The sheet-lamination class of the additive manufacturing process includes ultrasonic additive manufacturing (UAM) and laminated object manufacturing (LOM). The successfully fabrication of gradient materials using the sheet-lamination technique was reported by using the ultrasonic consolidation process. Three sheet materials include stainless steel, aluminium, and Copper foils were used in this study and the formation of the gradient structure was demonstrated. The main disadvantages of the lamination techniques is that the finishes achievable depend seriously on the material used and a long post-processing is required to achieve the desired surface finish.

Although above four techniques have been successfully demonstrated to fabricate functionally gradient materials, they suffer from their own disadvantages and have not been used in dental printing with gradient color change.

There is a need to provide a 3D printing method for functionally graded materials that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

There is provided a method of three-dimensional printing an object having a varying degree of transmissivity to light along an axis of the object, the method comprising the steps of (a) providing a liquefied polymer resin having a plurality of particles therein, the particles being distributed in the liquefied polymer resin based on the density of the particles; and (b) polymerizing the liquefied polymer resin under conditions to form the object layer-by-layer.

In one aspect, the present disclosure refers to a method of three-dimensional printing an object having a varying degree of transmissivity to light along an axis of said object, the method comprising the steps of: (a) providing a liquefied polymer resin having a plurality of particles therein, wherein said particles have densities in the range of 3 to 12 g/cm^3; said particles being distributed in said liquefied polymer resin based on the density of said particles; and (b) polymerizing said liquefied polymer resin under conditions to form said object layer-by-layer.

The method may involve the Vat photopolymerization technique. Vat photopolymerization based printing techniques include laser-based stereolithography (SLA) and digital light processing (DLP) 3D printing. Both techniques can provide high printing resolutions and high surface smoothness, making them ideal techniques for bio-related printing such as dental and bone 3D printing.

Advantageously, the method can be used to print artificial teeth with naturally gradient color change. Therefore, the method provides a 3D printing solution to solve the problem of single color dental prosthesis composite whereby the method can be used to produce a functionally graded artificial tooth with colour gradient from the base of the tooth to the top of the tooth. This enables artificial teeth to be similar in colour and shade as compared to natural teeth.

~~In another aspect, t~~The present disclosure refers to a formulation for three-dimensional printing comprising: (i) 60 to 95 wt% liquefied polymer resin; (ii) 5 to 40 wt% particles; (iii) 0.1 to 5 wt% photoinitiator; and (iv) 0 to 0.2 wt% photoadditive, based on the weight of the

formulation; wherein said particles comprise a plurality of particles having various density values; and wherein said particles have densities in the range of 3 g/cm^3 to 12 g/cm^3.

In another aspect, the present disclosure refers to a formulation for three-dimensional printing comprising: (i) 60 to 95 wt% liquefied polymer resin; (ii) 5 to 40 wt% particles; (iii) 0.1 to 5 wt% photoinitiator; and (iv) 0 to 0.2 wt% photoadditive, based on the weight of the formulation; wherein said particles comprise a plurality of particles having various density values; wherein said particles have densities in the range of 3 g/cm^3 to 12 g/cm^3;and wherein said particles are distributed in said liquefied polymer resin based on the density of said particles.

There is provided a three-dimensional printed object having a varying degree of transmissivity to light along an axis of the object.

In yet another aspect, the present disclosure refers to a three-dimensional printed object having a varying degree of transmissivity to light along an axis of said object; wherein along said axis, the transparency of said object varies gradationally from opaque or partially opaque on one end to translucent or transparent on the opposite end; and wherein said object is formed from the formulation as defined herein.

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 method of three-dimensional printing an object having a varying degree of transmissivity to light along an axis of said object, the method comprising the steps of:
   (a) providing a liquefied polymer resin having a plurality of particles therein, wherein said particles have densities in the range of 3 to 12 g/cm^3; said particles being distributed in said liquefied polymer resin based on the density of said particles; and
   (b) polymerizing said liquefied polymer resin under conditions to form said object layer-by-layer.

2. The method according to claim 1, further comprising, before said providing step (a), the steps of:
   (a1) providing a homogenous suspension of said particles within said liquefied polymer resin; and
   (a2) allowing the particles to distribute within said liquefied polymer resin based on their density values after a period of time.

