carbon-fiber and uniformly distribute and transfer the external load. Both short carbon-fibers and continuous carbon-fiber reinforcements have been developed for 3D printing technologies. However, the low inter-laminar shear strength of the printed structures limit their applications in engineering products where isotropic reinforcement is required.

3D photopolymerization based techniques such as stereolithography (SLA), digital light processing (DLP) and continuous liquid interface production (CLIP) can help to eliminate the anisotropic mechanical problem as these technologies are based on using monomers or oligomers in a liquid state that can be cured or photopolymerized upon exposure to light source of specific wavelength and form thermosets. A photoinitiator or photoinitiator system is required to convert photolytic energy into the reactive species, a radical or cation, which can drive the chain growth via radical or cationic mechanism. Various photocurable formulations have been used in a 3D printing process, offering different chemical and mechanical properties. Although developed systems show great promise in 3D applications, they cannot fulfil all the desired requirements of the final products, particularly for engineering applicators due to the poor mechanical performance.

There is a need to provide a resin composition suitable for 3D printing that overcomes, or at least ameliorates, one or more of the disadvantages described above. Specifically, there is a need to provide a resin composition which upon 3D printing provides a product with enhanced mechanical performance.

Summary

There is provided a resin composition comprising at least one first monomeric or oligomeric component (A), at least one second monomeric or oligomeric component (B) and a photoinitiator,

wherein

the first monomeric or oligomeric component (A) has a formula $[(A_1)\text{-}(A_2)_b]_a\text{-}[(A_3)]_e$, wherein

A_1 is independently selected from an acrylate moiety or a methacrylate moiety,

A_2 is independently selected from the group consisting of a linear alkyl, a linear alkoxy ether and a linear poly(alkoxy ether) moiety, said linear alkyl, said linear alkoxy ether or said linear poly(alkoxy ether) moiety being optionally substituted by at least one hydroxyl substituent,

a is an integer selected from at least 2,

b is an integer selected from either 0 or at least 1,

e is an integer selected from at least 1, and

if a is 2, A_3 is selected from the group consisting of an aryl, a biaryl, a tricyclic alkyl and a urethane moiety, or

if a is 3 or more, A_3 is selected from the group consisting of an alkoxy ether, a saturated heterocycle or an alkyl moiety, and

the second monomeric or oligomeric component (B) has a formula $(B_1)_c\text{-}(B_2)_d$, wherein

B_1 is independently selected from an acrylate moiety or a methacrylate moiety,

B_2 is selected from the group consisting of an alkyl, an alkoxy ether, a thioalkyl, an aryl, an amino and a poly(alkoxy ether) moiety,

c is an integer selected from 1 or 2, and

d is an integer selected from at least 2,

wherein the second monomeric or oligomeric component (B) has a percentage composition by weight in the range of 20 wt% to 80 wt%, based on the weight of the resin composition.

In one aspect, there is provided a resin composition comprising at least one first monomeric or oligomeric component (A), at least one second monomeric or oligomeric component (B) and a photoinitiator,
wherein
the first monomeric or oligomeric component (A) has a formula $[(A_1)-(A_2)_b]_a-[(A_3)]_e$, wherein
A_1 is independently selected from an acrylate moiety or a methacrylate moiety,
A_2 is independently selected from the group consisting of a linear alkyl, a linear alkoxy ether and a linear poly(alkoxy ether) moiety, said linear alkyl, said linear alkoxy ether or said linear poly(alkoxy ether) moiety being optionally substituted by at least one hydroxyl substituent,
a is an integer selected from at least 2,
b is an integer selected from 0 or at least 1,
e is an integer selected from at least 1, and
if a is 2, A_3 is selected from the group consisting of an aryl, a biaryl, a tricyclic alkyl and a urethane moiety, or
if a is 3 or more, A_3 is selected from the group consisting of an alkoxy ether, a saturated heterocycle or an alkyl moiety,
and the second monomeric or oligomeric component (B) is selected from the group consisting of ethyl acrylate, butyl acrylate, ethyl 2-ethylacrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-carboxyethyl acrylate, 2-carboxyethyl acrylate oligomers, ethylene glycol methyl ether acrylate, ethyl 2-propylacrylate, hexyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl acrylate, isodecyl acrylate, isooctyl acrylate, lauryl acrylate, methyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, octadecyl acrylate, pentafluorophenyl acrylate, poly(propylene glycol) acrylate, tetrahydrofurfuryl acrylate, 2-tetrahydropyranyl acrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 3,3'-diethoxypropyl methacrylate, 2-(diethylamino)ethyl methacrylate, 2-ethoxyethyl methacrylate, ethylene glycol dicyclopentenyl ether methacrylate, di(ethylene glycol) methyl ether methacrylate, ethylene glycol methyl ether methacrylate, ethyl methacrylate, furfuryl methacrylate, glycidyl methacrylate, hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-isocyanatoethyl methacrylate, isodecyl methacrylate, lauryl methacrylate, methyl methacrylate, phenyl methacrylate, poly(propylene glycol) methacrylate, propyl methacrylate, tetrahydrofurfuryl methacrylate, diethylene glycol diacrylate, 1,4-butanediol diacrylate, tripropylene glycol diacrylate, 1,3-butanediol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, dipropylene glycol diacrylate, thiol diethylene glycol diacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and poly(propylene glycol) dimethacrylate,
wherein the second monomeric or oligomeric component (B) has a percentage composition by weight in the range of 20 wt% to 80 wt%, based on the weight of the resin composition.

