

Curable Compositions

Cross-Reference to Related Application

5 This application claims the benefit of priority of Singapore application no. 10202100797W filed on 25 January 2021, the contents of it being hereby incorporate by reference in its entirety for all purpose.

Technical Field

10 The present invention generally relates to curable compositions. The present invention also relates to curable compositions useful for forming shape memory polymers.

Background Art

15 Shape memory polymer (SMP) is a stimuli-responsive elastomer that can maintain a temporary shape when deformed by external forces, and be triggered to recover its original shape, usually via heat. The ability to stay deformed and recover allows SMPs to have the potential to serve the needs of robotics and medical devices, but it has yet to be fully realised in these applications.

20 More recently, SMP has been used in 3D printing which allows for fabricating sophisticated geometries at high rate. Among all the 3D printing technology, vat photopolymerization has one of the fastest printing processes, as well as smoothest surface finishes. However, the mechanical properties of the printed parts tend to be inferior when compared to other 3D printing methods. One of the issues with vat photopolymerization is the increase in brittleness after post-treatment or long exposure of light and heat. The use of additives in vat photopolymerization is also challenging due to a variety of reasons, such as
25 the dispersion of particles and the detrimental effects on ultraviolet (UV) curing.

3D printing via Digital light processing (DLP) is well known for its fast printing speed, by UV projection of pixels instead of a moving laser. This enables DLP printers to instantly print the whole layer at once, eliminating the need for UV light to move across the layer. Along with the new developments of photopolymerizable resins, DLP printing has
30 seen great growth and wide adoption in industries such as dentistry and automotive.

However, DLP printing suffers from poor dimensional and geometrical accuracy and therefore has shortcomings in medical applications where accuracy of internal structures for medical devices is important.

35 Photoabsorbing dyes are commonly used in UV curable resins to improve dimensional accuracies. They can be used to reduce the cure depth, thus preventing unwanted cure due to excessive UV exposures. However, photoabsorbers tend to also increase the critical energy of the resin, which the minimum amount of energy needed for the resin to start curing. This could result in longer exposure time, as well as the overall printing time.

There is a need to provide a curable composition that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary of Invention

5 According to a first aspect, there is provided a curable composition comprising (i) a resin composition, wherein the resin composition comprises:

a compound C1 having an X group and an optionally substituted aryl group;

a compound C2 having an X group and an optionally substituted carbocyclyl group;

10 a compound C3 having at least two X groups; and

a photoinitiator,

wherein X is acrylate or methacrylate.

15 In another aspect of the present disclosure, there is provided a method of forming a shape memory polymer, the method comprising exposing a curable composition disclosed herein to ultraviolet light.

In a further aspect of the present disclosure, there is provided a shape memory polymer comprising the curable composition disclosed herein, wherein the curable composition has been cured by ultraviolet light.

20 Advantageously, the curable compositions of the present disclosure allow for fast UV curing into shape memory polymers (SMP). The working temperature of the SMP may be brought closer to body temperature, even after extensive post-treatment is applied. This advantageously makes it easier to trigger its shape memory effect without having to heat the SMP to high temperatures. Further advantageously, the SMPs may have high recovery ratio of 99% at 40 °C.

25 In an example, the curable compositions of the present disclosure may further comprise metal oxides, such as zinc oxide. The addition of metal oxide not only speeds up the curing process, it also helps to improve the print quality of the product by reducing flashes. It also provides slight improvement in the mechanical properties at both room temperature and body temperature.

30 The addition of metal oxide also advantageously reduces the amount of energy needed to cure a layer of resin, while preventing excessive unwanted cure during the printing process. In addition, the inclusion of metal oxide increases the toughness of the material, with some compromise on the tensile strength and Young's Modulus.

35 Also advantageously, the curable compositions of the present disclosure do not contain photoabsorbers, such as 1-phenylazo-2-naphthol (Sudan I), 1-[4-(phenylazo)phenylazo]-2-naphthol (Sudan III), and C₂₈H₃₁ClN₂O₃ (Rhodamine B). Although they can be used to reduce the cure depth (thus preventing unwanted cure due to excessive UV exposures), photoabsorbers tend to also increase the critical energy of the resin, which the minimum amount of energy needed for the resin to start curing. This could result in longer exposure time, as well as the overall printing time, hence they are undesirable.

40

Definitions

The following words and terms used herein shall have the meaning indicated:

As used herein, the term "alkyl" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 6 carbon atoms, eg, 1, 2, 3, 4, 5 or 6 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl and the like. Alkyl groups may be optionally substituted.

As used herein, the term "alkenyl" refers to divalent straight chain or branched chain unsaturated aliphatic groups containing at least one carbon-carbon double bond and having from 2 to 6 carbon atoms, eg, 2, 3, 4, 5 or 6 carbon atoms. For example, the term alkenyl includes, but is not limited to, ethenyl, propenyl, butenyl, 1-butenyl, 2-butenyl, 2-methylpropenyl, 1-pentenyl, 2-pentenyl, 2-methylbut-1-enyl, 3-methylbut-1-enyl, 2-methylbut-2-enyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 2,2-dimethyl-2-butenyl, 2-methyl-2-hexenyl, 3-methyl-1-pentenyl, 1,5-hexadienyl and the like. Alkenyl groups may be optionally substituted.

As used herein, the term "alkynyl" refers to trivalent straight chain or branched chain unsaturated aliphatic groups containing at least one carbon-carbon triple bond and having from 2 to 6 carbon atoms, eg, 2, 3, 4, 5 or 6 carbon atoms. For example, the term alkynyl includes, but is not limited to, ethynyl, propynyl, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 1-hexyne, 2-hexyne, 3-hexyne, 3-methyl-1-pentyne or variants such as "aromatic group" or "arylene" as used herein refers to monovalent ("aryl") and divalent ("arylene") single, polynuclear, conjugated and fused residues of aromatic hydrocarbons having from 6 to 10 carbon atoms. Such groups include, for example, phenyl, biphenyl, naphthyl, phenanthrenyl, and the like. Aryl groups may be optionally substituted.

The terms "carbocycle", "carbocyclyl" or variants such as "carbocyclic ring" as used herein, includes within its meaning any stable 3, 4, 5, 6, or 7-membered monocyclic or bicyclic or 7, 8, 9, 10, 11, 12, or 13-membered bicyclic or tricyclic, any of which may be saturated, partially unsaturated, or aromatic. Examples of such carbocycles include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, cyclooctyl, [3.3.0]bicyclooctane, [4.3.0]bicyclononane, [4.4.0]bicyclodecane (decalin), [2.2.2]bicyclooctane, fluorenyl, phenyl, naphthyl, indanyl, adamantyl, or tetrahydronaphthyl (tetralin). Preferred carbocycles, unless otherwise specified, are cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenyl, naphthyl, and indanyl. When the term "carbocycle" is used, it is intended to include "aryl". Carbocycles may be optionally substituted.

When compounded chemical names, e.g. "arylalkyl" and "arylimine" are used herein, they are understood to have a specific connectivity to the core of the chemical structure. The group listed farthest to the right (e.g. alkyl in "arylalkyl"), is the group that is directly connected to the core. Thus, an "arylalkyl" group, for example, is an alkyl group substituted with an aryl group (e.g. phenylmethyl (i.e., benzyl)) and the alkyl group is attached to the core. An "alkylaryl" group is an aryl group substituted with an alkyl group (e.g., p-methylphenyl (i.e., p-tolyl)) and the aryl group is attached to the core.

The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups other than hydrogen provided that the indicated atom's normal valency is not exceeded, and that the substitution results in a stable compound. Such groups may be, for example, halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, aryl-4-alkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN- , $R^xOCO(CH_2)_m$, $R^xCON(R^y)(CH_2)_m$, $R^xR^yNCO(CH_2)_m$, $R^xR^yNSO_2(CH_2)_m$ or $R^xSO_2NR^y(CH_2)_m$ (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO-$ (wherein p is 1, 2, 3 or 4); wherein when the substituent is $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO$, R^x with at least one CH_2 of the $(CH_2)_p$ portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, alkyl.

