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(54) Title: THREE-DIMENSIONAL PRINTING

(57) Abstract: The present disclosure relates to a three-dimensional (3D) printing materials kit comprising: a first tailoring agent comprising at least one crosslinking agent; a second tailoring agent comprising at least one plasticizer, and a fusing agent. The present disclosure also relates to a printed structure comprising regions of relatively higher ductility and regions of relatively lower ductility. The regions of relatively higher ductility can be interspersed by the regions of relatively lower ductility, and the regions of relatively lower ductility can be formed from a crosslinked polymer and/or a polymer composition comprising a reinforcing filler, and/or the regions of relatively higher ductility can be formed from a polymer composition comprising a plasticizer. The present disclosure also relates to a method of three dimensional printing (3D) that can be used to print a 3D printed object comprising the printed structure described above.



THREE-DIMENSIONAL PRINTING

BACKGROUND

[0001] To be suitable for certain applications, a material may require a combination of material properties. For example, in some applications, a stiff, strong and tough material may be required. While a material may often exhibit compatible properties, e.g. stiffness and strength, in some instances, it can be more difficult to find a material that exhibits more contrasting properties, e.g. strength and toughness.

[0002] Natural materials can provide e.g. a strength-toughness balance and biological systems can be a good source of inspiration for the design of new smart materials. For instance, the architecture of bone has a significant influence on its mechanical properties, e.g. its combination of strength and toughness.

BRIEF DESCRIPTION OF THE DRAWING

[0003] Features of examples of the present disclosure will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though perhaps not identical, components. For the sake of brevity, reference numerals or features having a previously described function may or may not be described in connection with other drawings in which they appear.

[0004] FIG. 1 is an example reaction mechanism of an epoxide group and an amine group to illustrate an example crosslinking reaction;

[0005] FIG.2 is an example reaction mechanism of ethyleneglycol diglycidyl ether and a polyamide-6 polymer;

[0006] FIGS. 3 to 5 is a schematic view of an example 3D printing system that can be used in an example method of the present disclosure;

[0007] FIGS. 6 to 9 are schematic drawings of examples of structures that can be printed using examples of the methods of the present disclosure; and

[0008] FIG.S 10 and 11 are schematic drawings of example 3D printed objects produced in Example 3.

DETAILED DESCRIPTION

[0009] The present disclosure also relates a method for printing a three-dimensional (3D) printed object. The method comprises:

[0010] selectively applying a first tailoring agent to a build material; and

[0011] exposing the build material to radiation, thereby fusing at least part of the build material to form a layer.

[0012] The first tailoring agent comprises a reinforcing agent or a ductility-increasing agent, and the first tailoring agent is selectively applied to form regions of relatively lower ductility interspersed with regions of relatively higher ductility in the 3D printed object.

[0013] In some examples, the method further comprises selectively applying a fusing agent to the build material before exposing the build material to radiation.

[0014] The first tailoring agent may be selectively applied based on a three-dimensional (3D) object model. The fusing agent may be selectively applied based on a three-dimensional (3D) object model.

[0015] Where employed, the reinforcing agent may be a reinforcing filler or crosslinking agent. Suitable reinforcing fillers and crosslinking agents are described in further detail below. Where employed, the ductility-increasing agent may be a plasticizer. Suitable plasticizers are described in further detail below.

[0016] Where the first tailoring agent comprises a reinforcing agent, the reinforcing agent may be selectively applied to form regions of relatively lower ductility (e.g. stiff zones) in the 3D printed part. Regions of relatively higher ductility (e.g. ductile zones) may be formed from build material that is untreated with the reinforcing agent. These regions of relatively higher ductility (e.g. ductile zones) may be interspersed with regions of relatively lower ductility (e.g. stiff zones) in the 3D printed object.

[0017] Where the first tailoring agent comprises a ductility-increasing agent, the reinforcing agent may be selectively applied to form regions of relatively higher ductility (e.g. ductile zones) in the 3D printed part. Regions of relatively lower ductility (e.g. stiff zones) may be formed from build material that is untreated with the ductility-increasing agent. These regions of relatively lower ductility (e.g. stiff zones) may be interspersed with regions of relatively higher ductility (e.g. ductile zones) in the 3D printed object.

[0018] In one example, the method further comprises: selectively applying a second tailoring agent to the build material. In this example, the first tailoring agent comprises one of the reinforcing agent and a ductility-increasing agent, and the second tailoring agent comprises the other of the reinforcing agent and ductility-increasing agent. The first tailoring agent and second tailoring agent are selectively applied to form the regions of relatively lower ductility interspersed with the regions of relatively higher ductility.

[0019] The second tailoring agent may be selectively applied based on a three-dimensional (3D) object model. The three-dimensional (3D) object model may be or may be derived from a set of programming instructions defining how the 3D object should be printed.

[0020] The first tailoring agent may be applied to a first portion(s) of the build material and the second tailoring agent may be applied to a second portion(s) of the build material. The first portion(s) may be different from the second portion(s). In some examples, the first and second portions may be adjacent to one another. In some examples, the first and second portions are in contact with one another.

[0021] By selectively applying a tailoring agent onto portion(s) of the build material, regions of relatively lower ductility can be interspersed with regions of relatively higher ductility. This can allow relatively stiffer regions to be interspersed with relatively more ductile regions within the 3D printed object. The regions of relatively lower ductility can provide the 3D printed object with a degree of stiffness and/or strength, while the regions of relatively higher ductility can e.g. soften the material and/or reduce crack propagation. In some examples, this can provide the 3D printed object with a combination of mechanical properties, e.g. strength and toughness.

[0022] As the tailoring agent is selectively applied to the build material, the mechanical properties of the build material can be altered during the printing process. Accordingly, in some examples, the mechanical properties of a build material can be manipulated at the voxel level. Furthermore, as the tailoring agent is selectively applied to the build material, it is possible to build a structure or architecture comprising relatively lower ductility (e.g. stiff zones) interspersed with regions of relatively higher ductility (e.g. ductile zones). In some examples, this arrangement can provide alternating stiff and ductile regions, allowing a combination of contrasting properties to be achieved. In some examples, the arrangement can

result in a biomimetic and/or hierarchical structure. In some examples, such structures can impart a combination of mechanical properties, e.g. strength and toughness, to the material. Accordingly, the mechanical properties that can be achieved by arranging regions of relatively lower ductility and regions of relatively higher ductility in a predetermined manner can, in some instances, surpass the mechanical properties that would be expected from the mechanical properties of the build material itself. In some examples, therefore, the mechanical properties of the 3D printed object may be influenced not only by the nature of the material from which the 3D printed object is formed, but also the architecture (or structure (e.g. microstructure)) of the 3D printed object.

[0023] In some examples, the structure may comprise localized regions of relatively lower ductility (e.g. stiff zones) dispersed in a continuous region of relatively higher ductility (e.g. ductile zones). Alternatively, the structure may comprise localized regions of relatively higher ductility (e.g. ductile zones) dispersed in a continuous region of relatively lower ductility (e.g. stiff zones).

[0024] In some examples, the structure can comprise a network or web of stiff zones interspersed by ductile zones or a network or web of ductile zones interspersed by stiff zones.

[0025] In some examples, the 3D printed object may have a structure that comprises a cellular structure, and wherein a reinforcing agent is selectively applied to form cell walls having a relatively lower ductility (e.g. stiff zones), and/or wherein a ductility-increasing agent is applied to form regions having a relatively higher ductility (e.g. ductile zones) between the cell walls. Alternatively, the structure may comprise a cellular structure in which the regions of relatively higher ductility (e.g. ductile zones) are provided by cell walls and the regions of relatively lower ductility (e.g. stiff zones) are provided in regions between the cell walls. The cellular structure may be a cellular microstructure. The cellular structure may comprise an arrangement of repeating cell units. The cell units may be substantially round or substantially polygonal cell units. Examples of polygonal units include units that have a substantially square, triangular, rectangular, rhombus-shaped, kite-shaped, or hexagonal in cross-section. In some examples, the structure may be a biomimetic structure. In some examples, the structure may be a hierarchical structure. In some examples, the structure may be a microstructure.

[0026] The stiffness ratio (i.e. ratio of Young's Modulus) of the material used to form the regions of relatively lower ductility (e.g. stiff zones) to the material used to form the regions of relatively higher ductility (e.g. ductile zones) may be at least about 1.5, for example, at least about 2. In some examples, the stiffness ratio may be at least about 3, for example, at least about 4, at least about 5, at least about 6, at least about 7, at least about 8, at least about 9 or at least about 10. In some examples, the stiffness ratio may be at least about 20, at least about 30, at least about 40, at least about 50, at least about 60, at least about 70, at least about 80, at least about 90 or at least about 100. The stiffness ratio may be determined by any suitable method. In one example, a first sample may be made from the material used to form the regions of relatively lower ductility (e.g. stiff zones). A tensile test may be performed on this sample to determine its Young's Modulus. A corresponding tensile test may be performed on a second sample made from the material used to form the regions of relatively higher ductility (e.g. ductile zones). The Young's Modulus of the first sample may be divided by the Young's Modulus of the second sample to obtain the stiffness ratio.

[0027] The present disclosure also relates to a three-dimensional (3D) printing materials kit. The kit comprises a first tailoring agent comprising at least one crosslinking agent; a second tailoring agent comprising at least one plasticizer, and a fusing agent.

[0028] In some instances, examples of the kit(s) described in the present disclosure can be used in examples of the method(s) described in the present disclosure.

[0029] In some examples, the crosslinking agent may include compounds having a functional group selected from at least one of epoxy, amine, isocyanate, phosphine and aldehyde.

[0030] In some examples, the crosslinking agent can comprise an epoxy functional group and is selected from at least one of: 2-ethylhexyl glycidyl ether, phenol glycidyl ether, p-tert-butylphenyl glycidyl ether, dibromo phenyl glycidyl ether, lauryl alcohol glycidyl ether, resorcinol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol polyglycidyl ether, sorbitol polyglycidyl ether, diglycidyl terephthalate, diglycidyl-o-phthalate, N-glycidyl ether, and tris(4-hydroxyphenyl) methane triglycidyl ether.

[0031] In some examples, the crosslinking agent can comprise an amine functional group and is selected from at least one of: aniline, sulphonamide, tetraethylenepentamine, dipropylenediamine, diethylaminopropylamine, N-aminoethylpiperazine, bis(2-ethylhexyl)amine, methanediamine methylphenyl diamine, methylphenylenediamine, diaminodiphenyl sulfone, diethylenetriamine, and triethylenetetramine.

[0032] In some examples, the first tailoring agent can comprise a first crosslinking agent comprising an epoxy functional group, and a second crosslinking agent comprising an amine functional group. In some examples, the first crosslinking agent can comprise a mixture of ethyleneglycol diglycidyl ether and triphenylolmethane triglycidyl ether. In some examples, the second crosslinking agent can comprise 4,4-diaminodiphenyl sulfone. In some examples, the first tailoring agent can comprise a mixture of ethyleneglycol diglycidyl ether and triphenylolmethane triglycidyl ether, and the second crosslinking agent can comprise 4,4-diaminodiphenyl sulfone.