Advantageously, the polymer may display higher mechanical strength than that of market benchmark polymers such as RenShape®SL 7820, which possesses a tensile modulus of 2.0 to 2.5 GPa as a result of the polymer network of a hard and cross-linked three-dimensional network comprising component (A) interpenetrated by the polymer resulting from polymerization of the second monomeric or oligomeric component (B).

In another aspect, there is provided a method of preparing a polymer from the resin composition disclosed herein comprising the steps of (i) polymerizing the resin composition disclosed herein with light, and (ii) curing the polymer from step (i) with ultraviolet radiation. Advantageously, the polymer may be prepared by simply exposing the resin composition to light at room temperature, as both the monomeric or oligomeric components of the resin composition are polymerizable by light. Advantageously, polymerization of the resin composition may result in a polymer with isotropic mechanical properties.

Advantageously, the method of preparing a polymer from the resin composition disclosed herein results in spontaneous polymerization of the first monomeric or oligomeric component (A) followed by the second monomeric or oligomeric component (B) without the need for external control of the curing process for each component. Further advantageously, polymerization of the first monomeric or oligomeric component (A) does not result in aggregation or separation of the solid and liquid phases of the second monomeric or oligomeric component (B), thereby improving the interface interaction between the two components (A) and (B) and interpenetration of the two components (A) and (B) in the resulting polymer. The inventors have unexpectedly and surprisingly found that the method disclosed herein results in a fine polymer network with better interpenetration of the two components (A) and (B). This unexpected effect may be due to the polymerization of the second monomeric or oligomeric component (B) occurring immediately after or during the polymerization of the first monomeric or oligomeric component (A), such that there is no serious phase separation between the polymerized first monomeric or oligomeric component (A) and the unpolymerized second monomeric or oligomeric component (B) or assembly of the unpolymerized second monomeric or oligomeric component (B) into large liquid aggregates, thereby allowing for better interface interaction between components (A) and (B).

In another aspect, there is provided a method of forming a 3-dimensional printed article, comprising the steps of (i) polymerizing a resin composition described herein with light using a 3-dimensional printer, and (ii) curing the polymer from step (i) with ultraviolet radiation.

There is provided a kit comprising:

(i) at least one first monomeric or oligomeric component (A),
(ii) at least one second monomeric or oligomeric component (B), and
(iii) a photoinitiator,

wherein

the first monomeric or oligomeric component (A) has a formula $[(A_1)\text{-}(A_2)_b]_a\text{-}[(A_3)]_e$, wherein

