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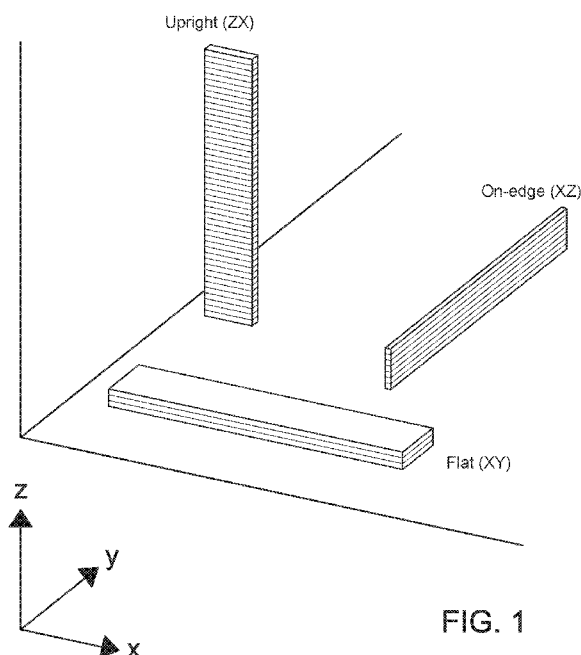


FIG. 1

(57) Abstract: The present disclosure provides improved manufacturing methods for ABS -containing filaments that exhibit reduced beard growth during manufacturing and improved color qualities in additive-manufactured articles formed from the filaments.

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IMPROVED ABS RESIN COMPOSITION FOR ADDITIVE MANUFACTURING

TECHNICAL FIELD

[0001] The present disclosure relates to the field of additive manufacturing and to the field of acrylonitrile butadiene styrene resins.

BACKGROUND

[0002] Fused filament fabrication (FFF) is an additive manufacturing technology that uses thermoplastic monofilaments, pellets, or metal wires to build parts or articles in a layer by layer manner. In some aspects, material from a spool is fed by an extrusion nozzle that is heated to melt the material, which melted material is then deposited by a controlled mechanism in horizontal and vertical directions.

[0003] ABS (acrylonitrile-butadiene-styrene) resins are a suitable choice for three dimensional (3D) printing applications. For some 3D printing applications, an important color in the finished article is white, specifically for FFF. Existing resins are, however, limited by their tendency to experience so-called beard growth (also known as die lip build-up) during extrusion of 3D filaments and/or during printing.

[0004] Beard growth is a phenomenon characterized by chunks of resin that accumulate around the die and then break off on the surface of the filament, or become enveloped by the filament. The defective filament, characterized by larger or variable filament diameter, then has the disadvantages of, variously, (1) effecting incorrect or uneven filament feed, (2) causing printer jams in the 3D printing system, and (3) negatively affecting printed part performance.

[0005] During the printing of a part, similar resin build-up can occur on the printer nozzle through which the filament is extruded. This may present the disadvantages of the filament fragments breaking off on the surface of the part or becoming enveloped in the part. Additionally, in some cases, the nozzle build-up may result in inability to print since the printer may sense the build-up on the nozzle as a clog, and therefore stop the print job.

[0006] In addition, the problem of beard growth can be exacerbated by the presence in the resin of pigments that are necessary for colored resin, for example, carbon black and titanium dioxide. Accordingly, the available color space for 3D printed parts that include ABS is limited by the pigment levels that can be tolerated. Low pigment loadings, however, may result in resins that are not truly opaque, are not as strongly colored as they otherwise could be, and/or are subject to the increased resin color variations that stem from base resin color variability and the

effectiveness (or lack thereof) of equipment cleaning procedures. Accordingly, there is a long-felt need in the art for compositions with reduced beard growth and that accommodate increased colorant loadings.

SUMMARY

[0007] In one aspect, the present disclosure provides polymeric compositions for additive manufacturing, comprising: acrylonitrile-butadiene-styrene (ABS) resin; styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 grams per mole (g/mol) as measured by gel permeation chromatography (GPC) with polystyrene standards; a population of acid scavenger particles; a lubricant; optionally, one or more of an antioxidant, a colorant, and a stabilizer; and the polymeric composition being in a filament or a pellet form.

[0008] In another aspect, the present disclosure provides methods, comprising additively manufacturing at least a portion of an article using a composition according to the present disclosure.

[0009] Also provided are additively-manufactured articles made according to the disclosed methods.

[0010] Additionally disclosed are systems, the systems comprising a dispenser having disposed within an amount of a polymeric composition according to the present disclosure; and a substrate, one or both of the dispenser and substrate being capable of controllable motion relative to the other.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 depicts exemplary additive manufacturing (for example, FFF) part orientations (upright, on edge, and flat) with reference to X, Y, and Z axes; as shown, parts may be built in the XY (flat), XZ (on edge), or ZX (upright) orientations.

[0012] FIG. 2 provides an exemplary filament (raster) fill pattern for a part layer made by a filament-based additive manufacturing process; this pattern may apply to any print orientation. The parameters shown in FIG. 2 are known to those of skill in the art. In FIG. 2, layer thickness (not labeled) is the thickness of the layer deposited by the nozzle. Raster angle (not labeled) is the direction of raster with respect to the contours. Raster-to-raster air gap is the distance between two adjacent deposited filaments in the same layer. The perimeter (contours) is the number of filaments deposited along the outer edge of a part. Filament (raster) width is the width of the filament deposited by the nozzle. The print head may operate such that the print

head changes its angle of travel with each successive layer, for example, by 45 degrees (45 °) with each successive layer, such that roads on successive layers are criss-crossed relative to one another.

[0013] FIG. 3 provides a tabular summary of experimental results.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0014] The present disclosure may be understood more readily by reference to the following detailed description taken in connection with the accompanying figures and examples, which form a part of this disclosure. It is to be understood that this disclosure is not limited to the specific devices, methods, applications, conditions or parameters described and/or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of the disclosed subject matter.

[0015] It is to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term “comprising” can include the embodiments “consisting of” and “consisting essentially of.” Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined herein.

[0016] Also, as used in the specification including the appended claims, the singular forms “a,” “an,” and “the” include the plural, and reference to a particular numerical value includes at least that particular value, unless the context clearly dictates otherwise. Any documents mentioned herein are incorporated herein in their entireties for any and all purposes.

[0017] The term “plurality”, as used herein, means more than one. When a range of values is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. All ranges are inclusive and combinable. When referring to a value, the term “about” means the value and all other values within 10% of the value. For example, “about 10” means from 9 to 11 and all intermediate values, including 10. Weight percentages should be understood as not exceeding a combined weight percent value of 100 wt. %. Where a standard is mentioned and

no date is associated with that standard, it should be understood that the standard is the most recent standard in effect on the date of the present filing.

[0018] Ranges can be expressed herein as from one value (first value) to another value (second value). When such a range is expressed, the range includes in some aspects one or both of the first value and the second value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0019] As used herein, the terms “about” and “at or about” mean that the amount or value in question can be the designated value, approximately the designated value, or about the same as the designated value. It is generally understood, as used herein, that it is the nominal value indicated $\pm 10\%$ variation unless otherwise indicated or inferred. The term is intended to convey that similar values promote equivalent results or effects recited in the claims. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but can be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is “about” or “approximate” whether or not expressly stated to be such. It is understood that where “about” is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0020] The present disclosure provides techniques for using improved ABS resin compositions for filament production in additive manufacturing (for example 3D printing) applications, specifically fused deposition modeling (FFF). These compositions exhibit, variously, improved filament extrusion and printing ability, as a result of reduced bead growth (die lip or nozzle build-up), and a tolerance for higher colorant loading levels that allow a wider color palette and increased color consistency.

[0021] The disclosed filaments also allow for higher loading levels of other materials, for example, conductive materials such as copper chromite and other conductive materials. This ability to accommodate higher loading in turn enables the use of the disclosed filaments and methods in laser-directed structuring, a process which allows for the formation of a conductive pathway in an article.

[0022] These disclosed compositions also permit more robust printing with fewer printer jams and production of more uniform, higher quality printed parts, which can lead to improved part performance. In addition, the use of the disclosed compositions provides a number of ways to improve the bead growth or nozzle build-up tendency of ABS resins in 3D printing filament applications and methods of manufacture.