The term "substituted" as used herein means the group to which this term refers is substituted with one or more groups other than hydrogen provided that the indicated atom's normal valency is not exceeded, and that the substitution results in a stable compound. Such groups may be, for example, halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN- , $R^xOCO(CH_2)_m$, $R^xCON(R^y)(CH_2)_m$, $R^xR^yNCO(CH_2)_m$, $R^xR^yNSO_2(CH_2)_m$ or $R^xSO_2NR^y(CH_2)_m$ (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO-$ (wherein p is 1, 2, 3 or 4); wherein when the substituent is $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO$, R^x with at least one CH_2 of the $(CH_2)_p$ portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, alkyl.

Any carbon or heteroatom with unsatisfied valences in the text, schemes, examples, structural formulae, and any Tables herein is assumed to have the hydrogen atom or atoms to satisfy the valences.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated

value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig.1

[Fig. 1] is a graph showing the cure depth versus exposure time for curable compositions with and without zinc oxide (ZnO).

Fig.2

[Fig. 2] is a series of photographs comparing the printing quality of structures 3D-printed from curable compositions containing ZnO (right) and without ZnO (left) with small defining features (2mm, 3.2 mm and 6.0 mm circles/ squares and 2.2 mm, 3.5 mm and 6 mm diamonds).

Fig.3

[Fig. 3] is an image showing a square array with different UV exposure for measuring cure depth.

Fig.4a

[Fig. 4a] is a graph showing the cure depth versus energy input for different curable compositions with varying amounts of ZnO added.

Fig.4b

[Fig. 4b] is a series of graphs showing the critical energy and penetration depth for the different curable compositions with varying amounts of ZnO added.

Fig.5

- 5 [Fig. 5] is a diagram of an overhanging structure used to measure unwanted cure in the vertical direction, with increasing bottom exposures from left to right.

Fig.6

[Fig. 6] are microscopic images of the overhanging structure after certain amounts of bottom exposure.

- 10 **Fig.7a**

[Fig. 7a] is a graph showing the measured versus theoretical flash height for the UV-curable resins with an exposure time of 1.5 seconds.

Fig.7b

- 15 [Fig. 7b] is a graph showing the measured versus theoretical flash height for curable compositions with an exposure time of 2 seconds.

Fig.8a

- 20 [Fig. 8a] is a graph showing the stress-strain curves of the curable compositions of Example 1 60 minutes post curing.

Fig.8b

[Fig. 8b] is a series of graphs showing the tensile properties of the curable compositions of Example 1 60 minutes post curing.

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Fig.8c

[Fig. 8c] is a series of graphs showing the tensile properties of the curable compositions of Example 1 180 minutes post curing.

- 30 **Fig.9a**

[Fig. 9a] is a graph showing the tensile properties of the curable compositions of Example 1 with no post curing.

Fig.9b

- 35 [Fig. 9b] is a graph showing the cumulative normalized energy exposure during printing of the samples of Example 6.

Fig.9c

- 40 [Fig. 9c] is a graph showing the total and normalized energy exposures of the samples of Example 6 without post curing.

Fig.10a

[Fig. 10a] is a graph showing the programming of shape memory polymer in the shape of an octahedron cube, by compression the cube to 40% strain at 40 °C.

5 Fig.10b

[Fig. 10b] is a graph measuring the recovery stress while the octahedron cube of Example 7 is maintained at 27% strain based on the position of the cube.

Fig.10c

10 [Fig. 10c] is a graph measuring the recovery of the shape memory polymer in the shape of an octahedron cube, wherein the strain is returned to 0% based on the position at 40 °C.

Fig.10d

15 [Fig. 10d] is a diagram of the shape memory polymer in the shape of an octahedron cube used in the shape memory effect analysis.

Fig.11

20 [Fig. 11] is an image of a 3D-printed stent from ZnO-containing shape memory polymer, with a smallest feature size of 0.4 mm.

Fig.12

[Fig. 12] are images of a 3D-printed stent printed with shape memory polymer without ZnO, before and after compression at 40 °C.

25

Detailed Description

Exemplary, non-limiting embodiments of the present invention will now be disclosed.

30 The present invention relates to a curable composition comprising (i) a resin composition, wherein the resin composition comprises:

a compound C1 having an X group and an optionally substituted aryl group;

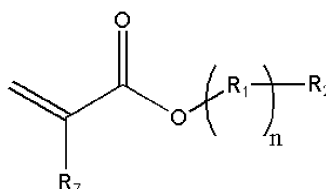
a compound C2 having an X group and an optionally substituted carbocyclyl group;

a compound C3 having at least two X groups; and

35 a photoinitiator,

wherein X is acrylate or methacrylate.

Compound C1 may be represented by the following Formula (I):



Formula (I)

5 wherein

R₁ is optionally substituted alkylene, or -R_{1a}-O-, wherein R_{1a} is optionally substituted alkylene;

R₂ is optionally substituted aryl;

R₇ is H or methyl; and

10 n represents an integer of 1 to 4.

R₁ and R_{1a} may each be unsubstituted or substituted C₁ to 6-alkylene (i.e. C₁, C₂, C₃, C₄, C₅, or C₆ alkylene).

n may be 1, 2, 3 or 4.

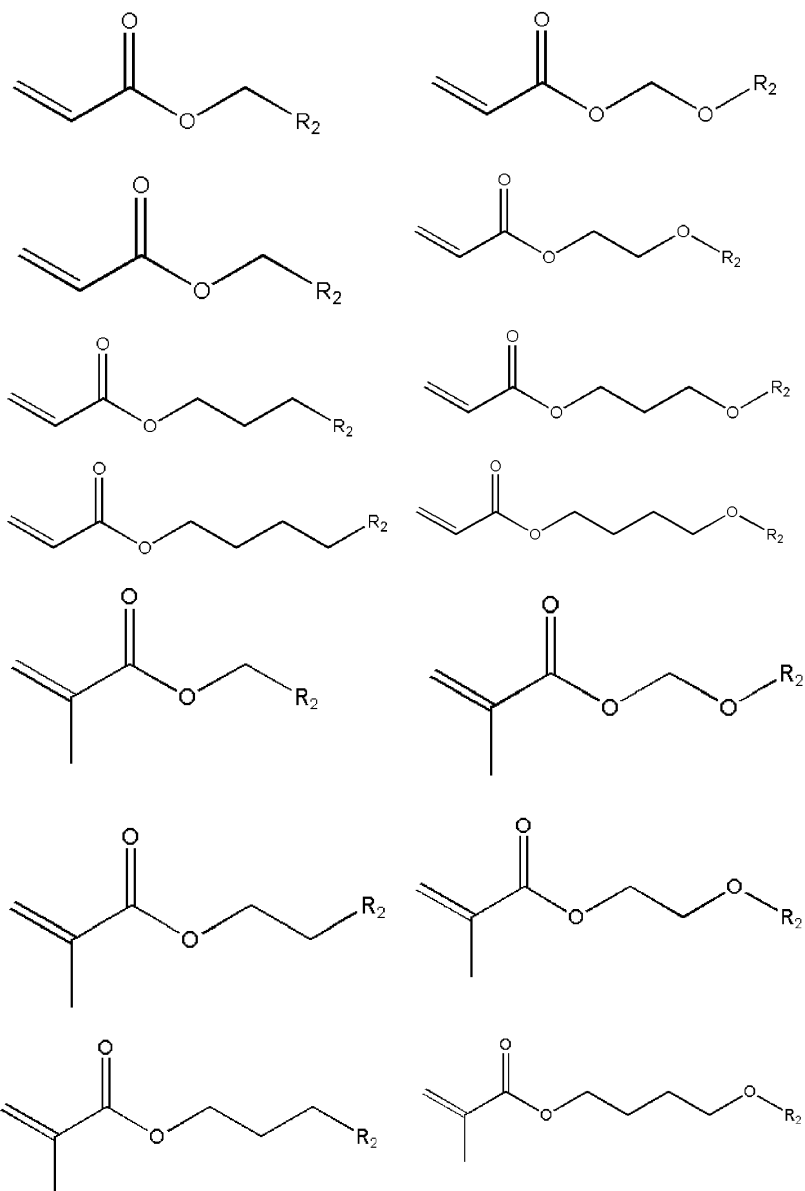
15 R₂ may be unsubstituted or substituted aryl. R₂ may be a substituted or unsubstituted C₆-₁₂ aryl group (i.e. a C₆, C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ aryl group).

