dyes interfered with the polymerization of the liquid resin and decreased printing accuracy. Therefore, it is a challenge to develop printable luminescent resins for the liquid based 3D printing techniques.

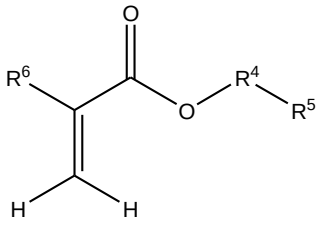
There is a need to provide a resin formulation that overcomes, or at least ameliorates, one or more of the disadvantages described above. There is also a need to provide a 3D print that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

There is provided a resin formulation comprising a) a resin precursor, b) a crosslinking additive, c) a photoinitiator, and d) at least one luminescent dye, wherein the crosslinking additive of b) comprises a functional group selected from the group consisting of hydroxyl, alkoxyl, carboxylic acid, amine, amide, alkylacrylate, acrylate, epoxy, alkyl and heterocycloalkyl.

According to one aspect, there is provided a resin formulation consisting essentially of a) a resin precursor, b) a crosslinking additive, c) a photoinitiator, and d) at least one luminescent dye, wherein the crosslinking additive b) comprises a solubilizing acrylate monomer or a solubilizing acrylate oligomer comprising a plurality of said solubilizing acrylate monomers,

wherein the solubilizing acrylate monomer or each of said plurality of solubilizing acrylate monomer is of formula (IIIa):



(IIIa)

wherein

R^4 is independently an optionally substituted alkyl group, an optionally substituted arylalkyl group, an optionally substituted alkoxyl group, an optionally substituted arylalkoxyl group, an optionally substituted alkylamine group, an optionally substituted arylalkylamine group, an optionally substituted alkylsilane group, an optionally substituted arylalkylsilane group, an optionally substituted alkylcarboxylic acid group, an optionally substituted arylalkylcarboxylic acid group, an optionally substituted ester group, an optionally substituted alkylacrylate group, an optionally substituted acrylate group, an optionally substituted alkylester group, an optionally substituted arylalkylester group, an optionally substituted carbonyl group, an optionally substituted alkylether group, or an optionally substituted arylalkylether group;

R^5 is selected from the group consisting of hydroxyl, alkoxyl, carboxylic acid, amine, amide, acrylate and heterocycloalkyl; andR^6 is hydrogen or an alkyl group,

wherein when said cross-linking additive (b) is the solubilizing acrylate oligomer, each R^4 is the same as or different from each other, or each R^5 group is the same as or different

from each other.

Advantageously, the crosslinking additive of the resin formulation may help to homogeneously disperse the luminescent dye in the resin by improving the miscibility and polarity between the resin precursor and the luminescent dye. For example, the solubilizing acrylate monomer may be selected based on “like dissolves like” principle, wherein if the luminescent dye is structurally polar, the solubilizing acrylate monomer having polar functional groups like hydroxyl and carboxylic acid may be selected for the particular reaction and vice versa where the nonpolar luminescent dye will require a nonpolar solubilizing acrylate monomer. More advantageously, the presence of the crosslinking additive may decrease the viscosity, thereby increasing the solidification rate of the resin formulation during 3D printing.

Advantageously, the presence of a photoabsorber or photostabilizer may help to control the curing depth of the resin formulation during 3D printing, and may produce more accurate 3D prints.

Further, electromagnetic radiation emitted from luminescent dyes may initiate a reaction between the photoinitiator and the resin formulation, which may interfere with the light initiation polymerization process during the printing process. More advantageously, the presence of a photoabsorber may enhance the printing accuracy of the printed object or article by absorbing the interfering light emitted from the luminescent dye.

According to another aspect, there is provided a method of preparing a resin formulation as described herein, comprising the step of stirring a resin precursor, a crosslinking additive, a photoinitiator, and at least one luminescent dye in the absence of light for a period of time to form a reaction mixture; and optionally ultrasonicating the reaction mixture.

According to yet another aspect, there is provided a method of printing a luminescent object comprising exposing the resin formulation as described herein to a light source.