[0033] In some examples, the plasticizer may be selected from at least one of 2-pyrrolidone, dimethyl sulfoxide, methyl 4-hydroxybenzoate, dioctyl phthalate, N-methyl-2-pyrrolidone, N-2-hydroxyethyl-2-pyrrolidone, urea, ethylene carbonate, propylene carbonate, lactones, diethylene glycol, triethylene glycol, tetraethylene glycol, decalin, gamma-butyrolactone, dimethylformamide, phenylmethanol, dimethyl sulfoxide (DMSO), 2-methyl-benzene sulphonamide, 4-methyl benzene, 2-methyl-benzene sulphonamide, N-butylbenzenesulfonamide, N-ethylbenzenesulfonamide, N-propylbenzenesulfonamide, N-butyl-N-dodecylbenzenesulfonamide, N,N-dimethylbenzenesulfonamide, p-methylbenzenesulfonamide, o/p-toluene sulphonamide, p-toluene sulphonamide, 2-ethylhexyl-4-hydroxybenzoate, hexadecyl-4-hydroxybenzoate, 1-butyl-4-hydroxybenzoate, dioctyl phthalate, diisodecyl phthalate, di(-2-ethylhexyl) adipate, and tri(-2-ethylhexyl) phosphate. In some examples, the plasticizer comprises methyl benzene sulfonamide.

[0034] In some examples, the kit further comprises a build material comprising polymer particles.

[0035] In some examples, the polymer of the build material may be selected from at least one of polyamide, polyolefin, thermoplastic polyurethane, polyester, polycarbonate, polyether ketone, polyacrylate and polystyrene. In some examples, the polymer of the build material may be a polyamide.

[0036] In some examples, the first tailoring agent of the kit comprises about 5 to about 40 weight % of crosslinking agent dispersed in a liquid carrier. In some examples, the second tailoring agent of the kit comprises about 5 to about 40 weight % of a plasticizer dispersed in a liquid carrier.

[0037] The present disclosure also relates to a 3D printed structure comprising regions of relatively higher ductility and regions of relatively lower ductility, wherein the regions of relatively higher ductility are interspersed by the regions of relatively lower ductility, and wherein the regions of relatively lower ductility are formed from a crosslinked polymer and/or a polymer composition comprising a reinforcing filler, and/or wherein the regions of relatively higher ductility are formed from a polymer composition comprising a plasticizer.

[0038] In some examples, the structure may be a microstructure. In some examples, the structure may be a biomimetic structure. In some examples, the structure may be a hierarchical structure. The structure may comprise localized regions of relatively lower ductility (e.g. stiff zones) dispersed in a continuous region of relatively higher ductility (e.g. ductile zones). Alternatively, the structure may comprise localized regions of relatively higher ductility (e.g. ductile zones) dispersed in a continuous region of relatively lower ductility (e.g. stiff zones).

[0039] In some examples, the structure comprises a network or web of stiff zones interspersed of ductile zones or a network or web of ductile zones interspersed by stiff zones.

[0040] In some examples, the structure is a cellular structure. In some examples, the structure is a cellular structure (e.g. cellular microstructure), wherein the cell walls form the regions of relatively low ductility, and/or regions between the cell walls form the regions of relatively high ductility.

Reinforcing agent

[0041] The tailoring agent (e.g. first or second tailoring agent) may comprise a reinforcing agent. The tailoring agent may comprise a reinforcing agent dispersed in a liquid carrier.

[0042] The reinforcing agent may be present in the tailoring agent in an amount of at least about 0.5 weight %, for example, at least about 1 weight % or at least about 2 weight %. In some examples, the reinforcing agent may be present in the tailoring

agent in an amount of at most about 70 weight %, at least about 60 weight %, or at least about 50 weight %. In some examples, the reinforcing agent may be present in the tailoring agent in an amount of about 0.5 weight % to about 70 weight %, about 1 weight % to about 60 weight % or about 2 weight % to about 50 weight %. In some examples, the reinforcing agent may be present in the tailoring agent in an amount of about 5 weight % to about 45 weight %, about 10 weight % to about 40 weight % or about 15 weight % to about 30 weight %.

[0043] The tailoring agent may also include at least one of the following additives: surfactant(s), antimicrobial agent(s), anti-kogation agent(s), chelating agent(s), humectant(s) and/or water.

[0044] As mentioned above, the reinforcing agent may be a reinforcing filler. The reinforcing filler may comprise particles, for instance, nanoparticles. The particles of the reinforcing agent may have a particle size of about 1 micron or less. Suitable particle sizes range from about 0.01 to about 1 microns, for example, about 0.05 to about 0.8 microns.

[0045] Examples of suitable reinforcing filler particles include particles of at least one of the following materials: boron, boron nitride materials, silica, alumina, titanium dioxide, glass, carbon nanomaterials, montmorillonite, talc, basalt, silicon carbide, metal carbide, silicon nitride, metal nitride, polyaramid, metal, metal alloy, diamond, boron carbide, mica, wollastonite, and ceramic.

[0046] The reinforcing filler particles may be selectively applied to the build material to form regions of relatively lower ductility (or increased stiffness) in the 3D printed object.

[0047] Where a reinforcing filler is employed, the amount of reinforcing filler in the tailoring agent may be about 1 to about 50 weight %, for example, about 5 to about 40 weight % or about 10 to about 30 weight %.

[0048] In some examples, the reinforcing agent may be a crosslinking agent. A crosslinking agent may be employed, for example, when a polymer build material is employed.

[0049] The crosslinking agent may be selectively applied to the build material and reacted with functional groups in e.g. the polymer build material to form regions of relatively lower ductility (or increased stiffness) in the 3D printed object.

Alternatively, the reinforcing agent may comprise a first crosslinking agent and a second crosslinking agent. The first crosslinking agent and the second crosslinking

agent may be selectively applied to the build material and crosslinked to form regions of relatively lower ductility (or increased stiffness) in the 3D printed object. The first crosslinking agent and the second crosslinking agent may be provided as separate agents, e.g. separate inkjet compositions.

[0050] In some examples, the crosslinking agent may include compounds having a functional group selected from at least one of epoxy, amino (e.g. -NHR, -NR₂ or -NH₂), isocyanate, phosphine and aldehyde. Examples of crosslinking agents having isocyanate, phosphine or aldehyde functional groups include: methyl isocyanate, ethyl isocyanate, toluene isocyanate, hexamethylene diisocyanate, acetaldehyde, glutaraldehyde, or tris(hydroxymethyl)phosphine.

[0051] Where the crosslinking agent includes an epoxy functional group (epoxy crosslinking agent), the epoxy crosslinking agent may have one or more epoxy groups. Epoxy groups can be highly reactive with amino groups. Accordingly, when an epoxy compound comes in contact with a compound having an amino functional group, the epoxy compound can react.

[0052] In some examples, an epoxy crosslinking agent may be employed when the build material comprises an amino functional group. In some examples, such a crosslinking agent may be employed together with a further crosslinking agent having an amino group (amino crosslinking agent). In these examples, the epoxy crosslinking agent and the amino crosslinking agent may both be selectively applied to selected regions of the build material and reacted to form regions of relatively lower ductility (or increased stiffness) in the 3D printed object. For instance, the tailoring agent may comprise a first crosslinking agent comprising an epoxy crosslinking agent and a second crosslinking agent comprising an amino crosslinking agent. The first and second crosslinking agents may be provided as separate agents (e.g. inkjet compositions)

[0053] FIG. 1 shows an example reaction mechanism of an epoxy compound reacting with an amine compound. The epoxy compound that is included in the tailoring agent can have multiple epoxide groups so that when the multiple epoxide groups react with amino groups, a cross-linked network may form.

[0054] By way of illustration, FIG. 2 shows an example reaction between ethyleneglycol diglycidyl ether and nylon 6 polymer (i.e. PA-6 polymer). The ethyleneglycol diglycidyl ether is one example of an epoxy compound having multiple epoxide groups and the nylon 6 polymer is one example of an amine compound

having multiple amino groups. As shown in the figure, two nylon 6 polymer chains can be crosslinked by reaction between the amino groups of the nylon 6 polymer chains with the epoxide groups at either end of the ethyleneglycol diglycidyl ether molecule. Additional molecules of ethyleneglycol diglycidyl ether can crosslink to additional nylon 6 polymer chains, forming a crosslinked network.

[0055] Examples of epoxy crosslinking agents that can be used as the reinforcing agent include 2-ethylhexyl glycidyl ether, phenol glycidyl ether, p-tert-butylphenyl glycidyl ether, dibromo phenyl glycidyl ether, lauryl alcohol glycidyl ether, resorcinol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol polyglycidyl ether, trimethylolpropane polyglycidyl ether, pentaerythritol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, diglycidyl terephthalate, diglycidyl o-phthalate, N-glycidyl phthalimide, ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, tris(4-hydroxyphenyl) methane triglycidyl ether, and combinations thereof. In some examples, the epoxy compound can have two epoxide groups. In other examples, the epoxy compound can have three or more epoxide groups. In further examples, a mixture of epoxy compounds can be used. For example, an epoxy compound having exactly two epoxide groups can be used together with an epoxy compound having three or more epoxide groups. In a particular example, the epoxy compound can include a combination of ethyleneglycol diglycidyl ether and triphenylolmethane triglycidyl ether.

[0056] Where an epoxy crosslinking agent is employed, the tailoring agent can include the epoxy crosslinking agent in an amount from about 5 wt% to about 40 wt%, or from about 10 wt% to about 30 wt%, or from about 15 wt% to about 25 wt%.

[0057] Where the crosslinking agent includes an amino functional group (amino crosslinking agent), the amino compound may have one or more amino groups. Such amino compounds may be employed together with a further crosslinking agent having an epoxy group (epoxy crosslinking agent). In these examples, the epoxy crosslinking agent and the amino crosslinking agent may both be selectively applied to selected regions of the build material and reacted to form regions of relatively lower ductility (or increased stiffness) in the 3D printed object.

[0058] In some examples, the crosslinking agent including an amino functional group (amino crosslinking agent) can include aniline sulfonamide, tetraethylenepentamine, dipropylenediamine, diethylaminopropylamine, N-

aminoethylpiperazine, bis(2-ethylhexyl)amine, methanediamine methylphenyl diamine, methylphenylenediamine, diaminodiphenyl sulfone, diethylenetriamine, triethylenetetramine, or a combination thereof. In a particular example, the amine compound can be diaminodiphenyl sulfone.

[0059] The tailoring agent can include the amino crosslinking agent in an amount from about 5 wt% to about 30 wt%, or from about 10 wt% to about 20 wt%.

[0060] The reinforcing agent may include a liquid carrier. As described above, the reinforcing filler or crosslinking agent may be dispersed in the liquid carrier. In some examples, the reinforcing agent may be an inkjet ink composition. The reinforcing agent may comprise more than one agent, for instance, one agent comprising a first crosslinking agent (e.g. epoxy crosslinking agent) and a further agent comprising a second crosslinking agent (e.g. amino crosslinking agent).

[0061] The liquid carrier of the reinforcing agent may be water. The liquid carrier (e.g. water) may be present in an amount of from about 10 to about 95 weight %, for example, from about 10 to about 70 weight %, about 15 to about 60 weight %, about 20 to about 50 weight %, or from about 25 to about 45 weight %.

[0062] The reinforcing agent may include a humectant. Suitable humectants include diethylene glycol butyl ether, polyethylene glycol, 2-pyrrolidone, N-methyl 2-pyrrolidone, hydroxyethyl 2-pyrrolidone, and combinations thereof. The humectant may be present in an amount of about 20 to about 60 weight %, about 30 to about 50 weight % or about 35 to about 45 weight %.

[0063] A surfactant, or combination of surfactants, can also be present in the reinforcing agent. Examples of surfactants include alkyl polyethylene oxides, alkyl phenyl polyethylene oxides, polyethylene oxide block copolymers, acetylenic polyethylene oxides, polyethylene oxide (di)esters, polyethylene oxide amines, protonated polyethylene oxide amines, protonated polyethylene oxide amides, dimethicone copolyols, substituted amine oxides, and the like. Other surfactants can include liponic esters such as Tergitol™ 15-S-12, Tergitol™ 15-S-7 available from Dow Chemical Company, LEG-1 and LEG-7; Triton™ X-100; Triton™ X-405 available from Dow Chemical Company; and sodium dodecylsulfate.

