(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 May 2018 (24.05.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/094185 A1

(51) International Patent Classification:
B33Y 70/00 (2015.01) ***B29C 64/118*** (2017.01)
C08K 7/24 (2006.01)

(21) International Application Number:
PCT/US2017/062251

(22) International Filing Date:
17 November 2017 (17.11.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

62/423,522	17 November 2016 (17.11.2016)	US
62/436,783	20 December 2016 (20.12.2016)	US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM,

(54) Title: COMPOSITIONS INCLUDING POLYMER AND HOLLOW CERAMIC MICROSPHERES AND METHOD OF MAKING A THREE-DIMENSIONAL ARTICLE

(57) Abstract: The method of making a three-dimensional article includes heating a composition comprising a polymer and hollow ceramic microspheres, extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three-dimensional article, and extruding at least a second layer of the composition in molten form from the extrusion head onto at least the portion of the first layer to make at least a portion of the three-dimensional article. Three-dimensional articles are also described. A composition including a polymer and hollow ceramic microspheres is also described. The composition may be a filament. The polymer is at least one of a low-surface-energy polymer or polyolefin. The composition can be useful, for example, in melt extrusion additive manufacturing, for example, fused filament fabrication.

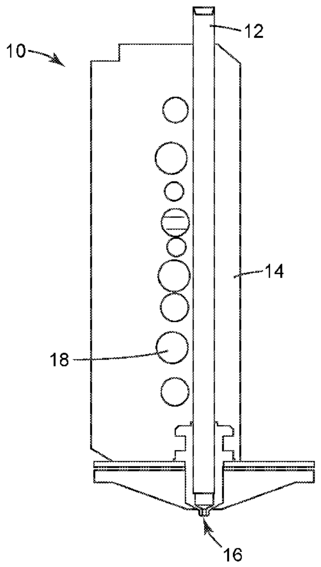

Fig. 1

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AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

COMPOSITIONS INCLUDING POLYMER AND HOLLOW CERAMIC MICROSPHERES AND METHOD OF MAKING A THREE-DIMENSIONAL ARTICLE

Cross-Reference to Related Application

This application claims priority to U.S. Provisional Application Nos. 62/423,522, filed November 17, 2016, and 62/436,738, filed December 20, 2016, the disclosures of which are incorporated by reference in their entirety herein.

Background

Hollow ceramic microspheres (e.g., hollow glass microspheres also commonly known as "glass microbubbles", "glass bubbles ", "hollow glass beads", or “glass balloons”) having an average diameter of less than about 500 micrometers are widely used in industry, for example, as additives to polymeric compositions. In many industries, hollow glass microspheres are useful, for example, for lowering weight and improving processing, dimensional stability, and flow properties of a polymeric composition.

Composites including hollow glass microspheres and reinforcing fibers dispersed in a polymer phase and methods of making such composites are disclosed in U.S. Pat. Appl. Pub. No. 2016/0002468 (Heikkila et al.).

Fused Filament Fabrication, which is also known under the trade designation “FUSED DEPOSITION MODELING” from Stratasys, Inc., Eden Prairie, Minn., is a process that uses a thermoplastic strand fed through a hot can to produce a molten aliquot of material from an extrusion head. The extrusion head extrudes a bead of material in 3D space as called for by a plan or drawing (e.g., a computer aided drawing (CAD file)). The extrusion head typically lays down material in layers, and after the material is deposited, it fuses. Similar processes can use other input materials, such as thermoplastic pellets.

Summary

There are several problems that can arise with the many independently fused layers made in a fused filament fabrication process or other melt extrusion additive manufacturing processes. We have observed poor interlayer adhesion between layers of low-surface-energy polymers formed by successive passes of the extruder head, which results in delamination of layers in the three-dimensional article. Without wishing to be bound by theory, it is believed that the low-surface-energy and typically low polarity in such polymers can prevent interlayer adhesion from one pass of the extruder head to the next. This can cause sliding or deformation of the new semi-molten layer, resulting in waviness, warpage, and dimensional instability.

Other problems can occur in melt extrusion additive manufacturing processes, especially with semi-crystalline thermoplastics. For example, the time it takes for a polymer to fuse solidly enough to act as a support for the next bead can be excessive. If the printer has to be run at a slow speed to allow for solidification and densification, the cost of making a part may be increased beyond a level where melt extrusion additive manufacturing can compete. Another problem that occurs is shrinkage or differential shrinkage (x-y plane vs. z plane) as the thermoplastic densifies upon solidification. This also can cause dimensional instability, warpage, and waviness, which may prevent certain polymer types or structures from being printed.

Polypropylene is a semi-crystalline thermoplastic that can exhibit a high degree of variation in percent crystallinity due to environmental or chemical factors. For example, some inorganic materials like talc are known to nucleate polypropylene to provide greater than 60 percent crystalline material. Quick thermal quenching of polypropylene can result in less than 40 percent crystalline material. Due to this high variation, polypropylene, an economical commodity plastic, is typically not used in a fused filament fabrication process or other melt extrusion additive manufacturing processes.

In one aspect, the present disclosure provides a method of making a three-dimensional article. The method includes heating a composition comprising a low-surface-energy polymer and hollow ceramic microspheres, extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three-dimensional article, and extruding at least a second layer of the composition in molten form from the extrusion head onto at least the portion of the first layer to make at least a portion of the three-dimensional article. In some embodiments, the method includes at least partially melting the low-surface-energy polymer in the extrusion head to provide the composition in molten form. The composition may be provided, for example, as a filament, pellet, or granules.

In another aspect, the present disclosure provides a method of making a three-dimensional article. The method includes heating a composition comprising a polyolefin and hollow ceramic microspheres; extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three-dimensional article; and extruding at least a second layer of the composition in molten form onto at least the portion of the first layer to make at least a portion of the three-dimensional article. In some embodiments, the method includes at least partially melting the polyolefin in the extrusion head to provide the composition in molten form. The composition may be provided, for example, as a filament, pellet, or granules.

In another aspect, the present disclosure provides a three-dimensional article made by either of the aforementioned methods.

In another aspect, the present disclosure provides a filament for use in fused filament fabrication. The filament includes a low-surface-energy polymer and hollow ceramic microspheres.

In another aspect, the present disclosure provides a filament for use in fused filament fabrication. The filament includes a polyolefin and hollow ceramic microspheres.

In another aspect, the present disclosure provides a filament having an ovality of up to 10%. The filament includes a low-surface-energy polymer and hollow ceramic microspheres.

In another aspect, the present disclosure provides a filament having an ovality of up to 10%. The filament includes a polyolefin and hollow ceramic microspheres.

In another aspect, the present disclosure provides a composition including a low-surface-energy polymer and hollow ceramic microspheres for use in melt extrusion additive manufacturing. The composition may be useful, for example, for lowering the specific gravity of a three-dimensional article in comparison to a comparative three-dimensional article comprising the low-surface-energy polymer but no hollow ceramic microspheres.

In another aspect, the present disclosure provides a composition including a polyolefin and hollow ceramic microspheres for use in material extrusion printing. The composition may be useful, for example, for lowering the specific gravity of a three-dimensional article in comparison to a comparative three-dimensional article comprising the polyolefin but no hollow ceramic microspheres.

Typically and advantageously, when hollow ceramic microspheres are added to compositions for melt extrusion additive manufacturing made from low-surface-energy polymers or polyolefins, good flow properties of the low-surface-energy polymers or polyolefins are observed, resulting in good adhesion between deposited layers. In contrast, when the composition did not contain hollow ceramic microspheres, poor interlayer adhesion was observed, and air pockets and voids were observed within the deposited layers. Also advantageously, in some embodiments, the filament for use in fused filament fabrication has improved ovality when compared to filaments that do not include the hollow ceramic microspheres.