[0023] The disclosed technology differs from existing approaches in a number of ways. Some illustrative differences include, for example: (1) use of a magnesium oxide stabilizer – in some aspects – of relatively small particle size (for example, less than (<) 10 micrometers (microns), or even less than 8 microns); (2) an increased level of ethylene bisstearamide wax or other lubricant, for example, more than, for example, 0.5 parts per hundred (pph) or even 1.0 pph; (3) incorporation of hindered phenol anti-oxidant (for example, Lowinox™ CPL) and, in some aspects, a secondary anti-oxidant phosphite stabilizer (for example, Irgafos™168).

[0024] Illustrative Aspects

[0025] The following aspects of the disclosed invention are illustrative only and do not limit the scope of the present disclosure.

[0026] Aspect 1. A polymeric composition, comprising: acrylonitrile-butadiene-styrene (ABS) resin; styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards; a population of acid scavenger particles; a lubricant; optionally, one or more of an antioxidant, a colorant, and a stabilizer; and the polymeric composition being in a filament or a pellet form.

[0027] Aspect 1A. A polymeric composition, consisting of: acrylonitrile-butadiene-styrene (ABS) resin; styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards; a population of acid scavenger particles; a lubricant; optionally, one or more of an antioxidant, a colorant, and a stabilizer; and the polymeric composition being in a filament or a pellet form.

[0028] Aspect 1. A polymeric composition, consisting essentially of: acrylonitrile-butadiene-styrene (ABS) resin; styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards; a population of acid scavenger particles; a lubricant; optionally, one or more of an antioxidant, a colorant, and a stabilizer; and the polymeric composition being in a filament or a pellet form.

[0029] The SAN resin may have a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol, from about 150,000 to about 200,000 g/mol, from about 155,000 to about 195,000 g/mol, from about 160,000 to about 190,000 g/mol, from about 165,000 to about 185,000 g/mol, from about 170,000 to about 180,000 g/mol, or even about 170,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards. In some embodiments, the styrene/acrylonitrile (S/AN) weight ratio may be in the range of from about 80/20 to 60/40; a S/AN ratio of about 72/28 S/AN is considered especially suitable.

[0030] Acrylonitrile-butadiene-styrene (“ABS”) refers to an acrylonitrile-butadiene-styrene polymer which can be an acrylonitrile-butadiene-styrene terpolymer or a blend of styrene-butadiene rubber and styrene-acrylonitrile copolymer. It should be understood that ABS may, in some aspects, include recycled acrylonitrile-butadiene-styrene polymer” or “recycled ABS,” which refers to a recycled acrylonitrile-butadiene-styrene that comprises at least one impurity not present in a corresponding, substantially similar or identical virgin acrylonitrile-butadiene-styrene or polystyrene polymer.

[0031] ABS graft copolymers may contain two or more polymeric parts of different compositions, which are bonded chemically. The graft copolymer is specifically prepared by first polymerizing a conjugated diene, such as butadiene or another conjugated diene, with a monomer copolymerizable therewith, such as styrene, to provide a polymeric backbone. After formation of the polymeric backbone, at least one grafting monomer, and specifically two, is polymerized in the presence of the polymer backbone to obtain the graft copolymer. These resins are prepared by methods well known in the art. (Further disclosure regarding ABS is found in United States published patent application nos. 2014/0275382 and 2014/0357769, the entireties of which applications are incorporated herein by reference for any and all purposes.)

[0032] For example, ABS can be made by one or more of emulsion or solution polymerization processes, bulk/mass, suspension and/or emulsion-suspension process routes. In addition, ABS materials can be produced by other process techniques such as batch, semi batch

and continuous polymerization for reasons of either manufacturing economics or product performance or both. In order to reduce point defects or inclusions in the inner layer of the final multi-layer article, the ABS is produced by bulk polymerization. In some aspects, ABS is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can, in some aspects, vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene, though these proportions are not a requirement.

[0033] ABS made by emulsion polymerization is considered especially suitable for the disclosed technology. Emulsion polymerization of vinyl monomers gives rise to a family of addition polymers. In many instances the vinyl emulsion polymers are copolymers containing both rubbery and rigid polymer units. Mixtures of emulsion resins, especially mixtures of rubber and rigid vinyl emulsion derived polymers are useful in blends.

[0034] Such rubber modified thermoplastic resins made by an emulsion polymerization process can comprise a discontinuous rubber phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the rubber phase. Such a rubbery emulsion polymerized resin can be further blended with a vinyl polymer made by an emulsion or bulk polymerized process.

[0035] Suitable rubbers for use in making a vinyl emulsion polymer blend are rubbery polymers having a glass transition temperature (T_g) of less than or equal to 25 °C., more preferably less than or equal to 0 °C., and even more preferably less than or equal to -30 °C. As referred to herein, the T_g of a polymer is the T_g value of polymer as measured by differential scanning calorimetry (heating rate 20 °C/minute, with the T_g value being determined at the inflection point). In another aspect, the rubber comprises a linear polymer having structural units derived from one or more conjugated diene monomers. Suitable conjugated diene monomers include, but are not limited to, 1,3-butadiene, isoprene, 1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-pentadiene, 1,3-hexadiene, 2,4-hexadiene, dichlorobutadiene, bromobutadiene and dibromobutadiene as well as mixtures of conjugated diene monomers. In a preferred aspect, the conjugated diene monomer is 1,3-butadiene.

[0036] The emulsion polymer may, optionally, include structural units derived from one or more copolymerizable monoethylenically unsaturated monomers selected from (C2 – C12) olefin monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers and (C2 – C12) alkyl (meth)acrylate monomers. As used herein, the term “(C2-C12) olefin monomers” means a compound having from 2 to 12 carbon atoms per molecule and having a single site of ethylenic unsaturation per molecule. Suitable (C2-C12) olefin monomers

include, e.g., ethylene, propene, 1-butene, 1-pentene, heptene, 2-ethyl-hexylene, 2-ethyl-heptene, 1-octene, and 1-nonene. As used herein, the term “(C1-C12) alkyl” means a straight or branched alkyl substituent group having from 1 to 12 carbon atoms per group and includes, e.g., methyl, ethyl, n-butyl, sec-butyl, t-butyl, n-propyl, isopropyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl, and the terminology “(meth)acrylate monomers” refers collectively to acrylate monomers and methacrylate monomers.

[0037] The rubber phase and the rigid thermoplastic phase of the emulsion modified vinyl polymer may, optionally include structural units derived from one or more other copolymerizable monoethylenically unsaturated monomers such as, for example, monoethylenically unsaturated carboxylic acids such as, for example, acrylic acid, methacrylic acid, itaconic acid, hydroxy (C1-C12) alkyl (meth)acrylate monomers such as, for example, hydroxyethyl methacrylate; (C5-C12) cycloalkyl (meth)acrylate monomers such as for example, cyclohexyl methacrylate; (meth)acrylamide monomers such as for example, acrylamide and methacrylamide; maleimide monomers such as, for example, N-alkyl maleimides, N-aryl maleimides, maleic anhydride, vinyl esters such as, for example, vinyl acetate and vinyl propionate. As used herein, the term “(C5-C12) cycloalkyl” means a cyclic alkyl substituent group having from 5 to 12 carbon atoms per group and the term “(meth)acrylamide” refers collectively to acrylamides and methacrylamides.

[0038] In some cases the rubber phase of the emulsion polymer is derived from polymerization of a butadiene, C4-C12 acrylates or combination thereof with a rigid phase derived from polymerization of styrene, C1-C3 acrylates, methacrylates, acrylonitrile or combinations thereof where at least a portion of the rigid phase is grafted to the rubber phase. In other instances more than half of the rigid phase will be grafted to the rubber phase.

[0039] Suitable vinyl aromatic monomers include, for example, styrene and substituted styrenes having one or more alkyl, alkoxy, hydroxyl or halo substituent group attached to the aromatic ring, including, for example, -methyl styrene, p-methyl styrene, vinyl toluene, vinyl xylene, trimethyl styrene, butyl styrene, chlorostyrene, dichlorostyrene, bromostyrene, p-hydroxystyrene, methoxystyrene and vinyl-substituted condensed aromatic ring structures, such as, for example, vinyl naphthalene, vinyl anthracene, as well as mixtures of vinyl aromatic monomers. As used herein, the term “monoethylenically unsaturated nitrile monomer” means an acyclic compound that includes a single nitrile group and a single site of ethylenic unsaturation per molecule and includes, for example, acrylonitrile, methacrylonitrile, a-chloro acrylonitrile.

