Summary

In an aspect, the present disclosure refers to a method of making a three-dimensional object by additive manufacturing, comprising:

(a) applying a light polymerizable resin to a build surface of a growing three-dimensional object to form a build segment, said applying carried out with a moving roller resin applicator or a moving film resin applicator;

(b) exposing said build segment to patterned light to polymerize said build segment and form a new build surface, said new build surface having edge portions, said edge portions carrying excess, polymerized or unpolymerized, material thereon;

(c) exposing said excess material to an ablation light (*e.g.*, laser light) at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) sufficient to remove said excess material from said edge portions (*e.g.*, by ablation or melting); and

(d) sequentially repeating steps (a) through (c), with step (c) optionally omitted during some of said sequentially repeating steps but included during at least a plurality of said sequentially repeating steps, until said three-dimensional object is formed.

In an aspect, the present disclosure refers to a method of making a three-dimensional object by additive manufacturing, comprising:

(a) applying a light polymerizable resin to a build surface of a growing three-dimensional object to form a build segment, and with said applying carried out with a moving roller resin applicator or a moving film resin applicator;

(b) exposing said build segment to patterned light to polymerize said build segment and form a new build surface,

(c) exposing said new build surface to an ablation light (*e.g.*, laser light) to physically and/or chemically modify said new build surface; and

(d) sequentially repeating steps (a) through (c), with step (c) optionally omitted during some of said sequentially repeating steps but included during at least a plurality of said sequentially repeating steps, until said three-dimensional object is formed.

In an aspect, the present disclosure refers to a three-dimensional object produced by the method of any of the above aspects.

In an aspect, the present disclosure refers to an apparatus for additively manufacturing a three-dimensional object from a light polymerizable resin, comprising:

(a) a build platform on which a growing three-dimensional object can be produced, the object having a build segment, the build segment including an edge portion and a build surface;

(b) an applicator configured to apply a light-polymerizable resin to said build surface to form a new build segment including a new edge portion and a new build surface, wherein said applicator comprises a moving roller resin applicator or a moving film resin applicator;

(c) a resin supply configured for applying said light polymerizable resin to said applicator;

(d) a first, additive light source configured for polymerizing said light polymerizable resin on said build segment; and

(e) a second, subtractive light source configured for delivering a dosage of light to said edge portion(s) and/or said build surface(s).

Examples of the present disclosure are directed methods of making a three-dimensional object by additive manufacturing. In some examples, the method includes (a) applying a light polymerizable resin to a build surface of a growing three-dimensional object to form a build segment, the applying carried out with a moving roller resin applicator or a moving film resin applicator; (b) exposing the build segment to patterned light to polymerize the build segment and form a new build surface, the new build surface having edge portions, the edge portions carrying excess, polymerized or unpolymerized, material thereon; (c) exposing the excess material to an ablation light (e.g., laser light) at a dosage (i.e., an exposure pattern, wavelength, intensity and duration) sufficient to remove the excess material from the edge portions (e.g., by ablation or melting); and (d) sequentially repeating steps (a) through (c), with step (c) optionally omitted during some of the sequentially repeating steps but included during at least a plurality of the sequentially repeating steps, until the three-dimensional object is formed.

In some examples, the excess material includes polymerized resin.

In some examples, the excess material includes unpolymerized resin.

Additional examples of the present disclosure are directed to methods of making a three-dimensional object by additive manufacturing. In some examples, the method includes (a) applying a light polymerizable resin to a build surface of a growing three-dimensional object to form a build segment, and with the applying carried out with a moving roller resin applicator or a moving film resin applicator; (b) exposing the build segment to patterned light to polymerize the build segment and form a new build surface, (c) exposing the new build surface

to an ablation light (e.g., laser light) to physically and/or chemically modify the new build surface; and (d) sequentially repeating steps (a) through (c), with step (c) optionally omitted during some of the sequentially repeating steps but included during at least a plurality of the sequentially repeating steps, until the three-dimensional object is formed.