In this application, terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terms "a", "an", and "the" are used interchangeably with the term "at least one". The phrases "at least one of" and "comprises at least one of" followed by a list refers to any one of the items in the list and any combination of two or more items in the list. All numerical ranges are inclusive of their endpoints and integral and non-integral values between the endpoints unless otherwise stated (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

The term “ceramic” as used herein refers to glasses, crystalline ceramics, glass-ceramics, and combinations thereof.

"Low-surface-energy" describes polymers that are nonwettable by aqueous liquids (i.e., liquids comprising water) in contact with the surface of the polymer. Typically, a polymer will be considered to have low surface energy if the contact angle of water on the surface of the polymer is about 90 degrees or greater. Low-surface-energy polymers may have a surface energy of up to 36, 35, or 30 dynes per centimeter as measured by DIN ISO 8296 (2008-03-00) Plastics - Film and sheeting - Determination of wetting tension (ISO 8296:2003).

Additive manufacturing, also known as “3D printing”, refers to a process to create a three-dimensional object by sequential deposition of materials in defined areas, typically by generating successive layers of material. The object is typically produced under computer control from a 3D model or other electronic data source by an additive printing device typically referred to as a 3D printer.

"Alkyl group" and the prefix "alk-" are inclusive of both straight chain and branched chain groups and of cyclic groups having up to 30 carbons (in some embodiments, up to 20, 15, 12, 10, 8, 7, 6, or 5 carbons) unless otherwise specified. Cyclic groups can be monocyclic or polycyclic and, in some embodiments, have from 3 to 10 ring carbon atoms.

The term "perfluoroalkyl group" includes linear, branched, and/or cyclic alkyl groups in which all C-H bonds are replaced by C-F bonds.

The phrase "interrupted by one or more -O- groups", for example, with regard to an alkyl, alkylene, or arylalkylene refers to having part of the alkyl, alkylene, or arylalkylene on both sides of the one or more -O- groups. An example of an alkylene that is interrupted with one -O- group is $-CH_2-CH_2-O-CH_2-CH_2-$.

The term "aryl" as used herein includes carbocyclic aromatic rings or ring systems, for example, having 1, 2, or 3 rings, optionally containing at least one heteroatom (e.g., O, S, or N) in the ring, and optionally substituted by up to five substituents including one or more alkyl groups having up to 4 carbon atoms (e.g., methyl or ethyl), alkoxy having up to 4 carbon atoms, halo (i.e., fluoro, chloro, bromo or iodo), hydroxy, or nitro groups. Examples of aryl groups include phenyl, naphthyl, biphenyl, fluorenyl as well as furyl, thienyl, oxazolyl, and thiazolyl. "Arylalkylene" refers to an "alkylene" moiety to which an aryl group is attached. "Alkylarylene" refers to an "arylene" moiety to which an alkyl group is attached.

The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure. The description that follows more particularly exemplifies illustrative embodiments. It is to be understood, therefore, that the following description should not be read in a manner that would unduly limit the scope of this disclosure.

Brief Description of the Drawings

FIG. 1 is a schematic sectional view of an embodiment of an extrusion head useful in the method of the present disclosure;

FIG. 2 is a sectional view of an embodiment of a strand die extruding a filament according to the present disclosure;

FIG. 3 is a micrograph at a magnification of 75 X of deposited layers of polypropylene including hollow glass microspheres prepared in Example 4;

FIG. 4 is a micrograph at a magnification of 75 X of deposited layers of polypropylene not including hollow glass microspheres prepared in Comparative Example C;

FIG. 5 illustrates an embodiment of a system for carrying out the method of the present disclosure; and

FIG. 6 illustrates another embodiment of a system for carrying out the method of the present disclosure.

Detailed Description

Extrusion-based layered deposition systems (e.g., fused filament fabrication systems and other melt extrusion additive manufacturing processes) are useful for making three-dimensional articles in the method of the present disclosure. The three-dimensional articles can be made, for example, from computer-aided design (CAD) models in a layer-by-layer manner by extruding a composition including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres. Movement of the extrusion head with respect to the substrate onto which the substrate is extruded is performed under computer control, in accordance with build data that represents the three-dimensional article. The build data is obtained by initially slicing the CAD model of the three-dimensional article into multiple horizontally sliced layers. Then, for each sliced layer, the host computer generates a build path for depositing roads of the composition including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres to form the three-dimensional article.

The composition can be extruded through a nozzle carried by an extrusion head and deposited as a sequence of roads of molten material on a substrate in an x-y plane. The roads can be in the form of continuous beads or in the form of a series of droplets (e.g., as described in U.S. Pat. Appl. No. 2013/0071599 (Kraibühler et al.)). The extruded composition fuses to previously deposited composition as it solidifies upon a drop in temperature. This can provide at least a portion of the first layer of the three-dimensional article. The position of the extrusion head relative to the first layer is then incremented along a z-axis (perpendicular to the x-y plane), and the process is repeated to form at least a second layer of the composition on at least a portion of the first layer. Changing the position of the extrusion head relative to the deposited layers may be carried out, for example, by lowering the substrate onto which the layers are deposited. The process can be repeated as many times as necessary to form a three-dimensional article resembling the CAD model. Further details can be found, for example, Turner, B.N. et al., "A review of melt extrusion additive manufacturing processes: I. process design and modeling"; *Rapid Prototyping Journal* 20/3 (2014) 192-204.

In some embodiments, a (e.g., non-transitory) machine-readable medium is employed in the method of making a three-dimensional article of the present disclosure. Data is typically stored on the machine-readable medium. The data represents a three-dimensional model of an article, which can be accessed by at least one computer processor interfacing with additive manufacturing equipment (e.g., a 3D printer, a manufacturing device, etc.). The data is used to cause the additive manufacturing equipment to create the three-dimensional article.

Data representing an article may be generated using computer modeling such as computer aided design (CAD) data. Image data representing the three-dimensional article design can be exported in STL format, or in any other suitable computer processable format, to the additive manufacturing equipment. Scanning methods to scan a three-dimensional object may also be employed to create the data representing the article. One exemplary technique for acquiring the data is digital scanning. Any other suitable scanning technique may be used for scanning an article, including X-ray radiography, laser scanning, computed tomography (CT), magnetic resonance imaging (MRI), and ultrasound imaging. Other possible scanning methods are described, e.g., in U.S. Patent Application Publication No. 2007/0031791 (Cinader, Jr., et al.). The initial digital data set, which may include both raw data from scanning operations and data representing articles derived from the raw data, can be processed to segment an article design from any surrounding structures (e.g., a support for the article).

Often, machine-readable media are provided as part of a computing device. The computing device may have one or more processors, volatile memory (RAM), a device for reading machine-readable media, and input/output devices, such as a display, a keyboard, and a pointing device. Further, a computing device may also include other software, firmware, or combinations thereof, such as an operating system and other application software. A computing device may be, for example, a workstation, a laptop, a personal digital assistant (PDA), a server, a mainframe or any other general-purpose or application-specific computing device. A computing device may read executable software instructions from a computer-readable medium (such as a hard drive, a CD-ROM, or a computer memory), or may receive instructions from another source logically connected to computer, such as another networked computer.

In some embodiments, the method of making a three-dimensional article of the present disclosure comprises retrieving, from a (e.g., non-transitory) machine-readable medium, data representing a model of a desired three-dimensional article. The method further includes executing, by one or more processors interfacing with a manufacturing device, manufacturing instructions using the data; and generating, by the manufacturing device, the three-dimensional article.