[0040] In an alternative aspect, the rubber is a copolymer, preferably a block copolymer, comprising structural units derived from one or more conjugated diene monomers and up to 90 percent by weight (“wt. % or wt. %”) structural units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers, such as, a styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer or a styrene-butadiene-acrylonitrile copolymer. In another aspect, the rubber is a styrene-butadiene block copolymer that contains from 50 to 95 wt. % structural units derived from butadiene and from 5 to 50 wt. % structural units derived from styrene.

[0041] The emulsion derived polymers can be further blended with non-emulsion polymerized vinyl polymers, such as those made with bulk or mass polymerization techniques. A process to prepare mixtures containing polycarbonate, an emulsion derived vinyl polymer, along with a bulk polymerized vinyl polymers, is also contemplated.

[0042] The rubber phase can be made by aqueous emulsion polymerization in the presence of a radical initiator, a surfactant and, optionally, a chain transfer agent and coagulated to form particles of rubber phase material. Suitable initiators include conventional free radical initiator such as, for example, an organic peroxide compound, such as for example, benzoyl peroxide, a persulfate compound, such as, for example, potassium persulfate, an azonitrile compound such as, for example, 2,2'-azobis-2,3,3-trimethylbutyronitrile, or a redox initiator system, such as, for example, a combination of cumene hydroperoxide, ferrous sulfate, tetrasodium pyrophosphate and a reducing sugar or sodium formaldehyde sulfoxylate. Suitable chain transfer agents include, for example, a (C9-C13) alkyl mercaptan compound such as nonyl mercaptan, t-dodecyl mercaptan. Suitable emulsion aids include, linear or branched carboxylic acid salts, with about 10 to 30 carbon atoms. Suitable salts include ammonium carboxylates and alkaline carboxylates; such as ammonium stearate, methyl ammonium behenate, triethyl ammonium stearate, sodium stearate, sodium isostearate, potassium stearate, sodium salts of tallow fatty acids, sodium oleate, sodium palmitate, potassium linoleate, sodium laurate, potassium abieate (rosin acid salt), sodium abietate and combinations thereof. Often mixtures of fatty acid salts derived from natural sources such as seed oils or animal fat (such as tallow fatty acids) are used as emulsifiers.

[0043] In one aspect, the emulsion polymerized particles of rubber phase material have a weight average particle size of 50 to 800 nanometers (“nm”), more preferably, of from 100 to 500 nm, as measured by light transmission. The size of emulsion polymerized rubber particles

can optionally be increased by mechanical, colloidal or chemical agglomeration of the emulsion polymerized particles, according to known techniques.

[0044] The rigid thermoplastic phase comprises one or more vinyl derived thermoplastic polymers and exhibits a glass transition temperature T_g of greater than 25 °C, preferably greater than or equal to 90 °C. and even more preferably greater than or equal to 100 °C.

[0045] In various aspects, the rigid thermoplastic phase comprises a vinyl aromatic polymer having first structural units derived from one or more vinyl aromatic monomers, preferably styrene, and having second structural units derived from one or more monoethylenically unsaturated nitrile monomers, preferably acrylonitrile. In other cases, the rigid phase comprises from 55 to 99 wt. %, still more preferably 60 to 90 wt. %, structural units derived from styrene and from 1 to 45 wt. %, still more preferably 10 to 40 wt. %, structural units derived from acrylonitrile.

[0046] The amount of grafting that takes place between the rigid thermoplastic phase and the rubber phase can vary with the relative amount and composition of the rubber phase. In one aspect, from 10 to 90 wt. %, often from 25 to 60 wt. %, of the rigid thermoplastic phase is chemically grafted to the rubber phase and from 10 to 90 wt. %, preferably from 40 to 75 wt. % of the rigid thermoplastic phase remains “free,” i.e., non-grafted.

[0047] The rigid thermoplastic phase of the rubber modified thermoplastic resin can be formed solely by emulsion polymerization carried out in the presence of the rubber phase or by addition of one or more separately polymerized rigid thermoplastic polymers to a rigid thermoplastic polymer that has been polymerized in the presence of the rubber phase.

[0048] In other cases, the rubber modified thermoplastic resin comprises a rubber phase having a polymer with structural units derived from one or more conjugated diene monomers, and, optionally, further comprising structural units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers, and the rigid thermoplastic phase comprises a polymer having structural units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers. In one aspect, the rubber phase of the rubber modified thermoplastic resin comprises a polybutadiene or poly(styrene-butadiene) rubber and the rigid thermoplastic phase comprises a styrene-acrylonitrile copolymer. Vinyl polymers free of alkyl carbon-halogen linkages, specifically bromine and chlorine carbon bond linkages can provide melt stability.

[0049] In some instances it is desirable to isolate the emulsion vinyl polymer or copolymer by coagulation in acid. In such instances the emulsion polymer can be contaminated by residual acid, or species derived from the action of such acid, for example carboxylic acids derived from fatty acid soaps used to form the emulsion. The acid used for coagulation can be a mineral acid; such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid or mixtures thereof. In some cases the acid used for coagulation has a pH less than about 5.

[0050] Exemplary elastomer-modified graft copolymers include those formed from styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), styrene-ethylene-butadiene-styrene (SEBS), ABS (acrylonitrile-butadiene-styrene), acrylonitrile-ethylene-propylene-diene-styrene (AES), styrene-isoprene-styrene (SIS), methyl methacrylate-butadiene-styrene (MBS), methacrylate-butadiene (MB) and styrene-acrylonitrile (SAN).

[0051] Aspect 2. The composition of aspect 1A-C, wherein the ABS resin is present at from about 10 wt. % to about 50 wt. %, as measured against the total weight of the composition, for example, at from about 15 to about 45 wt. %, from about 20 to about 40 wt. %, from about 25 to about 35 wt. %, or even about 30 wt. %, as measured against the total weight of the composition.

[0052] Aspect 3. The composition of any of aspects 1A-2, wherein the SAN resin is present at from about 50 to about 80 wt. %, measured against the total weight of the composition, for example, at from about 55 to about 75 wt. %, from about 60 to about 70 wt. %, or even at about 70 wt. %.

[0053] Aspect 4. The composition of any of aspects 1A-3, wherein the SAN resin has a weight-average molecular weight in the range of about 150,000 to about 200,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards.

[0054] Aspect 5. The composition of any of aspects 1A-4, wherein the acid scavenger comprises magnesium oxide, zinc oxide, calcium stearate, zinc stearate, magnesium stearate, or any combination thereof.

[0055] Aspect 6. The composition of any of aspects 1A-5, wherein the population of acid scavenger particles has a number average diameter of less than about 10 micrometers, for example, about 9, about 8, about 7, about 6, about 5, about 4, about 3, about 2, or even about 1 micrometer. Populations of acid scavenger particles having a number average diameter of 8 micrometers or less are considered especially suitable. A population may be uni-, bi-, or multimodal.

[0056] Aspect 7. The composition of any of aspects 1A-6, wherein the lubricant is present at from about 1 to about 5 wt. %, as measured against the total weight of the composition.

[0057] Aspect 8. The composition of any of aspects 1A-7, wherein the lubricant comprises a wax. Suitable waxes include primary fatty amides, for example, ethylene bisstearamide wax. A composition may include a non-primary fatty amide lubricant. Some suitable non-primary fatty amide lubricants include, for example, fluorinated polymers, mineral oil, a metallic salt of stearic acid, or any combination thereof.

[0058] A fluoropolymer can include a fibril forming or non-fibril forming fluoropolymer such as polytetrafluoroethylene (PTFE). The fluoropolymer can optionally be encapsulated by a rigid copolymer, for example styrene-acrylonitrile (SAN). PTFE encapsulated in SAN is known as TSAN. Encapsulated fluoropolymers can be made by polymerizing the encapsulating polymer in the presence of the fluoropolymer, for example, in an aqueous dispersion. TSAN can provide significant advantages over PTFE, in that TSAN can be more readily dispersed in the composition. A suitable TSAN can comprise, for example, about 50 wt. % PTFE and about 50 wt % SAN, based on the total weight of the encapsulated fluoropolymer. Alternatively, the fluoropolymer can be pre-blended in some manner with a second polymer, such as for, example, an aromatic polycarbonate resin or SAN to form an agglomerated material for use as an anti-drip agent. Either method can be used to produce an encapsulated fluoropolymer.