According to a further aspect, there is provided a use of the resin formulation as described herein as a material for three-dimensional printing.

According to another aspect, there is provided a three-dimensional printed article comprising the resin formulation as described herein, wherein said resin formulation is in a cured state.

There is provided a method of tuning a colour of a three-dimensional printed article comprising the step of mixing a resin precursor, a crosslinking additive, a photoinitiator, and two or more luminescent dyes in the absence of light.

According to another aspect, there is provided a method of tuning a colour of a three-dimensional printed article comprising the step of mixing a mixture consisting essentially of a resin precursor, a crosslinking additive, a photoinitiator, and two or more luminescent dyes in the absence of light, wherein said resin precursor, said crosslinking additive, said photoinitiator and said luminescent dyes are as described herein.

Advantageously, addition of two or more luminescent dye may enable the colour of the three-dimensional printed article to be modified i.e. when blue and green luminescent dyes are combined, indigo luminescent colour may be achieved, when blue and red luminescent dyes are combined, violet luminescent colour may be achieved, when green and red luminescent dyes are combined, yellow luminescent colour may be achieved and when blue and red luminescent dyes are combined, white luminescent colour may be achieved.

Definitions

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

The term “resin formulation” is to be interpreted broadly to include a material or a mixture prepared according to a formula comprising a synthetic organic polymer. The resin formulation may be used as a material for 3D printing where the resin formulation forms a printed object when exposed to a curing agent.

The term “luminescence” or “fluorescence” as used herein refers to the emission of light by a substrate or a substance that has not been heated, as in fluorescence and phosphorescence.

The term “photoabsorber” or “photostabilizer” as used herein refers to a substrate or a substance to control the curing depth during the 3D printing process.

The term “photoinitiator” as used herein refers to a compound that undergoes a photoreaction on absorption of light, producing reactive species. Such compounds are capable of initiating or catalyzing chemical reactions that may result in significant changes in the solubility and physical properties of suitable formulations.

The following are some definitions that may be helpful in understanding the description of the present invention. These are intended as general definitions and should in no way limit the scope of the present invention to those terms alone, but are put forth for a better understanding of the following description.

Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated step or element or integer or group of steps or elements or integers, but not the exclusion of any other step or element or integer or group of elements or integers.

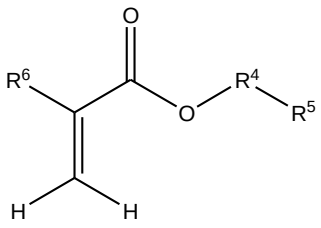
Thus, in the context of this specification, the term “comprising” means “including principally, but not necessarily solely”.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in

Claims

1. A resin formulation consisting essentially of a) a resin precursor, b) a crosslinking additive, c) a photoinitiator, and d) at least one luminescent dye, wherein the crosslinking additive b) comprises a solubilizing acrylate monomer or a solubilizing acrylate oligomer comprising a plurality of said solubilizing acrylate monomers,

wherein the solubilizing acrylate monomer or each of said plurality of solubilizing acrylate monomer is of formula (IIIa):



(IIIa)

wherein

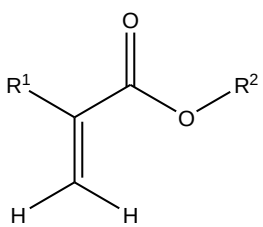
R^4 is independently an optionally substituted alkyl group, an optionally substituted arylalkyl group, an optionally substituted alkoxyl group, an optionally substituted arylalkoxyl group, an optionally substituted alkylamine group, an optionally substituted arylalkylamine group, an optionally substituted alkylsilane group, an optionally substituted arylalkylsilane group, an optionally substituted alkylcarboxylic acid group, an optionally substituted arylalkylcarboxylic acid group, an optionally substituted ester group, an optionally substituted alkylacrylate group, an optionally substituted acrylate group, an optionally substituted alkylester group, an optionally substituted arylalkylester group, an optionally substituted carbonyl group, an optionally substituted alkylether group, or an optionally substituted arylalkylether group;