In some examples, the exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that textures at least a portion (*e.g.*, a major portion) of the new build surface (*e.g.*, the pattern configured to enhance adhesion of a subsequent build segment to the new build surface).

In some examples, the light polymerizable resin includes an additive (*e.g.*, a thermoplastic material such as nylon powder, a natural or synthetic rubber, ceramic particles, etc.), and the exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that selectively melts or sinters the additive (*e.g.*, to form a co-

continuous secondary material network) in at least a portion (*e.g.*, a major portion) of the new build surface and modify the material properties of the three-dimensional object (e.g., such as increase toughness, and/or promoting interlayer adhesion, strength or toughness).

In some examples, the light polymerizable resin is a dual cure resin including a first polymerizable component and a second polymerizable component and the exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that initiates polymerization of the second polymerizable component in at least a portion (*e.g.*, a major portion) of the new build surface to modify the mechanical properties of the three-dimensional object (*e.g.*, in the green and/or final steps) (in some examples theses exposure dosages may be patterned, spatially and/or temporally, to create control of and modify the spatial distribution of material properties in the three-dimensional object).

In some examples, the exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that modifies material properties (*e.g.*, modifies glass transition temperature) in at least a portion (*e.g.*, a major portion) of the new build surface (*e.g.*, to modify internal stresses in the object and thereby modify final object geometry).

In some examples, the exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that activates surface chemicals (*e.g.*, modifies glass transition temperature) in at least a portion (*e.g.*, a major portion) of the new build surface (*e.g.*, to promote adhesion, modify the surface energy, and/or control the wettability of the resin.

In some examples, the light polymerizable resin includes a filler (*e.g.*, a porogen or microballoon), and the exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that selectively expands the filler (*e.g.*, to thereby counteract shrinkage and/or warpage of the object) in at least a portion (*e.g.*, a major portion) of the new build surface.

In some examples, the light polymerizable resin includes a filler (*e.g.*, solid fillers including fiber fillers, spherical fillers, elliptical fillers, etc.).

In some examples, the filler is a solid particulate filler including glass fibers, carbon fibers, aramid fibers, basalt fibers, thermoplastic or thermoset polymer fibers (*e.g.*, polyamide, cellulose, or nanocellulose fibers, etc.).

In some examples, the light polymerizable resin has a viscosity of 1,000, 2,000, 10,000 or 20,000 centipoise or more at 25 degrees Centigrade and 1 atmosphere pressure.

In some examples, the light polymerizable resin has a viscosity of from 100,000 centipoise to 1,000,000 or 2,000,000 centipoise or more, at 25 degrees Centigrade and 1 atmosphere pressure.

In some examples, the applying step is carried out with a bottom-up or top-down additive manufacturing apparatus.

In some examples, the applying step is carried out with a moving roller resin applicator.

In some examples, the applying step (a) is carried out with the moving film resin applicator (e.g., where the moving film is a light-transmissive film, through which the patterned light, and optionally the ablation light, is projected).

In some examples, the ablation light is a laser light.

In some examples, the laser light is at a dosage which is absorbed by the excess material and/or the new build surface in single photon or multiphoton absorption process.

In some examples, the laser light is delivered to the excess material and/or the new build surface as a shaped beam.

In some examples, the laser light is delivered to the excess material and/or the new build surface as a continuous wave or pulsed laser beam.

In some examples, the method further includes the steps of detecting a current property (*e.g.*, focal field, focal length, wavelength, intensity) of the ablation light; comparing the current property to a desired property (*e.g.*, focal field, focal length, wavelength, intensity) and modifying the ablation light so that the current property more closely corresponds to the desired property.

Additional examples of the present disclosure are directed to a three-dimensional object produced by the methods described herein.