[0059] Aspect 9. The composition of any of aspects 1A-8, wherein the colorant is present at from about 0.0001 to about 15 wt. % (or from about 0.0001 pph to about 15 pph), measured against the total weight of the composition. Suitable colorants include, e.g., dyes, pigments, and the like. Carbon black, titanium dioxide TiO_2 , mixed metal oxides such as chrome antimony titanium buff rutile, metal oxides such as iron oxide, and ultramarine blue are all considered suitable colorants. Colorant loadings may be, for example, 0.5 – 15 pph (for example, 0.5 to 5 pph). As one example, TiO_2 in ABS resin may be present at up to about 15 pph (or 15 wt. %). Carbon black, when present, may be present at 1.0 pph or less (1 wt. % or less), but the carbon black may be present at up to about 2.0 pph (2 wt. %).

[0060] Aspect 10. The composition of aspect 9, wherein the colorant comprises TiO_2 , the TiO_2 being present at from about 0.01 wt. % to about 15 wt. %, measured against the total weight of the composition. It should be understood, however, that a composition need not

contain any colorant. In some aspects, the composition may be characterized as having a color other than unpigmented natural.

[0061] Aspect 11. The composition of any of aspects 1A-10, wherein the antioxidant comprises a primary antioxidant or “stabilizer” (for example, a hindered phenol and/or secondary aryl amine) and, optionally, a secondary antioxidant (for example, a phosphate and/or thioester). Suitable antioxidant additives include, for example, organophosphites such as tris(nonyl phenyl)phosphite, tris(2,4-di-*t*-butylphenyl)phosphite, bis(2,4-di-*t*-butylphenyl)pentaerythritol diphosphite, distearyl pentaerythritol diphosphite or the like; alkylated monophenols or polyphenols; alkylated reaction products of polyphenols with dienes, such as tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane, or the like; butylated reaction products of para-cresol or dicyclopentadiene; alkylated hydroquinones; hydroxylated thiodiphenyl ethers; alkylidene-bisphenols; benzyl compounds; esters of beta-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols; esters of beta-(5-*tert*-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols; esters of thioalkyl or thioaryl compounds such as distearylthiopropionate, dilaurylthiopropionate, ditridecylthiodipropionate, octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate or the like; amides of beta-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionic acid or the like, or combinations comprising at least one of the foregoing antioxidants. Compositions according to the present disclosure may also comprise a secondary antioxidant. In one specific aspect, a composition may include, for example, a hindered phenol anti-oxidant (for example, Lowinox CPL™) and, in some aspects, a secondary anti-oxidant phosphite stabilizer (for example, Irgafos 168™). Additional disclosure related to antioxidants and stabilizers is provided elsewhere herein.

[0062] Aspect 12. The composition of any of aspects 1A-11, wherein the antioxidant is present at up to about 0.5 wt. %, measured against the total weight of the composition, for example, at about 0.1, 0.2, 0.3, or even about 0.4 wt. %.

[0063] Aspect 13. The composition of any of aspects 1A-12, wherein the composition is (a) in the form of a filament that has a diameter in the range of from about 0.1 to about 5 mm, (b) in the form of a filament that has along a length of the filament of 0.5 cm, a standard deviation in diameter of less than about 0.1 mm, or both (a) and (b).

[0064] Aspect 14. The composition of any of aspects 1A-12, wherein the composition is in the form of a pellet, the pellet comprising a cross-sectional dimension in the range of from

about 0.1 millimeter (mm) to about 50 mm, an aspect ratio in the range of from about 1 to about 10, or any combination thereof.

[0065] Aspect 15. The composition of any of aspects 1A-14, wherein the composition exhibits a melt strength of greater than about 20 centiNewtons (cN), for example, about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, or even about 110 cN, as well as all intermediate values and ranges. In some aspects, the composition may have a melt strength greater than about 110 cN. (It should be understood that the foregoing may apply to compositions in filament or pellet form.) The improved melt strength helps with the filament extrusion process when extruding filaments for FFF, and nozzle extrusion when printing parts for FFF or large format additive manufacturing (LFAM) using filaments or pellets.

[0066] Aspect 16A. A method, comprising at least one of (a) additively manufacturing at least a portion of an article using a composition according to any of aspects 1-15; or (b) additively manufacturing at least a portion of an article using a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form.

[0067] Aspect 16B. A method consisting of at least one of: (a) additively manufacturing at least a portion of an article using a composition according to any of aspects 1-15; or (b) additively manufacturing at least a portion of an article using a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form.

[0068] Aspect 16C. A method consisting essentially of at least one of: (a) additively manufacturing at least a portion of an article using a composition according to any of aspects 1-15; or (b) additively manufacturing at least a portion of an article using a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene

standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form.

[0069] It should be understood that if the polymeric composition is in pellet form, the composition may include one or more of the features recited in any of the foregoing aspects (for example, aspects 2-12 and aspect), for example, wherein the acid scavenger of the composition comprises magnesium oxide, zinc oxide, calcium stearate, zinc stearate, magnesium stearate, or any combination thereof.

[0070] Aspect 17. The method of aspect 16A-C, wherein the additively manufacturing comprises at least one of fused filament fabrication (FFF) with the polymeric composition being in filament form or large format additive manufacturing (LFAM) with the polymeric composition being in pellet form. Both FFF and LFAM are known in the art and are described in additional detail elsewhere herein.

[0071] Aspect 18. The method of any of aspects 16A-17, wherein the additive manufacturing comprises effecting relative motion between a dispenser of the composition and a substrate. As one example, a dispenser (for example, a nozzle) may move while the substrate or build platform remains stationary. As another example, the build platform may move while the dispenser remains stationary. In some aspects, both the dispenser and the substrate move relative to one another. Movement may be in any of the three dimensions, and may also include rotation and tilting.

[0072] Aspect 19. The method of aspect 18, wherein the dispenser is adapted to dispense molten polymeric composition from at least one of pellet form or filament form. The dispenser may comprise a heating element (for example, a heated wire) disposed within or on the dispenser. In some aspects, the polymeric composition is rendered molten before the polymeric composition arrives at the dispenser.

[0073] Aspect 20. The method of any of aspects 16-19, wherein the dispensed amount of the polymeric composition, following solidification, is characterized as attached to the substrate.

[0074] Aspect 21. The method of any of aspects 17-20, wherein the additive manufacturing comprises large format additive manufacturing that extrudes molten composition from a nozzle at a rate of from about 1 to about 100 kg of molten composition per hour, for example, about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or even about 95 kg/hr. The foregoing range is illustrative only, and does not serve to limit the extrusion rate of the disclosed technology.

[0075] Aspect 22A. An additively manufactured article, made according to any of aspects 16A-21. Exemplary articles include, for example, drain, waste, and vent pipes, pipe fittings, camper tops, truck bed liners, appliances (such as, for example, refrigerator components), vehicle interiors and other vehicle components, luggage, business and consumer electronics, packaging, and communications.

[0076] Aspect 22B. An additively manufactured article, made according to any of aspects 16A-21. Exemplary articles include, for example, drain, waste, and vent pipes, pipe fittings, camper tops, truck bed liners, appliances (such as, for example, refrigerator components), vehicle interiors and other vehicle components, luggage, business and consumer electronics, packaging, and communications.

[0077] Aspect 22C. An additively manufactured article, made according to any of aspects 16A-21. Exemplary articles include, for example, drain, waste, and vent pipes, pipe fittings, camper tops, truck bed liners, appliances (such as, for example, refrigerator components), vehicle interiors and other vehicle components, luggage, business and consumer electronics, packaging, and communications.

[0078] Aspect 23. The additively manufactured article according to aspect 22, wherein the additively manufactured article comprises an amount of TiO_2 as a colorant and, when printed in a flat orientation, an on-edge orientation, or an upright orientation, has a Notched Izod Impact, per ASTM D256 at 23 °C, that is within about 30% (in J/m) of the Notched Izod Impact, per ASTM 256 at 23 °C, of an additively manufactured article printed in a corresponding orientation and formed from a corresponding composition that is essentially free of TiO_2 .

[0079] Aspect 24. The additively manufactured article according to any of aspects 22-23, wherein the additively manufactured article comprises an amount of TiO_2 as a colorant and, when printed in a flat orientation, an on-edge orientation, or an upright orientation, has a tensile strength at break, per ASTM D638 at 23 °C, that is within about 15% (in MPa) of the tensile strength at break, per ASTM D638 at 23 °C, of an additively manufactured article printed in a corresponding orientation formed from a corresponding composition that is essentially free of TiO_2 .