[0064] The amount of surfactant in the reinforcing agent may range from about 0.01 wt% to about 20 wt%.

[0065] Various other additives can be employed to optimize the properties of the reinforcing agent. Such additives can be present in amounts of from about 0.01 wt%

to about 20 wt% of the reinforcing agent. Examples of these additives are those added to inhibit the growth of harmful microorganisms. These additives may be biocides, fungicides, and other microbial agents, which can be used in ink jet formulations. Examples of suitable microbial agents include NUOSEPT® (Nudex, Inc.), UCARCIDE™ (Union carbide Corp.), VANCIDE® (R.T. Vanderbilt Co.), PROXEL® (ICI America), and combinations thereof.

[0066] Sequestering agents, such as EDTA (ethylene diamine tetra acetic acid), may be included to eliminate the deleterious effects of heavy metal impurities. Buffers may also be used to control the pH of the composition. Viscosity modifiers may also be present.

Ductility-increasing agent

[0067] The tailoring agent may comprise a ductility-increasing agent. For example, the first tailoring agent may comprise a ductility-increasing agent. Alternatively, in an example where a first tailoring agent and a second tailoring agent are employed, the first tailoring agent may comprise a reinforcing agent and the second tailoring agent may comprise a ductility-increasing agent. In another example where a first tailoring agent and a second tailoring agent are employed, the first tailoring agent may comprise a ductility-increasing agent and the second tailoring agent may comprise a reinforcing agent.

[0068] Where a reinforcing agent and a ductility-increasing agent are employed, the reinforcing agent and ductility-increasing agent may be selectively applied to form the regions of relatively lower ductility (e.g. stiff zones) interspersed with the regions of relatively higher ductility (e.g. ductile zones). The stiff zones and ductile zones may be adjacent to one another. The stiff zones and ductile zones may be disposed in an alternating arrangement at least along one axis in at least part of the structure of the 3D printed object.

[0069] A suitable ductility-increasing agent may be a plasticizer. A plasticizer may be useful where a polymer build material is employed.

[0070] Suitable plasticizers include at least one of the following plasticizers: 2-pyrrolidone, dimethyl sulfoxide, methyl 4-hydroxybenzoate, dioctyl phthalate, N-methyl-2-pyrrolidone, N-2-hydroxyethyl-2-pyrrolidone, urea, ethylene carbonate,

propylene carbonate, lactones, diethylene glycol, triethylene glycol, tetraethylene glycol, decalin, gamma-butyrolactone, dimethylformamide, phenylmethanol, dimethyl sulfoxide (DMSO), 2-methyl-benzene sulphonamide, 4-methyl benzene, 2-methyl-benzene sulphonamide, N-butylbenzenesulfonamide, N-ethylbenzenesulfonamide, N-propylbenzenesulfonamide, N-butyl-N-dodecylbenzenesulfonamide, N,N-dimethylbenzenesulfonamide, p-methylbenzenesulfonamide, o/p-toluene sulphonamide, p-toluene sulphonamide, 2-ethylhexyl-4-hydroxybenzoate, hexadecyl-4-hydroxybenzoate, 1-butyl-4-hydroxybenzoate, dioctyl phthalate, diisodecyl phthalate, di(-2-ethylhexyl) adipate, and tri-(2-ethylhexyl) phosphate. An example of a plasticizer combination may be a mixture of 4-methyl benzene and 2-methyl benzene.

[0071] Where a plasticizer is used as a ductility-increasing agent, the plasticizer may be present in an amount of about 5 wt% to about 40 wt%, or from about 10 wt% to about 30 wt%, or from about 15 wt% to about 25 wt%.

[0072] The plasticizer may be dispersed or dissolved in a liquid carrier. The liquid carrier may be water. The liquid carrier (e.g. water) may be present in an amount of from about 10 to about 95 weight %, for example, from about 10 to about 70 weight %, about 15 to about 60 weight %, about 20 to about 50 weight %, or from about 25 to about 45 weight %.

[0073] The ductility-increasing agent may include a humectant. Suitable humectants include diethylene glycol butyl ether, polyethylene glycol, 2-pyrrolidone, N-methyl 2-pyrrolidone, hydroxyethyl 2-pyrrolidone, and combinations thereof. The humectant may be present in an amount of about 20 to about 60 weight %, about 30 to about 50 weight % or about 35 to about 45 weight %.

[0074] A surfactant, or combination of surfactants, can also be present in the ductility-increasing agent. Examples of surfactants include alkyl polyethylene oxides, alkyl phenyl polyethylene oxides, polyethylene oxide block copolymers, acetylenic polyethylene oxides, polyethylene oxide (di)esters, polyethylene oxide amines, protonated polyethylene oxide amines, protonated polyethylene oxide amides, dimethicone copolyols, substituted amine oxides, and the like. Other surfactants can include liponic esters such as Tergitol™ 15-S-12, Tergitol™ 15-S-7 available from Dow Chemical Company, LEG-1 and LEG-7; Triton™ X-100; Triton™ X-405 available from Dow Chemical Company; and sodium dodecylsulfate.

[0075] The amount of surfactant present in the ductility-increasing agent may range from about 0.01 wt% to about 20 wt%.

[0076] Various other additives can be employed to optimize the properties of the ductility-increasing agent. Such additives can be present in amounts of from about 0.01 wt% to 20 wt% of the ductility-increasing agent. Examples of these additives are those added to inhibit the growth of harmful microorganisms. These additives may be biocides, fungicides, and other microbial agents, which can be used in ink formulations. Examples of suitable microbial agents include NUOSEPT® (Nudex, Inc.), UCARCIDE™ (Union carbide Corp.), VANCIDE® (R.T. Vanderbilt Co.), PROXEL® (ICI America), and combinations thereof.

[0077] Sequestering agents, such as EDTA (ethylene diamine tetra acetic acid), may be included to eliminate the deleterious effects of heavy metal impurities. Buffers may also be used to control the pH of the composition. Viscosity modifiers may also be present.

Fusing Agents

[0078] In examples of the method of the present disclosure, the build material may be fused or bound by exposing the build material to radiation. In some examples of the method of the present disclosure, a fusing agent may be employed to facilitate fusing.

[0079] Where a fusing agent is employed, the fusing agent may be employed in addition to the tailoring agent(s) described above. The fusing agent can include a radiation absorber or pigment that can absorb electromagnetic radiation and convert that radiation into heat. The fusing agent can be selectively applied to areas of the build material (powder bed material) that are intended to be consolidated to become part of the solid 3D printed object.

[0080] The fusing agent can be applied, for example, by printing with a fluid or inkjet printhead. Accordingly, the fusing fluid can be applied with precision to selected areas of the build material to form a layer of the 3D printed object. After applying the fusing agent, the powder bed material can be irradiated with radiant energy. The radiation absorber can absorb this energy and convert it to heat, thereby heating any build material particles in contact with the radiation absorber of the

fusing agent. An appropriate amount of radiant energy can be applied so that the area of the build material that is printed with the fusing agent can heat up enough to bind or fuse the e.g. polymer particles. This can consolidate the particles into a solid layer. The build material that is not printed with the fusing agent can remain as a relatively loose powder.

[0081] The process of forming a single layer by applying fusing agent and bed of build material can be repeated with additional layers of fresh build material to form additional layers of the 3D printed object. This can allow the final 3D printed object to be built one layer at a time. As described above, the tailoring agent(s) can also be selectively applied to modify the mechanical properties of the build material at selected locations to form a structure comprising regions of relatively lower ductility (e.g. stiff zones) interspersed with regions of relatively higher ductility (e.g. ductile zones) in the 3D printed object. This structure (e.g. microstructure) can impart a desired balance of mechanical properties (e.g. strength and toughness) to the 3D printed object.

[0082] In the printing process, the build material surrounding the 3D printed object can act as a support material for the object. When the 3D printing is complete, the object can be removed from the bed and any loose build material on the object can be removed.

[0083] The radiation absorber of the fusing agent may be any suitable absorber. Examples of suitable absorbers include UV absorbers, infrared absorbers and near infrared absorbers. In some examples, infrared absorbers or near infrared absorbers are employed. In some examples, the infrared absorber or near infrared absorber may absorb electromagnetic radiation in the range of 700 nm to 1mm. In many cases, the infrared absorber or near infrared absorber can have a peak absorption wavelength in the range of 800 nm to 1400 nm.

[0084] In some examples, the absorber can be carbon black, tungsten bronze, molybdenum bronze, conjugated polymer, aminium dye, tetraaryldiamine dye, cyanine dye, phthalocyanine dye, dithiolene dye, metal phosphate, metal silicate or mixtures thereof.

[0085] The absorber may be a near infrared absorbing dye. Examples of absorbing dyes include aminium dyes, tetraaryldiamine dyes, cyanine dyes, phthalocyanine dyes, dithiolene dyes, and others.

[0086] In further examples, the absorber can be a near-infrared absorbing conjugated polymer such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), a polythiophene, poly(p-phenylene sulfide), a polyaniline, a poly(pyrrole), a poly(acetylene), poly(p-phenylene vinylene), polyparaphenylene, or combinations thereof. As used herein, "conjugated" refers to alternating double and single bonds between atoms in a molecule. Thus, "conjugated polymer" refers to a polymer that has a backbone with alternating double and single bonds.

[0087] Other examples of radiation absorbers or pigments can include phosphates having a variety of counterions such as copper, zinc, iron, magnesium, calcium, strontium, the like, and combinations thereof. Specific examples of phosphates can include $M_2P_2O_7$, $M_4P_2O_9$, $M_5P_2O_{10}$, $M_3(PO_4)_2$, $M(PO_3)_2$, $M_2P_4O_{12}$, and combinations thereof, where M represents a counterion having an oxidation state of +2, such as those listed above or a combination thereof. For example, $M_2P_2O_7$ can include compounds such as $Cu_2P_2O_7$, Cu/MgP_2O_7 , Cu/ZnP_2O_7 , or any other suitable combination of counterions. It is noted that the phosphates described herein are not limited to counterions having a +2 oxidation state. Other phosphate counterions can also be used to prepare other suitable radiation absorbers.

[0088] Other examples of radiation absorbers or pigments include silicates. The silicates can have the same or similar counterions as the phosphates. One non-limiting example can include M_2SiO_4 , $M_2Si_2O_6$, and other silicates where M is a counterion having an oxidation state of +2. For example, the silicate $M_2Si_2O_6$ can include $Mg_2Si_2O_6$, $Mg/CaSi_2O_6$, $MgCuSi_2O_6$, $Cu_2Si_2O_6$, $Cu/ZnSi_2O_6$, or other suitable combination of counterions. It is noted that the silicates described herein are not limited to counterions having a +2 oxidation state. Other silicate counterions can also be used to prepare other suitable pigments.

[0089] In some examples, the absorber may comprise carbon black.

[0090] In some examples, the radiation absorber, may be dissolved or dispersed in a liquid vehicle. The fusing agent may be a liquid composition comprising the radiation absorber, e.g. UV absorber, near infrared absorber or infrared absorber and a liquid carrier.

[0091] The liquid carrier can include water. In some examples, an additional co-solvent may also be present. In certain examples, a high boiling point co-solvent can be included in the fusing agent. The high boiling point co-solvent can be an organic

co-solvent that boils at a temperature higher than the temperature of the bed of build material during printing. In some examples, the high boiling point co-solvent can have a boiling point above 250 °C. In still further examples, the high boiling point co-solvent can be present at a concentration of at least about 1 wt %, for example, at least about 1.5 wt % of the total weight of the fusing agent. The co-solvent, where employed may be present in an amount of at most about 50 wt %, for example, at most 40 wt %, at most 35 wt % or at most 30 wt %. In some examples, the co-solvent may be present in an amount of from about 1 wt% to about 40 wt% of the total weight of the fusing agent.