Additional examples of the present disclosure are directed to an apparatus for additively manufacturing a three-dimensional object from a light polymerizable resin. The apparatus includes (a) a build platform on which a growing three-dimensional object can be produced, the object having a build segment, the build segment including an edge portion and a build surface; (b) an applicator configured to apply a light-polymerizable resin to the build surface to form a new build segment including a new edge portion and a new build surface, wherein the applicator includes a moving roller resin applicator or a moving film resin applicator; (c) a resin supply configured for applying the light polymerizable resin to the applicator; (d) a first, additive light source configured for polymerizing the light polymerizable

resin on the build segment; and (e) a second, subtractive light source configured for delivering a dosage of light to the edge portion(s) and/or the build surface(s).

In some examples, the subtractive light source includes an ultraviolet (UV) light source, vacuum UV light source, deep UV light source, or and high intensity infra-red (IR) light source.

In some examples, the subtractive light source includes a laser (*e.g.*, a gas laser, a solid-state laser, a fiber laser, a liquid laser, or a semiconductor laser).

In some examples, the applicator includes the moving roller resin applicator.

In some examples, the applicator includes the moving film resin applicator**.**

In some examples, the moving film resin applicator is light-transmissive and the first light source projects through the moving film resin applicator.

In some examples, the subtractive light source projects through the moving film resin applicator.

In some examples, the subtractive light source does not project through the moving film resin applicator (*e.g.*, by positioning on the opposite side of the moving film resin applicator from the additive light source, or by positioning adjacent the moving film resin applicator where the moving film resin applicator is not between the build platform and/or growing three-dimensional object).

In some examples, the apparatus further includes a detector operatively associated with the subtractive light source and configured to detect a current property (*e.g.*, focal field, focal length, wavelength, intensity) of the subtractive light; and a controller operatively associated with the detector and the subtractive light source, the controller configured to compare the current property to a desired property (*e.g.*, focal field, focal length, wavelength, intensity) and modify the subtractive light so that the current property more closely corresponds to the desired property.

In some examples, the subtractive (*e.g.*, laser) light source include a continuous wave light source or a pulsed laser light source; a single beam light source or a multi-beam light source, a free-standing laser or a fiber-optic based laser; and/or a single wavelength light source or a multi-wavelength light source.

In some examples, the subtractive (*e.g.*, laser) light source further includes a laser trepanning system; an XY stage for scanning or raster scanning of the laser beam; a beam expander, mirror, focusing lens, and/or air assist; a Z focusing component such as a motorized focusing mechanism; an additional optical element including a fiber optic element, diffraction optical elements and/or beam splitter; a beam focusing elements (*e.g.*, an to f-theta lens, motor

We claim:

1. A method of making a three-dimensional object by additive manufacturing, comprising:

(a) applying a light polymerizable resin to a build surface of a growing three-dimensional object to form a build segment, said applying carried out with a moving roller resin applicator or a moving film resin applicator;

(b) exposing said build segment to patterned light to polymerize said build segment and form a new build surface, said new build surface having edge portions, said edge portions carrying excess, polymerized or unpolymerized, material thereon;

(c) exposing said excess material to an ablation light (*e.g.*, laser light) at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) sufficient to remove said excess material from said edge portions (*e.g.*, by ablation or melting); and

(d) sequentially repeating steps (a) through (c), with step (c) optionally omitted during some of said sequentially repeating steps but included during at least a plurality of said sequentially repeating steps, until said three-dimensional object is formed.

2. The method of claim 1, wherein said excess material comprises polymerized resin.

3. The method of any preceding claim, wherein said excess material comprises unpolymerized resin.

4. A method of making a three-dimensional object by additive manufacturing, comprising:

(a) applying a light polymerizable resin to a build surface of a growing three-dimensional object to form a build segment, and with said applying carried out with a moving roller resin applicator or a moving film resin applicator;

(b) exposing said build segment to patterned light to polymerize said build segment and form a new build surface,

(c) exposing said new build surface to an ablation light (*e.g.*, laser light) to physically and/or chemically modify said new build surface; and

(d) sequentially repeating steps (a) through (c), with step (c) optionally omitted during some of said sequentially repeating steps but included during at least a plurality of said sequentially repeating steps, until said three-dimensional object is formed.

