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

According to a first 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 $[(A_1)\text{-}(A_2)_b]_a\text{-}[(A_3)]_e$, 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 another aspect, there is a polymer blend obtainable by the method disclosed herein, wherein the polymer blend comprises a first polymer, resulting from polymerization of the first monomeric or oligomeric component (A) of the resin composition disclosed herein, and a second polymer, resulting from polymerization of the second monomeric or oligomeric component (B) of the resin composition disclosed herein, interpenetrated with the first polymer.

The polymer blend may also be termed as an interpenetrating polymer network (IPN) where the second polymer formed from the second monomeric or oligomeric component (B) interpenetrates into the polymer network formed from the first monomeric or oligomeric component (A).

Advantageously, the functional groups in the first monomeric or oligomeric component (A) of the resin composition disclosed herein have a higher reactivity than the functional groups in the second monomeric or oligomeric component (B), which results in the first monomeric or oligomeric component (A) polymerizing faster than the second monomeric or oligomeric component (B) upon exposure of the resin composition to light. This sequential polymerization process leads to the first monomeric or oligomeric component (A) building a hard and cross-linked three-dimensional network, which is interpenetrated by the polymer resulting from polymerization of the second monomeric or oligomeric component (B) to form a ductile and tougher polymer matrix.

Advantageously, the proportion of the first monomeric or oligomeric component (A) and second monomeric or oligomeric component (B) may be adjusted to tune the strength and/or flexibility of the resulting interpenetrated polymer. By increasing the amount of first monomeric or oligomeric component (A), a tougher polymer may be obtained while increasing the amount of second monomeric or oligomeric component (B), a more flexible polymer may be obtained.

In the polymer blend, the first polymer can be regarded as a “rigid” polymer and the second polymer can be regarded as a “flexible” polymer whereby the second polymer interpenetrates into the first polymer. By having the second polymer interpenetrated with the first polymer, advantageously, this can strengthen the polymer by the spontaneous integration of the hard and soft regions in the resulting polymer matrix to result in a polymer showing a higher mechanical performance, which is much better than the mechanical properties of the individual polymer components. It is unexpected that the mechanical property of the polymer is better than that of the individual polymer components, as typically, when two polymer components are combined to form a new polymer, the mechanical property of the new polymer is typically influenced by the polymer component that has a lower mechanical property such that the mechanical property of the new polymer is lower than that of the polymer component with the lower mechanical property, as a result of immiscibility and poor interface interaction. In the present application, the inventors have surprisingly and unexpectedly found that the present polymer has a mechanical property that is actually higher than that of the polymer component with a lower mechanical property and is also higher than that of the polymer component with the higher mechanical property. This unexpected improvement in the mechanical property can be due to the sequential polymerization that controls the polymer networking formation leading to the strong interaction between the polymer components.

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.

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 $[(A_1)\text{-}(A_2)_b]_a\text{-}[(A_3)]_e$, 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.

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) 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 independently 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.

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), wherein d is 1, is selected from the group consisting of ethyl 2-ethylacrylate, ethylene glycol methyl ether acrylate, ethyl 2-propylacrylate,methyl 3-hydroxy-2-methylenebutyrate, 3,3'-diethoxypropyl methacrylate, di(ethylene glycol) methyl ether methacrylate, ethylene glycol dicyclopentenyl ether methacrylate, and ethylene glycol methyl ether methacrylate.

8. The resin composition of any one of claims 1 to 6, wherein the second monomeric or oligomeric component (B), wherein d is 2, is selected from the group consisting of diethylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, dipropylene glycol diacrylate, thiol diethylene glycol diacrylate, tetraethyleneglycol dimethacrylate, and tetraethylene glycol dimethacrylate .

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

10. The resin composition of any one of claims 1 to 9, 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).

11. The resin composition of any one of claims 1 to 10, wherein the resin composition has a viscosity of between 1 to 3000 cps.

12. A method of preparing a polymer from the resin composition of any one of claims 1 to 11 comprising the steps of (i) polymerizing the resin composition of any one of claims 1 to 11 with light, and (ii) curing the polymer from step (i) with ultraviolet radiation.

13. The method of claim 12, wherein the polymerizing step (i) is undertaken at a temperature in the range of about 20^{o}C to about 30^{o}C.

14. A polymer blend obtainable by the method of claim 12 or 13, 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 11, 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 11, interpenetrated with the first polymer.

15. The polymer of claim 14, wherein the polymer exhibits a Young's modulus of between 1.5 GPa to 5.0 GPa.

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

17. 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 11 with light using a 3-dimensional printer, and (ii) curing the polymer from step (i) with ultraviolet radiation.

18. 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,

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 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.