SMP) resin that exhibits shape memory properties. The resin may be suitable for 3D printing via UV curing.

[0061] Various embodiments may relate to an acrylate-based shape memory polymer mixture for 3D printing. Various embodiments may relate to a copolymer. The copolymer

may include or may be formed from a monomer and a cross-linker. The monomer may act as a soft segment to allow temporary change of shape. The cross-linker may act as a hard segment to define the permanent shape. The mixture may further include a photoinitiator to induce photopolymerization of the copolymer, and a photoabsorber to ensure controlled curing.

[0062] The testing and characterizations of the fabricated SMPs are described herein. Various embodiments may address the problems of limited availability of UV-curable materials suitable for 3D printing. These UV-curable materials are often thermoset-based, made up of highly cross-linked networks that are mainly glassy, rigid and brittle which cannot be reshaped once cured.

[0063] Moreover, most traditional SMP materials developed over the years are suited for photo-curing as a whole (not layer by layer) by exposure under UV lamps which takes up considerable time for polymerization. However, 3D printing emphasizes on fast curing of polymers for each layer within seconds. Fabrication using certain traditional SMP materials via UV laser curing layer by layer may not provide sufficient mechanical strength to build thin supports for overhanging structures. This may result in the fabricated part collapsing on its weight during the printing process.

[0064] Various embodiments may provide a method of synthesizing polymers based on a thermally induced one-way dual-SMP with phase switching mechanism. Various embodiments may relate to optimization of UV parameters in order to fabricate SMPs using stereo-lithography (SLA). SLA may be chosen as the 3D printing technique for fabrication since the open build parameters and easily accessible resin may offer more options for development and material modulation of thermoset SMPs.

[0065] In various embodiments, commercial tert-butyl acrylate (tBA) monomer may be mixed with di(ethylene glycol) diacrylate (DEGDA) cross-linker, UV photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) and Sudan I photoabsorber. The tBA-co-DEGDA network may form an acrylate-based photocurable system which polymerizes through free radical mechanism using BAPO photoinitiators. The rate of polymerization for radical curable acrylates may be distinctively fast and precise due to its high reactivity. Strong crosslinked polymers may be generated only in the illuminated areas, thus producing high resolution parts, especially with the use of intense laser scanning. The addition of photoabsorbers may also ensure that there is controlled curing so that any

complex or thin features can be printed precisely and accurately with no excess width. Furthermore, photoabsorbers may be able to prevent unwanted polymerization under ambient light by increasing the threshold curing intensity. The choice of the acrylate-based tBA-co-DEGDA system with its unique features may satisfy the requirements of stereo-lithography process to fabricate each cross-sectional layer within seconds. Various embodiments may also produce higher quality SMPs with lesser surface defects due to better surface finish, thus reducing the rate of polymer degradation, which can be observed through undergoing repeated thermomechanical cycles.

[0066] Various embodiments may relate to a thermoset memory polymer formed from a mixture including tBA (balanced amount), DEGDA (9 - 50 wt%), BAPO photoinitiator (1 - 10 wt%), and Sudan I photoabsorber (0.1 - 10 wt%). The resulting printed shape memory polymer may have a glass transition temperature (T_g) selected from a range of about 30 °C to about 90 °C.

[0067] The photopolymer resin may form a polymer network of tert-butyl acrylate copolymered with diethylene glycol diacrylate (tBA-co-DEGDA). Various embodiments may provide an acrylate-based photocurable system which polymerizes through free radical mechanism using photoinitiators (e.g. phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO)) and photoabsorbers (e.g. Sudan I).

[0068] The photopolymer may have certain curing characteristics that can be used on a standard resin based additive manufacturing process for building 3D objects layer by layer. This includes fast curing, suitable curing depth, sufficient strength during building process, and/or acceptable lifetime under ambient light.

[0069] The processing windows for fabricating shape memory polymers using resin based 3D printing techniques may require: (a) Threshold speed for UV laser based 3D printing systems: no less than 700 mms⁻¹ with power ranging from 40 – 80 mW/cm², (b) Exposure time for UV projection based 3D printing systems: 3 seconds or lesser with power ranging from 10 - 40 mW/cm², and a layer thickness of 25 μm or lesser.

[0070] The shape memory polymer produced may have thermally induced one-way dual-shape memory effect with phase switching mechanism within a temperature range from 30 to 90 °C, which can be tailored by change in composition.

[0071] FIG. 3A shows a photograph 300a of the permanent shape of a shape memory polymer (SMP) in the form of a bucky-ball according to various embodiments. FIG. 3B is a

photograph 300b showing a deformed shape of the shape memory polymer in the form of a flat shape according to various embodiments, which is formed after the bucky-ball in FIG. 3A is heated to above the transition temperature (T_g), opened up by force and cooled down. FIG. 3C is a photograph 300c showing the restored bucky-ball shape recovered after the flattened shape shown in FIG. 3B according to various embodiments is placed in hot water.

[0072] FIG. 3D is a photograph 300d showing another deformed shape of the shape memory polymer in the form of a flattened structure according to various embodiments, which is formed after the bucky-ball in FIG. 3A is heated to above the transition temperature (T_g), softened, and compressed. FIG. 3E is a photograph 300e showing the restored bucky-ball shape recovered after the flattened structure shown in FIG. 3D according to various embodiments is placed in hot water.

[0073] Various embodiments may provide an enabling formulation for printing SMPs for resin based 3D printing techniques. A photopolymer resin suitable for UV laser-scanning or UV projection may be developed to form a tBA-co-DEGDA network that exhibits excellent shape memory properties based on a thermally induced one-way dual-SMP with phase switching mechanism. The fabrication process may be first optimized by exploring the laser or projection parameters to ensure dimensional accuracy during the fabrication process.

[0074] For laser scanning techniques, printing at a threshold scanning speed of no less than 700 mm s^{-1} with power ranging from $40 - 80 \text{ mW/cm}^2$ may minimize occurrence of excess width, hence giving high dimensional accuracy of the printed SMPs. For projection type techniques, optimal printing may be achieved at 3 seconds or lesser with power ranging from $10 - 40 \text{ mW/cm}^2$. The concentrations of photoinitiators may also play a crucial role in determining both the curing depth of the SMPs and the layer thickness of the stereolithography process. Photoinitiators concentrations may be any value from a range from $1 - 10 \text{ wt\%}$, while the photoabsorbers added may be any value from a range of $0.1 - 10 \text{ wt\%}$ so as to give a curing depth larger than the layer thickness ($25 \text{ }\mu\text{m}$ or lesser) in order to fabricate SMPs without any presence of voids in between the layers.