R₂ may be substituted or unsubstituted phenyl, biphenyl, naphthyl, or phenanthrenyl.

20 R₂ may be an aryl group that is unsubstituted or substituted with one or more halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN-, R^xOCO(CH₂)_m, R^xCON(R^y)(CH₂)_m, R^xR^yNCO(CH₂)_m, R^xR^yNSO₂(CH₂)_m or R^xSO₂NR^y(CH₂)_m (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group R^xR^yN(CH₂)_p- or R^xR^yN(CH₂)_pO- (wherein p is 1, 2, 3 or 4); wherein when the substituent is R^xR^yN(CH₂)_p- or R^xR^yN(CH₂)_pO, R^x with at least one CH₂ of the (CH₂)_p portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, or alkyl.

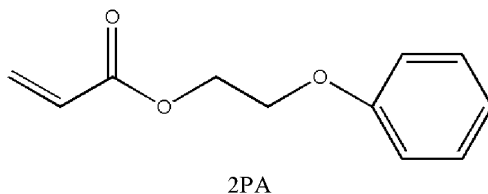
30 R₂ may be unsubstituted or substituted phenyl. R₂ may be unsubstituted phenyl.

Compound C1 may be selected from one of the following compounds:

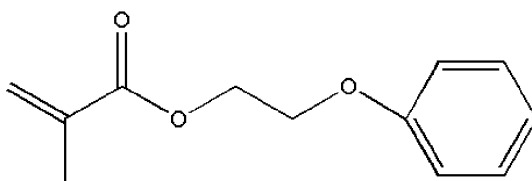


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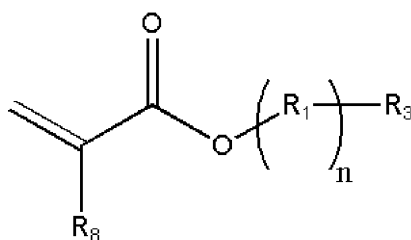
Compound C1 may be 2-phenoxyethyl acrylate (2PA):



5 Compound C1 may be 2-phenoxyethyl methacrylate:



Compound C2 may be represented by the following Formula (II):



10

Formula (II)

wherein

R₁ is optionally substituted alkylene;

R₃ is optionally substituted carbocyclyl;

R₈ is H or methyl; and

15 n represents an integer of 0 to 4.

R₁ may be unsubstituted or substituted C₁ to 6-alkylene (i.e. C₁, C₂, C₃, C₄, C₅, or C₆ alkylene).

n may be 0, 1, 2, 3 or 4.

20 R₁ may be alkylene unsubstituted or substituted with one or more halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl,

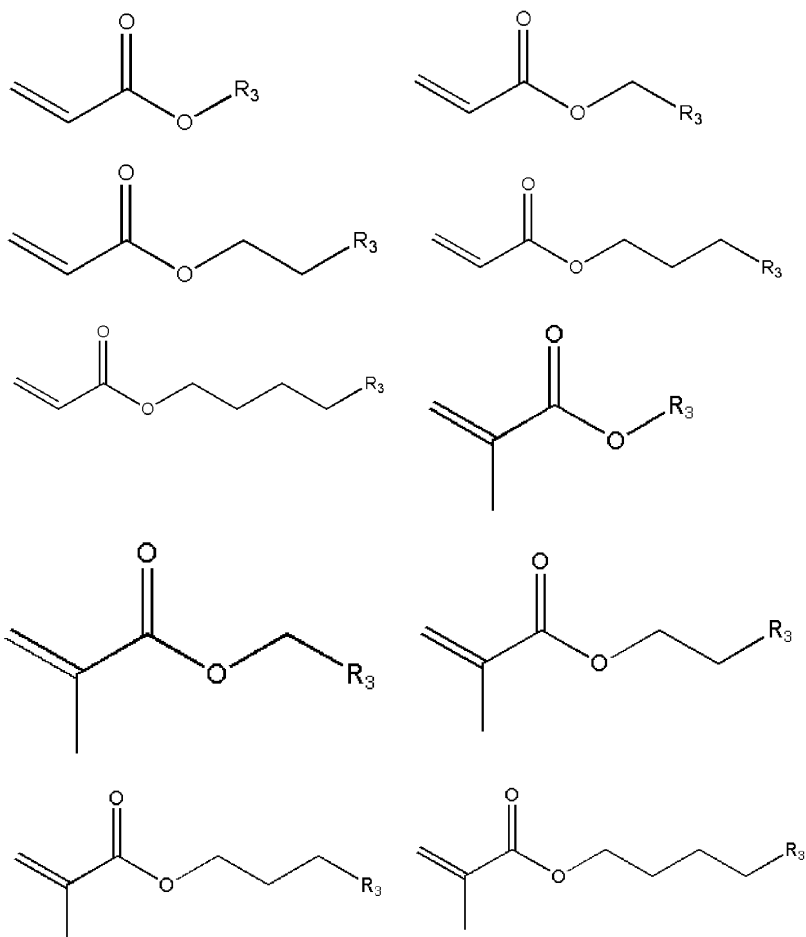
alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN- , $R^xOCO(CH_2)_m$, $R^xCON(R^y)(CH_2)_m$, $R^xR^yNCO(CH_2)_m$, $R^xR^yNSO_2(CH_2)_m$ or $R^xSO_2NR^y(CH_2)_m$ (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO-$ (wherein p is 1, 2, 3 or 4); wherein when the substituent is $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO$, R^x with at least one CH_2 of the $(CH_2)_p$ portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, or alkyl.

R_3 may be unsubstituted or substituted carbocyclyl. R_3 may be unsubstituted or substituted C_3 to C_{12} carbocyclyl group. The carbocyclyl may be a saturated, or partially saturated, mono or bicyclic carbon ring that contains 3 to 12 carbon atoms. The carbocyclyl may be a monocyclic ring containing 5 or 6 carbon atoms or a bicyclic ring containing 7 to 10 carbon atoms.

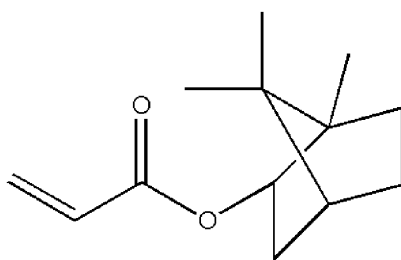
R_3 may be carbocyclyl group that is unsubstituted or substituted with one or more halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN- , $R^xOCO(CH_2)_m$, $R^xCON(R^y)(CH_2)_m$, $R^xR^yNCO(CH_2)_m$, $R^xR^yNSO_2(CH_2)_m$ or $R^xSO_2NR^y(CH_2)_m$ (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO-$ (wherein p is 1, 2, 3 or 4); wherein when the substituent is $R^xR^yN(CH_2)_p-$ or $R^xR^yN(CH_2)_pO$, R^x with at least one CH_2 of the $(CH_2)_p$ portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, or alkyl.