3. The method according to claim 1 or 2, wherein said liquefied polymer resin further comprises a photoinitiator.

4. The method according to any one of the preceding claims, wherein said liquefied polymer resin further comprises a photoadditive selected from a photoabsorber or a photostabilizer.

5. The method according to any one of the preceding claims, wherein said polymerizing step (b) comprises the step of:
   (b1) exposing each layer to light.

6. The method according to any one of the preceding claims, further comprising the step of:
   (c) post-treating the formed object.

7. A formulation for three-dimensional printing comprising:
   (i) 60 to 95 wt% liquefied polymer resin;
   (ii) 5 to 40 wt% particles;
   (iii) 0.1 to 5 wt% photoinitiator; and
   (iv) 0 to 0.2 wt% photoadditive, based on the weight of the formulation;
   wherein said particles comprise a plurality of particles having various density values; ~~and~~
   wherein said particles have densities in the range of 3 g/cm^3 to 12 g/cm^3; and ~~.~~ wherein said particles are distributed in said liquefied polymer resin based on the density of said particles.

8. The formulation according to claim 7, wherein said particles have a particle size in the range of 50 nm to 50 microns

9. The formulation according to claim 7 or 8, wherein said particles have a shape that is selected from the group consisting of spheres, rods, fibers, plates and star-shaped.

10. The formulation according to any one of claims 7 to 9, wherein said liquefied polymer resin comprises an acrylate.

11. The formulation according to claim 10, wherein said acrylate is a monomer or oligomer 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 (oligo), Bisphenol F ethoxylate diacrylate (oligo), Poly(ethylene glycol) diacrylate, Di(ethylene glycol) diacrylate, Tetra(ethylene glycol) diacrylate, 1,4-Butanediol diacrylate, Hydroxy ethylmethacrylate, 3,4-epoxy-cyclohexyl-methyl methacrylate (METHB), triethylene glycol dimethacrylate (TEGDMA), Tertiobutyl cyclohexanol methacrylate, 1,6-bis[2-(methacryloyloxy) ethoxycarbonylamino]-2,4,4-trimethylhexane (UDMA), 3,3,5-trimethyl cyclohexanol methacrylate, Dipentaerythritol penta-/hexa-acrylate and mixtures thereof.

12. The formulation according to any one of claims 7 to 11, wherein said particles are selected from the group consisting of metal oxides, metal nitrides, metal carbides, metalloid oxides, metalloid nitrides and metalloid carbides.

13. The formulation according to claim 12, wherein the metal or metalloid of said metal oxides, metal nitrides, metal carbides, metalloid oxides, metalloid nitrides or metalloid carbides is selected from Group 2, Group 3, Group 4, Group 5, Group 6, Group 8, Group 11, Group 12, Group 13, Group 14 or the lanthanide series of the Periodic Table of Elements.

14. The formulation according to claim 13, wherein said particles are selected from the group consisting of zinc oxide, Silicon carbide, Silicon nitride, Gallium nitride, Aluminium oxide, Titanium dioxide, Zirconium dioxide, Tin dioxide, Iron (III) oxide, Magnesium oxide, Indium (III) oxide, Tungsten trioxide, Tungsten (IV) oxide, Silver oxide, Vanadium (V) oxide, Vanadium (IV) oxide, Molybdenum trioxide, Yttrium (III) oxide, Cerium (IV) oxide and Copper (II) oxide.

15. The formulation according to any one of claims 7 to 14, wherein said photoinitiator is a type I or type II photoinitiator.

16. The formulation according to claim 15, wherein said photoinitiator is selected from the group consisting of bis(2,4, 6-trimethyl benzoyl)phenylphosphine oxide (IRGACURE 819), Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), 2,4,6-trimethylbenzoyl diphenyl phosphine (TPO), 2-hydroxy-2-methyl-1 -phenyl-1-propane (DAROCUR 1173) and benzophenone (BP).

17. The formulation according to any one of claims 7 to 16, wherein said photoadditive is a photoabsorber selected from the group consisting of Sudan I-IV, 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene, 4-methoxyphenol and butylated hyrdorxytoluene.

18. A three-dimensional printed object having a varying degree of transmissivity to light along an axis of said object;
wherein along said axis, the transparency of said object varies gradationally from opaque or partially opaque on one end to translucent or transparent on the opposite end;~~.~~ and wherein said object is formed from the formulation of claims 7 to 17.