FIG. 5 illustrates an embodiment of a system 2000 for carrying out some embodiments of the method according to the present disclosure. The system 2000 comprises a display 2062 that displays a model 2061 of a three-dimensional article; and one or more processors 2063 that, in response to the 3D model 2061 selected by a user, cause a manufacturing device 2065 to create the three-dimensional article 2017. Often, an input device 2064 (e.g., keyboard and/or mouse) is employed with the display 2062 and the at least one processor 2063, particularly for the user to select the model 2061.

Referring to FIG. 6, a processor 2162 (or more than one processor) is in communication with each of a machine-readable medium 2171 (e.g., a non-transitory medium), a manufacturing device 2165, and optionally a display 2162 for viewing by a user. The manufacturing device 2165 is configured to make one or more articles 2117 based on instructions from the processor 2163 providing data representing a model of the article 2117 from the machine-readable medium 2171.

A number of fused filament fabrication 3D printers may be useful for carrying out the method according to the present disclosure. Many of these are commercially available under the trade designation “FDM” from Stratasys, Inc., Eden Prairie, Minn., and subsidiaries thereof. Desktop 3D printers for idea and design development and larger printers for direct digital manufacturing can be obtained from Stratasys and its subsidiaries, for example, under the trade designations “MAKERBOT REPLICATOR”, “UPRINT”, “MOJO”, “DIMENSION”, and “FORTUS”. Other 3D printers for fused filament fabrication are commercially available from, for example, 3D Systems, Rock Hill, S.C., and Airwolf 3D, Costa Mesa, Cal.

Other printers useful for practicing the present disclosure use input materials other than filaments. For example, such printers can use pellets or granules comprising the low-surface-energy polymer or polyolefin and hollow ceramic microspheres as input materials. Accordingly, other examples of printers useful for practicing the present disclosure are a commercially available Freeformer from Arburg, Lossburg, Germany, useful for carrying out a process known under the trade designation "ARBURG PLASTIC FREEFORMING (APF)", and those described in U.S. Pat. No. 8,292,610 (Hehl et al.).

FIG. 1 is a sectional view of an embodiment of an extrusion head 10 useful in the method of the present disclosure. Extrusion head 10 includes extrusion channel 12, heating block 14, and extrusion tip 16. Ports 18 in the heating block 14 may be useful, for example, for measurement and control of the temperature of the heating block 14 as needed. The extrusion head 10 can be a component, for example, of an extrusion-based layered deposition system, including those described in any of the above embodiments.

Extrusion channel 12 is a channel extending through heating block 14 for feeding a composition comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres. In some embodiments, the composition introduced to the heating block 14 is a filament comprising the low-surface-energy polymer or polyolefin and the hollow ceramic microspheres. Filaments may be introduced to the heating block 14 using a pinch roller mechanism, for example. In other embodiments, the composition introduced to the heating block 14 is in the form of pellets or granules, which may be introduced to the heating block 14 using a feed screw, for example. Heating block 14 is useful for at least partially melting the composition (in some embodiments, the filament) to a desired extrusion viscosity based on a suitable thermal profile along heating block 14. The temperature of the heating block 14 can be adjusted based on the melting temperature and melt viscosity of at least the low-surface-energy polymer or polyolefin in the composition. In some embodiments, the heating block is heated at a temperature of at least 180 °C, at least 200 °C, at least 220 °C, up to about 325 °C, 300 °C, or 275 °C. Examples of suitable heating blocks 14 include those commercially available in "FUSED DEPOSITION MODELING" systems under the trademark "FDM TITAN" from Stratasys, Inc.

Extrusion tip 16 is the tip extension of extrusion channel 12, which shears and extrudes the composition in molten form to make the three-dimensional article. The size and shape of the extrusion tip may be designed as desired for the size and shape of the extruded roads of the composition. Extrusion tip 16 has tip inner dimensions useful for depositing roads of the composition comprising the low-surface-energy polymer or polyolefin and the hollow ceramic microspheres, where the road widths and heights are based in part on the tip inner dimensions. In some embodiments, the extrusion tip has a round opening. In some of these embodiments, suitable tip inner diameters for extrusion tip 16 can range from about 100 micrometers to about 1000 micrometers. In some dimensions, the extrusion tip has a square or rectangular opening. In some of these embodiments, the extrusion tip can have at least one of a width or a thickness ranging from about 100 micrometers to about 1,000 micrometers.

The temperature of the substrate onto which the composition comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres can be deposited may be room temperature or may be adjusted to promote the fusing of the roads of the deposited composition. In the method according to the present disclosure, the temperature of the substrate may be, for example, at least about 25 °C, 50 °C, 75 °C, 100 °C, 110 °C, 120 °C, 130 °C, or 140 °C up to 300 °C, 200 °C, 175 °C or 150 °C.

In fabricating three-dimensional articles by depositing layers of the composition including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres, supporting layers or structures may be built underneath overhanging portions or in cavities of the three-dimensional articles that are not supported by the composition itself. A support structure may be built utilizing the same deposition techniques by which the composition comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres is deposited. The host computer can generate additional structure acting as a support for the overhanging or free-space segments of the three-dimensional article being formed. Support material can then be deposited from a second extrusion tip according to the generated structure during the build process. Generally, the support material adheres to the composition during fabrication but is removable from the three-dimensional article when the build process is complete.

In contrast to other forming process such as injection molding, blow molding, and sheet extrusion, the three-dimensional article made according to the method disclosed herein may have a high surface roughness with vertical deviation of at least 0.01 millimeters (mm), particularly when a fused filament fabrication method is used to make the three-dimensional article. The rough surface has very regular appearance that may be useful or attractive in some applications. In situations where a smoother surface is desired, the initially formed rough grooved surface may be removed in subsequent operations, examples of which include sanding, peening, shot blasting, or laser peening.

The three-dimensional object prepared by the method according to the present disclosure may be an article useful in a variety of industries, for example, the aerospace, apparel, architecture, automotive, business machines products, consumer, defense, dental, electronics, educational institutions, heavy equipment, jewelry, medical, and toys industries.

The present disclosure provides compositions including at least one low-surface-energy polymer or polyolefin and hollow ceramic microspheres that may be useful, for example, for melt extrusion additive manufacturing (in some embodiments, fused filament fabrication). The compositions can be in the form of filaments, pellets, or granules, for example. Examples of low-surface-energy polymers useful for the methods and compositions disclosed herein include polyolefins and fluoropolymers.

Examples of polyolefins useful for the compositions and methods disclosed herein include those made from monomers having the general structure $CH_2{=}CHR^{10}$, wherein R^{10} is a hydrogen or alkyl. In some embodiments, R^{10} is alkyl having up to 10 carbon atoms or from one to six carbon atoms. Examples of suitable polyolefins include polyethylene; polypropylene; poly (l-butene); poly (3-

methylbutene); poly (4-methylpentene); copolymers of ethylene with propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 4-methyl-1-pentene, and 1-octadecene; and blends of polyethylene and polypropylene. In some embodiments, the polyolefin comprises at least one of polyethylene or polypropylene. It should be understood that a polyolefin comprising polyethylene may be a polyethylene homopolymer or a copolymer containing ethylene repeating units. Similarly, it should be understood that a polyolefin comprising polypropylene may be a polypropylene homopolymer or a copolymer containing propylene repeating units. The polyolefin comprising at least one of polyethylene or polypropylene may also be part a blend of different polyolefins that includes at least one of polypropylene or polyethylene. Useful polyethylene polymers include high density polyethylene (e.g., those having a density of such as from 0.94 to about 0.98 g/cm^3) and linear or branched low-density polyethylenes (e.g. those having a density of such as from 0.89 to 0.94g/cm^3). In some embodiments, the polyolefin comprises polypropylene. Useful polypropylene polymers include low impact, medium impact, or high impact polypropylene. A high impact polypropylene may be a copolymer of polypropylene including at least 80, 85, 90, or 95% by weight propylene repeating units, based on the weight of the copolymer. The polyolefin may comprise mixtures of stereo-isomers of such polymers (e.g., mixtures of isotactic polypropylene and atactic polypropylene). Suitable polypropylene can be obtained from a variety of commercial sources, for example, LyondellBasell, Houston, TX, under the trade designations "PRO-FAX" and "HIFAX", and from Pinnacle Polymers, Garyville, LA, under the trade designation "PINNACLE". Suitable polyethylene can be obtained from a variety of commercial sources, for example, Braskem S. A., Sao Paolo, Brazil.