R^5 is selected from the group consisting of hydroxyl, alkoxyl, carboxylic acid, amine, amide, acrylate and heterocycloalkyl; andR^6 is hydrogen or an alkyl group,

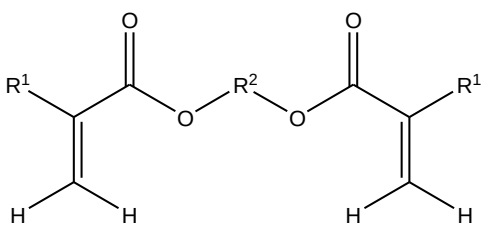
wherein when said cross-linking additive (b) is the solubilizing acrylate oligomer, each R^4 is the same as or different from each other, or each R^5 group is the same as or different from each other.

2. The resin formulation of claim 1, wherein the resin precursor is selected from the group consisting of a base acrylate monomer, a base acrylate oligomer, a base epoxy monomer and a base epoxy oligomer.

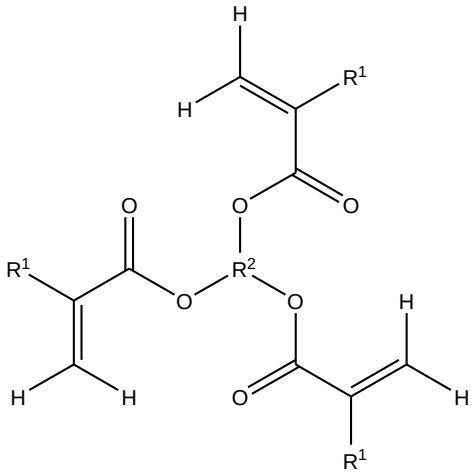
3. The resin formulation of claim 2, wherein the base acrylate monomer is of formula (Ia), (Ib), (Ic) or (Id):



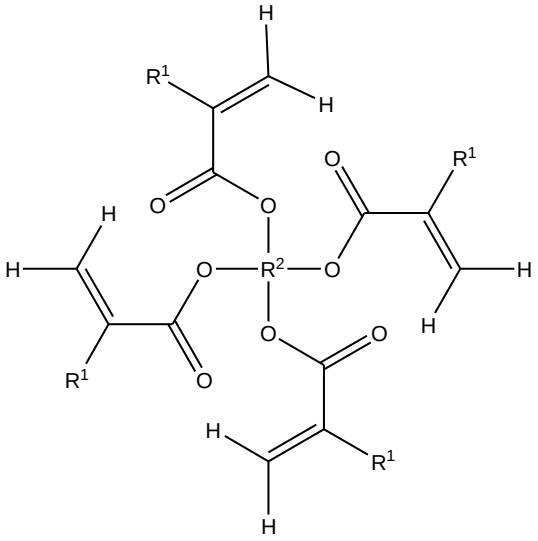
(Ia),



(Ib),



(Ic)



(Id)

wherein

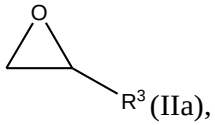
R^1 is hydrogen or an alkyl group;

R^2 in formula (Ia), (Ib) or (Ic) is independently an optionally substituted alkyl group, an optionally substituted arylalkyl group, an optionally substituted alkoxyl group, an optionally substituted arylalkoxyl group, an optionally substituted alkylamine group, an optionally substituted arylalkylamine group, an optionally substituted alkylsilane group, an optionally substituted arylalkylsilane group, an optionally substituted alkylcarboxylic acid group, an optionally substituted arylalkylcarboxylic acid group, an optionally substituted ester group, an optionally substituted carbonyl group, an optionally substituted alkylether group, or an optionally substituted arylalkylether group; or

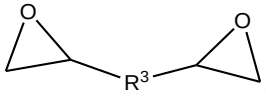
R^2 in formula (Id) is a carbon atom.

4. The resin formulation of claim 2 or 3, wherein the base acrylate monomer is selected from the group consisting of poly(ethylene glycol) diacrylate, di(ethylene glycol) diacrylate, tri(ethylene glycol) diacrylate, tetra(ethylene glycol) diacrylate and di(ethylene glycol) dimethacrylate.