[0075] Testing and characterizations in terms of thermal, mechanical and thermomechanical analysis have been carried out on the printed SMPs. The T_g of the SMPs is found to be approximately $53.96 \text{ }^\circ\text{C}$, while the SMPs may start to soften when temperature reaches above $45.3 \text{ }^\circ\text{C}$. For mechanical properties, the SMPs exhibit a large difference in maximum tensile strength below and at T_g . Further, the elongation at break of the SMPs at T_g

may be up to 18.2 %, which is at least twice of that at room temperature due to better molecular mobility in the polymer chains when it is heated. The mechanical properties of the printed SMPs may be in fact comparable to commercial thermoset SMPs. The SMPs have also been characterized using several thermomechanical cyclic tests to determine its shape memory properties. The SMPs show excellent shape recovery and fixity properties, in which they may be able to undergo repeated folding and unfolding thermomechanical cyclic tests for up to at least 20 cycles before failure.

[0076] Various embodiments may relate to the development and fabrication of SMPs using stereo-lithography (SLA) or digital light processing (DLP) processes, which may not only be able to overcome the limitations in geometric complexity which traditional methods struggle to achieve, but also expand material processing to include a new class of smart and responsive materials for 4D printing.

[0077] In summary, a photosensitive resin or formulation suitable for layer by layer UV curing to form a 3D shape that exhibits shape memory properties may be developed. The resin or formulation may be suitable to be printed using resin based 3D printing. Various embodiments may relate to a formulation or resin for printing the shape memory polymer using resin based 3D printing techniques. The formulation or resin may include an acrylate monomer such as tBA (balanced amount), a cross-linker such as DEGDA (about 9 – 50 wt%), a photoinitiator such as BAPO (about 1 - 10 wt %), and a suitable photoabsorber such as Sudan I (about 0.1 – 10 wt%).

[0078] Various embodiments may relate to specific ratios of constituents and/or methods using controlled process parameters so that a shape memory polymer may be printed using a resin-based 3D printing technique such as SLA or DLP. Various embodiments may relate to specific ratios of constituents and/or methods using controlled process parameters so that a high quality shape memory polymer may be printed.

[0079] The threshold speed for an UV laser based printing system may be no less than 700 mm s^{-1} with power ranging from 40 – 80 mW/cm^2 . For a UV projection based printing system, the exposure time may be 3 seconds or less with power ranging from 10 – 40 mW/cm^2 . The layer thickness may be 25 μm or less. With the inclusion of photoabsorbers, the shape memory polymers in the resin state may not cure easily under ambient lighting. However, rapid curing may be achieved during the printing process provided that the process windows are met.

[0080] To date, research and developments in 4D printing are largely based on the more widespread commercial systems in the market, which are the fused deposition modeling or FDM (which produces thermoplastic SMPs) or inkjet printing (which produces thermoset SMPs), such as Objet and PolyJet. However, FDM is known to produce thermoplastic parts with poorer surface finish, especially when the parts require supports for overhanging features. Surface defects may occur in these parts during folding and unfolding, resulting in shorter shape memory thermomechanical cycles. Parts formed by FDM may also experience more chances of delamination due to poorer dimensional precision such that layer thickness is generally more than 100 μ m.

[0081] In contrast, the developed resin with tBA-co-DEGDA system according to various embodiments may form higher quality SMPs with lesser surface defects due to better surface finish, thus reducing the rate of polymer degradation, which can be observed through undergoing multiple consecutive thermomechanical cycles.

[0082] On the other hand, inkjet printing systems make use of multiple materials that are cured heterogeneously as the conventional thermoset materials alone do not react to external stimulus. Hence, the shape memory effects depend principally on the design of the components. This induces a limiting factor in the smartness of the materials since the extent of the shape memory changes in multi-material components are determined by the design in terms of stretching, compression, bending or twisting. Inkjet printing systems are liquid based additive manufacturing (AM) techniques that generally use photo-sensitive resins which cure under UV exposure. In terms of shape memory properties, the printed parts form thermoset SMPs that are much stiffer with better recoverability and reproducibility as compared to thermoplastics since they exhibit inherent lower creep properties due to cross-linkages formed. However, for thermoset multi-material inkjet printers, the materials available are digitized and a single material alone cannot form SMP because the material is either too rubbery or too rigid. Rigid materials contain highly cross-linked networks, are mainly glassy and brittle, and cannot be reshaped once cured. In order to form thermoset SMPs, a mixture of elastomeric matrix with rigid plastic may have to be cured heterogeneously.

[0083] There are not very few single thermoplastic materials for 4D printing (which are recognized as “4D ready” materials which can reshaped when heated, solidified when cooled). There are also few thermoset materials suitable for 3D printing. Further, there is limited range and availability of single homogeneous thermoset SMPs with shape memory

properties as inkjet printers are mostly closed systems which restrict material processing for new class of smart and responsive materials.

[0084] The difference between 4D printing of a single material and multiple materials lies in the ‘smartness’ of the smart materials which determines how readily the printed materials react upon activation. Multi-materials are prone to failures due to interface or boundary cracks in dissimilar materials. Hence, a single homogenous photo-curable thermoset resin that exhibits shape memory properties with rapid curing characteristics described herein may have significant advantages over conventional materials. The resin developed may be suitable for resin based 3D printing techniques. Various embodiments may address and demonstrate the possibility of regulating material compositions and types of materials to fabricate UV curable SMPs of tunable properties for specific applications and/or widen the spectrum of available materials for 4D printing.

[0085] Experimental Results

[0086] Commercial tert-butyl acrylate (tBA) monomer were mixed with di(ethylene glycol) diacrylate (DEGDA) cross-linker, UV photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) and Sudan I photoabsorbers. The tBA-co-DEGDA networks were synthesized by free radical polymerization using a bottom-up UV scanning laser. FIG. 4 is a schematic 400 illustrating the chemical structure of the crosslinking between tert-butyl acrylate (tBA) monomer molecules and di(ethylene glycol) diacrylate (DEGDA) cross-linker molecules according to various embodiments.

[0087] The polymer is based on a thermally induced one-way dual-SMP with phase switching mechanism. The shape memory polymer formed may include hard segments (netpoints) including covalent bonds or intermolecular interactions that define the permanent shape, and soft segments (switching segments) made up of chains, which enable fixation of a temporary shape. The tBA monomer molecules may make up the soft segment since tBA monomer molecules form shorter chains which are less bulky, hence increasing mobility of the molecular chains for easier deformation when the material changes from rigid plastic at room temperature to soft rubber at temperatures above its glass transition temperature (T_g). The DEGDA cross-linker molecules may act as the netpoints, ensuring that a network structure is established within the SMP. The higher thermal transition temperature of the cross-linker molecules may also provide stability in the network structure to withstand the thermomechanical conditions encountered in the shape memory process without breakage.