[0080] Aspect 25. The additively manufactured article according to any of aspects 22-24, wherein the additively manufactured article comprises an amount of TiO_2 as a colorant and, when printed in a flat orientation, an on-edge orientation, or an upright orientation, has a tensile modulus, per ASTM D638 at 23 °C, that is within about 15%, or within about 10%, or within about 5% (in megapascals, MPa) of the tensile modulus, per ASTM D638 at 23 °C, of an

additively manufactured article printed in a corresponding orientation formed from a corresponding composition that is essentially free of TiO₂.

[0081] Characteristics (for example, the foregoing characteristics in aspects 23-25) may be suitably measured on, for example, parts printed on a Fortus 400 MC™ or 900 MC™ printer in a flat (XY), on-edge (XZ), or upright (ZX) print orientation under standard ABS conditions and measured using ASTM D256 or ASTM D638 test protocols, at a model temperature of 315 °C., at an oven temperature of about 95 °C, using a tip size of 0.0254 centimeters (cm) (0.010 inches, ") (T16), a layer thickness (resolution) of 0.0254 cm (0.010") (T16), a contour and raster width of 0.0508 cm (0.020"), a speed of about 30.48 cm/second (12 inches/sec), and an air gap of from -0.00254 cm to 0 cm (-0.0010" to 0.0000"). It should be understood that the foregoing is an exemplary measurement method only and does not limit the scope of the present disclosure.

[0082] FIG. 1 provides an illustration of various print orientations for additive-manufactured articles, showing the positions of the component layers in various print orientations. FIG. 2 provides an exemplary filament (raster) fill pattern for a part layer; this pattern may apply to any print orientation.

[0083] Aspect 26A. A system, comprising: a dispenser having disposed within (a) an amount of the polymeric composition of any of aspects 1-15 or (b) a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form; and a substrate, one or both of the dispenser and substrate being capable of controllable motion relative to the other. It should be understood that if the polymeric composition is in pellet form, the composition may include one or more of the features recited in any of aspects 2-12 and aspect 14 above, for example, wherein the acid scavenger of the composition comprises magnesium oxide, zinc oxide, calcium stearate, zinc stearate, magnesium stearate, or any combination thereof.

[0084] Aspect 26B. A system, comprising: a dispenser having disposed within (a) an amount of the polymeric composition of any of aspects 1-15 or (b) a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene

standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form; and a substrate, one or both of the dispenser and substrate being capable of controllable motion relative to the other. It should be understood that if the polymeric composition is in pellet form, the composition may include one or more of the features recited in any of aspects 2-12 and aspect 14 above, for example, wherein the acid scavenger of the composition comprises magnesium oxide, zinc oxide, calcium stearate, zinc stearate, magnesium stearate, or any combination thereof.

[0085] Aspect 26C. A system, comprising: a dispenser having disposed within (a) an amount of the polymeric composition of any of aspects 1-15 or (b) a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form; and a substrate, one or both of the dispenser and substrate being capable of controllable motion relative to the other. It should be understood that if the polymeric composition is in pellet form, the composition may include one or more of the features recited in any of aspects 2-12 and aspect 14 above, for example, wherein the acid scavenger of the composition comprises magnesium oxide, zinc oxide, calcium stearate, zinc stearate, magnesium stearate, or any combination thereof.

[0086] Aspect 27. The system of aspect 26A, wherein the dispenser is configured to render molten and dispense the polymeric composition. As described elsewhere herein, the system may be configured as a FFF system or as an LFAM system.

[0087] Additive manufacturing using the disclosed technology presents a number of unexpected advantages over existing additive manufacturing techniques. One such advantage is that additively-manufactured parts according to the disclosed technology may exhibit improved warpage relative to parts made by other, commonly-used materials. As one example, pellets according to the present disclosure were used in an LFAM process to print a 10.2 cm wide x 182.9 cm long x 10.2 cm high single-walled box, the box comprising about 30 layers. Defining warpage by measuring the amount of lift off of the build plate at each end of the part, and then dividing by the length in that direction, this example part exhibited about warpage of about 0.254

cm (0.1 inches) of lift per linear foot at 30 layers, a favorable result. (It should be understood that this result is illustrative only and is not limiting of the present disclosure.)

[0088] Another advantage is that additively-manufactured parts according to the present disclosure display comparatively favorable surface finish characteristics when compared to filled materials that are commonly used for LFAM, such as glass-filled or carbon fiber-filled ABS. As one example, a part additively-manufactured according to the present disclosure exhibited an improved surface roughness when compared to a comparable additively-manufactured part made according to an existing filled ABS material.

[0089] Additive Manufacturing

[0090] The disclosed compositions (for example, in pellet and/or filament form) are suitable for use in a variety of additive manufacturing processes. Suitable additive manufacturing processes include those processes that use filaments, pellets, and the like, and suitable processes will be known to those of ordinary skill in the art; the disclosed compositions may be used in virtually any additive manufacturing process that uses filament or pellet build material.

[0091] Although additive manufacturing techniques are known to those in the art, the present disclosure will provide additional information on such techniques for the sake of convenience.

[0092] In some additive manufacturing techniques, a plurality of layers is formed in a preset pattern by an additive manufacturing process. “Plurality” as used in the context of additive manufacturing includes 2 or more layers. The maximum number of layers can vary and may be determined, for example, by considerations such as the size of the article being manufactured, the technique used, the capabilities of the equipment used, and the level of detail desired in the final article. For example, 20 to 100,000 layers can be formed, or 50 to 50,000 layers can be formed.

[0093] As used herein, “layer” is a term of convenience that includes any shape, regular or irregular, having at least a predetermined thickness. In some aspects, the size and configuration of two dimensions are predetermined, and on some aspects, the size and shape of all three dimensions of the layer is predetermined. The thickness of each layer can vary widely depending on the additive manufacturing method. In some aspects the thickness of each layer as formed differs from a previous or subsequent layer. In some aspects, the thickness of each layer is the same. In some aspects, the thickness of each layer as formed is 0.1 millimeters (mm) to 5 mm. In other aspects, the article is made from a monofilament additive manufacturing process.

For example, the monofilament may comprise a thermoplastic polymer with a diameter of from 0.1 to 5.0 mm.

[0094] The preset pattern can be determined from a three-dimensional digital representation of the desired article as is known in the art and described in further detail below. Such a representation may be created by a user, or may be based – at least in part – on a scan made of a three-dimensional real object.

[0095] Any additive manufacturing process can be used, provided that the process allows formation of at least one layer of a thermoplastic material that is fusible to the next adjacent layer. The plurality of layers in the predetermined pattern may be fused to provide the article. Any method effective to fuse the plurality of layers during additive manufacturing can be used. In some aspects, the fusing occurs during formation of each of the layers. In some aspects the fusing occurs while subsequent layers are formed, or after all layers are formed.

[0096] In some aspects, an additive manufacturing technique known generally as material extrusion can be used. In material extrusion, an article can be formed by dispensing a material (“the build material”, which may be rendered flowable) in a layer-by-layer manner and fusing the layers. “Fusing” as used herein includes the chemical or physical interlocking of the individual layers, and provides a “build structure.” Flowable build material can be rendered flowable by dissolving or suspending the material in a solvent. In other aspects, the flowable material can be rendered flowable by melting. In other aspects, a flowable prepolymer composition that can be crosslinked or otherwise reacted to form a solid can be used. Fusing can be by removal of the solvent, cooling of the melted material, or reaction of the prepolymer composition.

[0097] In one particular aspect, an article may be formed from a three-dimensional digital representation of the article by depositing the flowable material as one or more roads on a substrate in an x-y plane to form the layer. The position of the dispenser (for example, a nozzle) relative to the substrate is then incremented along a z-axis (perpendicular to the x-y plane), and the process is then repeated to form an article from the digital representation. The dispensed material is thus also referred to as a “modeling material” as well as a “build material.”

[0098] In some aspects, a support material as is known in the art can optionally be used to form a support structure. In these aspects, the build material and the support material can be selectively dispensed during manufacture of the article to provide the article and a support structure. The support material can be present in the form of a support structure, for example, a so-called scaffolding that may be mechanically removed or washed away when the layering

process is completed to a desired degree. The dispenser may be movable in one, two, or three dimensions, and may also be rotatable. Similarly, the substrate may also be moveable in one, two, or three dimensions, and may also be rotatable.

[0099] Systems for material extrusion are known. One exemplary material extrusion additive manufacturing system includes a build chamber and a supply source for the thermoplastic material. The build chamber may include a build platform, a gantry, and a dispenser for dispensing the thermoplastic material, for example an extrusion head.