[0092] Classes of co-solvents that can be used can include organic co-solvents including aliphatic alcohols, aromatic alcohols, diols, glycol ethers, polyglycol ethers, caprolactams, formamides, acetamides, and long chain alcohols. Examples of such compounds include primary aliphatic alcohols, secondary aliphatic alcohols, 1,2-alcohols, 1,3-alcohols, 1,5-alcohols, ethylene glycol alkyl ethers, propylene glycol alkyl ethers, higher homologs (C₆-C₁₂) of polyethylene glycol alkyl ethers, N-alkyl caprolactams, unsubstituted caprolactams, both substituted and unsubstituted formamides, both substituted and unsubstituted acetamides, and the like. Specific examples of solvents that can be used include 2-pyrrolidinone, N-methylpyrrolidone, 2-hydroxyethyl-2-pyrrolidone, 2-methyl-1,3-propanediol, tetraethylene glycol, 1,6-hexanediol, 1,5-hexanediol and 1,5-pentanediol.

[0093] A surfactant, or combination of surfactants, can also be present in the fusing agent. Examples of surfactants include alkyl polyethylene oxides, alkyl phenyl polyethylene oxides, polyethylene oxide block copolymers, acetylenic polyethylene oxides, polyethylene oxide (di)esters, polyethylene oxide amines, protonated polyethylene oxide amines, protonated polyethylene oxide amides, dimethicone copolyols, substituted amine oxides, and the like. Other surfactants can include liponic esters such as Tergitol™ 15-S-12, Tergitol™ 15-S-7 available from Dow Chemical Company, LEG-1 and LEG-7; Triton™ X-100; Triton™ X-405 available from Dow Chemical Company; and sodium dodecylsulfate.

[0094] The amount of surfactant present in the fusing agent may range from about 0.01 wt% to about 20 wt%.

[0095] Various other additives can be employed to optimize the properties of the fusing agent for specific applications. Such additives can be present at from about 0.01 wt% to about 20 wt% of the fusing agent. Examples of these additives are

those added to inhibit the growth of harmful microorganisms. These additives may be biocides, fungicides, and other microbial agents, which can be used in ink jet formulations. Examples of suitable microbial agents include NUOSEPT® (Nudex, Inc.), UCARCIDE™ (Union carbide Corp.), VANCIDE® (R.T. Vanderbilt Co.), PROXEL® (ICI America), and combinations thereof.

[0096] Sequestering agents, such as EDTA (ethylene diamine tetra acetic acid), may be included to eliminate the deleterious effects of heavy metal impurities. Buffers may also be used to control the pH of the composition. Viscosity modifiers may also be present.

[0097] The amount of radiation absorber, e.g. UV absorber, infrared absorber or near infrared absorber, in the fusing agent can vary depending on the type of absorber. In some examples, the concentration of infrared absorber or near infrared absorber in the fusing agent can be from about 0.1 wt% to about 20 wt% of the fusing agent. In one example, the concentration of absorber in the fusing ink can be from about 0.1 wt% to about 15 wt%. In another example, the concentration can be from about 0.1 wt% to about 8 wt%. In yet another example, the concentration can be from about 0.5 wt% to about 2 wt%. In a particular example, the concentration can be from about 0.5 wt% to about 1.2 wt%.

[0098] The fusing agent can have a temperature boosting capacity. In the case of a polymer build material, this temperature boosting capacity may be used to increase the temperature of the polymer in the bed of build material above the melting or softening point of the polymer. As used herein, "temperature boosting capacity" refers to the ability of a fusing agent to convert electromagnetic radiation, for example, infrared or near-infrared energy into thermal energy. When fusing agent is applied to the powder bed material (e.g. by printing), this temperature boosting capacity can be used to increase the temperature of the treated (e.g. printed) portions of the powder bed material over and above the temperature of the untreated (e.g. unprinted) portions of the powder bed material. The particles of the powder bed material can be at least partially bound or coalesced when the temperature increases to or above the melting point of the polymer.

[0099] As used herein, "melting point" refers to the temperature at which a polymer transitions from a crystalline phase to a pliable, amorphous phase. Some polymers do not have a single melting point, but rather have a range of temperatures over which the polymers soften. When the fusing agent is selectively applied to at

least a portion of the polymer powder, the fusing agent can heat the treated portion to a temperature at or above the melting or softening point, while the untreated portions of the polymer powder remain below the melting or softening point. This allows the formation of a solid 3D printed part, while the loose powder can be easily separated from the finished printed part.

[0100] In one example, the fusing agent can have a temperature boosting capacity from about 10°C to about 70°C for a polymer with a melting or softening point of from about 100°C to about 350°C. If the powder bed is at a temperature within about 10°C to about 70°C of the melting or softening point, then such a fusing agent can boost the temperature of the printed powder up to the melting or softening point, while the unprinted powder remains at a lower temperature. In some examples, the powder bed can be preheated to a temperature from about 10°C to about 70°C lower than the melting or softening point of the polymer. The fusing agent can then be applied (e.g. printed) onto the powder and the powder bed can be irradiated with e.g. infrared or near-infrared light to coalesce the treated (e.g. printed) portion of the powder.

[0101] In some examples, the fusing agent is applied to areas of the bed of build material that has or is intended to be treated with the tailoring agent(s), for example, the first tailoring agent and/or second tailoring agent. The fusing agent may also be applied to areas of the bed of build material where tailoring agent(s) are absent.

Build Material

[0102] The build material (also referred to as “powder bed material”) is in the form of particles or powder.

[0103] The particles may have an average particle size of at least about 10 μm , for example, at least about 15 μm , at least about 20 μm , at least about 30 μm , at least about 40 μm or at least about 50 μm . The particles may have an average particle size of at most about 120 μm , for example, at most about 110 μm , at most about 100 μm , at most about 90 μm , at most about 80 μm or at most about 75 μm .

[0104] In some examples, the build material may have an average particle size of from about 10 to about 120 μm , for example, about 15 to about 110 μm . In some examples, the powder bed material may have an average particle size of from about

20 to about 100 μm , about 30 to about 90 μm , about 40 to about 80 μm or about 50 to about 75 μm . As used in the present disclosure, "average" with respect to properties of particles refers to a volume average unless otherwise specified. Accordingly, "average particle size" refers to a volume average particle size. Additionally, "particle size" refers to the diameter of spherical particles, or to the longest dimension of non-spherical particles. Particle size may be determined by any suitable method, for example, by laser diffraction spectroscopy.

[0105] In accordance with some examples, the volume-based particle size distribution of the build material can be as follows: D50 can be from about 45 μm to about 75 μm , from about 55 μm to about 65 μm , or about 60 μm ; D10 can be from about 20 μm to about 50 μm , from about 30 μm to about 40 μm , or about 35 μm ; and D90 can be from about 75 μm to about 100 μm , from about 80 μm to about 95 μm , or about 90 μm . "D50" is defined as the median particle diameter (by volume). "D10" is defined as the tenth-percentile by volume of powder that is below a given particle size, e.g., from about 20 μm to about 50 μm . "D90" is defined as the ninetieth-percentile by volume of powder that is below a given particle size, e.g., about 75 μm to about 100 μm .

[0106] In one example, the particle size distribution of the build material is as follows:

- a. D50 is from about 45 μm to about 70 μm ,
- b. D10 is from about 20 μm to about 50 μm , and
- c. D90 is from about 75 μm to about 100 μm .

[0107] In certain examples, the particles of the powder bed material can have a variety of shapes, such as substantially spherical particles or irregularly-shaped particles. In some examples, the particles can be capable of being formed into 3D printed parts with a resolution of about 10 to about 120 μm , for example about 20 to about 100 μm or about 20 to about 80 μm . As used herein, "resolution" refers to the size of the smallest feature that can be formed on a 3D printed part. The particles can form layers from about 10 to about 120 μm or 100 μm thick, allowing the fused layers of the printed part to have roughly the same thickness. This can provide a resolution in the z-axis direction of about 10 to about 100 μm . The particles can also

have a sufficiently small particle size and sufficiently regular particle shape to provide about 10 to about 100 μm resolution along the x-axis and y-axis.

[0108] In some examples, the build material comprises a polymer powder, for instance, a thermoplastic polymer powder. The polymer can have a melting or softening point from about 70°C to about 350°C. In further examples, the polymer can have a melting or softening point from about 150°C to about 200°C. A variety of thermoplastic polymers with melting points or softening points in these ranges can be used. For example, the polymer powder can be a polyamide. Suitable polyamides include PA- 6, PA- 9, PA-11, PA-12, PA-66 and PA-612. Other suitable polymer powders include polyethylene powder, wax, thermoplastic polyurethane powder, acrylonitrile, butadiene styrene powder, amorphous polyamide powder, polymethylmethacrylate powder, ethylene-vinyl acetate powder, polyacrylate powder, silicone rubber, polypropylene powder, polyester powder, polycarbonate powder, copolymers of polycarbonate with acrylonitrile butadiene styrene, copolymers of polycarbonate with polyethylene terephthalate polyether ketone powder, polyacrylate powder, polystyrene powder, or mixtures thereof. In an example, the polymer powder can be a polyamide powder, e.g. PA-11 or PA-12. In another example, the polymer powder can be thermoplastic polyurethane.

[0109] As mentioned above, in certain examples, the polymer powder can include a polymer having amino groups as a part of the polymer itself. Such amino groups can crosslink with epoxy groups present, for example, if an epoxy crosslinking agent is employed. This crosslinking can result in an increase in stiffness compared to the polymer in un-crosslinked form.

[0110] An example of a polymer having amino groups is polyamide. Suitable polyamides include PA- 6, PA- 9, PA-11, PA- 12, PA- 66, and PA- 612. In some examples, polymers that include multiple amino groups can include from about 2 to about 1,000 amino groups per molecule. In further examples, the polymer can be made up of polymerized monomer units, wherein the individual monomer units include an amino group or multiple amino groups per monomer unit. Additionally, all or a portion of the amino groups of the monomer units can be available for reaction with epoxide groups after the monomers have polymerized (i.e., the amino groups of the monomers are not consumed during the polymerization of the monomers). Alternatively, the monomers may not include amino groups before polymerization,

but the polymerization reaction may create amino groups on the polymer molecule, wherein the amino groups are available for reaction with epoxide groups.

[0111] In some examples, the polymer powder can be pre-mixed with a separate amine compound or an epoxy compound. If the polymer powder is pre-mixed with an amine compound, an epoxy compound may be used as a crosslinking agent in the tailoring agent. For instance, the epoxy compound can be selectively applied as the tailoring agent to crosslink with the amine compound mixed with the polymer powder. This crosslinking reaction can form a crosslinked polymer network that can increase the stiffness of the build material at desired locations within the 3D printed object. Conversely, if the polymer powder is pre-mixed with an epoxy compound, an amine compound may be used as a crosslinking agent in the tailoring agent. The amine compound can be selectively applied as the tailoring agent to crosslink with the epoxy compound mixed with the polymer powder. This crosslinking reaction can form a crosslinked polymer network that can increase the stiffness of the build material at desired locations within the 3D printed object. In another alternative, the epoxy compound and amine compound are used as separate crosslinking agents. These agents can be selectively applied to the build material at coincident locations to initiate crosslinking at desired locations within the 3D printed object. In some examples, therefore, a first crosslinking agent and a second crosslinking agent may be selectively applied at coincident locations on the bed of build material. These crosslinking agents may react to form a crosslinked polymer network that can increase the stiffness of the build material at the selected locations. The combination of first and second crosslinking agent, therefore, may act as the first or second tailoring agent.