Accordingly, the hard segments in the SMP constituting the permanent shape of the SMP may be made of the cross-linker molecules.

[0088] The tBA-co-DEGDA network may form from an acrylate-based photocurable system. The tBA-co-DEGDA network may be formed by polymerization through free radical mechanism using BAPO photoinitiators. It may be necessary to introduce the photosensitive initiators to kick off the photo-polymerization upon exposure to UV as the monomers do not generate sufficient initiating species for polymerization. The rate of polymerization for radical curable acrylates may be distinctively fast and precise due to its high reactivity. Strong crosslinked polymers may be generated only in the illuminated areas, thus producing high resolution parts, especially with the use of intense laser scanning. The addition of photoabsorbers may also ensure that there is controlled curing so that any complex or thin features can be printed precisely and accurately with no excess width. Furthermore, the photoabsorbers may also be able to prevent unwanted polymerization under ambient light by increasing the threshold curing intensity. Unlike cationic polymerization which is common in epoxy-based monomers, acrylate-based systems may be more stable due to sensitivity towards atmospheric oxygen and may not exhibit post-polymerization which tends to proceed even in the dark without UV exposure. The acrylate-based tBA-co-DEGDA system may be compatible with the requirements of stereo-lithography process to fabricate each individual cross-sectional layer within seconds. However, high shrinkage may be experienced during fabrication. Hence, the photopolymerizable formulations based on dual-SMP mechanism for stereo-lithography process are further studied for optimization.

[0089] Optimization Of Laser Parameters

[0090] Mixtures of tBA-co-DEGDA with 1 wt% photoinitiators were cured by the UV laser beam at different scanning velocities of 100 to 1360 mm s^{-1} with a layer thickness of 50 μm to form specimens size of 17.5 mm x 11.9 mm x 2 mm. FIG. 5 is a plot 500 of excess width (millimeters or mm) as a function of laser scanning speed (millimeter per second or mm/s) showing the excess width of the cured specimens in x and y directions measured using digital caliper. When the laser is set at its lowest speed, there is loss in dimensional accuracy caused by presence of excess width due to prolonged laser scanning. The excess width of the specimens decreased exponentially with increasing laser scanning velocities. Therefore, the threshold scanning speed for fabricating a SMP is determined to be 700 mm s^{-1} or higher so as to keep the accuracy of the printed parts within 0.1 mm.

[0091] The curing depths of polymerization may be strongly determined by not only the penetration of incident light by the laser source, but also the photoinitiator concentration which is explained by Jacobs' Equations:

$$C_d = D_p \ln \left(\frac{E_{\max}}{E_c} \right) \quad (1)$$

$$D_p \propto \frac{2}{2.303 \ln [PI]} \quad (2)$$

where C_d is the curing depth, D_p is the depth of penetration, $E_{\max}$ is the energy dose per area, E_c represents a critical energy dosage and $[PI]$ stands for concentration of photoinitiators. The curing depth may determine the layer thickness suitable for stereo-lithography fabrication and hence the total number of layers required to build the part completely. The curing depth of the printed parts may have to be larger than the layer thickness so as to ensure good adherence to the previous layer printed such that the unreacted monomers on the solidified structure in the previous layer printed polymerize with the UV scanned resin in the subsequent printed layer. This may also minimise the chances of delamination between each layer.

[0092] Upon specifying the laser to be set at its threshold scanning speed of 700 mm s^{-1} , solutions with varying concentrations of photoinitiators at 0.5, 1, 2, 4 and 5 wt% were cured to form single layer square laminates of 10 mm by 10 mm. The curing depths measured for 0.5 and 1 wt% photoinitiator concentrations respectively fluctuate slightly above 10 μm and below 10 μm . However, dramatic shrinkage may be observed in the printed parts due to the low curing depths. Given that the concentration of photoinitiators is relatively low, generation of free radicals is also reduced, hence a loosely crosslinked polymer is being formed, leading to a large amount of shrinkage. Therefore, photoinitiator concentrations of 0.5 and 1 wt% were not considered for formulation of the SMPs.

[0093] FIG. 6 is a plot of thickness (in micrometres or μm) as a function of length (in millimetres or mm) showing the curing depths of square laminates according to various embodiments with varying concentrations of photoinitiators. FIG. 6 shows the curing depths for photoinitiator concentrations of 2, 4 and 5 wt%. An increase in the concentration of the photoinitiators may yield a deeper curing depth, as the photon absorption is greater and the initiation of free radicals is more localized, thus producing a tightly cross-linked polymer that

undergoes little shrinkage. The lowest curing depths achievable for 2, 4 and 5 wt% photoinitiator concentration are 28.10 μm , 35.45 μm and 38.85 μm respectively.

[0094] To ensure that the parts are fabricated without any presence of voids in between layers, the layer thickness of the stereolithography process is set to be 25 μm so that tBA-formulation or mixture including 2 wt% photoinitiator may be used for all stereo-lithography fabrication of test specimens. Given that the layer thickness is smaller than the minimum curing depth attained by the 2 wt% photoinitiator concentration, there may be a slight overlap curing between layers, hence preventing formation of internal voids.

[0095] Thermogravimetric Analysis

[0096] FIG. 7A is a plot 700a of weight percentage (in percent or %) of the original weight and the derivative of the weight percentage (in weight percent per degree Celsius or $\text{wt\%} / ^\circ\text{C}$) of the printed shape memory polymer (SMP) according to various embodiments as a function of temperature (in degrees Celsius or $^\circ\text{C}$). The thermal decomposition temperature for the printed SMPs may be obtained from the thermogravimetric analysis (TGA) data as shown in FIG. 7A. The SMP may start to decompose upon reaching 226.74°C , hence for subsequent characterizations of the SMPs, temperatures were kept below 200°C . The presence of only 2 peaks may indicate that the tBA monomer has chemically reacted with the DEGDA cross-linker to form tBA-co-DEGDA system as shown by the first peak. The second peak may relate to the decomposition of unreacted photoinitiators.