5. The method of claim 4, wherein said exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that textures at least a portion (*e.g.*, a major portion) of said new build surface (*e.g.*, the pattern configured to enhance adhesion of a subsequent build segment to said new build surface).

6. The method of claim 4 or 5, wherein said light polymerizable resin comprises an additive (*e.g.*, a thermoplastic material such as nylon powder, a natural or synthetic rubber, ceramic particles, etc.), and said exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that selectively melts or sinters said additive (*e.g.*, to form a co-continuous secondary material network) in at least a portion (*e.g.*, a major portion) of said new build surface and modify the material properties of the three-dimensional object (*e.g.*, such as increase toughness, and/or promoting interlayer adhesion, strength or toughness).

7. The method of any one of claims 4 to 6, wherein said light polymerizable resin is a dual cure resin comprising a first polymerizable component and a second polymerizable component and said exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that initiates polymerization of said second polymerizable component in at least a portion (*e.g.*, a major portion) of said new build surface to modify the mechanical properties of said three-dimensional object (*e.g.*, in the green and/or final steps) (in some embodiments theses exposure dosages may be patterned, spatially and/or temporally, to create control of and modify the spatial distribution of material properties in the three-dimensional object).

8. The method of any one of claims 4 to 7, wherein said exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that modifies material properties (*e.g.*, modifies glass transition temperature) in at least a portion (*e.g.*, a major portion) of said new build surface (*e.g.*, to modify internal stresses in the object and thereby modify final object geometry).

9. The method of any one of claims 4 to 8, wherein said exposing step (c) is carried out at a dosage (*i.e.*, an exposure pattern, wavelength, intensity and duration) that activates surface chemicals (*e.g.*, modifies glass transition temperature) in at least a portion (*e.g.*, a

major portion) of said new build surface (*e.g.,* to promote adhesion, modify the surface energy, and/or control the wettability of the resin.

10. The method of any one of claims 4 to 9, wherein said light polymerizable resin comprises a filler (*e.g.,* a porogen or microballoon), and said exposing step (c) is carried out at a dosage (*i.e.,* an exposure pattern, wavelength, intensity and duration) that selectively expands said filler (*e.g.,* to thereby counteract shrinkage and/or warpage of said object) in at least a portion (*e.g.,* a major portion) of said new build surface.

11. The method of any preceding claim, wherein said light polymerizable resin comprises a filler (*e.g.,* solid fillers including fiber fillers, spherical fillers, elliptical fillers, etc.).

12. The method of claim 11, wherein said filler is a solid particulate filler comprising glass fibers, carbon fibers, aramid fibers, basalt fibers, thermoplastic or thermoset polymer fibers (*e.g.,* polyamide, cellulose, or nanocellulose fibers, etc.).

13. The method of any preceding claim, wherein said light polymerizable resin has a viscosity of 1,000, 2,000, 10,000 or 20,000 centipoise or more at 25 degrees Centigrade and 1 atmosphere pressure.

14. The method of any preceding claim, wherein said light polymerizable resin has a viscosity of from 100,000 centipoise to 1,000,000 or 2,000,000 centipoise or more, at 25 degrees Centigrade and 1 atmosphere pressure.

15. The method of any preceding claim, wherein said applying step is carried out with a bottom-up or top-down additive manufacturing apparatus.

16. The method of any preceding claim, wherein said applying step is carried out with a moving roller resin applicator.

17. The method of any one of claims 1 to 15, wherein said applying step (a) is carried out with said moving film resin applicator (*e.g.,* where the moving film is a light-transmissive film, through which the patterned light, and optionally the ablation light, is projected).

18. The method of any preceding claim, wherein said ablation light is a laser light.

19. The method of claim 18, wherein said laser light is at a dosage which is absorbed by said excess material and/or said new build surface in single photon or multiphoton absorption process.