[00100] The build platform is a platform on which the article is built, and desirably moves along a vertical z-axis based on signals provided from a computer-operated controller. The gantry is a guide rail system that can be configured to move the dispenser in a horizontal x-y plane within the build chamber, for example based on signals provided from a controller. The horizontal x-y plane is a plane defined by an x-axis and a y-axis where the x-axis, the y-axis, and the z-axis are orthogonal to each other.

[00101] Alternatively, the platform can be configured to move in the horizontal x-y plane and the extrusion head can be configured to move along the z-axis. Other similar arrangements can also be used such that one or both of the platform and extrusion head are moveable relative to each other. The build platform can be isolated or exposed to atmospheric conditions. The distance between the platform and head may be adjustable, as may be the orientation of the head and platform relative to one another. It should be understood that the platform may be heated, cooled or maintained at ambient temperature, depending on the user's needs.

[00102] In some aspects, both the build structure and the support structure of the article formed can include a fused expandable layer. In other aspects, the build structured includes a fused expandable layer and the support material does not include an expandable layer. In still other aspects, the build structure does not include an expandable layer and the support structure does include a fused expandable layer. In those aspects where the support structure includes an expandable layer, the lower density of the expanded layer can allow for the support material to be easily or more easily broken off than the non-expanded layer, and re-used or discarded.

[00103] In some aspects, the support structure can be made purposely breakable, to facilitate breakage where desired. For example, the support material may have an inherently lower tensile or impact strength than the build material. In other aspects, the shape of the support structure can be designed to increase the breakability of the support structure relative to the build structure.

[00104] For example, in some aspects, the build material can be made from a round print nozzle or round extrusion head. A round shape as used herein means any cross-sectional shape that is enclosed by one or more curved lines. A round shape includes circles, ovals, ellipses, and the like, as well as shapes having an irregular cross-sectional shape. Three dimensional articles formed from round shaped layers of build material can possess strong structural strength. In other aspects, the support material for the articles can be made from a non-round print nozzle or non-round extrusion head. A non-round shape means any cross-sectional shape enclosed by at least one straight line, optionally together with one or more curved lines. A non-round shape can include squares, rectangles, ribbons, horseshoes, stars, T-head shapes, X-shapes, chevrons, and the like. These non-round shapes can render the support material weaker, brittle and with lower strength than round shaped build material.

[00105] The above material extrusion techniques include techniques such as fused deposition modeling and fused filament fabrication as well as others as described in ASTM F2792-12a. In fused material extrusion techniques, an article can be produced by heating a thermoplastic material to a flowable state that can be deposited to form a layer. The layer can have a predetermined shape in the x-y axis and a predetermined thickness in the z-axis. The flowable material can be deposited as roads as described above, or through a die to provide a specific profile. The layer cools and solidifies as it is deposited. A subsequent layer of melted thermoplastic material fuses to the previously deposited layer, and solidifies upon a drop in temperature. Extrusion of multiple subsequent layers builds the desired shape. In some aspects at least one layer of an article is formed by melt deposition, and in other aspects, more than 10, or more than 20, or more than 50 of the layers of an article are formed by melt deposition, up to and including all of the layers of an article being formed by melt deposition.

[00106] In some aspects the thermoplastic polymer is supplied in a melted form to the dispenser. The dispenser can be configured as an extrusion head. The extrusion head can deposit the thermoplastic composition as an extruded material strand to build the article. Examples of average diameters for the extruded material strands can be from 1.27 millimeters (0.050 inches) to 3.0 millimeters (0.120 inches). The foregoing dimensions are exemplary only and do not serve to limit the scope of the present disclosure.

[00107] So-called large format additive manufacturing (LFAM) systems are also within the scope of the present disclosure, as such systems may utilize pellets of polymeric material according to the present disclosure to form parts.

[00108] In a LFAM system, a comparatively large extruder converts pellets to a molten form that are then deposited on a table. A LFAM system may comprise a frame or gantry that in turn includes a print head that is moveable in the x, y and/or z directions. (The print head may also be rotatable.) Alternately, the print head may be stationary and the part (or the part support) is moveable in the x, y and/or z axes. (The part may also be rotatable.)

[00109] A print head may have a feed material in the form of pellets and/or filament and a deposition nozzle. The feed material may be stored in a hopper (for pellets) or other suitable storage vessel nearby to the print head or supplied from a filament spool.

[00110] An LFAM apparatus may comprise a nozzle for extruding a material. The polymeric material is heated and extruded through the nozzle and directly deposited on a building surface, which surface may be a moveable (or stationary) platform or may also be previously-deposited material. A heat source may be positioned on or in connection with the nozzle to heat the material to a desired temperature and/or flow rate. The platform or bed may be heated, cooled, or left at room temperature.

[00111] In one non-limiting aspect, a nozzle may be configured to extrude molten polymeric material (from melted pellets) at about 4.54 kg/hr – 45.36 kg/hr (10 – 100 lbs/hr) through a nozzle onto a print bed. The size of a print bed may vary depending on the needs of the user and can be room-sized. As one example, a print bed may be sized at about 406.4 cm by 203.2 cm by 86.36 cm (160 x 80 x 34 inches). A LFAM system may have one, two, or more heated zones. A LFAM system may also comprise multiple platforms and even multiple print heads, depending on the user's needs.

[00112] One exemplary LFAM method is known as big area additive manufacturing (BAAM). LFAM systems may utilize filaments, pellets, or both as feed materials. Exemplary description of a BAAM process may be found in, for example, US 2015/0183159, US 2015/0183138, US 2015/0183164, and US 8,951,303, all of which are incorporated herein by reference in their entireties. The disclosed compositions are also suitable for droplet-based additive manufacturing systems, for example, the Freeformer™ system by Arburg (

[00113] Additive manufacturing systems may use materials in filament form as the build material. Such a system may, as described, effect relative motion between the filament (and/or molten polycarbonate) and a substrate. By applying the molten material according to a pre-set schedule of locations, the system may construct an article in a layer-by-layer fashion, as is familiar to those of ordinary skill in the art. As described elsewhere herein, the build material may also be in pellet form.

[00114] Filaments according to the present disclosure may be disposed about a spool. In some additive manufacturing processes, material from a spool is fed by an extrusion nozzle that is heated to melt the material, which melted material is then deposited in a controlled fashion in horizontal and vertical directions.

[00115] As described elsewhere herein, additive manufacturing may be performed according to a pre-programmed computer-aided design (CAD) model. The additive manufacturing may be performed so as to give rise to an article for food service, computer hardware, medical devices, aerospace, sporting goods, consumer electronics, mobile phones, toys, automotive parts, mounting brackets, fans, conduit boxes, construction industries, prototypes, architectural models, medical models, lighting, or any combination thereof.

[00116] Exemplary Embodiments

[00117] The following embodiments are exemplary only and do not serve to limit the scope of the present disclosure.

[00118] **Table 1: Exemplary composition:**

Component	Wt. %
ABS resin	1-50
SAN resin	50-90
Acid scavenger	0.01 - 10
Wax	0.1 - 5
Antioxidants, stabilizers, colorants	0.001 - 20

[00119] Illustrative experiments are shown in FIG. 3. EX1 represents a commercially-available injection molding material grade commercially available and commonly used for 3D printing. EX2 is an extrusion grade expected to decrease issues with die build-up/beard growth during filament extrusion and/or printing, especially with white color packages containing TiO₂. The principal differences between EX1 and EX2 are that EX2 includes a higher molecular weight Mw SAN resin, a smaller particle size acid scavenger, and a higher amount of wax (mold release).

[00120] In comparing EX1 and EX2, filament extrusion showed no significant differences in die build-up, but EX2 had noticeably better melt strength. In one illustrative experiment, a sample according to EX1 white exhibited a draw ratio of 11.73, and a melt

strength of 19.31 cN. A sample according to EX2 white exhibited a draw ratio of 9.95, and a melt strength of 87.37 cN. The foregoing values are, of course, illustrative only and do not serve to limit the scope of the disclosed compositions.

[00121] To collect the preceding data, the following approach was used.

[00122] Hardware

[00123] Apparatus: Göttfert Rheograph 50™ (barrel diameter: 15 mm; capillary 30/2 (length/diameter, l/d), length 30 mm, diameter 2 mm, entrance angle 180° (flat); pressure transducer: max 500 bar.

[00124] Apparatus: Rheotens 71.97™ (acceleration: 2.4 mm/s², V₀: 50 mm/s)

[00125] Operation

[00126] Filling time ca. 45-60 sec; melting time: 300 sec.