The optionally substituted carbocyclyl group may be a bicyclic C_7 carbocyclyl substituted with at least 1 alkyl group. The optionally substituted carbocyclyl group may be a bicyclic C_7 carbocyclyl substituted with 1, 2, or 3 alkyl groups. The alkyl groups may be selected from methyl, ethyl, propyl or butyl. The optionally substituted carbocyclyl group may be a bicyclic C_7 carbocyclyl substituted with 1, 2, or 3 methyl groups. The optionally substituted carbocyclyl group may be a bicyclic C_7 carbocyclyl substituted with 3 methyl groups.

Compound C2 may be selected from one of the following compounds:

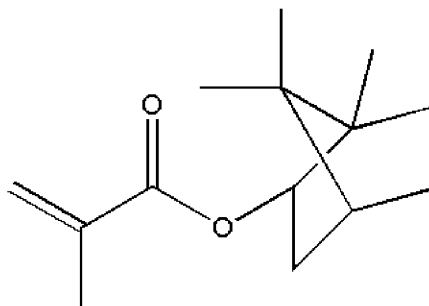


Compound C2 may be isobornyl acrylate (IBOA):

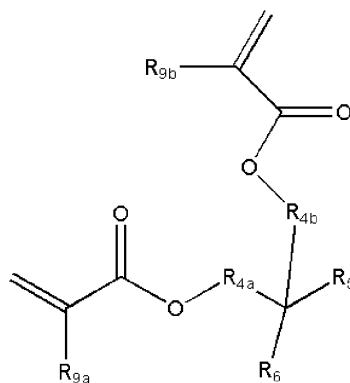


IBOA

Compound C2 may be isobornyl methacrylate:



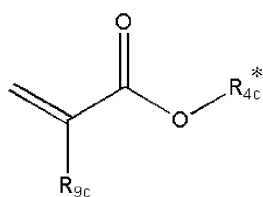
Compound C3 be represented by the following Formula (III):



Formula (III)

wherein

R₅ is optionally substituted alkyl, alkenyl or alkynyl;



R₆ is H or

R_{4a}, R_{4b} and R_{4c} are each independently optionally substituted alkylene, or -R_{4d}-O-,
 wherein R_{4d} is optionally substituted alkylene; and

R_{9a}, R_{9b} and R_{9c} are each independently H or methyl.

Compound C3 may have at least 2 acrylate or methacrylate groups. Compound C3 may have
 at least 3 acrylate or methacrylate groups. Compound C3 may have 3 acrylate or methacrylate

groups. Compound C3 may have at least 2 acrylate groups. Compound C3 may have at least 3 acrylate groups. Compound C3 may have 3 acrylate groups.

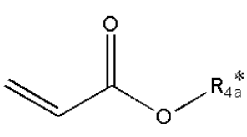
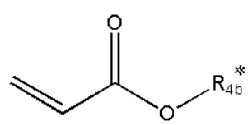
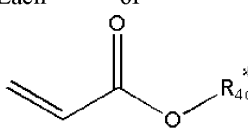
R₅ may be unsubstituted or substituted C₁₋₆ alkyl (i.e. C₁, C₂, C₃, C₄, C₅, or C₆ alkyl), C₂₋₆ alkylene (i.e. C₂, C₃, C₄, C₅, or C₆ alkenyl), or C₂₋₆ alkynyl (i.e. C₂, C₃, C₄, C₅, or C₆ alkynyl).

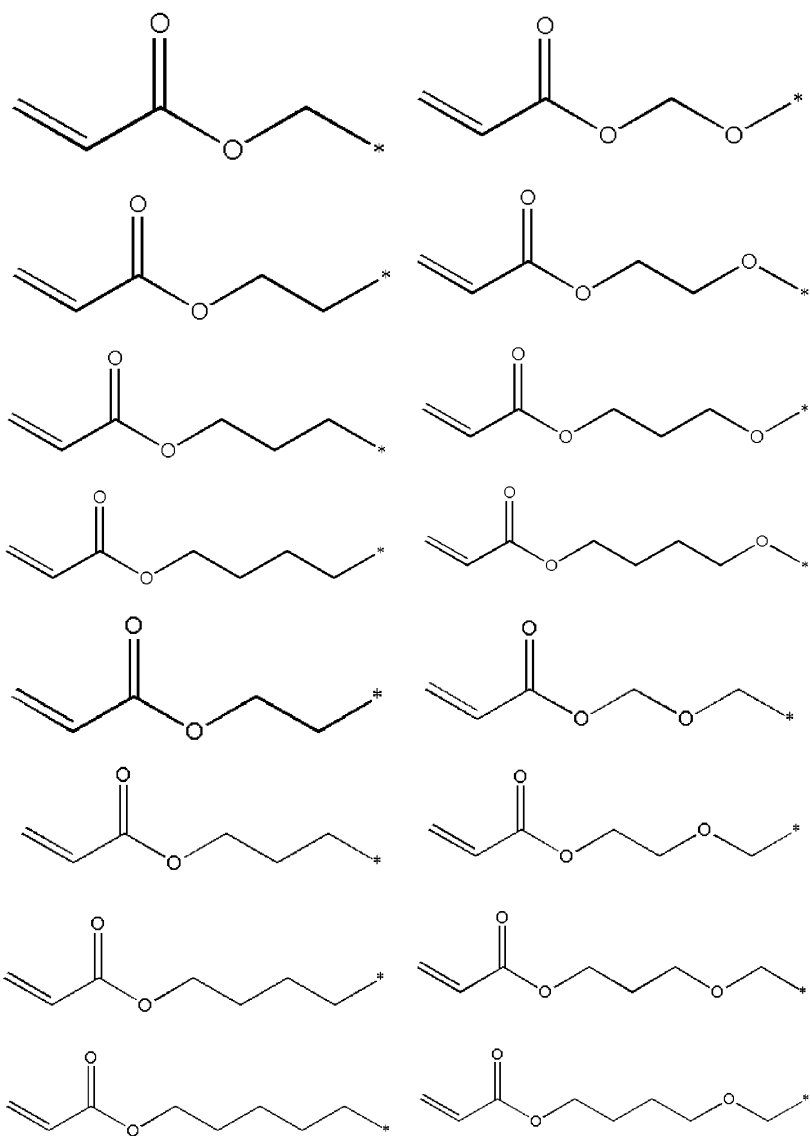
5 R₅ may be unsubstituted or substituted methyl, ethyl, or propyl.