[0112] In examples where the polymer powder is mixed with an epoxy compound, the polymer powder can be mixed with an epoxy compound selected from at least one of the following: 2-ethylhexyl glycidyl ether, phenol glycidyl ether, p-tert-butylphenyl glycidyl ether, dibromo phenyl glycidyl ether, lauryl alcohol, glycidyl ether, resorcinol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol polyglycidyl ether, trimethylolpropane, polyglycidyl ether, pentaerythritol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, diglycidyl terephthalate, diglycidyl o-phthalate, N-glycidyl phthalimide, ethylene glycol diglycidyl ether, polyethylene glycol

diglycidyl ether, tris(4-hydroxyphenyl) methane triglycidyl ether, or combinations thereof.

[0113] In examples where the polymer powder is mixed with an amine compound, the polymer powder can be mixed with an amine compound selected from at least one of the following: aniline sulfonamide, tetraethylenepentamine, dipropylenediamine, diethylaminopropylamine, N-aminoethylpiperazine, bis(2-ethylhexyl)amine, methanediamine methylphenyl diamine, methylphenylenediamine, diaminodiphenyl sulfone, diethylenetriamine, triethylenetetramine, or a combination thereof.

[0114] When the powder bed material includes polymer powder mixed with an amine compound or an epoxy compound, the amount of amine or epoxy compound can be from about 0.1 wt% to about 10 wt% of the total weight of the powder bed material.

[0115] The powder bed material may also include an anti-oxidant. The anti-oxidant can be sterically hindered phenol derivatives. The anti-oxidant can, for example be in the form of fine particles, e.g., 5 μm or less, that are e.g. dry blended with the remaining particles of the powder bed material. The anti-oxidant may be present at a concentration of at least about 0.01 wt %, for example, at least about 0.05 wt %, at least about 0.1 wt % or at least about 0.2 wt %. The anti-oxidant may be present at a concentration of at most about 2 wt %, for example, at most about 1.5 wt % or at most about 1 wt %. In some examples, the anti-oxidant may be present in an amount of e.g., from about 0.01 wt% to about 2 wt% or from about 0.2 wt% to about 1 wt% of the powder bed material.

[0116] The powder bed material can, in some cases, also comprise a filler. The filler can include inorganic particles such as alumina, silica, glass, and/or other similar fillers. In some examples, the filler can include a free-flow filler, anti-caking filler, or the like. Such fillers can prevent packing of the powder bed material, and/or coat the particles of the powder bed material and smooth edges to reduce inter-particle friction, and/or absorb moisture. In some examples, a weight ratio of thermoplastic polymer to filler particles in the powder bed material can be from about 99: 1 to about 1 :2, from about 10: 1 to about 1:1, or from about 5:1 to about :1.

3D Printing

[0117] FIGS. 3-5 illustrate one example method of making a 3D printed object. FIG. 3 shows a 3D printing system 800 that includes a build platform 802 supporting a powder bed of build material powder 804. A partially printed object 806 is made up of fused build material powder in the powder bed. This figure shows a cross-sectional view of the partially printed article and the powder bed. A layer of fresh build material powder is supplied over the top of the partially printed object from a build material supply 808. Fluids (e.g. inkjet inks) are applied to the layer of fresh build material, including fusing agent 810 from a fusing agent jet 812, an epoxy crosslinking agent 820 from a first reactive agent jet 822, an amine crosslinking agent 830 from a second reactive agent jet 832, and a ductility-increasing agent 840 from a third reactive agent jet 842. The fluid jets are moveable within the printing system so that the fluid jets can move across the powder bed to apply the fluids in specific, desired locations. The system also includes an electromagnetic energy source 852.

[0118] FIG. 4 shows the 3D printing system 800 after the fluids have been jetted onto portions of the build material powder 804. An upper layer of build material includes areas jetted with epoxy crosslinking agent 820 and amine crosslinking agent 830, and areas jetted with ductility-increasing agent 840. These agents are selectively applied to produce an architecture or structure (e.g. microstructure) in the 3D printed object comprising crosslinked regions of lower ductility (stiff zones) interspersed with regions of higher ductility (ductile zones). Although an epoxy crosslinking agent 820, an amine crosslinking agent 830 and a ductility-increasing agent 840 can be used to form the structure in this example, it should be understood that, in some examples, the structure can be produced with fewer agents. For example, the ductility-increasing agent 840 may be used to soften the polymer in selected regions, such that regions of higher ductility can be interspersed with stiffer regions that remain untreated by the ductility-increasing agent 840. In another example, the epoxy crosslinking agent 820 amine crosslinking agent 830 may be used to selectively crosslink selected areas of the powder bed to form stiffer zones interspersed with ductile zones that remain untreated by the combination of epoxy 820 and amine crosslinking agent 830. In yet another example, just one of the epoxy crosslinking agent 820 or amine crosslinking agent 830 may be

required, e.g. if the build material already contains a corresponding epoxy or amino functional group.

[0119] FIG.5 shows the 3D printing system 800 after fusing the upper layer to form a 3D printed object 1006. Fusing can be carried out by exposing the powder bed to electromagnetic energy 950 from an energy source 852, such as an infrared lamp. Once fused, the object 1006 can be removed from the powder bed and cleaned to remove loose powder bed material from the article.

[0120] Suitable fusing lamps for use in the 3D printing system can include commercially available infrared lamps and halogen lamps. The fusing lamp can be a stationary lamp or a moving lamp. For example, the lamp can be mounted on a track to move horizontally across the powder bed. Such a fusing lamp can make multiple passes over the bed depending on the amount of exposure used to fuse individually printed layer. The fusing lamp can be configured to irradiate the entire powder bed with a substantially uniform amount of energy. This can selectively fuse the portions printed with the fusible fluid while leaving the unprinted portions of the polymer powder below the fusing temperature.

[0121] In one example, the fusing lamp can be matched with the radiation absorber in the fusing agent so that the source emits wavelengths of light that match the peak absorption wavelengths of the radiation absorber. A radiation absorber with a narrow peak at a particular near-infrared wavelength can be used with an electromagnetic radiation fusing source that emits a narrow range of wavelengths at approximately the peak wavelength of the fusing agent. Similarly, a radiation absorber that absorbs a broad range of near-infrared wavelengths can be used with an electromagnetic radiation fusing source that emits a broad range of wavelengths. Matching the radiation absorber and the electromagnetic radiation fusing source in this way can increase the efficiency of fusing the polymer particles with the fusing agent printed thereon, while the unprinted polymer particles do not absorb as much light and remain at a lower temperature.

[0122] In some examples, the three-dimensional printing system can also include preheaters for preheating the polymer powder to a temperature near the fusing temperature. In one example, the system can include a print bed heater to heat the print bed during printing. The preheat temperature used can depend on the type of polymer used. In some examples, the print bed heater can heat the print bed to a temperature from about 50 °C to about 250 °C. The system can also include a

supply bed, where polymer particles can be stored before being spread in a layer onto the print bed. The supply bed can have a supply bed heater. In some examples, the supply bed heater can heat the supply bed to a temperature from about 80 °C to about 140 °C.

[0123] Depending on the amount of radiation absorber present in the polymer powder, the absorbance of the radiation absorber, the preheat temperature, and the fusing temperature of the polymer, an appropriate amount of irradiation can be supplied from the electromagnetic energy source or fusing lamp. In some examples, the fusing lamp can irradiate individual layers from about 0.1 to about 10 seconds per pass. In further examples, the fusing lamp can move across the powder bed at a rate of about 2.5 cm per second to about 130 cm per second to fuse the individual layers. In still further examples, the fusing lamp can move across the powder bed at a rate of about 15 cm per second to about 50 cm per second.

[0124] In various examples, the fusing agent 810, epoxy crosslinking agent 820 (if used), amine crosslinking agent reactive agent 830 (if used), and ductility-increasing agent 840 (if used) can be applied to the powder bed material in any order.

[0125] In one example, the fusing agent, epoxy crosslinking agent 820 and the amine crosslinking agent 830 can be applied to the powder bed material before irradiating the powder bed material 804. In another example, the fusing agent 810 can be applied to the powder bed material first. The powder bed material 804 can then be irradiated to soften the polymer particles that were printed with the fusing agent. After melting the polymer particles, the epoxy crosslinking agent 820 and amine crosslinking agent 830 can be applied. In a particular example, the powder bed 804 can then be irradiated a second time. The additional heating from irradiating the powder bed 804 a second time can help cure the epoxy and amine compounds.

[0126] In further examples, additional heating can help complete the curing reaction between the epoxy compound and the amine compound. In some examples, the completed 3D printed object can be post-cured by heating in an oven or similar heater for a period of time. In one example, the 3D printed object can be post-cured at a temperature from about 100 °C to about 200 °C for a time of from about 30 minutes to about 24 hours. This can allow for more reaction between the epoxy and amine compounds to form more crosslinking and strengthen selected regions of the 3D printed object.

[0127] FIGS. 6 to 9 are schematic drawings that show examples of structures that can be printed using examples of the methods of the present disclosure. FIG. 6 depicts a structure (e.g. a microstructure) comprising regions of relatively higher ductility (ductile zones) interspersed with regions of relatively lower ductility (stiff zones). The stiff zones 10 are localized regions dispersed in a continuous matrix of ductile zones 12. The stiff zones 10 provide stiffness and strength to the structure (e.g. microstructure), while the ductile zones 12 reduce the risk of crack propagation. Thus, in the event of a fracture in a stiff zone 10, crack propagation is limited by the softer nature of the ductile zone 12. Overall, therefore, the structure can provide a desirable balance of strength and toughness.

[0128] FIG. 7 shows an alternative structure (e.g. a microstructure) comprising regions of relatively higher ductility (ductile zones) interspersed with regions of relatively lower ductility (stiff zones). In this example, the structure is a cellular structure (e.g. microstructure). The cell walls constitute the stiff zones 10. The regions between the cell walls constitute the ductile zones 12. In the event of a fracture in a stiff zone 10, crack propagation is limited by the softer nature of the ductile zone 12. Overall, therefore, the structure can provide a desirable balance of strength and toughness. In this example, the cells have a triangular shape. However, the cells may have any shape, for example, they may have a hexagonal shape.

[0129] FIG. 8 shows an alternative structure comprising regions of relatively higher ductility (ductile zones) interspersed with regions of relatively lower ductility (stiff zones). In this example, the ductile zones 12 are present along a path 14 that provides controlled crack propagation. The stiff zones 10, 10' are interspersed by the ductile zones 12 along this path. As shown in FIG. 9, this example structure can be used to control cracking within a 3D printed object e.g. an attachment bracket 16. In FIG. 9, the attachment bracket is coupled to two parts 18, 20 via rings 22. Stress would normally concentrate in the region 24, where the rings 22 are coupled to the holes of the printed bracket 16. Thus, if fatigue cracking occurs, cracks are more likely appear in this region 24 of stress concentration, causing the parts 18, 20 to become completely detached. By providing ductile zones 12 along the path 14, cracking can be controlled along the path, avoiding failure at the holes and reducing the risk of the parts 18, 20 becoming completely detached from the bracket 16.

Definitions

[0130] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise.

[0131] As used herein, the term "about" is used to provide flexibility to a range endpoint by providing that a given value may be "a little above" or "a little below" the endpoint. The degree of flexibility of this term can be dictated by the particular variable and can be determined based on experience and the associated description herein.

[0132] As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each individual member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a *de facto* equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary.