In some embodiments, compositions comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres useful for practicing the present disclosure are copolymers of olefins described above in any of their embodiments and dienes. The low-surface-energy polymer or polyolefin in the composition disclosed herein may also be part of a blend of different polyolefins, at least one of which includes a diene monomer. Examples of useful diene monomers include 1,2-propadiene (i.e., allene) isoprene (i.e., 2-methyl-1,3-butadiene, the precursor to natural rubber), 1,3-butadiene, 1,5-cyclooctadiene, norbornadiene, dicylopentadiene, and linoleic acid. In some embodiments, the composition comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres includes a polyolefin that comprises units of ethylene, propylene, and at least one of dicyclopentadiene, ethylidene norbornene, and vinyl norbornene (i.e., the composition includes EPDM).

In some embodiments, compositions comprising polyolefins and hollow ceramic microspheres useful for practicing the present disclosure are copolymers of olefins described above in any of their embodiments and at least one polar copolymerizable monomer. In these embodiments, the polyolefin can include ethylene and acrylic acid copolymers; ethylene and methyl acrylate copolymers; ethylene and ethyl acrylate copolymers; ethylene and vinyl acetate copolymers; ethylene, acrylic acid, and ethyl acrylate copolymers; and ethylene, acrylic acid, and vinyl acetate copolymers. Such polar copolymerizable monomers tend to increase the surface energy of the polymer. Accordingly, in some of these embodiments, the copolymer has at least 80, 85, 90, 95, 97.5 or 99% by weight olefin repeating units (that is, those having the formula $CH_2=CHR^{10}$, based on the weight of the copolymer. The polyolefin in the composition disclosed herein may also be part of a blend of different polyolefins, at least one of which includes a polar copolymerizable monomer. In some embodiments, a low-surface-energy polyolefin useful for practicing the present disclosure is substantially free of such polar copolymerizable monomers. That is, the low-surface-energy polyolefin may be free of polar monomers (in some embodiments, acrylic acid, methacrylic acid, acrylates, methacrylates, or vinyl acetate) or contain less than 5%, 2.5%, 1%, or 0.5% by weight of the polar monomer, based on the weight of the copolymer.

Fluoropolymers useful for the compositions and methods disclosed herein include amorphous fluoropolymers and semi-crystalline fluorothermoplastics. Fluoropolymers useful for practicing the present disclosure can comprise interpolymerized units derived from at least one partially fluorinated or perfluorinated ethylenically unsaturated monomer represented by formula $R^aCF=CR^a_2$, wherein each R^a is independently fluoro, chloro, bromo, hydrogen, a fluoroalkyl group (e.g. perfluoroalkyl having from 1 to 8, 1 to 4, or 1 to 3 carbon atoms and optionally interrupted by one or more oxygen atoms), a fluoroalkoxy group (e.g. perfluoroalkoxy having from 1 to 8, 1 to 4, or 1 to 3 carbon atoms, optionally interrupted by one or more oxygen atoms), alkyl having up to 10 carbon atoms, alkoxy having up to 8 carbon atoms, or aryl having up to 8 carbon atoms. Examples of useful fluorinated monomers represented by formula $R^aCF=CR^a_2$ include vinylidene fluoride (VDF), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), chlorotrifluoroethylene, 2-chloropentafluoropropene, trifluoroethylene, vinyl fluoride, dichlorodifluoroethylene, 1,1-dichlorofluoroethylene, 1-hydropentafluoropropylene, 2-hydropentafluoropropylene, tetrafluoropropylene, perfluoroalkyl perfluorovinyl ethers, perfluoroalkyl perfluoroallyl ethers, and mixtures thereof.

In some embodiments, the fluoropolymer useful for practicing the present disclosure includes units from one or more monomers independently represented by formula $CF_2=CFORf$, wherein Rf is perfluoroalkyl having from 1 to 8, 1 to 4, or 1 to 3 carbon atoms, optionally interrupted by one or more -O- groups. Perfluoroalkoxyalkyl vinyl ethers suitable for making a fluoropolymer include those represented by formula $CF_2=CF(OC_nF_{2n})_zORf_2$, in which each n is independently from 1 to 6, z is 1 or 2, and Rf_2 is a linear or branched perfluoroalkyl group having from 1 to 8 carbon atoms and optionally interrupted by one or more -O- groups. In some embodiments, n is from 1 to 4, or from 1 to 3, or from 2 to 3, or from 2 to 4. In some embodiments, n is 1 or 3. In some embodiments, n is 3. C_nF_{2n} may be linear or branched. In some embodiments, C_nF_{2n} can be written as $(CF_2)_n$, which refers to a linear perfluoroalkylene group. In some embodiments, C_nF_{2n} is $–CF_2-CF_2-CF_2-$. In some embodiments, C_nF_{2n} is branched, for example, $–CF_2-CF(CF_3)-$. In some embodiments, $(OC_nF_{2n})_z$ is represented by $–O-(CF_2)_{1-4}-[O(CF_2)_{1-4}]_{0-1}$. In some embodiments, Rf_2 is a linear or branched perfluoroalkyl group having from 1 to 8 (or 1 to 6) carbon atoms that is optionally interrupted by up to 4, 3, or 2 -O- groups. In some embodiments, Rf_2 is a perfluoroalkyl group having from 1 to 4 carbon atoms optionally interrupted by one -O- group. Suitable monomers represented by formula $CF_2=CFORf$ and $CF_2=CF(OC_nF_{2n})_zORf_2$

include perfluoromethyl vinyl ether, perfluoroethyl vinyl ether, perfluoropropyl vinyl ether, $CF_2=CFOCF_2OCF_3$, $CF_2=CFOCF_2OCF_2CF_3$, $CF_2=CFOCF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2CF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2OCF_2CF_3$, $CF_2=CFOCF_2CF_2CF_2OCF_2CF_3$, $CF_2=CFOCF_2CF_2CF_2CF_2OCF_2CF_3$, $CF_2=CFOCF_2CF_2OCF_2OCF_3$, $CF_2=CFOCF_2CF_2OCF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2OCF_2CF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2OCF_2CF_2CF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2OCF_2CF_2CF_2CF_2CF_2OCF_3$, $CF_2=CFOCF_2CF_2(OCF_2)_3OCF_3$, $CF_2=CFOCF_2CF_2(OCF_2)_4OCF_3$, $CF_2=CFOCF_2CF_2OCF_2OCF_2OCF_3$, $CF_2=CFOCF_2CF_2OCF_2CF_2CF_3$ $CF_2=CFOCF_2CF_2OCF_2CF_2OCF_2CF_2CF_3$, $CF_2=CFOCF_2CF(CF_3)\text{-}O\text{-}C_3F_7$ (PPVE-2), $CF_2=CF(OCF_2CF(CF_3))_2\text{-}O\text{-}C_3F_7$ (PPVE-3), and $CF_2= CF(OCF_2CF(CF_3))_3\text{-}O\text{-}C_3F_7$ (PPVE-4). Many of these perfluoroalkoxyalkyl vinyl ethers can be prepared according to the methods described in U.S. Pat. Nos. 6,255,536 (Worm et al.) and 6,294,627 (Worm et al.).