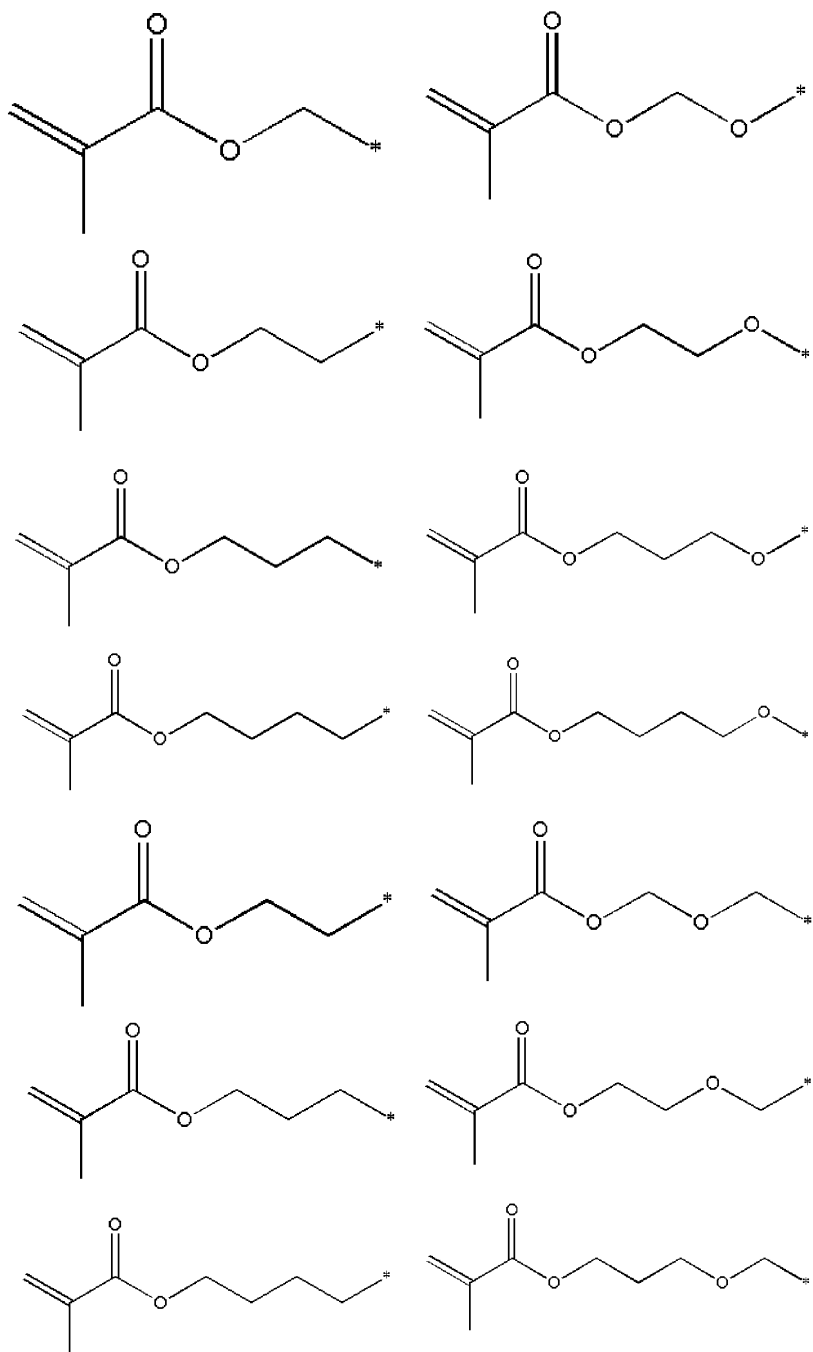
R₅ may be alkyl, alkenyl or alkynyl unsubstituted or substituted with one or more halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, 10 arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN-, R^xOCO(CH₂)_m, R^xCON(R^y)(CH₂)_m, R^xR^yNCO(CH₂)_m, R^xR^yNSO₂(CH₂)_m or R^xSO₂NR^y(CH₂)_m (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part 15 of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group R^xR^yN(CH₂)_p- or R^xR^yN(CH₂)_pO- (wherein p is 1, 2, 3 or 4); wherein when the substituent is R^xR^yN(CH₂)_p- or R^xR^yN(CH₂)_pO, R^x with at least one CH₂ of the (CH₂)_p portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, or alkyl.

20 R_{4a}, R_{4b}, R_{4c}, R_{4d} may each be unsubstituted or substituted C_{1 to 6}-alkylene (i.e. C₁, C₂, C₃, C₄, C₅, or C₆ alkylene).

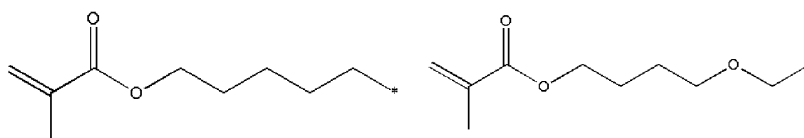
R_{4a}, R_{4b}, R_{4c}, R_{4d} may be alkylene unsubstituted or substituted with one or more halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, arylalkoxy, alkylthio, hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxy carbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, 25 arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl-4-alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl, a group R^xR^yN-, R^xOCO(CH₂)_m, R^xCON(R^y)(CH₂)_m, R^xR^yNCO(CH₂)_m, R^xR^yNSO₂(CH₂)_m or R^xSO₂NR^y(CH₂)_m (where each of R^x and R^y is independently selected from hydrogen or alkyl, or where appropriate R^xR^y forms part 30 of carbocyclic or heterocyclic ring and m is 0, 1, 2, 3 or 4), a group R^xR^yN(CH₂)_p- or R^xR^yN(CH₂)_pO- (wherein p is 1, 2, 3 or 4); wherein when the substituent is R^xR^yN(CH₂)_p- or R^xR^yN(CH₂)_pO, R^x with at least one CH₂ of the (CH₂)_p portion of the group may also form a carbocyclyl or heterocyclyl group and R^y may be hydrogen, or alkyl.

Each of , , and , may be selected from one of the following compounds:

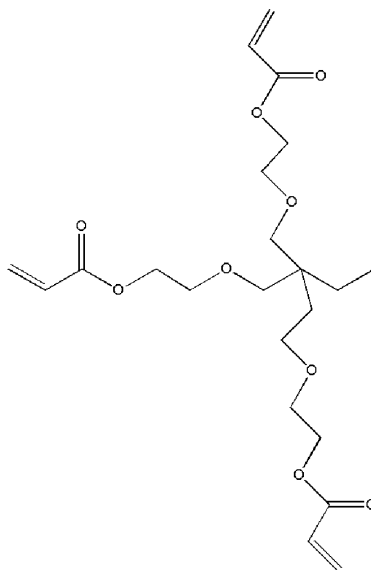




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Compound C3 may be trimethylolpropane ethoxylate triacrylate (TMPEOTA):



TMPEOTA

- 5 The photoinitiator may be bis (2, 4, 6-trimethylbenzoyl) phosphine oxide (BAPO), or diphenyl 2,4,6- trimethylbenzoyl phosphine oxide.

The curable composition may further comprise metal oxide. The metal of the metal oxide may be selected from the group consisting of aluminium, magnesium, chromium, iron, cobalt, nickel, and zinc. The metal oxide may be zinc oxide.

- 10 The metal oxide may be in the form of nanoparticles. The nanoparticles may have a particle size less than about 250 nm. The particle size may be about 10 nm to about 250 nm, about 20 nm to about 250 nm, about 30 nm to about 250 nm, about 40 nm to about 250 nm, about 50 nm to about 250 nm, about 60 nm to about 250 nm, about 70 nm to about 250 nm, about 80 nm to about 250 nm, about 90 nm to about 250 nm, about 100 nm to about 250 nm,
- 15 about 110 nm to about 250 nm, about 120 nm to about 250 nm, about 130 nm to about 250 nm, about 140 nm to about 250 nm, about 150 nm to about 250 nm, about 160 nm to about 250 nm, about 170 nm to about 250 nm, about 180 nm to about 250 nm, about 190 nm to about 250 nm, about 200 nm to about 250 nm, about 210 nm to about 250 nm, about 220 nm to about 250 nm, about 230 nm to about 250 nm, about 240 nm to about 250 nm, about 10 nm to about 240 nm, about 10 nm to about 230 nm, about 10 nm to about 220 nm, about 10 nm to about 210 nm, about 10 nm to about 200 nm, about 10 nm to about 190 nm, about 10
- 20

nm to about 180 nm, about 10 nm to about 170 nm, about 10 nm to about 160 nm, about 10 nm to about 150 nm, about 10 nm to about 140 nm, about 10 nm to about 130 nm, about 10 nm to about 120 nm, about 10 nm to about 110 nm, about 10 nm to about 100 nm, about 10 nm to about 90 nm, about 10 nm to about 80 nm, about 10 nm to about 70 nm, about 10 nm to about 60 nm, about 10 nm to about 50 nm, about 10 nm to about 40 nm, about 10 nm to about 30 nm, about 10 nm to about 20 nm, about 10 nm, about 20 nm, about 30 nm, about 40 nm, about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, about 100 nm, about 110 nm, about 120 nm, about 130 nm, about 140 nm, about 150 nm, about 160 nm, about 170 nm, about 180 nm, about 190 nm, about 200 nm, about 210 nm, about 220 nm, about 230 nm, about 240 nm, about 250 nm, or any value or range therebetween.