A_1 is independently selected from an acrylate moiety or a methacrylate moiety,

A2 is independently selected from the group consisting of a linear alkyl, a linear alkoxy ether and a linear poly(alkoxy ether) moiety, said linear alkyl, said linear alkoxy ether or said linear poly(alkoxy ether) moiety being optionally substituted by at least one hydroxyl substituent,

a is an integer selected from at least 2,
b is an integer selected from 0 or at least 1,
e is an integer selected from at least 1, and
if a is 2, A3 is selected from the group consisting of an aryl, a biaryl, a tricyclic alkyl and a urethane moiety, or
if a is 3 or more, A3 is selected from the group consisting of an alkoxy ether, a saturated heterocycle or an alkyl moiety,

the second monomeric or oligomeric component (B) has a formula $(B_1)_c$-$(B_2)_d$, wherein
B1 is independently selected from an acrylate moiety or a methacrylate moiety,
B2 is independently selected from the group consisting of an alkoxy ether, a thioalkyl, an aryl, an amino and a poly(alkoxy ether) moiety,
c is an integer selected from 1 or 2, and
d is an integer selected from at least 2,
wherein the second monomeric or oligomeric component (B) has a percentage composition by weight in the range of 30 wt% to 80 wt%, based on the weight of the resin composition.

In another aspect, there is provided a kit comprising:
(i) at least one first monomeric or oligomeric component (A),
(ii) at least one second monomeric or oligomeric component (B), and
(iii) a photoinitiator,
wherein

the first monomeric or oligomeric component (A) has a formula $[(A_1)$-$(A_2)_b]_a$-$[(A_3)]_e$, wherein
A_1 is independently selected from an acrylate moiety or a methacrylate moiety,
A_2 is independently selected from the group consisting of a linear alkyl, a linear alkoxy ether and a linear poly(alkoxy ether) moiety, said linear alkyl, said linear alkoxy ether or said linear poly(alkoxy ether) moiety being optionally substituted by at least one hydroxyl substituent,
a is an integer selected from at least 2,
b is an integer selected from 0 or at least 1,
e is an integer selected from at least 1, and
if a is 2, A_3 is selected from the group consisting of an aryl, a biaryl, a tricyclic alkyl and a urethane moiety, or
if a is 3 or more, A_3 is selected from the group consisting of an alkoxy ether, a saturated heterocycle or an alkyl moiety,

and the second monomeric or oligomeric component (B) is selected from the group consisting of ethyl acrylate, butyl acrylate, ethyl 2-ethylacrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-carboxyethyl acrylate, 2-carboxyethyl acrylate oligomers, ethylene glycol methyl ether acrylate, ethyl 2-propylacrylate, hexyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl acrylate, isodecyl acrylate, isooctyl acrylate, lauryl acrylate, methyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, octadecyl acrylate, pentafluorophenyl acrylate, poly(propylene glycol) acrylate, tetrahydrofurfuryl acrylate, 2-tetrahydropyranyl acrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 3,3'-diethoxypropyl methacrylate, 2-(diethylamino)ethyl methacrylate, 2-ethoxyethyl methacrylate, ethylene glycol dicyclopentenyl ether methacrylate, di(ethylene glycol) methyl ether methacrylate, ethylene glycol methyl ether methacrylate, ethyl methacrylate, furfuryl methacrylate, glycidyl methacrylate, hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-isocyanatoethyl methacrylate, isodecyl

methacrylate, lauryl methacrylate, methyl methacrylate, phenyl methacrylate, poly(propylene glycol) methacrylate, propyl methacrylate, tetrahydrofurfuryl methacrylate, diethylene glycol diacrylate, 1,4-butanediol diacrylate, tripropylene glycol diacrylate, 1,3-butanediol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, dipropylene glycol diacrylate, thiol diethylene glycol diacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and poly(propylene glycol) dimethacrylate,
wherein the second monomeric or oligomeric component (B) has a percentage composition by weight in the range of 30 wt% to 80 wt%, based on the weight of the resin composition.

Definitions

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

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.