[0097] Dynamic Mechanical Analysis (DMA)

[0098] FIG. 7B is a plot 700b of storage modulus (in mega Pascals or MPa), tan delta ($\tan \delta$), and loss modulus (in mega Pascals or MPa) as a function of temperature (in degree Celsius or $^\circ\text{C}$) showing the dynamic mechanical analysis (DMA) curves of the shape memory polymers according to various embodiments in which the glass transition temperature (T_g) and viscoelasticity of the shape memory polymers may be determined. T_g may be defined by the peak of the tan delta curve, and may have a value of 53.96°C . The tan delta curve or $\tan \delta$ curve may be formed by calculating the tangent ($\tan$) function of the phase lag between stress and strain (δ).

[0099] It may be observed that the storage moduli of the SMPs change as a function of temperature. At temperatures below the T_g , the SMPs may be in their solid rigid state, hence the storage modulus measured is at the highest point of 641.97 MPa. However, when the

SMPs are heated to above its T_g , the SMPs may soften due to increased mobility of the molecular chains, therefore lowering the storage modulus.

[00100] Current literature has highlighted such that a large and sharp change in storage modulus is necessary when the SMP changes from glassy to rubbery state. FIG. 7B shows that the SMP may experience a change in storage modulus of more than 2 orders of magnitude when temperatures are increased from below T_g to above T_g , thus demonstrating that the SMP possess good shape memory behaviour.

[00101] Thermomechanical Analysis (TMA)

[00102] Thermomechanical Analysis (TMA) may be conducted to determine the onset of temperature at which the SMP starts to soften and become rubbery. FIG. 7C is a plot 700c of dimension change (in micrometres or μm) as a function of temperature (in degrees Celsius or $^{\circ}\text{C}$) indicating the softening temperature of the shape memory polymer (SMP) according to various embodiments.

[00103] FIG. 7C shows that there is a dramatic drop in the thickness of the SMP sample when it reaches about 45.3°C . At temperatures below this, there is slight increase in the thickness due to thermal expansion of the part. However, when the temperature passes above 45.3°C , the thickness reduces drastically from $-1.22\ \mu\text{m}$ to $-8.41\ \mu\text{m}$, indicating the onset of softening in the SMP. Thus, the point at which the SMP encounters a large dimensional change may define the softening temperature. As shown by FIG. 7C, the softening temperature may be about 45.3°C , approximately 10°C below T_g .

[00104] Mechanical Properties

[00105] SMPs are known to change from a glassy state to rubbery state so as to undergo a deploying process to recover back to its original shape. To examine the mechanical properties of the printed SMPs under the 2 different states, mechanical characterizations were carried out by performing uniaxial tensile tests below and at T_g . FIG. 8A is a table 800a showing tensile properties of printed shape memory polymers according to various embodiments at room temperature (r.t.p) and at glass transition temperature (T_g). FIG. 8B shows a plot 800b of stress (mega-Pascals or MPa) as a function of strain (in percent or %) showing stress-strain curves of the shape memory polymers according to various embodiments at room temperature (r.t.p) and at glass transition temperature (T_g). σ represents the tensile strength, ϵ represent the breaking strain, and E represents the Young Modulus.

[00106] From FIG. 8A, the SMPs tested at room temperature exhibit higher tensile strength of 20.2 MPa, as compared to the tensile strength measured at T_g , which is 2 orders lower in magnitude. This denotes that the SMPs may be able to withstand higher maximum stress when the SMPs are in a rigid glassy state, but only a small amount of stress is required to initiate the deploying process when they are heated to above T_g .

[00107] Moreover, FIG. 8B displays the tensile behaviour of the SMPs tested at T_g with a larger breaking strain of 18.2 ± 0.343 %, which is approximately more than twice the breaking strain of 8.79 ± 0.95 % at room temperature. The SMPs tested at room temperature may experience necking due to localized deformation and may induce a fracture at low strain or elongation. However, at T_g , the heating may activate the molecular mobility which allows the molecules to stretch and align easily in the direction of the tensile pull, thus resulting in larger strain or elongation at break. Various embodiments may meet the requirements of large deformation during the deploying process and may be suitable for shape memory applications.

[00108] The mechanical properties obtained based on the SLA-printed SMPs may be comparable with commercial thermoset SMPs. FIG. 8C is a table 800c comparing properties of stereo-lithography (SLA) printed shape memory polymers according to various embodiments and properties of a commercial thermoset Veriflex shape memory polymer.

[00109] Shape Memory Properties

[00110] The fabricated SMPs are studied by undergoing thermomechanical cyclic tests using dynamic mechanical analysis (DMA) single cantilever mode until the samples fail upon fracture. The shape fixity and shape recovery ratio can be readily determined by using the following equations:

$$R_f = \frac{\epsilon}{\epsilon_{load}} \times 100\% \quad (3)$$

$$R_r = \frac{\epsilon - \epsilon_{rec}}{\epsilon} \times 100\% \quad (4)$$

[00111] FIG. 9 shows a plot 900 of fixity (in percent or %) as a function of cycles of a printed shape memory polymer (SMP) according to various embodiments. FIG. 9 shows that SMPs under deformation force of 0.3 N may be able to undergo repeated folding and unfolding for up to at least 20 cycles. At higher deformation force of 0.7 N, the SMPs may also withstand up to 10 cycles, suggesting that the SMPs possess good shape memory

properties. The deformation force of 0.3 N exerts an approximated 12% ϵ_{load} on the SMP. However, upon removal of the load force after cooling to below its T_g , there is a slight elastic spring back causing a drop in the shape fixity. The ϵ recorded is below 12%, which gives R_f of only 85% but there is a rising trend in the fixity up to 92% at the 6th cycle. The fixity then further drops to about 86% at the 7th cycle and stays relatively constant for the subsequent cycles. At the incipient stage, the shape fixity may be lower in ratio as the release of constrained force is followed by restrictive force due to heavy friction among molecules to retain the temporary shape hence generating spring back by the SMP. After the 7th cycle, the repeated movement of the cross-linked structures during repeated cycles may reduce the friction among the molecules. Molecular chain mobility may become easier and the molecules may be locked in deformed chain conformation, which results in smaller spring back, thus giving better shape fixity ratio. However, the fixity remains relatively constant for subsequent cycles, indicating that repeated thermal mechanical cycles may have little effects on the SMP's ability to retain its temporary shape.