In an embodiment, the curable composition does not contain photoabsorber. In an embodiment, the curable composition does not contain 1-phenylazo-2-naphthol (Sudan I), 1-[4-(phenylazo)phenylazo]-2-naphthol (Sudan III), or $C_{28}H_{31}ClN_2O_3$ (Rhodamine B).

The resin composition may comprises about 40 wt% to about 50 wt% of compound C1, based on the total weight of the resin composition. The resin composition may comprise 40 wt% to about 50 wt% of compound C1, or about 41 wt% to about 50 wt%, about 42 wt% to about 50 wt%, about 43 wt% to about 50 wt%, about 44 wt% to about 50 wt%, about 45 wt% to about 50 wt%, about 46 wt% to about 50 wt%, about 47 wt% to about 50 wt%, about 48 wt% to about 50 wt%, about 41 wt% to about 50 wt%, about 41 wt% to about 50 wt%, about 59 wt% to about 50 wt%, about 40 wt% to about 49 wt%, about 40 wt% to about 48 wt%, about 40 wt% to about 47 wt%, about 40 wt% to about 46 wt%, about 40 wt% to about 45 wt%, about 40 wt% to about 44 wt%, about 40 wt% to about 43 wt%, about 40 wt% to about 42 wt%, about 40 wt% to about 41 wt%, or about 42 wt%, about 43 wt%, about 44 wt%, about 45 wt%, about 46 wt%, about 47 wt%, about 48 wt%, about 49 wt%, about 50 wt%, or any value or range therebetween.

The resin composition may comprise about 30 wt% to about 50 wt% of compound C2, based on the total weight of the resin composition. The resin composition may comprise about 30 wt% to about 50 wt% of compound C2, about 35 wt% to about 50 wt%, about 40 wt% to about 50 wt%, about 45 wt% to about 50 wt%, about 30 wt% to about 45 wt%, about 30 wt% to about 40 wt%, about 30 wt% to about 35 wt%, or about 40 wt%, about 45 wt%, about 50 wt%, or any value or range therebetween.

The resin composition may comprise about 15 wt% to about 25 wt% of compound C3, based on the total weight of the resin composition. The resin composition may comprise about 15 wt% to about 25 wt% of compound C3, about 16 wt% to about 25 wt%, about 17 wt% to about 25 wt%, about 16 wt% to about 25 wt%, about 16 wt% to about 25 wt%, about 18 wt% to about 25 wt%, about 19 wt% to about 25 wt%, about 20 wt% to about 25 wt%, about 21 wt% to about 25 wt%, about 22 wt% to about 25 wt%, about 23 wt% to about 25 wt%, about 24 wt% to about 25 wt%, about 15 wt% to about 24 wt%, about 15 wt% to about 23 wt%, about 15 wt% to about 22 wt%, about 15 wt% to about 21 wt%, about 15 wt% to about 20 wt%, about 15 wt% to about 19 wt%, about 15 wt% to about 18 wt%, about 15 wt% to about 17 wt%, about 15 wt% to about 16 wt%, or any value or range therebetween.

The weight ratio of resin composition to metal oxide is about 200:1 to about 5:1, about 200:10 to about 5:1, about 200:20 to about 5:1, about 200:30 to about 5:1, about 200:1 to about 200:30, about 200:1 to about 200:20, about 200:1 to about 200:10, or about 200:1,

about 200:10, about 200:20, about 200:30, about 200:40 (5:1), or any value or range therebetween.

The present disclosure also relates to a method of forming a shape memory polymer, the method comprising exposing a curable composition described above to ultraviolet light. The shape memory polymer may further undergo a post-curing step.

The present invention also relates to a shape memory polymer formed or obtained or obtainable by the method disclosed herein.

The shape memory polymer may be 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 an external force; and wherein the shape memory polymer is configured to switch from the second shape to the first shape upon application of an external stimulus. The predetermined temperature may be any value selected from a range of about 30°C to about 90 °C.

The present invention also relates to a device comprising the shape memory polymer disclosed herein. The device may be a suture, stent or dental aligner.

The present invention also relates to a shape memory polymer comprising the curable composition disclosed herein, wherein the curable composition has been cured by ultraviolet light.

Examples

Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Preparation of Curable Compositions

Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO), 2-phenoxyethyl acrylate (2PA) and isobornyl acrylate (IBOA) were purchased from Tokyo Chemical Industry (TCI). Trimethylolpropane ethoxylate triacrylate (TMPEOTA) with an average Mn of 428, ZnO nanoparticles (ZnONP) with particle size <100 nm and Sudan I photoabsorber were purchased from Sigma-Aldrich.

2PA, IBOA, TMPEOTA and BAPO were mixed using a magnetic stirrer for 30 minutes to form a resin composition. ZnONP was added into smaller batches of resin composition with different concentrations (see Table 1). The mixtures underwent another round of magnetic stirring for 1 hour, followed by an ultrasonic bath for 30 minutes to ensure even dispersion of the ZnONP.

The concentrations of ZnONP and Sudan I are determined with respect to the mass of the resin composition. For example in sample Z1, for every 100 g of resin composition, there was 1 g of ZnONP. Thus, the concentration of ZnONP is 1 wt/wt% with respect to the resin composition.

Exemplary embodiments of a curable composition of the present invention are shown in Table 1:

[Table 1]

Curable Composition Sample No.	Component	Amount
Z0	2PA	43.00 wt% based on total weight of Z0
	IBOA	37.00 wt% based on total weight of Z0 based on total weight of Z0
	TMPEOTA	19.00 wt% based on total weight of Z0
	BAPO	1.00 wt% based on total weight of Z0
Z1	Z0 + 1 wt/wt% ZnONP	1 wt/wt% ZnONP
Z2.5	Z0 + 2.5 wt/wt% ZnONP	2.5 wt/wt% ZnONP
Z5	Z0 + 5 wt/wt% ZnONP	5 wt/wt% ZnONP
S0.1	Z0 + 0.10 wt/wt% Sudan I	0.10 wt/wt% Sudan I

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Example 2: Preparation of Shape Memory Polymers (SMP)

10 Z0 resin was prepared by combining 2PA, IBOA, TMPEOTA and BAPO together to form a mixture. The mixture is magnetically stirred for 1 hour at room temperature. Z1, Z2.5 and Z5 were prepared by adding ZnONP into Z0, followed by magnetic stirring for 30 minutes and ultrasonication for 30 minutes to ensure dispersion of the ZnONP.

15 After the resin was mixed, the shape memory polymer (SMP) was 3D printed using an Asiga Max Digital Light Processing (DLP) printer (UV wavelength: 405 nm, intensity: 11 mW/cm²). The 3D printed SMP then underwent a post-curing step using Formlabs Form Cure, 60 minutes of UV radiation at 60 °C.

Example 3: Curing Characteristics

Figure 1 shows the cure depths of the curable compositions of Example 1 using the Asiga Max Digital Light Processing (DLP) printer (wavelength: 405 nm, intensity: 11 mW/cm²). To

achieve a layer thickness of 200 μm for a typical printing parameter, only 3.5 seconds of exposure time is required for Z0. This can translate to a print job taking less than 4 minutes to achieve a height of 1 cm (50 layers). The addition of ZnONP increases the initial rate of cure (Z1, Z2.5, Z5). It decreases the exposure time required to achieve the same layer thickness of 200 μm by 1 second, which is 28% faster than Z0. This is due to the nature of ZnONP acting as both a light scatterer and a photocatalyst. ZnONP has a refractive index of 1.9 at 400 nm wavelength, which causes the UV rays to scatter within the printed layer.

At the same time, ZnONP reduces excess unwanted cure, which is represented by the decrease in cure depth for exposure time greater than 5 seconds. This shows that ZnO acts as an effective light blocking element for better printing accuracy without hindering the printing process. The improvements in print quality can be observed in Figure 2, where the printed parts with ZnO (Figure 2, right) show less flashes (unwanted cure) on unsupported segments of the printed parts with small shape features compared to the neat formulation (Figure 2, left).