20. The method of claim 18 or 19, wherein said laser light is delivered to said excess material and/or said new build surface as a shaped beam.

21. The method of any one of claims 18 to 20, wherein said laser light is delivered to said excess material and/or said new build surface as a continuous wave or pulsed laser beam.

22. The method of any preceding claim, further comprising the steps of:

detecting a current property (*e.g.*, focal field, focal length, wavelength, intensity) of said ablation light;

comparing said current property to a desired property (*e.g.*, focal field, focal length, wavelength, intensity) and

modifying said ablation light so that said current property more closely corresponds to said desired property.

23. A three-dimensional object produced by the method of any preceding claim.

24. An apparatus for additively manufacturing a three-dimensional object from a light polymerizable resin, comprising:

(a) a build platform on which a growing three-dimensional object can be produced, the object having a build segment, the build segment including an edge portion and a build surface;

(b) an applicator configured to apply a light-polymerizable resin to said build surface to form a new build segment including a new edge portion and a new build surface, wherein said applicator comprises a moving roller resin applicator or a moving film resin applicator;

(c) a resin supply configured for applying said light polymerizable resin to said applicator;

(d) a first, additive light source configured for polymerizing said light polymerizable resin on said build segment; and

(e) a second, subtractive light source configured for delivering a dosage of light to said edge portion(s) and/or said build surface(s).

25. The apparatus of claim 24, wherein said subtractive light source comprises an ultraviolet (UV) light source, vacuum UV light source, deep UV light source, or and high intensity infra-red (IR) light source.

26. The apparatus of claim 24 or 25, wherein said subtractive light source comprises a laser (*e.g.*, a gas laser, a solid-state laser, a fiber laser, a liquid laser, or a semiconductor laser).

27. The apparatus of any one of claims 24 to 26, wherein said applicator comprises said moving roller resin applicator.

28. The apparatus of any one of claims 24 to 26, wherein said applicator comprises said moving film resin applicator.

29. The apparatus of claim 28, wherein said moving film resin applicator is light-transmissive and said first light source projects through said moving film resin applicator.

30. The apparatus of claim 29, wherein said subtractive light source projects through said moving film resin applicator.

31. The apparatus of claim 29, wherein said subtractive light source does not project through said moving film resin applicator (*e.g.*, by positioning on the opposite side of said moving film resin applicator from said additive light source, or by positioning adjacent the moving film resin applicator where the moving film resin applicator is not between the build platform and/or growing three-dimensional object).

32. The apparatus of any preceding claim, further comprising:

a detector operatively associated with said subtractive light source and configured to detect a current property (*e.g.*, focal field, focal length, wavelength, intensity) of said subtractive light; and

a controller operatively associated with said detector and said subtractive light source, said controller configured to compare said current property to a desired property (*e.g.*, focal field, focal length, wavelength, intensity) and modify said subtractive light so that said current property more closely corresponds to said desired property.

33. The apparatus of any preceding claim, wherein said subtractive (*e.g.*, laser) light source comprises:

a continuous wave light source or a pulsed laser light source;

a single beam light source or a multi-beam light source,

a free-standing laser or a fiber-optic based laser; and/or

a single wavelength light source or a multi-wavelength light source.

34. The apparatus of any preceding claim, wherein said subtractive (*e.g.*, laser) light source further comprises:

a laser trepanning system;

an XY stage for scanning or raster scanning of the laser beam;

a beam expander, mirror, focusing lens, and/or air assist;

a Z focusing component such as a motorized focusing mechanism;

an additional optical element comprising a fiber optic element, diffraction optical elements and/or beam splitter;

a beam focusing elements (*e.g.*, an to f-theta lens, motor driven z-focusing component, etc.); and/or

a beam shaping components (*e.g.*, a refractive beam shaping element, diffractive beam shaping element, laser beam integrators, axicons for generating Bessel beams, cylinder lenses and anamorphic prism pairs for circularizing beams, etc.).