[00127] Measuring conditions

[00128] Measuring temperature 220 °C; V_{piston}: 0.44 mm/s (shear-rate 99.9 1/s with 30/2 capillary).

[00129] Differences were observed between EX1 and EX2 in die build-up on nozzle during printing. “Stringing” was observed with EX1 on-edge and vertical parts, and the machine stopped the print because of high build-up around the nozzle. Only flat orientation parts could be printed with EX1. Parts in all three orientations could be printed with EX2, and no nozzle build-up was observed.

[00130] The parts of FIG. 3 were printed at standard ABS extrusion and oven temperatures, using a Stratasys Fortus 400mc™ or 900mc™ machine, under the following conditions: standard/default ABS conditions; model temp (315 °C) and oven temp (95 °C); tip size: 0.0254 cm (0.010”) (T16); layer thickness (resolution): 0.0254cm (0.010”) (T16); contour and raster width: 0.020”; approximate speed: 12 in/sec. FIG. 1 – described elsewhere herein – provides an illustration of layer alignment in exemplary printed articles, and FIG. 2 provides an illustration of layer construction in an exemplary additive manufacturing system. FIG. 1 presents the dimensions upright (ZX), on-edge (XZ), and flat (XY). FIG. 2 presents the first layer 202, the second layer 204, and the print head (nozzle) 206 for printing the article. Arrows between the first layer 202 and second layer 204 show the direction of the print head movement. In the enlarged portion of FIG. 2, the filament (raster width) W and the raster to raster air gap (G) is shown at the perimeter or contours 208. Without being bound to any particular theory, EX2 had not only improved melt strength over EX1 for filament extrusion, but also allows for higher

colorant loadings to be added without nozzle build-up during printing. Experimental results are provided in FIG. 3 attached hereto.

[00131] As shown in FIG. 3, EX1 white samples could not be printed in on-edge and upright orientations due to nozzle build-up, machine sensed this as a clog and stopped print. The Notched Izod impact (NII) strength of EX1 white decreased significantly in flat orientation vs. EX1 natural samples; EX1 natural samples were the same composition as EX1 white without a TiO₂ color package. NII of EX2 white (i.e., with white color package) was similar to EX1 natural, and was about two times higher than EX1 with white color package when printed in flat orientation. Surprisingly, EX2 white had an improved impact strength while containing high TiO₂, which is known to decrease impact strength. EX1 white had 50% decrease in notched Izod impact strength with the inclusion of a white color package compared to EX1 natural, while EX2 white impact strength decreased by about 20% with inclusion of a white color package compared to EX2 natural. Again without being bound to any particular theory, EX2 thus allows higher impact strength (while maintaining tensile properties) and improved processability (printing performance) while also allowing for comparatively high colorant loadings. Tensile properties were comparable for all samples.

[00132] While typical aspects have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

[00133] It will be apparent to those skilled in the art that various modifications and variations can be made in the present disclosure without departing from the scope or spirit of the disclosure. Other embodiments of the disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the disclosure disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the disclosure being indicated by the following claims.

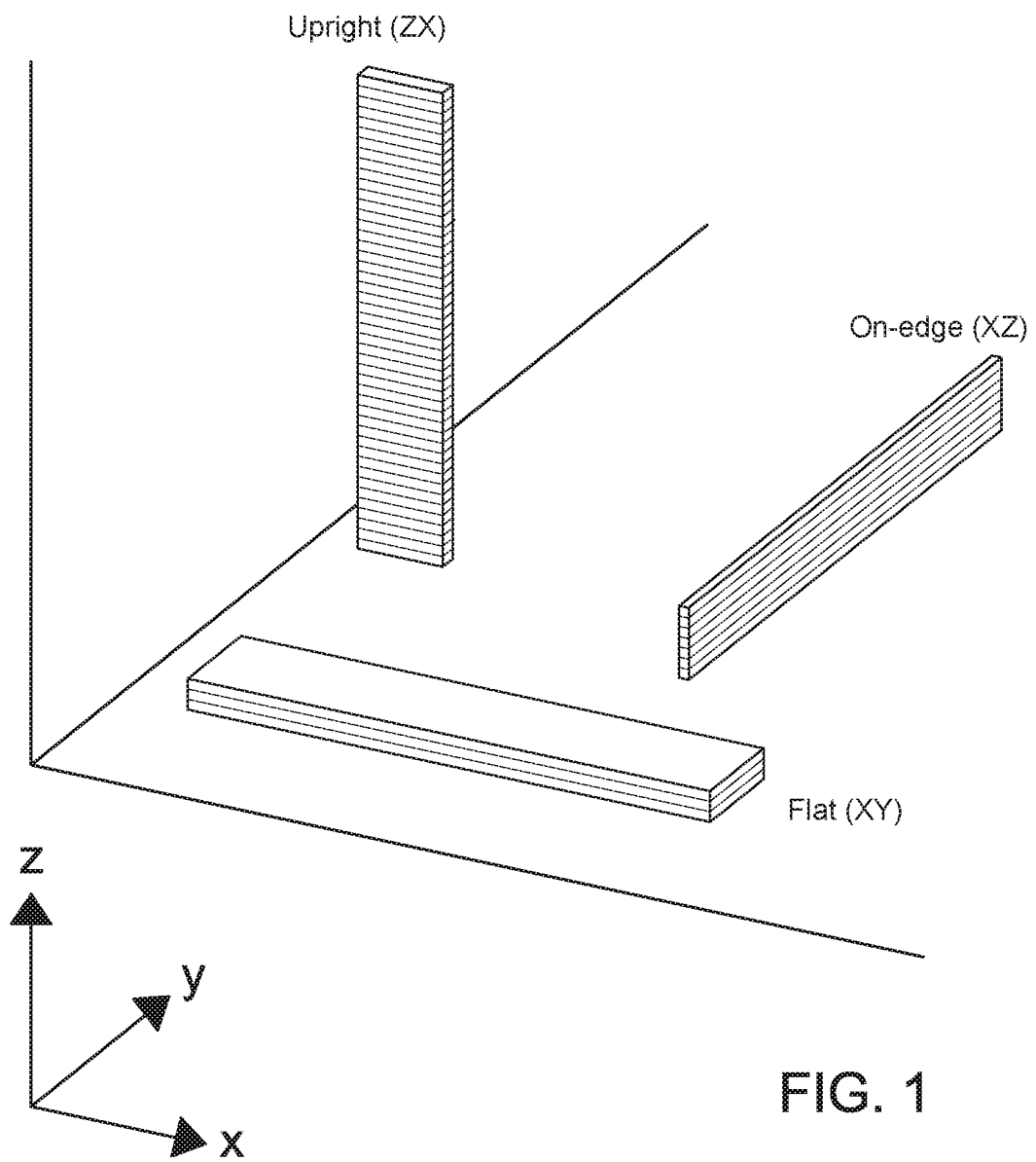
[00134] The patentable scope of the disclosure is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

What is Claimed:

1. A polymeric composition for additive manufacturing, comprising:
acrylonitrile-butadiene-styrene (ABS) resin;
styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 g/mol to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards;
a population of acid scavenger particles;
a lubricant;
optionally, one or more of an antioxidant, a colorant, and a stabilizer; and
the polymeric composition being in a filament form.
2. The composition of claim 1, wherein the ABS resin is present at from about 10 wt. % to about 50 wt. %, as measured against the total weight of the composition.
3. The composition of any of claims 1-2, wherein the SAN resin is present at from about 50 to about 80 wt. %, measured against the total weight of the composition.
4. The composition of any of claims 1-3, wherein the SAN resin has a weight-average molecular weight in the range of about 150,000 to about 200,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards.
5. The composition of any of claims 1-4, wherein the acid scavenger comprises magnesium oxide, zinc oxide, calcium stearate, zinc stearate, magnesium stearate, or any combination thereof.
6. The composition of any of claims 1-5, wherein the population of acid scavenger particles has a number average diameter of less than about 10 micrometers.
7. The composition of any of claims 1-6, wherein the lubricant is present at from about 1 to about 5 wt. %, as measured against the total weight of the composition.
8. The composition of any of claims 1-7, wherein the lubricant comprises a wax.
9. The composition of any of claims 1-8, wherein the colorant is present at from about 0.0001 to about 15 wt. %, measured against the total weight of the composition.