[00112] On the other hand, the deformation force on the SMPs may have a significant effect on the fixity ratio. When the force is doubled to 0.7 N, there may be a huge elastic spring back which leads to a fixity of only 69%. The deformation introduced is relatively large such that it may result in an entropic change in the polymer chains, in which the cooling stage may serve as a kinetic trap to store this entropic energy, and may only release the energy during reheating for recovery. However, the energy state in the SMPs may be too high due to the large deformation imposed on the permanent shape (i.e. first shape) together with the initial restrictive friction among molecules, hence the cooling of SMPs may be unable to fully trap the entropic energy, which may result in some loss of entropic energy that causes the huge spring back. The friction among molecules may be reduced after repeated cycles, therefore fixity ratio rises up to 86% but the polymer may still be unable to fully “memorize” the deformed shape (i.e. second shape).

[00113] FIG. 10 is a plot 1000 of recovery percentage (in percent or %) as a function of cycles showing the shape recovery properties of the shape memory polymers (SMPs) according to various embodiments over several cycles until the shape memory polymers fail to recover. As shown in FIG. 10, the SMPs under a deformation force of 0.3 N may be able to fully recover to the original permanent shape (i.e. first shape) for the first 14 thermomechanical cycles. However, the netpoints which are responsible for defining the

permanent shape may become less stable from the 15th cycle onwards due to thermomechanical conditions and fatigue encountered in the shape recovery process. Therefore, as shown in FIG. 10, the SMPs may be unable to fully recover starting from the 15th cycle. Nevertheless, the recovery ratio may range between about 97% and about 99%. Hence, the SMPs may be considered as excellent shape memory material because the SMPs are able to meet the requirements of shape memory ratio being more than 90%. In other words, the shape memory polymer according to various embodiments may have a shape memory ratio above 90%.

[00114] On the contrary, the SMPs under deformation force of 0.7 N may not be able to recover completely beginning with the first cycle. The SMPs may only be able to recover at most 95% of the original permanent shape, and may be able to withstand up to only 10 thermomechanical cycles. This indicates that the deformation force imposed may be so large such that it causes slippage in the polymer chains that lead to macroscopic deformation instead of entropic change. As such, full 100% recovery may not be possible.

[00115] The shape memory performance of the printed SMPs is illustrated by three-dimensional (3D) plots in FIGS. 11A and 11B. FIG. 11A is a three-dimensional (3D) plot 1100a of strain (in percent or %) as a function of temperature (in degrees Celsius or °C) and stress (in mega-Pascals or MPa) showing a thermomechanical cyclic test of a shape memory polymer (SMP) according to various embodiments under 0.3N deformation force. FIG. 11B is another three-dimensional (3D) plot 1100b of strain (in percent or %) as a function of temperature (in degrees Celsius or °C) and stress (in mega-Pascals or MPa) showing a thermomechanical cyclic test of a shape memory polymer (SMP) according to various embodiments under 0.7N deformation force.

[00116] The thermomechanical cyclic tests may be carried out using dynamic mechanical analysis (DMA). The samples may be bent and recovered in the DMA furnace under 2 different forces, 0.3N and 0.7N force until the samples fail. FIG. 11A shows that the sample under 0.3N force may be able to recover almost fully since the graph looped back to the original point, and the sample may undergo at least 20 cycles for all samples tested. However, FIG. 11B shows that the graph of the sample under higher force of 0.7N may not loop back to the original point, indicating that there is no complete recovery of the original shape. Nevertheless, the sample may withstand up to 10 cycles under 0.7N. The thermomechanical

cyclic experiments show the robustness of the shape memory performance, and illustrate that repeated fixing and recovery cycles could be realized.

[00117] The 3D representations of the thermomechanical cycles clearly illustrate the various deformation-fixing-recovering stages which the SMPs have undergone, and also depict whether the SMPs may recover completely, indicated by whether the curves loop back to the original strain value.

[00118] Tunable SMP Thermomechanical Properties

[00119] By controlling the material compositions, the flexibility of the tBA-co-DEGDA network according to various embodiments may enable tunable thermomechanical properties, which may include glass transition temperatures and/or storage modulus.

[00120] FIG. 12A is a plot 1200a of exotherm (in arbitrary units or a.u.) as a function of temperature (in degree Celsius or °C) showing the digital scanning calorimetry (DSC) results of shape memory polymers formed with different concentration of the cross linkers according to various embodiments. FIG. 12A indicates the amorphous nature of the shape memory polymer according to various embodiments. No endothermic peak representing crystal melting may be observed, indicating the highly cross-linked nature of the printed SMP with no crystalline domains. Moreover, only one single step on each curve was observed, showing the SMPs are amorphous copolymers exhibiting glass transition temperatures (T_g).

[00121] The optimal T_g may be determined by the temperature at which the relaxation peak of the $\tan \delta$ curves of DMA occur, as shown in FIG. 12B. δ may refer to the phase lag between stress and strain.

[00122] FIG. 12B is a plot 1200b of tangent delta ($\tan \delta$) as a function of temperature (in degree Celsius or °C) showing the tangent delta ($\tan \delta$) ratios shape memory polymers according to various embodiments with different concentrations of cross-linker molecules. The T_g of the SMP with 10 wt% of cross-linker is 53.9°C. For every 10 wt% of additional cross-linker, an approximate 5°C increase in T_g may be observed. The peak height may decrease and the peak may shift towards higher temperatures with increasing concentration of cross-linker molecules, since more energy may be required for regaining the chain mobility for more crosslinked polymers.

[00123] The peak heights may also correspond to the storage modulus which determines the molecular mobility of the polymers. The curves become flatter with increasing DEGDA

content, thus showing that flexibility of the SLA SMP reduces with higher amount of cross-linkers.

[00124] Two important aspects of SMPs may be the ability to fix a temporary shape (fixity), and to subsequently recover its original shape by an external stimulus (recovery). Variations in concentration of the DEGDA cross-linkers may not only influence the glass transition temperatures of the SLA SMPs, but may also affect the shape fixity and recovery properties, which may be critical in defining the suitability of the materials for shape memory applications.

[00125] FIG. 13A is a plot 1300a of fixity ratio R_f (in percent or %) as a function of number of cycles illustrating the effect of increasing concentrations of cross-linkers on shape fixity of the shape memory polymers according to various embodiments. FIG. 13B is a plot 1300b of recovery ratio R_r (in percent or %) as a function of number of cycles illustrating the effect of increasing concentrations of cross-linkers on shape recovery properties of the shape memory polymers according to various embodiments. FIGS. 13A-B show the effect of DEGDA cross-linker concentrations on shape fixity and shape recovery properties, as well as the cycle life of each composition for the developed SMPs.