[0133] Concentrations, dimensions, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include the numerical values explicitly recited as the limits of the range, and also to include all the individual numerical values or sub-ranges encompassed within that range as if the numerical value and sub-range is recited. For example, a weight ratio range of about 1 wt% to about 20 wt% should be interpreted to include the explicitly recited limits of 1 wt% and about 20 wt%, and also to include individual weights such as 2 wt%, 11 wt%, 14 wt%, and sub-ranges such as 10 wt% to 20 wt%, 5 wt% to 15 wt%, etc.

[0134] As a further note, in the present disclosure, it is noted that when discussing the fluids, materials, and methods described herein, these discussions can be considered applicable to the various examples, whether or not they are explicitly discussed in the context of that example. Thus, for example, in discussing details about the methods of making 3D printed objects, such discussion also refers to the 3D printing kits, and *vice versa*.

[0135] As used herein, a “kit” may comprise one or more components where the different components are contained in one or more containers, separately or in any combination, prior to and during printing but these components can be combined together during printing. The containers can be any type of a vessel, box, or receptacle made of any material.

[0136] Where selective jetting of an agent is performed based on a 3D object model, the 3D object model may comprise at least one of: a 3D object model created using Computer Aided Design (CAD) or similar software; or a file, for example, a Standard Tessellation Language file generated based on output of the CAD software, providing one or more processors of a 3D printer with instructions to form the 3D object

EXAMPLES

Example 1 - Epoxy Crosslinking Agent and Amino Crosslinking Agent

[0137] An epoxy crosslinking agent having the composition shown in Table 1 below was prepared:

Ingredient Type	Specific Ingredient	Concentration (wt %)
Epoxy	1:1 weight ratio of ethyleneglycol diglycidyl ether and triphenylolmethane triglycidyl ether	20
Humectant	Diethylene glycol butyl ether	40
Liquid Carrier	Ink carrier containing water, humectant, surfactant, biocide and anti-kogation agent	40

[0138] An amino crosslinking agent was prepared having the composition shown in Table 2 below:

Ingredient Type	Specific Ingredient	Concentration (wt %)
Amine	4,4-diaminodiphenyl sulfone	15
Humectant	2-pyrrolidone	45
Liquid Carrier	Ink carrier containing water, humectant, surfactant, biocide and anti-kogation agent	10
Solvent	Water	30

Example 2 – Ductility-increasing agent

[0139] A ductility-increasing agent was produced from the stock solution shown in Table 3 below:

Ingredient Type	Specific Ingredient	Concentration (wt %)
Plasticizer	Methyl-benzene sulfonamide	40
Humectant	2-pyrrolidone	40
Liquid Carrier	Water-based solvent	20

[0140] The above stock solution was mixed in a 1:1 weight ratio with the composition shown in Table 4 below to form the ductility-increasing agent:

Ingredient Type	Specific Ingredient	Concentration (wt %)
Co-solvent	1-methyl-2-pyrrolidone	40
Anti-kogation agent	CRODAFOS® O3A	1
Surfactants	Surfonyl® SEF	1.5
	Capstone®FS-35	0.10
Scale inhibitor/Anti-deceleration agent	DOWFAX™ 2A1	0.2
Chelating agent	TRILON® M	0.08
Biocide	PROXEL®GXL	0.36
	Water	Balance

Example 3 – 3D printing

[0141] In this example, a 3D printing method according to an example of the present disclosure was used to print an impact bar having a honeycomb microstructure and a dog bone having the same honeycomb microstructure. Figure 10 is a schematic drawing of the impact bar that was printed. Figure 11 is a schematic drawing of the impact bar that was printed.

[0142] The powder bed material was a nylon-12 (polyamide-12 or "PA12") powder with a particle size ranging from about 10 microns to about 100 microns. The samples were formed by fusing together individual layers of polymer particles using a fusing agent that included a near IR dye as the radiation absorber.

[0143] The fusing agent was first jetted onto the powder bed. A backward pass was then performed in which the fusing lamp of the test bed was activated to heat the powder bed and melt the particles that were printed with the fusing agent. A second forward pass was then performed. In this forward pass, the epoxy crosslinking agent and the amino crosslinking agent of Example 1 agent were jetted onto the molten/softened polymer particles to delineate the hexagonal walls of the microstructure. The ductility-increasing agent of Example 2 was jetted onto the molten/softened polymer particles in the regions within the hexagonal walls. A second backward pass was then performed during which the fusing lamp was activated to heat the powder bed material to cause the epoxy and amine compounds to react. Fresh powder bed material was then applied and the process repeated until the desired thickness (4 mm) of the part was achieved.

[0144] When the 3D printed dog bone was back lit, the hexagonal walls of the microstructure appeared darker than the regions within the walls. This confirmed that the walls of the hexagonal structure were formed of a different material (crosslinked polymer) from the material (plasticized polymer) within the walls. (The material within the walls was more translucent because of the presence of plasticizer).

[0145] Impact testing was conducted on the impact bar, and the impact resistance values were recorded and compared to a control impact bar formed from the baseline PA12 with fusing agent (only). The average (over four samples) impact resistance value for the impact bar having the hexagonal microstructure was 6.33

kJ/m^2 . In comparison, the average (over four samples) impact resistance value for control impact bars formed from the baseline PA12 and fusing agent (only) was 3.52 kJ/m^2 .

[0146] Microscope images of the impact crack planes of the impact bars according to this example were compared with microscope images of the impact crack planes of the control impact bars. The microscope images of the impact crack planes of the impact bars according to this example showed longer crack planes and more chevron marks, demonstrating an increased propensity to absorb energy and an improved resistance to crack propagation.

Claims

1. A three-dimensional (3D) printing materials kit comprising:
a first tailoring agent comprising at least one crosslinking agent;
a second tailoring agent comprising at least one plasticizer, and
a fusing agent.
2. The kit according to claim 1, wherein the crosslinking agent comprises a functional group selected from at least one of epoxy, amine, isocyanate, phosphine and aldehyde.
3. The kit according to claim 2, wherein the crosslinking agent comprises an epoxy functional group and is selected from at least one of: 2-ethylhexyl glycidyl ether, phenol glycidyl ether, p-tert-butylphenyl glycidyl ether, dibromo phenyl glycidyl ether, lauryl alcohol glycidyl ether, resorcinol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol polyglycidyl ether, sorbitol polyglycidyl ether, diglycidyl terephthalate, diglycidyl-o-phthalate, N-glycidyl ether, and tris(4-hydroxyphenyl) methane triglycidyl ether.
4. The kit according to claim 2, wherein the crosslinking agent comprises an amine functional group and is selected from at least one of: aniline, sulphonamide, tetraethylenepentamine, dipropylenediamine, diethylaminopropylamine, N-aminoethylpiperazine, bis(2-ethylhexyl)amine, methanediamine methylphenyl diamine, methylphenylenediamine, diaminodiphenyl sulfone, diethylenetriamine, and triethylenetetramine.
5. The kit according to claim 2, wherein the first tailoring agent comprises a first crosslinking agent comprising an epoxy functional group, and a second crosslinking agent comprising an amine functional group.
6. The kit according to claim 1, wherein the plasticizer is selected from at least one plasticizer selected from: 2-pyrrolidone, dimethyl sulfoxide, methyl 4-hydroxybenzoate, dioctyl phthalate, N-methyl-2-pyrrolidone, N-2-

hydroxyethyl-2-pyrrolidone, urea, ethylene carbonate, propylene carbonate, lactones, diethylene glycol, triethylene glycol, tetraethylene glycol, decalin, gamma-butyrolactone, dimethylformamide, phenylmethanol, dimethyl sulfoxide (DMSO), 2-methyl-benzene sulphonamide, 4-methyl benzene, 2-methyl-benzene sulphonamide, N-butylbenzenesulfonamide, N-ethylbenzenesulfonamide, N-propylbenzenesulfonamide, N-butyl-N-dodecylbenzenesulfonamide, N,N-dimethylbenzenesulfonamide, p-methylbenzenesulfonamide, o/p-toluene sulphonamide, p-toluene sulphonamide, 2-ethylhexyl-4-hydroxybenzoate, hexadecyl-4-hydroxybenzoate, 1-butyl-4-hydroxybenzoate, dioctyl phthalate, diisodecyl phthalate, di-(2-ethylhexyl) adipate, and tri-(2-ethylhexyl) phosphate.

7. The kit according to claim 1, which further comprises a build material comprising polymer particles.

8. The kit according to claim 8, wherein the polymer of the build material is selected from at least one of polyamide, polyolefin, thermoplastic polyurethane, polyester, polycarbonate, polyether ketone, polyacrylate and polystyrene.

9. A printed structure comprising regions of relatively higher ductility and regions of relatively lower ductility, wherein the regions of relatively higher ductility are interspersed by the regions of relatively lower ductility, and wherein the regions of relatively lower ductility are formed from a crosslinked polymer and/or a polymer composition comprising a reinforcing filler, and/or wherein the regions of relatively higher ductility are formed from a polymer composition comprising a plasticizer.

10. The structure according to claim 9, which is a cellular microstructure cellular structure, wherein the cell walls form the regions of relatively low ductility, and/or regions between the cell walls form the regions of relatively high ductility.

11. A method for printing a three-dimensional (3D) printed object, the method comprising:
selectively applying a first tailoring agent to a build material;
and
exposing the build material to radiation, thereby fusing at least part of the build material to form a layer,
wherein the first tailoring agent comprises a reinforcing agent or a ductility-increasing agent, and
wherein the first tailoring agent is selectively applied to form regions of relatively higher ductility interspersed with regions of relatively lower ductility in the 3D printed object.

12. The method according to claim 11, which further comprises:
selectively applying a second tailoring agent to the build material;
wherein the first tailoring agent comprises one of the reinforcing agent and a ductility-increasing agent, and the second tailoring agent comprises the other of the reinforcing agent and ductility-increasing agent, and
wherein the first tailoring agent and second tailoring agent are selectively applied to form the regions of relatively higher ductility interspersed with the regions of relatively lower ductility.

13. The method according to claim 12, wherein the object has a structure that comprises a cellular structure, and wherein a reinforcing agent is selectively applied to form cell walls having a relatively lower ductility, and/or wherein a ductility-increasing agent is applied to form regions having a relatively higher ductility between the cell walls.

14. The method according to claim 11, wherein the reinforcing agent comprises a crosslinking agent or a reinforcing filler.

15. The method according to claim 14, wherein the reinforcing agent comprises a reinforcing filler and the reinforcing filler is selected from particles of at least one of boron, boron nitride materials, silica, alumina, titanium dioxide, glass, carbon nanomaterials, montmorillonite, talc, basalt,

silicon carbide, metal carbide, metal carbide, silicon nitride, metal nitride, polyaramid, metal, metal alloy, diamond, boron carbide, mica, wollastonite, and ceramic.