Example 4: Cure Depth

To gather further information on how ZnONP influences the curing of curable composition in a Digital Light Processing (DLP) process, various cure depth studies were carried out on the curable compositions of Example 1. Cure depth samples were prepared by printing a square array with different amounts of UV exposure. The samples were cured using the ASIGA MAX at 10 mW/cm^2 with varying exposure time. Figure 3 shows a model of the square array of different height, which represents the amount of UV exposure each square receives. The thickness of each square was measured using a digital thickness gauge with a precision of 0.001 mm.

The cure depth measurements were taken from three randomised square arrays and plotted against the exposure time/energy. Using the Jacob's cure depth equation (1), a logarithmic equation (2) was estimated via Originlabs Nonlinear Curve Fit Tool. The critical energy c and the depth of penetration p were derived from the constants from equation (2).

$$C_d = D_p \ln \frac{E}{E_c} \quad - (1)$$

$$y = b - a \ln x \quad - (2)$$

Figure 4a shows the cure depth against energy of curable compositions with various concentrations of ZnONP. Similar to the study on alumina nanowires, an increasing concentration of ZnONP resulted in a slower rate of increase in cure depth, thus lead to a decreasing trend of D_p . This could be the result of light absorption by ZnONP preventing the UV light from penetrating through the resin. The decrease in D_p can also be seen in sample S0.1.

Moreover, it can be observed that the E_c , as shown by the horizontal intersections in Figure 4a, was reduced when ZnONP is introduced into the resin. ZnONP caused a reduction the amount of UV energy required to start curing the resin and to achieve the desired cure depth for DLP printing. This can be attributed to the photoinitiating effect of ZnONP, which caused the resin to gel faster given the same amount of UV exposure. In addition, the effects of UV light scattering at low cure depth caused the layer to be exposed with additional reflected UV light,

resulting in faster generation of free-radicals and initiating the cure earlier. In contrast, the effects of Sudan I resulted in an increase in E_c (Figure 4b). Although both Z2.5 and S0.1 have similar D_p values, the E_c of S0.1 is approximately 10 times higher than Z2.5. This means that S0.1 required more energy to start curing. Moreover, S0.1 was not able to print any samples with 2 s exposure time, unlike the other resins. S0.1 required more than 10 s to achieve the same cure height as the other resin with exposure time of 2 s. This suggests that ZnONP could be a good replacement of photoabsorbers for preventing excessive cure, while ensuring that the printing time is not compromised.

10 Example 5: Measurement of Dimensional Accuracy

To measure the effects of ZnONP on dimensional accuracy, an overhanging structure, as shown in Figure 5, was printed with the resins. The structure contained hollow cuboids of 1.0 mm by 0.5 mm by 1.0 mm that can trap uncured resins during printing. The trapped resin would experience multiple UV exposure due to light penetration and result in unwanted cure inside the hollow cuboid. The height of the unwanted cure is then measured for comparison.

The structure is printed with a slice thickness of 0.050 mm, with 1.5 seconds and 2 seconds of exposure time per layer. After the parts were printed, they were soaked in an ethanol bath for 5 minutes to remove any uncured resins and dried for another 5 minutes. Post-curing was done in Form Cure by Formlabs, at 60 °C for 15 minutes. The printed structure was viewed under the optical microscope and height of the hollow gaps were measured. The unwanted cure height was calculated by subtracting the average of the measured gap height with the actual gap height of 0.5 mm.

Figure 6 shows the microscopic images of the benchmarking samples printed with 2 seconds exposure time. Significant amount of flash can be seen in the Z0 samples as compared to the Z1 and Z2.5 samples. As Z0 has the greatest transparency, the UV light during printing could penetrate through the cured layers. If the resin was trapped in the hollow gaps, it would be cured due to multiple UV exposures.

For a single UV exposure during printing, the Beer-Lambert law can be used to represent the amount of UV intensity exposed on a given height of the printed part. With the calculated values of D_p and E_c from Figure 4b, an expression for the amount of energy exposed n during exposure of layer n at plane height can be derived in equation (3). For this experiment, $z = 0$ refers to the plane where the 0.5 mm gap ends, as shown in Figures 7a and 7b. Equation (3) was then normalised into equation (4), and the summation of all the exposures lead to equation (5). Using equation (5), a theoretical value for the unwanted cure height was calculated and compared to the actual results.

$$E_n(z) = E_c e^{-(n+1)z_l - z}/D_p \quad - (3)$$

$$\Omega_n(E, z) \begin{cases} \frac{E}{E_c} e^{-\frac{[(n+1)z_l - z]}{D_p}}, & \text{for } (n+1) - \frac{z}{z_l} \geq 0 \\ 0 & \text{otherwise} \end{cases} \quad - (4)$$

$$\Omega = \sum_{n=0}^{N-1} \Omega_n \quad - (5)$$

From Figures 7a and 7b, the results indicated that the trapped Z0 resin gets cured rapidly from cumulative UV exposure, with each increasing number of bottom exposures resulting in a greater unwanted cure height. The unwanted cured height of Z0 reaches its maximum value after the second bottom exposure, which is significantly greater than the theoretical model. In contrast, the Z1 and Z2.5 samples prevented this light penetration and was able to limit the formation of flashes during the printing of subsequent layers. The measured unwanted cure heights of Z1 and Z2.5 were closer to the theoretical model, unlike Z0. This suggest that ZnONP effectively suppressed the growth of unwanted cure.

Example 6: Mechanical Properties

Initial tests were performed on the curable compositions of Example 1. As seen in Tables 2 and 3, the sample Z0 has a modulus of 1569 MPa at room temperature, which shows adequate rigidity at room temperature. When a SMP of Example 2 is soaked in a water bath at 37 °C, there is a huge drop in modulus. The softening of the SMP allows for programming (morphing into temporary shape) and recovering. With the right amount of ZnONP (1 w/wt%, Sample Z1), the mechanical properties of the shape memory polymer composite (SMPC) of Example 2 show slight improvements in both UTS and strain. Whereas when additional ZnONP (2.5 wt/wt%, Sample Z2.5) is added, the mechanical properties start to worsen.

[Table 2] Tensile Properties of SMPC at Room Temperature

Formula	Ultimate Tensile Strength (MPa)	Strain at Break (%)	Modulus (MPa)
Z0	23.15	10.27	1569
Z1	24.64	11.73	1821
Z2.5	21.87	10.06	1104

[Table 3] Tensile Properties of SMPC at 37 °C

Formula	Ultimate Tensile Strength (MPa)	Strain at Break (%)	Modulus (MPa)
Z0	5.88	12.51	243
Z1	6.76	14.32	281

The mechanical properties of the curable composition were further investigated using the samples of Example 1. Tensile tests were conducted with ASTM D638 Type V specimens, printed with 2 seconds exposure time (10 seconds for S0.1) and slice thickness of 0.050 mm. The specimens were lightly washed with ethanol after printing. Two sets of specimens were post-cured in Form Cure at 60 °C for 60 minutes and 180 minutes separately. In addition, a third set of

specimens were printed without post-curing. Known as green parts, these specimens were soaked in ethanol for 5 minutes, dried for 5 minutes and kept in a dark environment before being tested to prevent any further curing. The Instron 3366 with a fixed pulling rate of 2.5 mm/min was used.

Figures 8a and 8b shows the tensile properties of the post-cured specimens after 60 minutes. All the specimens exhibit both elastic and plastic deformation. The yield strength, which is the maximum stress in the elastic deformation, displays a decreasing trend with increasing concentration of ZnONP. This resulted in a decreasing trend in Young's modulus as well. However, the fracture strain, which is the maximum strain before fracture, shows an increasing trend with increasing concentration of ZnONP. This also led to greater toughness for specimens containing ZnONP compared to Z0.