Perfluoroalkyl alkene ethers and perfluoroalkoxyalkyl alkene ethers may also be useful for making a fluoropolymer for the composition, method, and use according to the present disclosure. In addition, the fluoropolymers may include interpolymerized units of fluoro (alkene ether) monomers, including those described in U.S. Pat. Nos. 5,891,965 (Worm et al.) and 6,255,535 (Schulz et al.). Such monomers include those represented by formula $CF_2=CF(CF_2)_m\text{-}O\text{-}R_f$, wherein m is an integer from 1 to 4, and wherein R_f is a linear or branched perfluoroalkylene group that may include oxygen atoms thereby forming additional ether linkages, and wherein R_f contains from 1 to 20, in some embodiments from 1 to 10, carbon atoms in the backbone, and wherein R_f also may contain additional terminal unsaturation sites. In some embodiments, m is 1. Examples of suitable fluoro (alkene ether) monomers include perfluoroalkoxyalkyl allyl ethers such as $CF_2=CFCF_2\text{-}O\text{-}CF_3$, $CF_2=CFCF_2\text{-}O\text{-}CF_2\text{-}O\text{-}CF_3$, $CF_2=CFCF_2\text{-}O\text{-}CF_2CF_2\text{-}O\text{-}CF_3$, $CF_2=CFCF_2\text{-}O\text{-}CF_2CF_2\text{-}O\text{-}CF_2\text{-}O\text{-}CF_2CF_3$, $CF_2=CFCF_2\text{-}O\text{-}CF_2CF_2\text{-}O\text{-}CF_2CF_2CF_2\text{-}O\text{-}CF_3$, $CF_2=CFCF_2\text{-}O\text{-}CF_2CF_2\text{-}O\text{-}CF_2CF_2\text{-}O\text{-}CF_2\text{-}O\text{-}CF_3$, $CF_2=CFCF_2CF_2\text{-}O\text{-}CF_2CF_2CF_3$. Suitable perfluoroalkoxyalkyl allyl ethers include those represented by formula $CF_2=CFCF_2(OC_nF_{2n})_zORf_2$, in which n, z, and Rf_2 are as defined above in any of the embodiments of perfluoroalkoxyalkyl vinyl ethers. Examples of suitable perfluoroalkoxyalkyl allyl ethers include $CF_2=CFCF_2OCF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2OCF_3$, $CF_2=CFCF_2OCF_2OCF_2CF_3$, $CF_2=CFCF_2OCF_2CF_2CF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_3$, $CF_2=CFCF_2OCF_2CF_2CF_2OCF_2CF_3$, $CF_2=CFCF_2OCF_2CF_2CF_2CF_2OCF_2CF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_2CF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_2CF_2CF_2CF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2(OCF_2)_3OCF_3$, $CF_2=CFCF_2OCF_2CF_2(OCF_2)_4OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2OCF_2OCF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_2CF_3$, $CF_2=CFCF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2CF_3$, $CF_2=CFCF_2OCF_2CF(CF_3)\text{-}O\text{-}C_3F_7$, and $CF_2=CFCF_2(OCF_2CF(CF_3))_2\text{-}O\text{-}C_3F_7$. Many of these perfluoroalkoxyalkyl allyl ethers can be prepared, for example, according to the methods described in U.S. Pat. No. 4,349,650 (Krespan).

Fluoropolymers useful for practicing the present disclosure may also comprise interpolymerized units derived from the interpolymerization of at least one monomer $R^aCF=CR^a_2$ with at least one non-fluorinated, copolymerizable comonomer represented by formula $R^b_2C=CR^b_2$, wherein each R^b is independently hydrogen, chloro, alkyl having from 1 to 8, 1 to 4, or 1 to 3 carbon atoms, a cyclic saturated alkyl group having from 1 to 10, 1 to 8, or 1 to 4 carbon atoms, or an aryl group of from 1 to 8 carbon atoms, or represented by formula $CH_2=CHR^{10}$, wherein R^{10} is as defined above. Examples of useful monomers represented by these formulas include ethylene and propylene.

Perfluoro-1,3-dioxoles may also be useful to prepare a fluoropolymer useful for practicing the present disclosure. Perfluoro-1,3-dioxole monomers and their copolymers are described in U. S. Pat. No. 4,558, 141 (Squire).

In some embodiments, the fluoropolymer useful for practicing the present disclosure is amorphous. Amorphous fluoropolymers typically do not exhibit a melting point and exhibit little or no crystallinity at room temperature. Useful amorphous fluoropolymers can have glass transition temperatures below room temperature or up to 280 °C. Suitable amorphous fluoropolymers can have glass transition temperatures in a range from -60 °C up to 280 °C, -60 °C up to 250 °C, from -60 °C to 150 °C, from -40 °C to 150 °C, from -40 °C to 100 °C, from -40 °C to 20 °C, from 80 °C to 280 °C, from 80 °C to 250 °C, or from 100 °C to 250 °C.

In some embodiments, useful amorphous fluoropolymers include copolymers of VDF with at least one terminally unsaturated fluoromonoolefin represented by formula $R^aCF=CR^a_2$ containing at least one fluorine atom on each double-bonded carbon atom. Examples of comonomers that can be useful with VDF include HFP, chlorotrifluoroethylene, 1-hydropentafluoropropylene, and 2-hydropentafluoropropylene. Other examples of amorphous fluoropolymers useful for practicing the present disclosure include copolymers of VDF, TFE, and HFP or 1- or 2-hydropentafluoropropylene and copolymers of TFE, propylene, and, optionally, VDF. Such fluoropolymers are described in U.S. Pat. Nos. 3,051,677 (Rexford) and 3,318,854 (Honn, et al.) for example. In some embodiments, the amorphous fluoropolymer is a copolymer of HFP, VDF and TFE. Such fluoropolymers are described in U.S. Pat. No. 2,968,649 (Pailthorp et al.), for example.

Amorphous fluoropolymers including interpolymerized units of VDF and HFP typically have from 30 to 90 percent by weight VDF units and 70 to 10 percent by weight HFP units. Amorphous fluoropolymers including interpolymerized units of TFE and propylene typically have from about 50 to 80 percent by weight TFE units and from 50 to 20 percent by weight propylene units. Amorphous fluoropolymers including interpolymerized units of TFE, VDF, and propylene typically have from about 45 to 80 percent by weight TFE units, 5 to 40 percent by weight VDF units, and from 10 to 25 percent by weight propylene units. Those skilled in the art are capable of selecting specific interpolymerized units at appropriate amounts to form an amorphous fluoropolymer. In some embodiments, polymerized units derived from non-fluorinated olefin monomers are present in the amorphous fluoropolymer at up to 25 mole percent of the fluoropolymer, in some embodiments up to 10 mole percent or up to 3 mole percent.

In some embodiments, polymerized units derived from at least one of perfluoroalkyl vinyl ether or perfluoroalkoxyalkyl vinyl ether monomers are present in the amorphous fluoropolymer at up to 50 mole percent of the fluoropolymer, in some embodiments up to 30 mole percent or up to 10 mole percent.

In some embodiments, amorphous fluoropolymers useful for practicing the present disclosure include a TFE/propylene copolymer, a TFE/propylene/VDF copolymer, a VDF/HFP copolymer, a TFE/VDF/HFP copolymer, a TFE/ perfluoromethyl vinyl ether (PMVE) copolymer, a TFE/CF_2=$CFOC_3F_7$ copolymer, a TFE/CF_2=$CFOCF_3$/CF_2=$CFOC_3F_7$ copolymer, a TFE/ethyl vinyl ether (EVE) copolymer, a TFE/butyl vinyl ether (BVE) copolymer, a TFE/EVE/BVE copolymer, a VDF/CF_2=$CFOC_3F_7$ copolymer, an ethylene/HFP copolymer, a TFE/ HFP copolymer, a CTFE/VDF copolymer, a TFE/VDF copolymer, a TFE/VDF/PMVE/ethylene copolymer, or a TFE/VDF/CF_2=$CFO(CF_2)_3OCF_3$ copolymer.