[00126] FIG. 13A shows the shape fixity curves of the SLA SMPs with concentrations of DEGDA cross-linkers ranging from 10 – 50 wt%. The SLA SMPs may maintain a high shape fixity of more than 85% when the amount of cross-linkers is 30 wt% or less. In the first cycle, the SLA SMPs with 10, 20 and 30 wt% cross-linkers may achieve considerably high shape fixity of 84.9%, 95.2% and 93.9% respectively.

[00127] The shape fixity of SMP with 10 wt% cross-linkers may gradually improve after several cycles due to the repeated movement through multiple cycles, which may reduce the friction among the molecules. Hence, molecular chain mobility may become easier and the molecules may be locked in deformed chain conformation, giving higher shape fixity close to 90% for subsequent cycles. The increase in cross-linker concentration within the polymer network may increase the rigidity of the SMP and may improve the ability in retaining the temporary shape at the incipient stage.

[00128] However, the SLA SMPs with higher concentration of cross-linkers may exhibit shorter cycle life and fracture after 8 cycles (20 wt%) and 6 cycles (30 wt%). This may be attributed to the low molecular weight ratio of tBA monomer within the network, indicating that the polymer chains have lower ability to coil. The amount of tBA monomer functioning

as softening agent may be imperative to enable the SMP to undergo large strain deformations without chain slippage (permanent deformation), thus contributing to its ability to recover. The presence of a very small amount of chemical crosslinking may potentially be a factor that determines the high shape memory performance and long lasting cycle life.

[00129] The results shown in FIG. 13A indicate that while a higher cross-linker concentration may give higher shape fixity at the beginning, a lower cross-linker concentration may overall be more favourable in the long term, as a lower cross-linker concentration may provide longer cycle life with comparatively high shape fixity.

[00130] The chemical composition may also affect the shape recovery properties of the SLA SMPs as shown in FIG. 13B. The ability to recover to its original shape may be highly dependent on the concentration of the cross-linkers within the SMP network. The SMP with lowest amount of cross-linkers may have 100% shape recovery in the initial 14 thermo-mechanical cycles, while maintaining stability within a high shape recovery range of 97 – 99% in the subsequent cycles. Therefore, a lower concentration of cross-linkers may result in a more loosely crosslinked covalent network that prevents catastrophic damage during shape deformation, hence achieving a more robust SLA SMPs with excellent shape recovery properties and longer cycle life. SLA SMPs with 10 wt% cross-linkers may exhibit an outstanding durability of 22 cycle life on average, which meets the criteria for commercial SMPs. Commercial SMPs may be tested using a series of at least twenty thermo-mechanical cycles for material confidence and robustness level.

[00131] FIG. 14 is a plot 1400 of recovery ratio (in percent or %) as a function of strain (in percent or %) comparing the shape recovery properties between the developed stereo-lithography shape memory polymers (SLA SMPs) according to various embodiments and other thermoset shape memory polymers (SMPs) fabricated using conventional methods such as injection molding and casting. The data presented relates to SLA-SMP with 10 wt% DEGDA cross-linkers and 2% PI, while the data for typical thermoset SMPs is obtained from various published information from well-known SMP companies as well as from several highly cited papers. FIG. 14 highlights that the performance of SLA SMPs according to various embodiments under the applied loading of 10% and 20% strain may exhibit highly comparative shape recovery properties as benchmarked against other thermoset SMPs of industrial grade.

[00132] There may be two approaches to improve and expand the applications of SMPs: 1) optimize the polymer system's mechanical, thermal and shape memory properties for the intended application and/or, 2) incorporate nanostructures or nanomaterials into the polymer to provide additional property enhancements. The SMPs may be reinforced with nanofillers.

[00133] These reinforced shape memory polymers (SMPs) or shape memory polymer composites (SMPCs) may be configured to bear a much higher mechanical load while maintaining shape memory effect (SME). Most of the fillers may significantly improve the elastic modulus and recovery stress of SMPs. While there are many different types of fillers based on sizes (micro- and nano-), shapes (rod-shaped and spherical-shape) and/or additional stimuli effects (electroactive, magnetic-active or water-active), various embodiments may include fillers that have chemical bonding with the SMP chains.

[00134] In various embodiments, the filler may be SiO₂ particles. SiO₂ particles may not only reinforce the SMPs by performing the function of cross-linking agents, but may also improve the shape memory properties.

[00135] In various embodiments, the formulation of tBA-co-DEGDA may have a low curing depth of 28.1 μm, which may only allow SMP layers with a layer thickness of 25 μm to be printed. This may eventually slow down the speed of the printing process as more layers are required to be printed to form or complete the entire part. Moreover, the fabricated part may be more likely to experience shrinkage due to high stress concentration formed from multiple layers. The addition of SiO₂ nanoparticles may improve the curing depths by allowing deeper penetration and curing of the resin bath.

[00136] FIG. 15A is an image 1500a of a stereo-lithography (SLA) printed part including a shape memory polymer (SMP) without addition of SiO₂ particles according to various embodiments. FIG. 15B is an image 1500b of another stereo-lithography (SLA) printed part including a shape memory polymer (SMP) without addition of SiO₂ particles according to various embodiments. FIG. 15C is an image 1500c of a stereo-lithography (SLA) printed part including a shape memory polymer (SMP) including SiO₂ particles according to various embodiments. FIG. 15D is an image 1500d of another stereo-lithography (SLA) printed part including a shape memory polymer (SMP) including SiO₂ particles according to various embodiments.

[00137] FIGS. 15A-D compare the printed parts with and without the addition of the nano SiO₂ particles. The presence of SiO₂ nanoparticles may influence the laser beam penetrating

into the resin. The refractive index of the particles (1.50) may be slightly higher than that of the resin (1.41). The laser beam entering regions of higher refractive index may be slowed down. The slowdown in the speed of light penetration may reduce ultraviolet (UV) scattering, and may reduce the refraction of light. Including the nanoparticles may thus lead to deeper curing depths and higher resolution printing.

[00138] The polymer including SiO₂ nanoparticles have been tested using Fourier transform infrared spectroscopy (FTIR) to determine the chemical bonding of the SiO₂ with the polymer chains. FIG. 16 is a plot 1600 of reflectance (in percent or %) as a function of wavenumbers (in per centimetres or cm⁻¹) showing the Fourier Transform Infra-red (FTIR) spectra of shape memory polymers with different amounts of silicon oxide (SiO₂) nanoparticles according to various embodiments. The reaction of the tBA-co-DEGDA with SiO₂ nanoparticles in which the SiO₂ nanoparticles form the Si-OH bonds with the polymer network is confirmed by the FTIR spectra shown in FIG. 16. The chemical bonding between the nanoparticles and the SMP chains may improve the mechanical properties and shape memory performance.