10. The composition of claim 9, wherein the colorant comprises TiO_2 , the TiO_2 being present at from about 0.01 to about 15 wt. %, measured against the total weight of the composition.
11. The composition of any of claims 1-10, wherein the antioxidant comprises a primary antioxidant.
12. The composition of any of claims 1-11, wherein the antioxidant is present at up to about 0.5 wt. %, measured against the total weight of the composition.
13. The composition of any of claims 1-12, wherein the composition is (a) in the form of a filament that has a diameter in the range of from about 0.1 to about 5 mm, (b) in the form of a filament that has along a length of the filament of 0.5 cm, a standard deviation in diameter of less than about 0.1 mm, or both (a) and (b).
14. The composition of any of claims 1-12, wherein the composition is in the form of a pellet, the pellet comprising a cross-sectional dimension in the range of from about 0.1 mm to about 50 mm, an aspect ratio in the range of from about 1 to about 10, or any combination thereof.
15. The composition of any of claims 1-14, wherein the composition has a melt strength of at least about 20 cN.
16. A method, comprising at least one of (a) additively manufacturing at least a portion of an article using a composition according to any of claims 1-14; or (b) additively manufacturing at least a portion of an article using a polymeric composition, in pellet form, that comprises acrylonitrile-butadiene-styrene (ABS) resin, styrene acrylonitrile (SAN) resin having a weight-average molecular weight in the range of from about 145,000 to about 205,000 g/mol as measured by gel permeation chromatography (GPC) with polystyrene standards, a population of acid scavenger particles, a lubricant, optionally, one or more of an antioxidant, a colorant, and a stabilizer and the polymeric composition being in a pellet form.
17. The method of claim 16, wherein the additively manufacturing comprises at least one of fused filament fabrication with the polymeric composition being in filament form or large format additive manufacturing with the polymeric composition being in pellet form.

18. The method of any of claims 16-17, wherein the polymeric composition is supplied in a melted form to a dispenser and wherein the dispenser is adapted to dispense molten polymeric composition from at least one of pellet form or filament form.
19. The method of any of claims 16-18, wherein the additive manufacturing comprises large format additive manufacturing that extrudes molten composition from a nozzle at a rate of from about 1 to about 100 kg of molten composition per hour.
20. An additively manufactured article according to any of claims 16-19, wherein the additively manufactured article comprises an amount of TiO_2 as a colorant and, when printed in a flat orientation, an on-edge orientation, or an upright orientation, has a Notched Izod Impact, per ASTM D256 at 23 °C, that is within about 30% (in J/m) of the Notched Izod Impact, per ASTM 256 at 23 °C, of an additively manufactured article printed in a corresponding orientation and formed from a corresponding composition that is essentially free of TiO_2 .



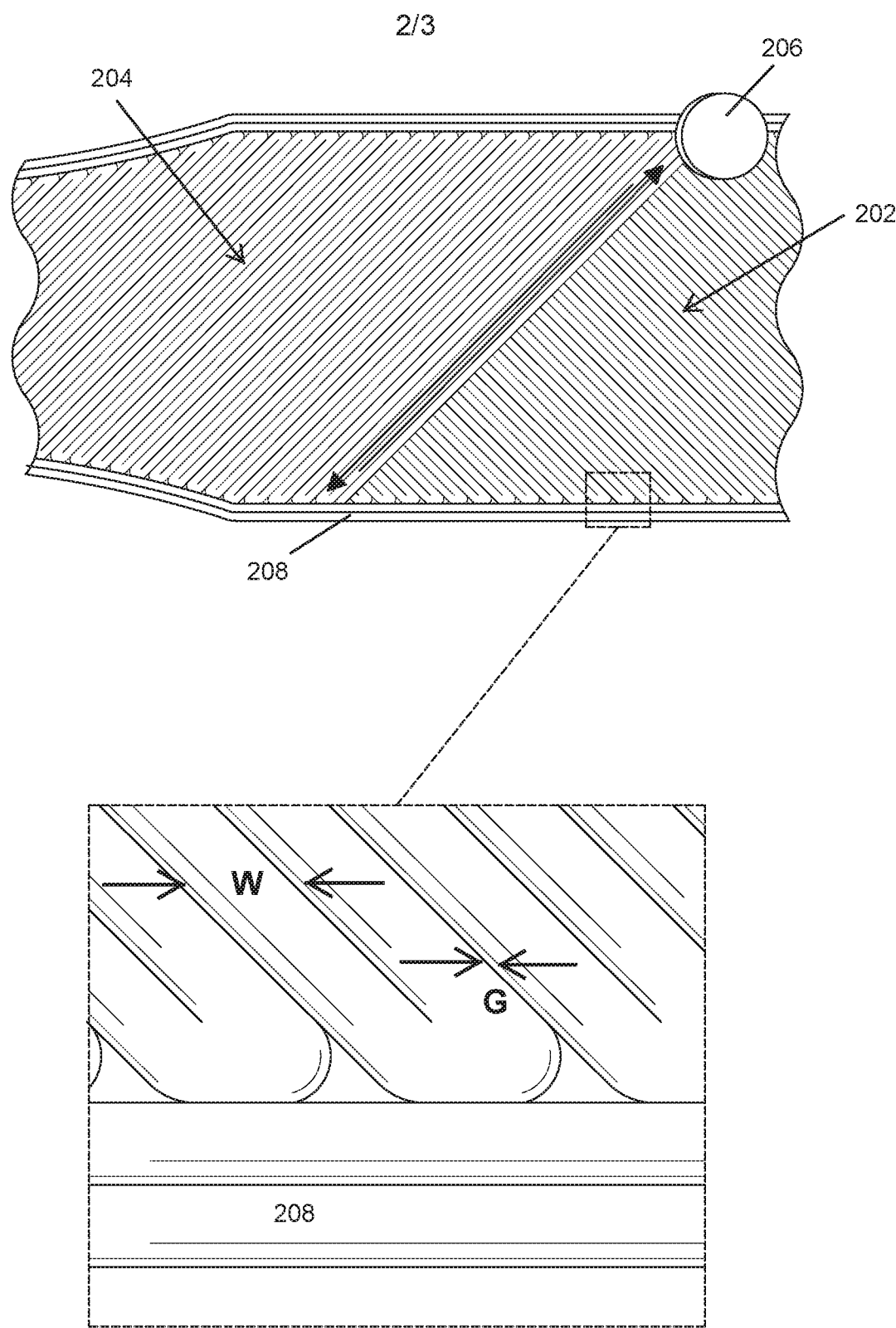


FIG. 2

TEST	UNIT	EX1 NATURAL			EX1 WHITE			EX2 NATURAL			EX2 WHITE		
		Flat	On-Edge	Upright	Flat	On-Edge	Upright	Flat	On-Edge	Upright	Flat	On-Edge	Upright
NII (ASTM), 23 °C	J/m	115	104	37	58			130	114	45	104	108	34
Std Dev		7	4	8	3			7	2	1	6	4	3
Tensile (ASTM), 23 °C Modulus	MPa	2065	2132	2030	2258	Nozzle build up, on-edge and upright samples could not be printed		1838	2030	2092	1974	2208	2204
Std Dev		47	48	47	47			45	20	65	68	33	74
Strength @ break	MPa	26	27	26	26			28	28	30	27	28	30
Std Dev		2	1	2	1			0.6	0.3	0.8	1	0	0
Elongation @ break	%	6.9	5.9	1.8	3.7			7.2	5.4	2.3	8.5	5.2	1.9
Std Dev		1.0	0.8	0.3	0.8			0.9	0.9	0.3	1.6	0.9	0.2

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/026321

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L25/12 C08L55/02 B29C64/00 B33Y70/00
ADD.

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)
C08L B29C B33Y

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/312022 A1 (NIESSNER NORBERT [DE] ET AL) 27 October 2016 (2016-10-27) page 8, paragraph 184 page 10, paragraph 246 page 13, paragraph 314 page 16; table 2 page 17; table 5 page 18, paragraph 405 claim 41	1-20
A	----- WO 2016/184765 A1 (INEOS STYROLUTION GROUP GMBH [DE]) 24 November 2016 (2016-11-24) table 1	1-20
A	----- CN 105 860 421 A (OU ZHENYUN) 17 August 2016 (2016-08-17) example 2 ----- -/-	1-20



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

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

26 June 2018

Date of mailing of the international search report

09/07/2018

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/026321

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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WO 2016184765 A1	24-11-2016	EP 3298079 A1	28-03-2018
		KR 20180006415 A	17-01-2018
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WO 2017158075 A1	21-09-2017	NONE	