Amorphous fluoropolymers useful for practicing the present disclosure also include those having glass transition temperatures in a range from 80 °C to 280 °C, from 80 °C to 250 °C, or from 100 °C to 250 °C. Examples of such fluoropolymers include copolymers of perfluorinated 1,3-dioxoles optionally substituted by perfluoroC_{1-4}alkyl or perfluoroC_{1-4}alkoxy with at least one compound of formula R^aCF=CR^a_2, in some embodiments, TFE. Examples of perfluorinated 1,3-dioxoles suitable for making amorphous fluoropolymers include 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, 2,2-bis(trifluoromethyl)-4-fluoro-5-trifluoromethoxy-1,3-dioxole, 2,4,5-trifluoro-2-trifluoromethyl-1,3-dioxole, 2,2,4,5-tetrafluoro-1,3-dioxole, and 2,4,5-trifluoro-2-pentafluoroethyl-1,3-dioxole. Some of these amorphous polymers are commercially available, for example, from The Chemours Company, Wilmington, Del., under the trade designation "TEFLON AF" and from Solvay, Brussels, Belgium, under the trade designation "HYFLON AD". Other useful amorphous fluoropolymers include poly(perfluoro-4-vinyloxy-1-butene), which is commercially available under the trade designation "CYTOP" from Asahi Glass, Tokyo, Japan, and poly(perfluoro-4-vinyloxy-3-methyl-1-butene). Several perfluoro-2-methylene-1,3-dioxolanes can be homopolymerized or copolymerized with each other and/or with compounds represented by formula R^aCF=CR^a_2 to provide useful amorphous fluoropolymers. Suitable perfluoro-2-methylene-1,3-dioxolane may be unsubstituted, substituted by at least one of perfluoroC_{1-4}alkyl or perfluoroC_{1-4}alkoxyC_{1-4}alkyl, or fused to a 5- or 6-membered perfluorinated ring, optionally containing an oxygen atom. One example of a useful substituted perfluoro-2-methylene-1,3-dioxolanes is poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane. Further examples and details about these amorphous fluoropolymers can be found in "Amorphous Fluoropolymers" by Okamot, et al., Chapter 16 in *Handbook of Fluoropolymer Science and Technology*, First Edition, Ed. Smith, D.W., Iacono, S.T., and Iyer, S., 2014, pp. 377 to 391.

In some embodiments, amorphous fluoropolymers have a glass transition temperature of up to 50 °C and have a Mooney viscosity in a range from 1 to 100 (ML 1+10) at 121 °C. Mooney viscosity is determined using ASTM D1646-06 Part A by a MV 2000 instrument (available from Alpha

Technologies, Ohio, USA) using a large rotor (ML 1+10) at 121 °C. Mooney viscosities specified above are in Mooney units.

In some embodiments, components useful for preparing an amorphous fluoropolymer further include a fluorinated bisolefin compound represented by the following formula:

$CY_2=CX-(CF_2)_a-(O-CF_2-CF(Z))_b-O-(CF_2)_c-(O-CF(Z)-CF_2)_d-(O)_e-(CF(A))_f-CX=CY_2$,

wherein a is an integer selected from 0, 1, and 2; b is an integer selected from 0, 1, and 2; c is an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, and 8; d is an integer selected from 0, 1, and 2; e is 0 or 1; f is an integer selected from 0, 1, 2, 3, 4, 5, and 6; Z is independently selected from F and CF_3; A is F or a perfluorinated alkyl group; X is independently H or F; and Y is independently selected from H, F, and CF_3. In a preferred embodiment, the highly fluorinated bisolefin compound is perfluorinated, meaning that X and Y are independently selected from F and CF_3. Examples of useful fluorinated bisolefin compounds include: $CF_2=CF-O-(CF_2)_2-O-CF=CF_2$, $CF_2=CF-O-(CF_2)_3-O-CF=CF_2$, $CF_2=CF-O-(CF_2)_4-O-CF=CF_2$, $CF_2=CF-O-(CF_2)_5-O-CF=CF_2$, $CF_2=CF-O-(CF_2)_6-O-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_2-O-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_3-O-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_4-O-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_5-O-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_6-O-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_2-O-CF_2-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_3-O-CF_2-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_4-O-CF_2-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_5-O-CF_2-CF=CF_2$, $CF_2=CF-CF_2-O-(CF_2)_6-O-CF_2-CF=CF_2$, $CF_2=CF-O-CF_2CF_2-CH=CH_2$, $CF_2=CF-(OCF_2CF(CF_3))-O-CF_2CF_2-CH=CH_2$, $CF_2=CF-(OCF_2CF(CF_3))_2-O-CF_2CF_2-CH=CH_2$, $CF_2=CF\ CF_2-O-CF_2CF_2-CH=CH_2$, $CF_2=CF\ CF_2-(OCF_2CF(CF_3))-O-CF_2CF_2-CH=CH_2$, $CF_2=CFCF_2-(OCF_2CF(CF_3))_2-O-CF_2CF_2-CH=CH_2$, $CF_2=CF-CF_2-CH=CH_2$, $CF_2=CF-O-(CF_2)_c-O-CF_2-CF_2-CH=CH_2$ wherein c is an integer selected from 2 to 6, $CF_2=CFCF_2-O-(CF_2)_c-O-CF_2-CF_2-CH=CH_2$ wherein c is an integer selected from 2 to 6, $CF_2=CF-(OCF_2CF(CF_3))_b-O-CF(CF_3)-CH=CH_2$ wherein b is 0, 1, or 2, $CF_2=CF-CF_2-(OCF_2CF(CF_3))_b-O-CF(CF_3)-CH=CH_2$ wherein b is 0, 1, or 2, $CH_2=CH-(CF_2)_n-O-CH=CH_2$ wherein n is an integer from 1-10, and $CF_2=CF-(CF_2)_a-(O-CF_2CF(CF_3))_b-O-(CF_2)_c-(OCF(CF_3)CF_2)_f-O-CF=CF_2$ wherein a is 0 or 1, b is 0, 1, or 2, c is 1, 2, 3, 4, 5, or 6, and f is 0, 1, or 2. In some embodiments, the fluorinated bisolefin compound is $CF_2=CF-O-(CF_2)_n-O-CF=CF_2$ where n is an integer from 2-6; $CF_2=CF-(CF_2)_a-O-(CF_2)_n-O-(CF_2)_b-CF=CF_2$ where n is an integer from 2-6 and a and b are 0 or 1; or a perfluorinated compound comprising a perfluorinated vinyl ether and a perfluorinated allyl ether. Useful amounts of the fluorinated bisolefin include 0.01 mol % to 1 mol % of the fluorinated bisolefin compound based on total moles of monomer incorporated. In some embodiments, at least 0.02, 0.05, or even 0.1 mol % of the fluorinated bisolefin compound is used and at most 0.5, 0.75, or even 0.9 mol % of a compound of the fluorinated bisolefin compound is used based on the total moles of monomer incorporated into the amorphous polymer.

In some embodiments, the amorphous fluoropolymer useful in the composition and method of the present disclosure includes polymerized units comprising a cure site. In these embodiments, cure site monomers may be useful during the polymerization to make the amorphous fluoropolymer. Such cure site monomers include those monomers capable of free radical polymerization. The cure site monomer can be perfluorinated to ensure adequate thermal stability of the resulting elastomer. Examples of useful cure sites include a Br cure site, an I cure site, a nitrile cure site, a carbon-carbon double bond, and combinations thereof. Any of these cure sites can be cured using peroxides as described below. However, in some cases in which multiple, different cure sites are present a dual cure system or a multi cure system may be useful. Other suitable cure systems that may be useful include bisphenol curing systems or triazine curing systems.