[00139] Dynamic Mechanical Analysis (DMA) may be used to determine the maximum strain the SMPCs can withstand when heated to above their glass transition temperature (T_g) in their rubbery state. FIG. 17 is a plot 1700 of stress (in mega Pascals or MPa) as a function of strain (in percent or %) showing the stress-strain curves of shape memory polymers with different concentrations of silicon oxide (SiO₂) nanoparticles according to various embodiments. FIG. 17 shows that there may be significant improvement in the maximum strain attainable when with the addition of SiO₂ nanoparticles. With increment of the concentration of nanoparticles from 0 wt% to 1 wt% to 2 wt%, the maximum strain may increase from 20.8% to 24.5% to 31.8% respectively.

[00140] The SiO₂ nanoparticles may not be homogeneously dispersed in the resin mixture or formulation. FIG. 18A is an image 1800a showing the agglomeration of the nanoparticles after a few print jobs to form large clusters which may affect the printed parts according to various embodiments. FIG. 18B is a plot 1800b of intensity (percent or %) as a function of size (in nanometres or nm) showing the particle size distribution in the mixture or formulation according to various embodiments. FIG. 18B shows the presence of large and small clusters of particles.

[00141] Experimental Details

[00142] Synthesis

[00143] Commercial tert-butyl acrylate (tBA) monomer (balanced amount) were synthesized with di(ethylene glycol) diacrylate (DEGDA) cross-linker (9-50 wt%) using UV photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) (1-10 wt%) and Sudan I photoabsorber (0.1-10 wt%). The chemicals were all ordered from Sigma Aldrich and used as received conditions without further purification. The DEGDA cross-linker were first added dropwise to the tBA monomer, subsequently with the addition of the photoinitiator and the photoabsorber in continuous mixing of the solution using magnetic stirring followed by planetary vacuum mixer at 1900 rpm until the photoinitiator and photoabsorber completely dissolved. The synthesis of the chemicals were performed in an ultra-violet (UV) proof environment to minimize pre-photopolymerization.

[00144] Characterization and Post Processing of Printed SMPs

[00145] Curing Properties and Characteristics

[00146] Objectives include determining the laser threshold scanning speed and optimal photoinitiator concentration to minimize excess width and determine the layer thickness for printing. The solutions with 1 wt% photoinitiators were prepared in the resin vat and cured by the UV laser beam at different scanning velocities ranging from minimum value of 100 to maximum value of 1360 mm s^{-1} with a layer thickness of 50 μm to form specimen size of 17.5 mm x 11.9 mm x 2 mm. Dimensional measurements of the cured specimens using digital caliper were recorded to determine the accuracy of the printed samples, so as to avoid over-curing from laser scanning which can cause printing of excess width.

[00147] Using the optimized laser parameters, solutions with varying concentrations of photoinitiators at 0.5, 1, 2, 4 and 5 wt% were prepared and pipetted onto a glass substrate which was placed above the laser beam. FIG. 19 is a schematic 1900 showing an experimental setup for determining curing depth. The samples were cured by scanning a single layer cross-hatched pattern to form square laminates of 10 mm x 10 mm. Two samples were produced for each concentration of photoinitiator for consistency purposes. After polymerization, the unreacted solutions were cleaned off with kimwipes, leaving behind the cured samples. The sample thickness corresponds to the curing depth which can be measured using a Stylus Profilometer (Taylor Hobson Talysurf Series 2, UK) to find out the minimum curing depth achievable by each sample of different photoinitiator concentrations.

[00148] Post Processing of Printed SMPs

[00149] With the optimized laser parameters and photoinitiator concentration, a batch of specimens with specific dimensions for thermal, mechanical and thermomechanical testings were printed. After the printing process, the specimens were removed off the platform and flushed with isopropyl alcohol (IPA) to wash off any unreacted monomers. They were then placed in a UV oven (CMET UV-600HL, Japan) for post-curing of 10 minutes, ensuring that the specimens are all fully polymerized.

[00150] Thermal Analysis of Printed SMPs

[00151] Thermogravimetric Analysis

[00152] A thermogravimetric analysis (TGA) was carried out on TA Instruments TGA Q500 equipment (USA) to find out the polymer decomposition temperature. The TGA results obtained can be used to anticipate the maximum temperature for the subsequent TMA and DMA tests. The samples with a mass of approximately 10 mg each were placed in a platinum pan which was heated up in the furnace from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

[00153] Dynamic Mechanical Analysis

[00154] Given that the shape memory effect of thermoset SMPs revolves around a temperature range centered at the glass transition temperature (T_g) in which the material is rigid below the T_g and become rubbery when above it, hence the T_g and viscoelasticity of the SMPs were determined using Dynamic Mechanical Analysis (TA Instruments DMA Q800, USA). Samples printed in the shape of rectangular bars with dimensions of 17.5 mm x 11.9 mm x 1.20 mm were placed into the DMA single cantilever clamping fixture under a dynamic load of 1 Hz with amplitude set at 15 μ m. The samples were heated from 20 °C to temperature well above the T_g at a heating rate of 3 °C min⁻¹. Glass transition temperature which is defined by the tan δ peak and storage modulus in both the glassy and rubbery state can be analysed from DMA.

[00155] Thermomechanical Analysis

[00156] To determine the temperature range in which the SMP changes from glassy to rubbery state, a Thermomechanical Analysis (TA Instruments TMA Q400, USA) is conducted to detect the onset of softening in the SMP. The sample with a thickness of 0.65 mm is placed on the quartz stage holder surrounded by a furnace and a quartz penetration probe rests on top of the sample with a small force of 0.02 N. The sample is cooled down to -20 °C before heated up to 80 °C at a heating rate of 5 °C min⁻¹. TGA measures the linear or

volumetric changes in the dimensions of a sample as a function of temperature when it is cooled or heated in a controlled atmosphere. A thermocouple placed next to the sample detects the softening temperature when there is a sudden drop in the dimensions of the sample.

[00157] Mechanical Properties

[00158] Tensile Tests

[00159] Tensile tests were performed on a Shimadzu AG-X Plus Series tensile tester (Japan) equipped with a thermostatic chamber to determine the mechanical properties of the printed dumbbell-shaped specimens at both room temperature and above T_g based on ISO 527-1:1996 standards. The tensile tests were run at a crosshead speed of 1 mm min^{-1} . For experimental runs above the T_g , the samples were placed inside the chamber to reach an equilibrium temperature above its T_g before the tests were carried out.