With prolonged post-curing up to 180 minutes (Figure 8c), the yield strengths of all the samples increase. The yield strengths of Z1 and Z2.5 become closer to Z0, while retaining greater fracture strains than Z0. This suggest that ZnONP slows down the degree of conversion and would require a longer period of post-curing to achieve high degree of conversion. The yield strength of Z5 specimen is still much lower than the other specimens, possibly due to the pronounced agglomeration of ZnONP. On the other hand, S0.1 showed poor mechanical properties, with most parameters being the lowest. Despite being post-cured, S0.1 could not achieve a high degree of conversion. This result in a weak polymer network that breaks easily.

To further investigate the effects of ZnONP on initial cure during printing, the tensile properties of the green parts are measured and compared, as shown in Figures 9a to 9c. The green parts only exhibited elastic deformation, unlike the post-cured specimens. While the tensile properties of with S0.1 being exposed to UV light for five times longer than the rest of the set, the cumulative normalised UV exposure of S0.1 specimens is close to the Z1 specimens. However, the tensile properties of S0.1 are poorer than the rest of the resins used, with a drastic decrease in tensile strength and Young's modulus. This shows that the light absorption of Sudan I inhibits the photopolymerization of the unreacted monomers, resulting in poorer mechanical properties.

Example 7: Thermomechanical Properties of Octahedron Cube

To demonstrate the recovery performance of the SMP formed from Z0, a compression Dynamic Mechanical Analyzer (DMA) test was performed to showcase the recovery force exerted by a programmed sample, as well as the maximum recovery that the sample can achieve. An octahedron cube was printed using the Z0 (Figure 10d) and was compressed up to 40% strain at 40 °C (Figure 10a to 10c). The compression plates were locked and the furnace was opened to cool down the sample. After cooling, the sample undergoes a temperature ramp up to 40 °C. The recovery stress is measured as the strain is maintained at 27%. The sample is cooled again after the run, before ramping the temperature to 40 °C again, this time to measure the recovery strain at very low applied force.

The sample was able to exhibit a maximum recovery stress of 29.46 kPa at 27% strain. In addition, the sample was able to return back to its original shape, as shown by the initial position of the deformation process and the final position of the recovery process.

Example 8: Thermomechanical Properties of Strut

Due to the working temperature being close to body temperature, this material can have potential uses in medical devices, such as stents. The print quality improvements by the addition of ZnO nanoparticles makes it possible for smaller features to be 3D printed without the need of internal supports. To demonstrate that a stent of 0.4 mm thickness and 25.6 mm length was synthesised (Figure 11). Figure 12 further shows the same stent before and after compression, where the 3D-printed structure was able to successfully undergo compression and return back to the initial shape without deformation.

ZnO nanoparticles were able to reduce the penetration of UV light in resins during DLP printing, which helped to eliminate any unwanted curing in the vertical direction. Moreover, the layer exposure time needed for printing resins containing ZnO nanoparticles did not increase, in contrast to the effect of photoabsorbers. Unlike the printed part with Sudan I (S0.1), the integrity of the mechanical properties were maintained when ZnONP were added into the resin. The ZnO nanocomposites showed some toughening effects, with only a slight decrease in tensile strength and Young's modulus.

Industrial Applicability

The present invention relates to curable compositions which are useful in forming shape memory polymers.

Advantageously, the curable compositions of the present disclosure allow for fast UV curing into shape memory polymers (SMP). The working temperature of the SMP may be brought closer to body temperature, even after extensive post-treatment is applied. This advantageously makes it easier to trigger its shape memory effect without having to heat the SMP to high temperatures. Further advantageously, the SMPs may have high recovery ratio of 99% at 40 °C.

In an example, the curable compositions of the present disclosure may further comprise metal oxides, such as zinc oxide. The addition of metal oxide not only speeds up the curing process, it also helps to improve the print quality of the product by reducing flashes. It also provides slight improvement in the mechanical properties at both room temperature and body temperature.

The addition of metal oxide also advantageously reduces the amount of energy needed to cure a layer of resin, while preventing excessive unwanted cure during the printing process. In addition, the inclusion of metal oxide increases the toughness of the material, with some compromise on the tensile strength and Young's Modulus.

Also advantageously, the curable compositions of the present disclosure do not contain photoabsorbers, such as 1-phenylazo-2-naphthol (Sudan I), 1-[4-(phenylazo)phenylazo]-2-naphthol (Sudan III), and $C_{28}H_{31}ClN_2O_3$ (Rhodamine B). Although they can be used to reduce the cure depth (thus preventing unwanted cure due to excessive UV exposures), photoabsorbers tend to also increase the critical energy of the resin, which the minimum amount of energy needed for the resin to start curing. This could result in longer exposure time, as well as the overall printing time, hence they are undesirable.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without

departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A curable composition comprising (i) a resin composition, wherein the resin composition comprises:
 - 5 a compound C1 having an X group and an optionally substituted aryl group;
 - a compound C2 having an X group and an optionally substituted carbocyclyl group;
 - a compound C3 having at least two X groups; and
 - a photoinitiator,
- 10 wherein X is acrylate or methacrylate.
2. The curable composition of claim 1, wherein the optionally substituted aryl group of compound C1 is an unsubstituted C₆₋₁₂ aryl group.
- 15 3. The curable composition of claim 1 or 2, wherein compound C1 is 2-phenoxyethyl acrylate (2PA).
4. The curable composition of any one of claims 1 to 3, wherein the optionally substituted carbocyclyl group of compound C2 is substituted C₃ to C₁₂ carbocyclyl group.
- 20 5. The curable composition of any one of claims 1 to 4, wherein the optionally substituted carbocyclyl group of compound C2 is substituted with at least one alkyl group.
- 25 6. The curable composition of any one of claims 1 to 5, wherein compound C2 is isobornyl acrylate (IBOA).
7. The curable composition of any one of claims 1 to 6, wherein compound C3 has at least three acrylate or methacrylate groups.
- 30 8. The curable composition of any one of claims 1 to 7, wherein compound C3 has at least three acrylate groups.
- 35 9. The curable composition of any one of claims 1 to 8, wherein compound C3 is trimethylolpropane ethoxylate triacrylate (TMPEOTA).
- 40 10. The curable composition of any one of claims 1 to 9, wherein the photoinitiator is bis (2, 4, 6-trimethylbenzoyl) phosphine oxide (BAPO) or diphenyl 2,4,6-trimethylbenzoyl phosphine oxide.

11. The curable composition of any one of claims 1 to 10, wherein the curable composition further comprises (ii) metal oxide.
- 5 12. The curable composition of claim 11, wherein the metal of the metal oxide is selected from the group consisting of aluminium, magnesium, chromium, iron, cobalt, nickel, and zinc.
- 10 13. The curable composition of claim 11 or 12, wherein the metal oxide is in the form of nanoparticles.
14. The curable composition of any one of claims 11 to 13, wherein the nanoparticles have a particle size less than about 100 nm.
- 15 15. The curable composition of any one of claims 11 to 14, wherein the metal oxide is zinc oxide.
16. The curable composition of any one of claims 11 to 15, wherein the curable composition does not contain a photoabsorber.
- 20 17. The curable composition of any one of claims 11 to 16, wherein the resin composition comprises about 40 wt% to about 50 wt% of compound C1, based on the total weight of the resin composition.
- 25 18. The curable composition of any one of claims 11 to 17, wherein the resin composition comprises about 30 wt% to about 50 wt% of compound C2, based on the total weight of the resin composition.
- 30 19. The curable composition of any one of claims 11 to 18, wherein the resin composition comprises about 15 wt% to about 25 wt% of compound C3, based on the total weight of the resin composition.
20. The curable composition of any one of claims 1 to 19, wherein the weight ratio of resin composition to metal oxide is about 200:1 to about 5:1.
- 35 21. A method of forming a shape memory polymer, the method comprising exposing a curable composition of any one of claims 1 to 20 to ultraviolet light.
22. A shape memory polymer comprising the curable composition of any one of claims 1 to 20, wherein the curable composition has been cured by ultraviolet light.
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