In some embodiments, the cure site monomer comprises an iodine capable of participating in a peroxide cure reaction, where, for example, the iodine atom capable of participating in the peroxide cure reaction is located at a terminal position of the backbone chain. One example of a useful fluorinated iodine containing cure site monomer is represented by the following formula:

$$CY_2=CX-(CF_2)_g-(O-CF_2CF(CF_3))_h-O-(CF_2)_i-(O)_j-(CF_2)_k-CF(I)-X \quad \text{(IV)}$$

wherein X and Y are independently selected from H, F, and CF_3; g is 0 or 1; h is an integer selected from 0, 2, and 3; i is an integer selected from 0, 1, 2, 3, 4, and 5; j is 0 or 1; and k is an integer selected from 0, 1, 2, 3, 4, 5, and 6. In one in embodiment, the fluorinated iodine containing cure site monomer is perfluorinated. Examples of suitable compounds of Formula (IV) include: $CF_2=CFOC_4F_8I$ (MV4I), $CF_2=CFOC_2F_4I$, $CF_2=CFOCF_2CF(CF_3)OC_2F_4I$, $CF_2=CF-(OCF_2CF(CF_3))_2-O-C_2F_4I$, $CF_2=CF-O-CF_2CFI-CF_3$, $CF_2=CF-O-CF_2CF(CF_3)-O-CF_2CFI-CF_3$, $CF_2=CF-O-(CF_2)_2-O-C_2F_4I$, $CF_2=CF-O-(CF_2)_3-O-C_2F_4I$, $CF_2=CF-O-(CF_2)_4-O-C_2F_4I$, $CF_2=CF-O-(CF_2)_5-O-C_2F_4I$, $CF_2=CF-O-(CF_2)_6-O-C_2F_4I$, $CF_2=CF-CF_2-O-CF_2-O-C_2F_4I$, $CF_2=CF-CF_2-O-(CF_2)_2-O-C_2F_4I$, $CF_2=CF-CF_2-O-(CF_2)_3-O-C_2F_4I$, $CF_2=CF-CF_2-O-(CF_2)_4-O-C_2F_4I$, $CF_2=CF-CF_2-O-(CF_2)_5-O-C_2F_4I$, $CF_2=CF-CF_2-O-(CF_2)_6-O-C_2F_4I$, $CF_2=CF-CF_2-O-C_4F_8I$, $CF_2=CF-CF_2-O-C_2F_4I$, $CF_2=CF-CF_2-O-CF_2CF(CF_3)-O-C_2F_4I$, $CF_2=CF-CF_2-(OCF_2CF(CF_3))_2-O-C_2F_4I$, $CF_2=CF-CF_2-O-CF_2CFI-CF_3$, $CF_2=CF-CF_2-O-CF_2CF(CF_3)-O-CF_2CFI-CF_3$, and combinations thereof. In some embodiments, the cure site monomer comprises at least one of $CF_2=CFOC_4F_8I$; $CF_2=CFCF_2OC_4F_8I$; $CF_2=CFOC_2F_4I$; $CF_2=CFCF_2OC_2F_4I$; $CF_2=CF-O-(CF_2)_n-O-CF_2-CF_2I$, or $CF_2=CFCF_2-O-(CF_2)_n-O-CF_2-CF_2I$ wherein n is an integer selected from 2, 3, 4, or 6. Examples of other useful cure site monomers include bromo- or iodo- (per)fluoroalkyl-(per)fluorovinylethers having the formula $ZRf-O-CX=CX_2$, wherein each X may be the same or different and represents H or F, Z is Br or I, Rf is a C_1-C_{12} (per)fluoroalkylene, optionally containing chlorine and/or ether oxygen atoms. Suitable examples include $ZCF_2-O-CF=CF_2$, $ZCF_2CF_2-O-CF=CF_2$, $ZCF_2CF_2CF_2-O-CF=CF_2$, $CF_3CFZCF_2-O-CF=CF_2$, wherein Z represents Br of I. Still other examples of useful cure site monomers include bromo- or iodo (per)fluoroolefins such as those having the formula $Z'-(Rf')_r-CX=CX_2$, wherein each X independently represents H or F, Z' is Br or I, Rf' is a C_1-C_{12} perfluoroalkylene, optionally containing chlorine atoms and r is 0 or 1. Suitable examples include bromo- or iodo-trifluoroethene, 4-bromo-perfluorobutene-1,4-iodo-perfluorobutene-1, or bromo- or iodo-fluoroolefins such as 1-iodo-2,2-difluroroethene, 1-bromo-2,2-difluoroethene, 4-iodo-3,3,4,4,-tetrafluorobutene-1 and 4-bromo-3,3,4,4-tetrafluorobutene-1. Non-fluorinated bromo and iodo-olefins such as vinyl bromide, vinyl iodide, 4-bromo-1-butene and 4-iodo-1-butene may also be useful as cure site monomers.

Useful amounts of the compound of Formula (IV) and the other cure site monomers described above include 0.01 mol % to 1 mol %, based on total moles of monomer incorporated may be used. In some embodiments, at least 0.02, 0.05, or even 0.1 mol % of a cure site monomer is used and at most 0.5, 0.75, or even 0.9 mol % of a cure site monomer is used based on the total moles of monomer incorporated into the amorphous fluoropolymer.

In some embodiments of the amorphous fluoropolymer useful in the composition and method of the present disclosure includes a nitrile cure site. Nitrile cure sites can be introduced into the polymer by using nitrile containing monomers during the polymerization. Examples of suitable nitrile containing monomers include those represented by formulas CF_2=CF-CF_2-O-Rf-CN; CF_2=CFO$(CF_2)_r$CN; CF_2=CFO$[CF_2CF(CF_3)O]_p(CF_2)_vOCF(CF_3)$CN; and CF_2=CF$[OCF_2CF(CF_3)]_kO(CF_2)_u$CN, wherein, r represents an integer of 2 to 12; p represents an integer of 0 to 4; k represents 1 or 2; v represents an integer of 0 to 6; u represents an integer of 1 to 6, Rf is a perfluoroalkylene or a bivalent perfluoroether group. Specific examples of nitrile containing fluorinated monomers include perfluoro (8-cyano-5-methyl-3,6-dioxa-1-octene), CF_2=CFO$(CF_2)_5$CN, and CF_2=CFO$(CF_2)_3$OCF(CF_3)CN. Typically these cure-site monomers, if used, are used in amounts of at least 0.01, 0.02, 0.05, or 0.1 mol % and at most 0.5, 0.75, 0.9, or 1 mol % based on the total moles of monomer incorporated into the amorphous fluoropolymer.

If the amorphous fluoropolymer is perhalogenated, in some embodiments perfluorinated, typically at least 50 mole percent (mol %) of its interpolymerized units are derived from TFE and/or CTFE, optionally including HFP. The balance of the interpolymerized units of the amorphous fluoropolymer (e.g., 10 to 50 mol %) is made up of one or more perfluoroalkyl vinyl ethers and/or perfluoroalkoxyalkyl vinyl ethers and/or perfluoroallyl ethers and/or perfluoroalkoxyallyl ethers, and, in some embodiments, a cure site monomer. If the fluoropolymer is not perfluorinated, it typically contains from about 5 mol % to about 90 mol % of its interpolymerized units derived from TFE, CTFE, and/or HFP; from about 5 mol % to about 90 mol % of its interpolymerized units derived from VDF, ethylene, and/or propylene; up to about 40 mol % of its interpolymerized units derived from a vinyl ether; and from about 0.1 mol % to about 5 mol %, in some embodiments from about 0.3 mol % to about 2 mol %, of a cure site monomer.