[00160] Shape Memory Characterization

[00161] Thermomechanical Cyclic Tests

[00162] The shape memory properties of the printed SMPs were examined using DMA (TA Instruments DMA Q800, USA) in single cantilever mode by carrying out thermomechanical cyclic tests of repeated deformation, cooling and reheating. Rectangular samples with dimensions of $17.5 \text{ mm} \times 11.9 \text{ mm} \times 1.20 \text{ mm}$ placed into the DMA fixture were thermally equilibrated at 28°C before being heated up to a deformation temperature $T_d = 65^\circ\text{C}$ ($T_g + 10^\circ\text{C}$) at a rate of 3°C min^{-1} and held isothermal for 15 min. The samples were then deformed under a ramped force at the rate of 0.05 N min^{-1} up to 2 different forces: 0.3 N and 0.7 N, so as to induce a strain under load of approximately 12% and 20% respectively which was held constant for 30 min to allow stress relaxation before the samples were cooled down to 30°C to fix the temporary shape. The force was unloaded to observe any elastic spring back ϵ by the sample. Lastly, under a stress free condition, the sample was reheated to 65°C ($T_g + 10^\circ\text{C}$) at a rate of 3°C min^{-1} so that the sample returned back to its permanent shape, leading to a recovered strain ϵ_{rec} , and the shape recovery R_r as well as the shape fixity ratio R_f are determined.

[00163] Applications

[00164] Various embodiments may provide a photocurable resin with shape memory properties suitable for resin based 3D printing via UV curing. The formulated resin may show a glass transition at 53.96°C which is considered in the near range of body temperature,

hence the fabricated SMPs may undergo low temperature deformation and may find potential in a wide range of medical applications such as self-tightening sutures and stents or dental applications, although specific biocompatibility tests have yet to be performed.

[00165] One potential application may be dental aligners (an alternative to braces) which allow adjustment of the teeth. FIG. 20A shows an image 2000a of a dental aligner including the shape memory polymer (SMP) according to various embodiments. FIG. 20B shows another image 2000b of the dental aligner including the shape memory polymer (SMP) according to various embodiments. The robustness of the formulated SMPs which can withstand repeated cycles may allow the dental aligners to be reused multiple times at different stages of the teeth adjustment, making it economically efficient.

[00166] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A formulation for forming a shape memory polymer, the formulation comprising:
 - an acrylate monomer;
 - a cross-linker for forming one or more cross-links with the acrylate monomer to form the shape memory polymer;
 - a photoinitiator for initializing the formation of the one or more cross-links upon exposure to ultraviolet light;
 - a photoabsorber for controlling a rate of formation of the one or more cross-links; and
 - one or more silicon oxide nanoparticles;wherein a concentration of the photoabsorber is any one value selected from a range of 0.1 weight percent to 10 weight percent of the formulation;
wherein a concentration of the photoinitiator is any one value selected from a range of 1 weight percent to 10 weight percent of the formulation;
wherein a concentration of the cross-linker is any one value selected from a range of 5 weight percent to 50 weight percent of the formulation; and
wherein the acrylate monomer, the cross-linker, the photoinitiator, the photoabsorber, and the one or more silicon oxide nanoparticles are configured to form the shape memory polymer.
2. The formulation according to claim 1,
 - wherein acrylate monomer is tert-butyl acrylate monomer or tert-butyl methacrylate monomer.
3. The formulation according to claim 1 or claim 2,
 - wherein the cross-linker is a compound comprising two or more functional groups.
4. The formulation according to claim 3,
 - wherein the two or more functional groups are acrylates or methacrylates.

5. The formulation according to any one of claims 1 to 4,
wherein the cross-linker is di(ethylene glycol) diacrylate.
6. The formulation according to any one of claims 1 to 5,
wherein the photoinitiator is phenyl bis (2, 4, 6-trimethylbenzoyl) phosphine oxide (BAPO).
7. The formulation according to any one of claims 1 to 6,
wherein the photoabsorber is configured to absorb the ultraviolet light.
8. The formulation according to any one of claims 1 to 7,
wherein the photoabsorber is any one selected from a group consisting of 1-phenylazo-2-naphthol (Sudan I), 1-[4-(phenylazo)phenylazo]-2-naphthol (Sudan III), and $C_{28}H_{31}ClN_2O_3$ (Rhodamine B).
9. A method of forming a shape memory polymer, the method comprising:
mixing a formulation according to claim 1; and
exposing the mixture to the ultraviolet light so that the cross-linker forms one or more cross-links with the acrylate monomer to form the shape memory polymer;
wherein the formation of the one or more cross-links upon exposure to the ultraviolet light is initialized by the photoinitiator; and
wherein a rate of formation of the one or more cross-links is controlled by the photoabsorber.
10. The method according to claim 9,
wherein exposing the mixture to the ultraviolet light comprises using a laser scanning system to provide an ultraviolet laser beam to form the shape memory polymer.
11. The method according to claim 10,

wherein the ultraviolet laser beam is moved across the mixture at a speed of at least 700 mms⁻¹.

12. The method according to claim 10 or claim 11,
wherein the ultraviolet laser beam has a surface power density of a value in the range of 40 mWcm⁻² to 80 mWcm⁻².
13. The method according to claim 9,
wherein exposing the mixture to the ultraviolet light comprises using a projection system to project the ultraviolet light to form the shape memory polymer.
14. The method according to claim 13,
wherein the ultraviolet light is projected for a duration of any value less than 3 seconds.
15. The method according to claim 13 or claim 14,
wherein the projected ultraviolet light has a surface power density of a value in the range of 10 mWcm⁻² to 40 mWcm⁻².
16. The method according to any one of claims 9 to 15,
wherein the shape memory polymer formed has a thickness of 25 µm or less.
17. A shape memory polymer formed by a method of any one of claims 9 to 16.
18. The shape memory polymer according to claim 17,
wherein the shape memory polymer is configured to switch from a first shape to a second shape upon the shape memory polymer being heated to a temperature above a predetermined temperature; and
wherein the shape memory polymer is configured to switch from the second shape to the first shape upon application of an external stimulus.

19. The shape memory polymer according to claim 18,
wherein the predetermined temperature is any value selected from a range of
30 °C to 90 °C.
20. The shape memory polymer according to any one of claims 17 to 19,
wherein the one or more silicon oxide nanoparticles are chemically bonded to
a polymer chain comprising the acrylate monomer and the cross-linker.
21. A device comprising a shape memory polymer according to any one of claims 17 to
20.
22. The device according to claim 21, wherein the device is any one of a suture, a stent,
and a dental aligner.