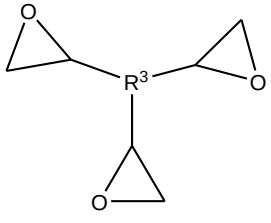
5. The resin formulation of claim 2, wherein the base epoxy monomer is of formula (IIa), (IIb), (IIc) or (IId):



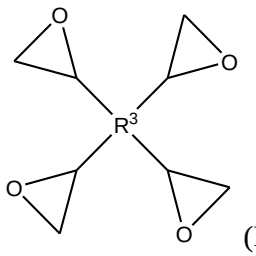
(IIa),



(IIb),



(IIc)



(IId)

wherein

R^3 in formula (IIa), (IIb) or (IIc) is independently an optionally substituted alkyl group, an optionally substituted arylalkyl group, an optionally substituted alkoxyl group, an optionally substituted arylalkoxyl group, an optionally substituted alkylamine group, an optionally substituted arylalkylamine group, an optionally substituted alkylsilane group, an optionally substituted arylalkylsilane group, an optionally substituted alkylcarboxylic acid group, an optionally substituted arylalkylcarboxylic acid group, an optionally substituted ester group, an optionally substituted carbonyl group, an optionally substituted alkylether group, or an optionally substituted arylalkylether group; or

R^3 in formula (IId) is a carbon atom.

6. The resin formulation of claim 2 or 5, wherein the base epoxy monomer is selected from the group consisting of poly(ethylene glycol) diglycidyl ether, di(ethylene glycol) diglycidyl ether, tri(ethylene glycol) diglycidyl ether, tetra(ethylene glycol) diglycidyl ether and poly(propylene glycol) diglycidyl ether.

7. The resin formulation of any one of claims 1 to 6, wherein the solubilizing acrylate monomer is selected from the group consisting of 2-carboxyethyl acrylate, 3-carboxypropyl acrylate, 4-carboxybutyl acrylate, 1,3-propanediol diacrylate, 1,4-butanediol diacrylate, 1,5-pentanediol diacrylate, 1,6-hexanediol diacrylate, tetrahydrofurfuryl methacrylate, and tetrahydrofurfuryl acrylate.

8. The resin formulation of any one of claims 2 to 7, wherein when the resin precursor is the base acrylate monomer, the crosslinking additive is the solubilizing acrylate monomer.

9. The resin formulation of any one of claims 1 to 8, wherein the photoinitiator is selected from the group consisting of bis(2,4,6-trimethyl benzoyl)phenylphosphine oxide (IRGACURE 819), benzoyl-diphenylphosphine oxide (BDPO), 2,4,6-trimethylbenzoyl-methoxy-phenylphosphine oxide (TMMPO), 2,4,6-trimethylbenzoyldiphenyl phosphine (TPO), 2-hydroxy-2-methyl-1-phenyl-1-propane (DAROCUR 1173), benzophenone (BP), 4,4'-bis(diethylamino)benzophenone, phenanthrenequinone, 2-chlorothioxanthen-9-one, 4,4'-bis(dimethylamino)-benzophenone, diphenyliodonium hexafluorophosphate, (4-tert-butylphenyl)diphenylsulfonium triflate, diphenyliodonium nitrate, diphenyliodonium p-toluenesulfonate, (4-fluorophenyl)diphenylsulfonium triflate, triphenylsulfonium triflate and bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate (DtBPIT).

10. The resin formulation of any one of claims 1 to 9, wherein the luminescent dye comprises an organic dye, an inorganic luminescence material or a combination thereof.