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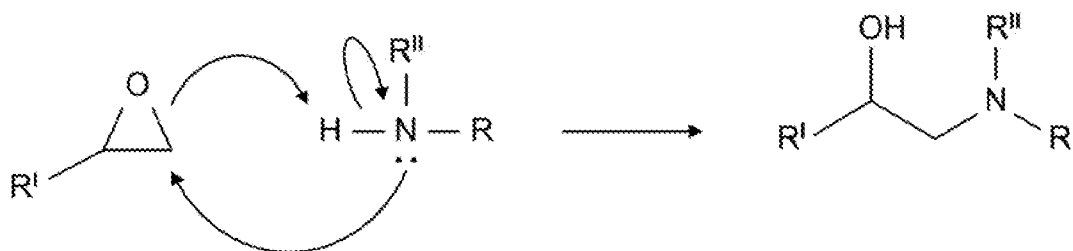


FIG. 1

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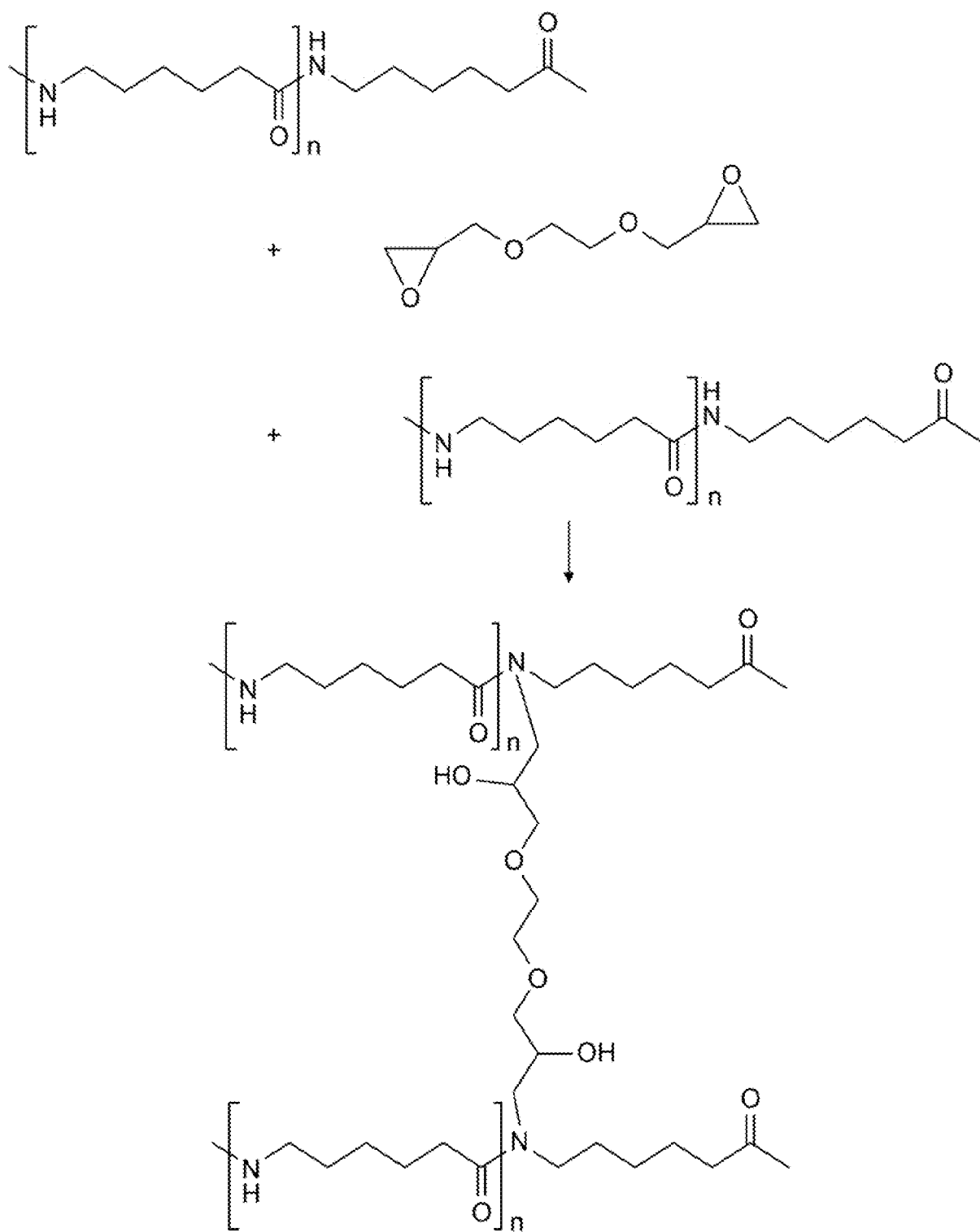


FIG. 2

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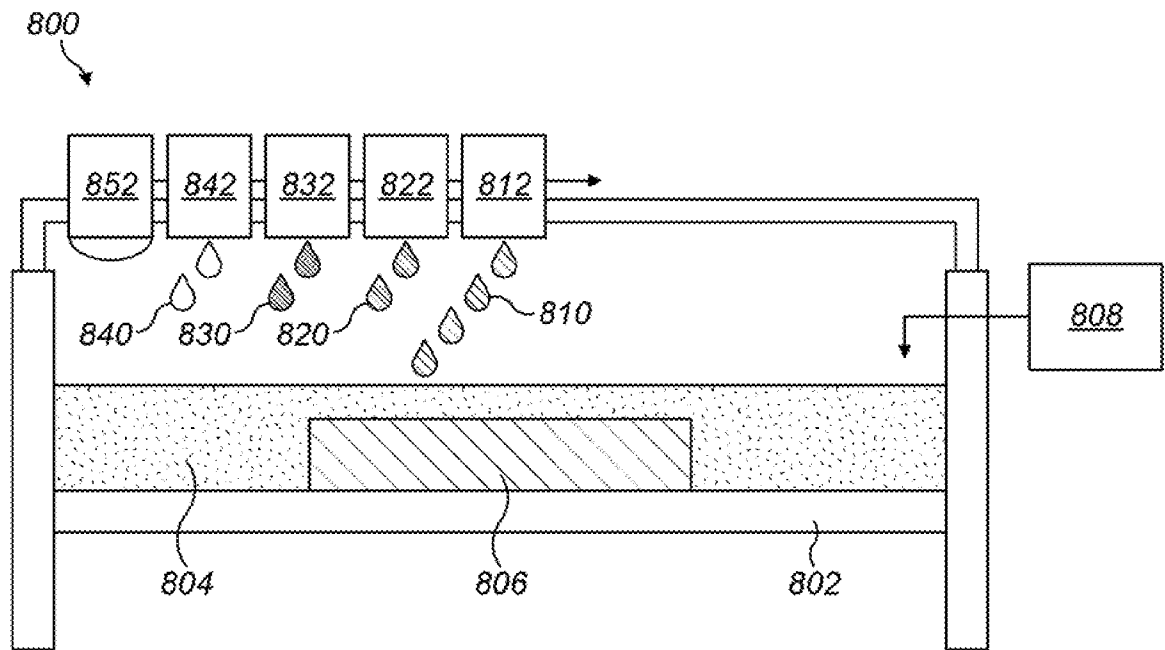


FIG. 3

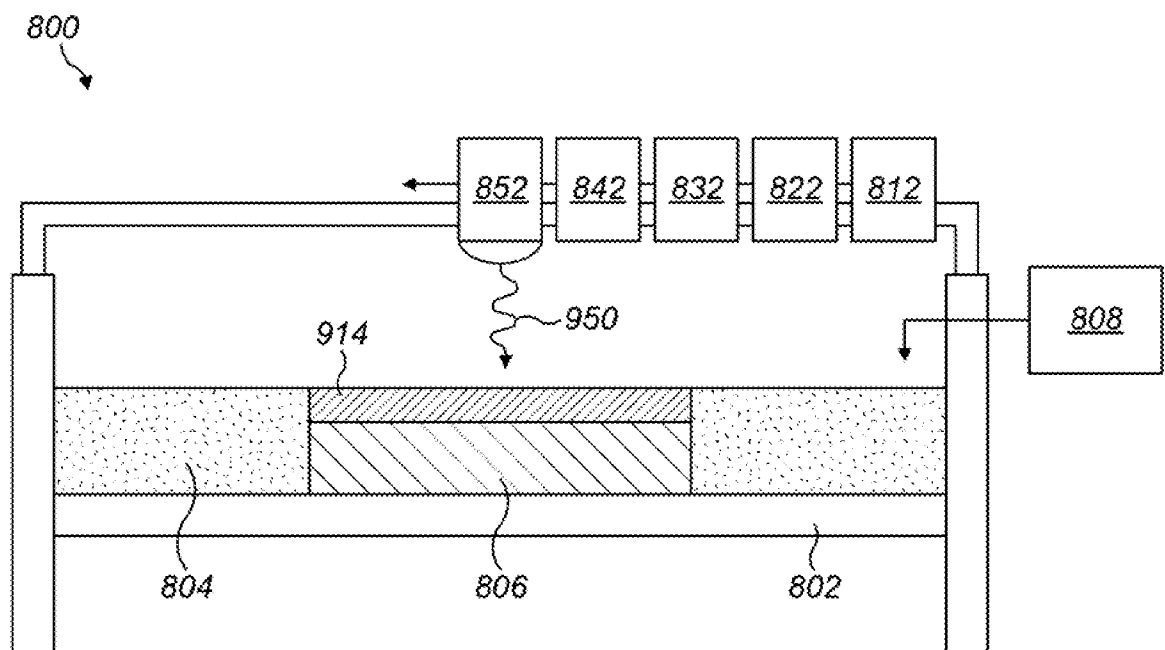


FIG. 4

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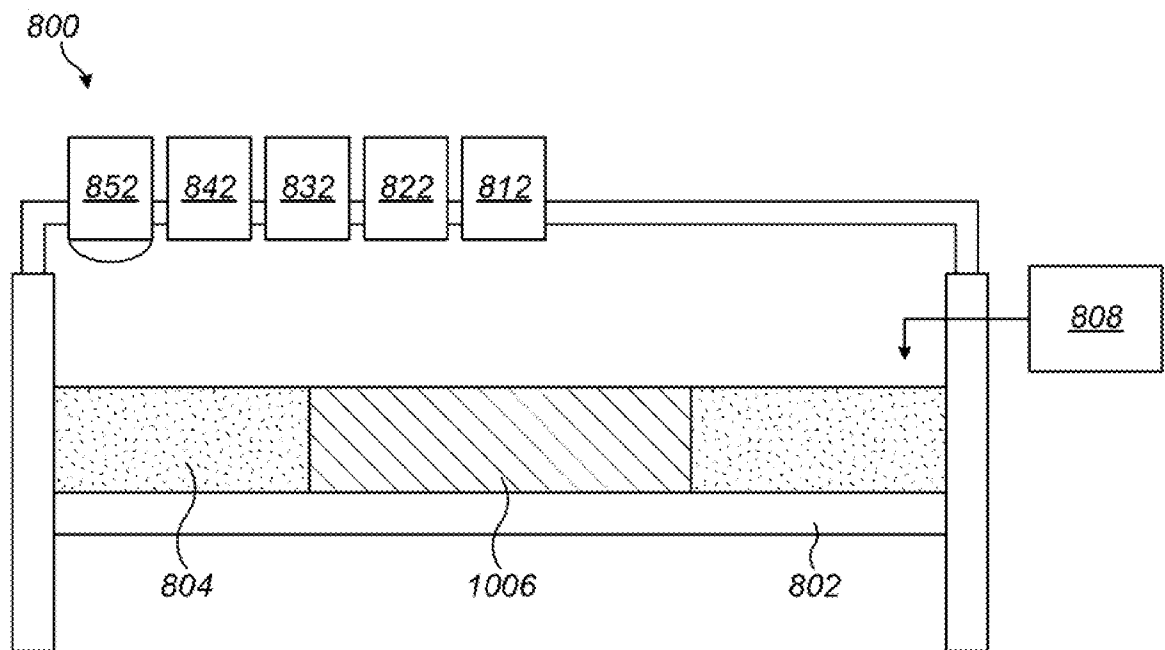