Claims

1. A resin composition comprising at least one first monomeric or oligomeric component (A), at least one second monomeric or oligomeric component (B) and a photoinitiator,
wherein
the first monomeric or oligomeric component (A) has a formula $[(A_1)\text{-}(A_2)_b]_a\text{-}[(A_3)]_e$, wherein
A_1 is independently selected from an acrylate moiety or a methacrylate moiety,
A_2 is independently selected from the group consisting of a linear alkyl, a linear alkoxy ether and a linear poly(alkoxy ether) moiety, said linear alkyl, said linear alkoxy ether or said linear poly(alkoxy ether) moiety being optionally substituted by at least one hydroxyl substituent,
a is an integer selected from at least 2,
b is an integer selected from 0 or at least 1,
e is an integer selected from at least 1, and
if a is 2, A_3 is selected from the group consisting of an aryl, a biaryl, a tricyclic alkyl and a urethane moiety, or
if a is 3 or more, A_3 is selected from the group consisting of an alkoxy ether, a saturated heterocycle or an alkyl moiety,
and the second monomeric or oligomeric component (B) is selected from the group consisting of ethyl acrylate, butyl acrylate, ethyl 2-ethylacrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-carboxyethyl acrylate, 2-carboxyethyl acrylate oligomers, ethylene glycol methyl ether acrylate, ethyl 2-propylacrylate, hexyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl acrylate, isodecyl acrylate, isooctyl acrylate, lauryl acrylate, methyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, octadecyl acrylate, pentafluorophenyl acrylate, poly(propylene glycol) acrylate, tetrahydrofurfuryl acrylate, 2-tetrahydropyranyl acrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 3,3'-diethoxypropyl methacrylate, 2-(diethylamino)ethyl methacrylate, 2-ethoxyethyl methacrylate, ethylene glycol dicyclopentenyl ether methacrylate, di(ethylene glycol) methyl ether methacrylate, ethylene glycol methyl ether methacrylate, ethyl methacrylate, furfuryl methacrylate, glycidyl methacrylate, hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-isocyanatoethyl methacrylate, isodecyl methacrylate, lauryl methacrylate, methyl methacrylate, phenyl methacrylate, poly(propylene glycol) methacrylate, propyl methacrylate, tetrahydrofurfuryl methacrylate, diethylene glycol diacrylate, 1,4-butanediol diacrylate, tripropylene glycol diacrylate, 1,3-butanediol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, dipropylene glycol diacrylate, thiol diethylene glycol diacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and poly(propylene glycol) dimethacrylate,
wherein the second monomeric or oligomeric component (B) has a percentage composition by weight in the range of 20 wt% to 80 wt%, based on the weight of the resin composition.

2. The resin composition of claim 1, wherein the first monomeric or oligomeric component (A) has a percentage composition by weight in the range of 10 wt% to 60 wt%, based on the weight of the resin composition.

3. The resin composition of claim 1 or 2, wherein the photoinitiator has a percentage composition by weight in the range of 0.1 wt% to 10 wt%, based on the weight of the resin composition.

4. The resin composition of any one of claims 1 to 3, wherein the first monomeric or oligomeric component (A) and the second monomeric or oligomeric component (B) each have an average molar mass of between 100 to 1200 g/mol.

5. The resin composition of any one of claims 1 to 4, wherein the first monomeric or oligomeric component (A) is selected from the group consisting of bisphenol A dimethacrylate (bis-DMA), bisphenol A diglycidyl ether methacrylate (bis-GMA), ethoxylated bisphenol-A dimethacrylate (bis-EMA), tricyclo[5.2.1.02,6]decanedimethanol diacrylate, bisphenol A glycerolate diacrylate, bisphenol A ethoxylate diacrylate, bisphenol A ethoxylate dimethacrylate (oligomer), bisphenol F ethoxylate diacrylate (oligomer), hydroquinone diacrylate, naphthalene-1,5- diyl diacrylate, tricyclodecane dimethanol diacrylate, urethane acrylate (oligomer), branched hexa-functional aliphatic urethane acrylate, di(trimethylolpropane) tetraacrylate, pentaerythritol triacrylate, 1,3,5-triacryloylhexahydro-1,3,5-triazine, trimethylolpropane propoxylate triacrylate, trimethylolpropane triacrylate and trimethylolpropane trimethacrylate.

6. The resin composition of any one of claims 1 to 5, wherein the first monomeric or oligomeric component (A) is bisphenol A dimethacrylate.

7. The resin composition of any one of claims 1 to 6, wherein the second monomeric or oligomeric component (B) is di(ethylene glycol) methyl ether methacrylate.

8. The resin composition of any one of claims 1 to 7, wherein the photoinitiator is selected from the group consisting of bis(2,4, 6-trimethyl benzoyl)phenylphosphine oxide (IRGACURE 819), 2,4,6-trimethylbenzoyl diphenyl phosphine (TPO), 2-hydroxy-2-methyl-1-phenyl-1-propane (DAROCUR 1173) and benzophenone (BP).