11. The resin formulation of claim 10, wherein the organic dye is selected from the group consisting of diaminostilbenesulfonic acid, distilbene, benzidine, benzidinesulfonic acid, diaminofluorene, imidazolone, triazole, p-quaterphenyl, p-terphenyl, 2,5-diphenyloxazole, 2-(1-naphthyl)-5-phenyloxazole, 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole, 3-phenyl-7-(1,2-2H-naphthotriazolyl)-coumarin, 3,7-bis(diethylamino)-phenoxazonium nitrate, 3,7-bis(diethylamino)phenoxazonium nitrate, europium-thenoyltrifluoroacetone chelate, basic yellow, rhodamine B, 6-bromoacetyl-2-dimethylaminonaphthalene; 5-carboxyfluorescein; 5 or 6-carboxyfluorescein; 6-carboxyfluorescein; fluorescein-6-isothiocyanate; 6-carboxy-2',4,4',5',7,7'-hexachlorofluorescein, 6-carboxy-2',4,7,7'-tetrachlorofluorescein, tetramethylrhodamine-5-(and-6)-isothiocyanate.

12. The resin formulation of claim 10, wherein the inorganic luminescence material is selected from the group consisting of $BaTiO_3$/Yb, La_2O_3/Yb, La_2O_3/Er, Lu_2O_3/Yb, Lu_2O_3/Er, Y_2O_3/Yb, Y_2O_3/Er, SrS/Ce, $Lu_3Al_5O_{12}$, $Y_3Al_5O_{12}$/Ce, SrB_4O_7/Eu, $Sr_2P_2O_7$/Eu, $BaMgAl_{10}O_{17}$/Eu, $SrAl_2O_4$/Eu, $CaGa_2S_4$, $Sr_2Si_5N_8$/Eu, $CaWO_4$, $MgWO_4$, luminescent quantum dot consisting of CdSe, CdTe, CdS, PbSe, InP/ZnS; ZnSe/ZnS; CdSe/ZnS; CdSe/ZnS; CdTs/ZnS; CdSe/ZnO and luminescent dyes doped silica or titania nanoparticles.

13. The resin formulation of any one of the preceding claims, wherein the resin formulation further comprises e) a photoabsorber.

14. The resin formulation of claim 13, wherein the photoabsorber is a photostabilizer selected from the group consisting of 1-phenylazo-2-naphthol (sudan I), 1-(2,4-dimethylphenylazo)-2-naphthol (sudan II), 1-(4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol (sudan III), 1-[{2-methyl-4-[(2-methylphenyl)diazenyl]phenyl}diazenyl]naphthalen-2-ol (sudan IV), (2,2-dimethyl-1,3-dihydroperimidin-6-yl)-(4-phenylazo-1-naphthyl)diazene (sudan black B), 1-(2-methoxyphenylazo)-2-naphthol (sudan red G), 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene, 4-methoxyphenol and butylatedhydroxytoluene.

15. A resin formulation of any one of claims 2 to 14, consisting of 83% to 95% by weight of the base acrylate monomer, 4% to 15% by weight of the crosslinking additive, 0.5% to 2% by weight of at least one photoinitiator, 0.01% to 0.5% by weight of at least one luminescence dyes, wherein the sum of the weight percentage of the base acrylate monomer, the crosslinking additive, the photoinitiator and the at least one luminescence dyes in the resin formulation is 100.

16. A method of preparing a resin formulation of any of the preceding claims, comprising the step of stirring a resin precursor, a crosslinking additive, a photoinitiator, and at least one luminescent dye in the absence of light for a period of time to form a reaction mixture; and optionally ultrasonicating the reaction mixture.

17. A method of printing a luminescent object comprising exposing the resin formulation of any one of claims 1 to 15 to a light source.

18. The method of claim 17, wherein the light source is selected from the group consisting of visible light, infra-red radiation and ultraviolet radiation.

19. Use of the resin formulation of any one of claims 1 to 15 as a material for three-dimensional printing

20. A three-dimensional printed article comprising the resin formulation of any one of claims 1 to 15, wherein said resin formulation is in a cured state.

21. A method of tuning a colour of a three-dimensional printed article comprising the step of mixing a mixture consisting essentially of a resin precursor, a crosslinking additive, a photoinitiator, and two or more luminescent dyes in the absence of light, wherein said resin precursor, said crosslinking additive, said photoinitiator and said luminescent dyes are as defined in any one of claims 1 to 15.