FIG. 5

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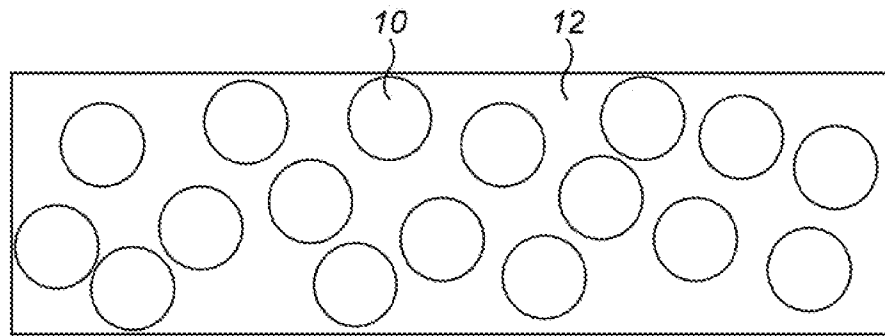


FIG. 6

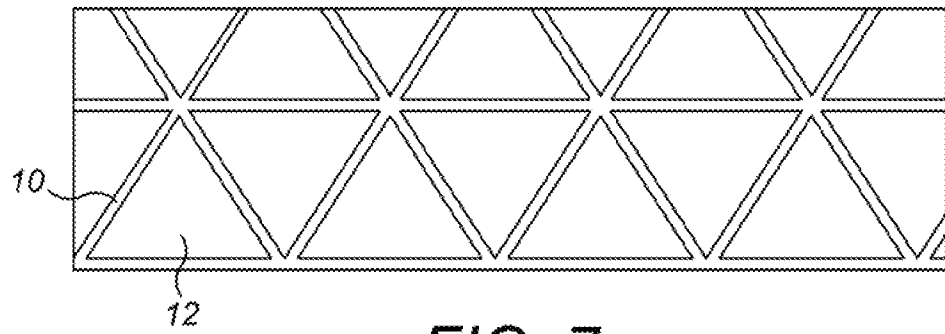


FIG. 7

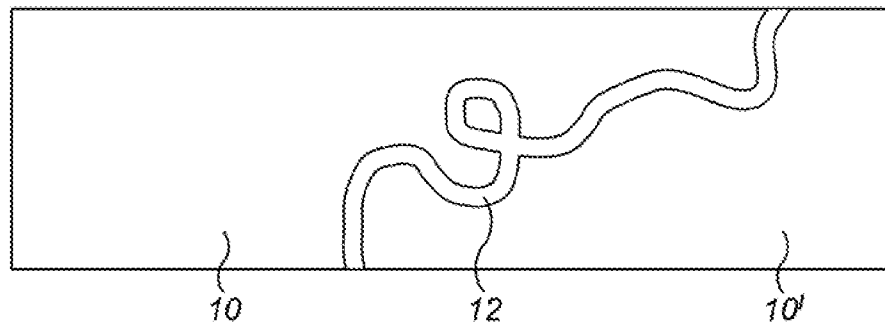


FIG. 8

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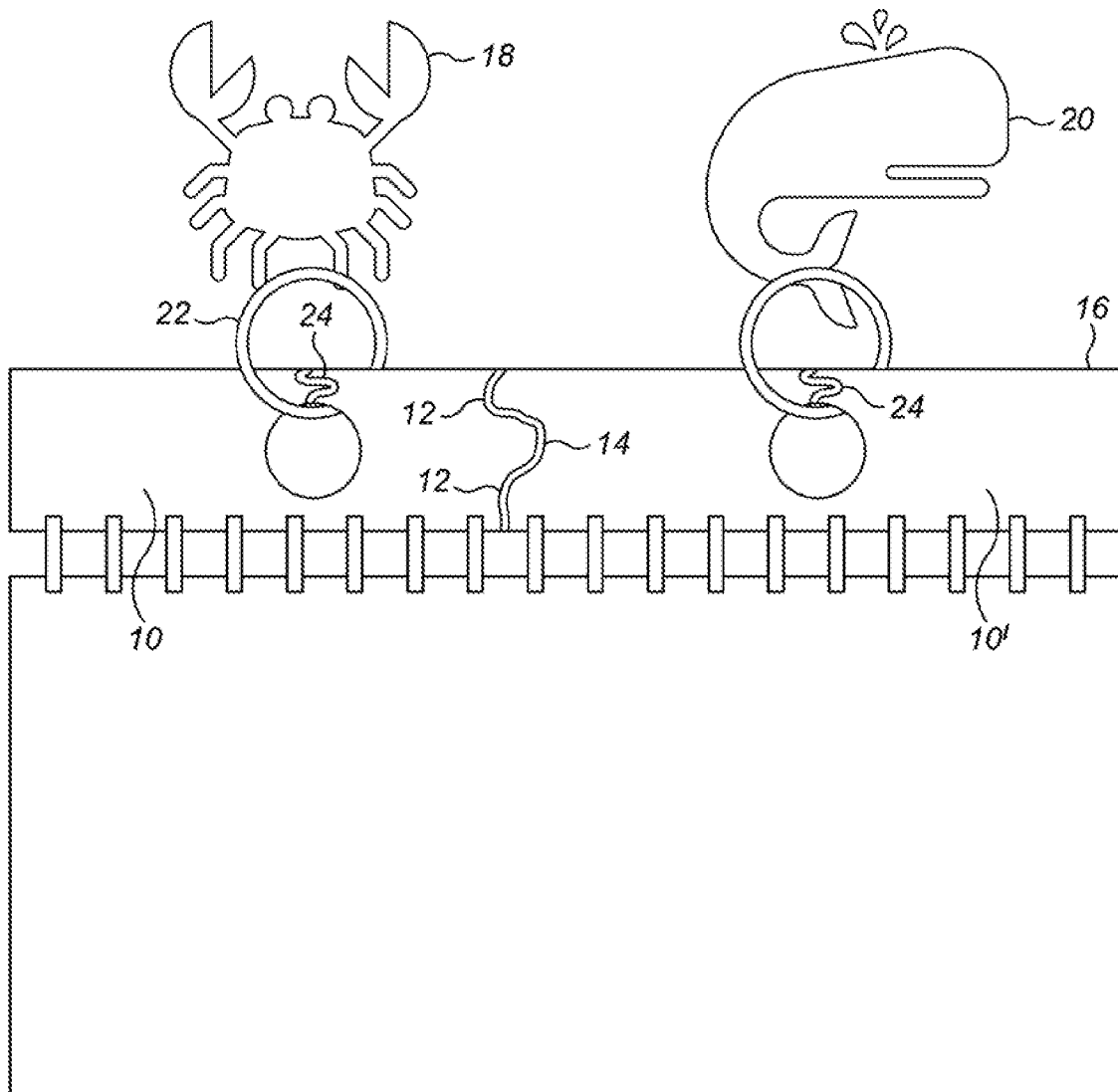


FIG. 9

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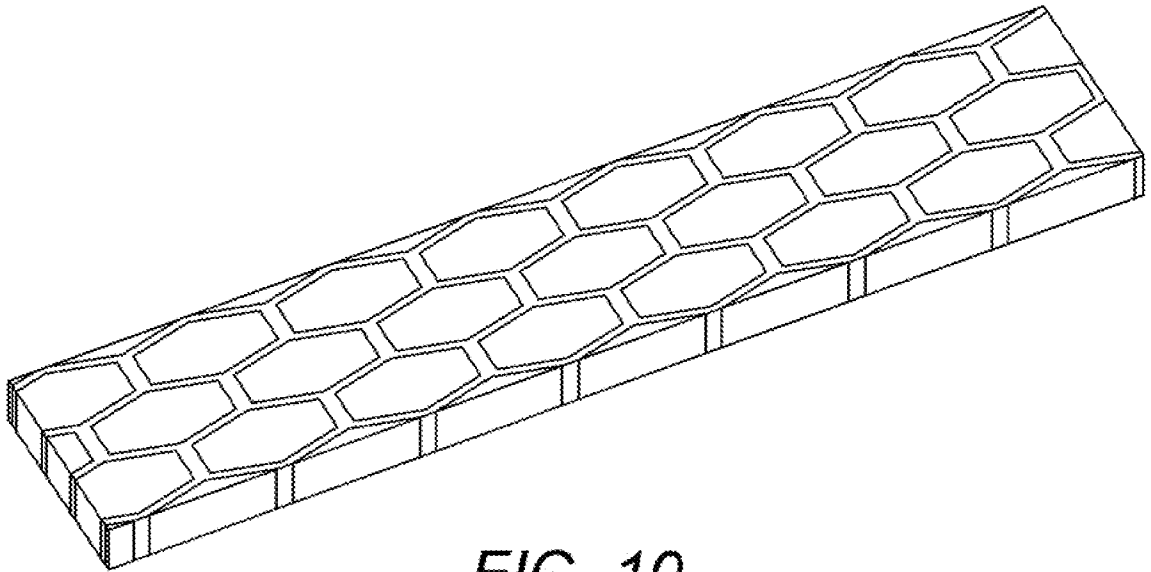


FIG. 10

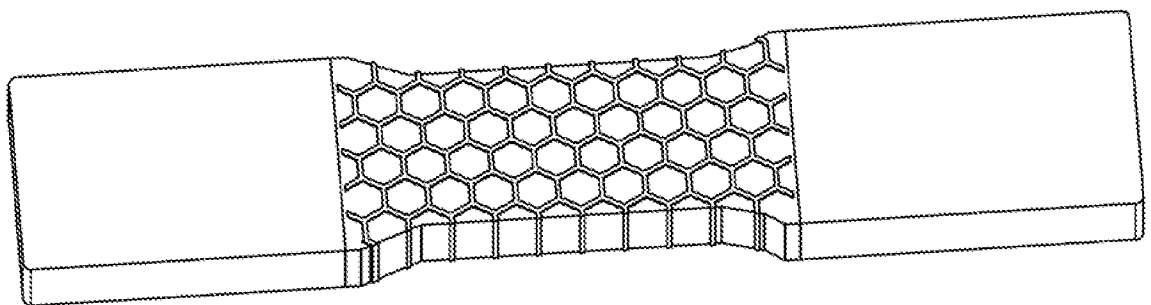


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2019/055501

A. CLASSIFICATION OF SUBJECT MATTER		
<i>B29C 64/165 (2017.01)</i> <i>C08K 5/17 (2006.01)</i> <i>C08K 5/1515 (2006.01)</i> <i>B33Y 70/00 (2015.01)</i> <i>B33Y 80/00 (2015.01)</i> <i>B33Y 10/00 (2015.01)</i>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B33Y 70/00, B33Y 80/00, B33Y 10/00, B29C 64/165, C08K 5/17, C08K 5/1515		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
PatSearch (RUPTO internal), USPTO, PAJ, K-PION, Espacenet, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/196330 A1 (HEWLETT-PACKARD DEVELOPMENT COMPANY, L.P.) 16.11.2017, paragraphs [0016]-[0030], [0052]-[0054], [0086], [0108],	1, 5-9, 11, 12, 14, 15
Y	[0116], [0122]-[0133], [0136], examples 3-5, fig. 1A-1D, 6A-6C,	2-4
A	claims 1, 6, 7, 9, 11	10, 13
Y	CN 109438746 A (HE YU) 08.03.2019, paragraph [0032]	2, 3
Y	CN 108148249 A (CHENGDU NEW KELI CHEM SCI CO) 12.06.2018, paragraph [0010]	4
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
*	Special categories of cited documents:	
“A”	document defining the general state of the art which is not considered to be of particular relevance	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E”	earlier document but published on or after the international filing date	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O”	document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search		Date of mailing of the international search report
16 December 2019 (16.12.2019)		23 January 2020 (23.01.2020)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer D. Ivanova Telephone No. 8(495)-531-64-81

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2019/055501

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/195974 A1 (APEX BIOMEDICAL COMPANY, LLC) 08.12.2016, paragraph [0028], claims 1, 13	1-15
A	WO 2019/005044 A1 (HEWLETT-PACKARD DEVELOPMENT COMPANY, L.P.) 03.01.2019, paragraphs [0009], [0012], [0013], [0040]	1-15