9. The resin composition of any one of claims 1 to 8, wherein the resin composition has a viscosity of between 1 to 3000 cps.

10. A method of preparing a polymer from the resin composition of any one of claims 1 to 9 comprising the steps of (i) polymerizing the resin composition of any one of claims 1 to 9 with light, and (ii) curing the polymer from step (i) with ultraviolet radiation.

11. The method of claim 10, wherein the polymerizing step (i) is undertaken at a temperature in the range of about 20^{o}C to about 30^{o}C.

12. A polymer blend obtainable by the method of claim 10 or 11, wherein the polymer blend comprises a first polymer, resulting from polymerization of the first monomeric or oligomeric component (A) of the resin composition of any one of claims 1 to 9, and a second polymer, resulting from polymerization of the second monomeric or oligomeric component (B) of the resin composition of any one of claims 1 to 9, interpenetrated with the first polymer.

13. The polymer of claim 12, wherein the polymer exhibits a Young’s modulus of between 1.5 GPa to 5.0 GPa.

14. The polymer of claim 12, wherein the polymer exhibits a flexure strength of between 40 MPa to 150 MPa.

15. A method of forming a 3-dimensional printed article, comprising the steps of (i) polymerizing a resin composition of any one of claims 1 to 9 with light using a 3-dimensional printer, and (ii) curing the polymer from step (i) with ultraviolet radiation.

16. A kit comprising:
(i) at least one first monomeric or oligomeric component (A),
(ii) at least one second monomeric or oligomeric component (B), and
(iii) a photoinitiator,
wherein
the first monomeric or oligomeric component (A) has a formula $[(A_1)\text{-}(A_2)_b]_a\text{-}[(A_3)]_e$, wherein

A_1 is independently selected from an acrylate moiety or a methacrylate moiety,
A_2 is independently selected from the group consisting of a linear alkyl, a linear alkoxy ether and a linear poly(alkoxy ether) moiety, said linear alkyl, said linear alkoxy ether or said linear poly(alkoxy ether) moiety being optionally substituted by at least one hydroxyl substituent,
a is an integer selected from at least 2,
b is an integer selected from 0 or at least 1,
e is an integer selected from at least 1, and
if a is 2, A_3 is selected from the group consisting of an aryl, a biaryl, a tricyclic alkyl and a urethane moiety, or
if a is 3 or more, A_3 is selected from the group consisting of an alkoxy ether, a saturated heterocycle or an alkyl moiety,

and the second monomeric or oligomeric component (B) is selected from the group consisting of ethyl acrylate, butyl acrylate, ethyl 2-ethylacrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-carboxyethyl acrylate, 2-carboxyethyl acrylate oligomers, ethylene glycol methyl ether acrylate, ethyl 2-propylacrylate, hexyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl acrylate, isodecyl acrylate, isooctyl acrylate, lauryl acrylate, methyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, octadecyl acrylate, pentafluorophenyl acrylate, poly(propylene glycol) acrylate, tetrahydrofurfuryl acrylate, 2-tetrahydropyranyl acrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 3,3'-diethoxypropyl methacrylate, 2-(diethylamino)ethyl methacrylate, 2-ethoxyethyl methacrylate, ethylene glycol dicyclopentenyl ether methacrylate, di(ethylene glycol) methyl ether methacrylate, ethylene glycol methyl ether methacrylate, ethyl methacrylate, furfuryl methacrylate, glycidyl methacrylate, hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-isocyanatoethyl methacrylate, isodecyl methacrylate, lauryl methacrylate, methyl methacrylate, phenyl methacrylate, poly(propylene glycol) methacrylate, propyl methacrylate, tetrahydrofurfuryl methacrylate, diethylene glycol diacrylate, 1,4-butanediol diacrylate, tripropylene glycol diacrylate, 1,3-butanediol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, dipropylene glycol diacrylate, thiol diethylene glycol diacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and poly(propylene glycol) dimethacrylate,

wherein the second monomeric or oligomeric component (B) has a percentage composition by weight in the range of 30 wt% to 80 wt%, based on the weight of the resin composition.