In some embodiments, the fluoropolymer useful for practicing the present disclosure is a semi-crystalline thermoplastic. Useful semi-crystalline fluoropolymers are melt processable with melt flow indexes in a range from 0.01 grams per ten minutes to 10,000 grams per ten minutes (20 kg/372 °C).

Suitable semi-crystalline fluoropolymers can have melting points in a range from 50 °C up to 325 °C, from 100 °C to 325 °C, from 150 °C to 325 °C, from 100 °C to 300 °C, or from 80 °C to 290 °C. Homopolymers of TFE and copolymers of TFE including less than one percent of a comonomer are not melt processable and cannot be extruded using the method of the present disclosure.

Examples of suitable semi-crystalline fluorinated thermoplastic polymers include fluoroplastics derived solely from VDF and HFP. These fluoroplastics typically have interpolymerized units derived from 99 to 67 weight percent of VDF and from 1 to 33 weight percent HFP, more in some embodiments, from 90 to 67 weight percent VDF and from 10 to 33 weight percent HFP. Another example of a useful fluoroplastic is a fluoroplastic having interpolymerized units derived solely from (i) TFE, (ii) more than 5 weight percent of one or more ethylenically unsaturated copolymerizable fluorinated monomers other than TFE. Copolymers of TFE and HFP with or without other perfluorinated comonomers are known in the art as FEP's (fluorinated ethylene propylene). In some embodiments, these fluoroplastics are derived from copolymerizing 30 to 70 wt. % TFE, 10 to 30 wt. %, HFP, and 5 to 50 wt. % of a third ethylenically unsaturated fluorinated comonomer other than TFE and HFP. For example, such a fluoropolymer may be derived from copolymerization of a monomer charge of TFE (e.g., in an amount of 45 to 65 wt. %), HFP (e.g., in an amount of 10 to 30 wt. %), and VDF (e.g., in an amount of 15 to 35 wt. %). Copolymers of TFE, HFP and vinylidenefluoride (VDF) are known in the art as THV. Another example of a useful fluoroplastic is a fluoroplastic derived from copolymerization of a monomer charge of TFE (e.g., from 45 to 70 wt %), HFP (e.g., from 10 to 20 wt %), and an alpha olefin hydrocarbon ethylenically unsaturated comonomer having from 1 to 3 carbon atoms, such as ethylene or propylene (e.g., from 10 to 20 wt. %). Another example of a useful fluoroplastic is a fluoroplastic derived from TFE and an alpha olefin hydrocarbon ethylenically unsaturated comonomer. Examples of polymers of this subclass include a copolymer of TFE and propylene and a copolymer of TFE and ethylene (known as ETFE). Such copolymers are typically derived by copolymerizing from 50 to 95 wt. %, in some embodiments, from 85 to 90 wt. %, of TFE with from 50 to 15 wt. %, in some embodiments, from 15 to 10 wt. %, of the comonomer. Still other examples of useful fluoroplastics include polyvinylidene fluoride (PVDF) and a VdF/TFE/CTFE including 50 to 99 mol % VdF units, 30 to 0 mol % TFE units, and 20 to 1 mol % CTFE units.

In some embodiments, the semi-crystalline fluorinated thermoplastic is a copolymer of a fluorinated olefin and at least one of a fluorinated vinyl ether or fluorinated allyl ether. In some of these embodiments, the fluorinated olefin is TFE. Copolymers of TFE and perfluorinated alkyl or allyl ethers are known in the art as PFA's (perfluorinated alkoxy polymers). In these embodiments, the fluorinated vinyl ether or fluorinated allyl ether units are present in the copolymer in an amount in a range from 0.01 mol% to 15 mol%, in some embodiments, 0.01 mol% to 10 mol%, and in some embodiments, 0.05 mol% to 5 mol%. The fluorinated vinyl ether or fluorinated allyl ether may be any of those described above. In some embodiments, the fluorinated vinyl ether comprises at least one of perfluoro (methyl vinyl) ether (PMVE), perfluoro (ethyl vinyl) ether (PEVE), perfluoro (n-propyl vinyl) ether (PPVE-1), perfluoro-2-

propoxypropylvinyl ether (PPVE-2), perfluoro-3-methoxy-n-propylvinyl ether, perfluoro-2-methoxy-ethylvinyl ether, or $CF_3-(CF_2)_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-CF_2-O-CF=CF_2$.

Semi-crystalline fluorinated thermoplastics described above in any of their embodiments may be prepared with or without cure site monomers as described above in any of their embodiments.

Fluoropolymers useful for practicing the present disclosure, including amorphous and semi-crystalline fluoropolymers described in any of the above embodiments, are commercially available and/or can be prepared by a sequence of steps, which can include polymerization, coagulation, washing, and drying. In some embodiments, an aqueous emulsion polymerization can be carried out continuously under steady-state conditions. For example, an aqueous emulsion of monomers (e.g,. including any of those described above), water, emulsifiers, buffers and catalysts can be fed continuously to a stirred reactor under optimum pressure and temperature conditions while the resulting emulsion or suspension is continuously removed. In some embodiments, batch or semibatch polymerization is conducted by feeding the aforementioned ingredients into a stirred reactor and allowing them to react at a set temperature for a specified length of time or by charging ingredients into the reactor and feeding the monomers into the reactor to maintain a constant pressure until a desired amount of polymer is formed. After polymerization, unreacted monomers are removed from the reactor effluent latex by vaporization at reduced pressure. The fluoropolymer can be recovered from the latex by coagulation.

The polymerization is generally conducted in the presence of a free radical initiator system, such as ammonium persulfate, potassium permanganate, AIBN, or bis(perfluoroacyl) peroxides. The polymerization reaction may further include other components such as chain transfer agents and complexing agents. The polymerization is generally carried out at a temperature in a range from 10 °C and 100 °C, or in a range from 30 °C and 80 °C. The polymerization pressure is usually in the range of 0.3 MPa to 30 MPa, and in some embodiments in the range of 2 MPa and 20 MPa.

When conducting emulsion polymerization, perfluorinated or partially fluorinated emulsifiers may be useful. Generally these fluorinated emulsifiers are present in a range from about 0.02% to about 3% by weight with respect to the polymer. An example of a useful fluorinated emulsifier is represented by formula:

$$Y\text{-}Rf\text{-}Z\text{-}M$$

wherein Y represents hydrogen, Cl or F; Rf represents a linear or branched perfluorinated alkylene having 4 to 10 carbon atoms; Z represents COO^- or SO_3^- and M represents an alkali metal ion or an ammonium ion. Such fluorinated surfactants include fluorinated alkanoic acid and fluorinated alkanoic sulphonic acids and salts thereof, such as ammonium salts of perfluorooctanoic acid and perfluorooctane sulphonic acid. Also contemplated for use in the preparation of the polymers described herein are fluorinated emulsifiers represented by formula:

$$[Rf\text{-}O\text{-}L\text{-}COO\text{-}]_iX^{i+}$$

wherein L represents a linear partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, Rf represents a linear partially or fully fluorinated aliphatic group or a linear partially or fully fluorinated group interrupted with one or more oxygen atoms, X^{i+} represents a cation having the valence i and i is 1,2 and 3. In one embodiment, the emulsifier is selected from CF_3-O-$(CF_2)_3$-O-CHF-CF_2-C(O)OH and salts thereof. Specific examples are described in US 2007/0015937. Other examples of useful emulsifiers include: $CF_3CF_2OCF_2CF_2OCF_2COOH$, $CHF_2(CF_2)_5COOH$, $CF_3(CF_2)_6COOH$, $CF_3O(CF_2)_3OCF(CF_3)COOH$, $CF_3CF_2CH_2OCF_2CH_2OCF_2COOH$, $CF_3O(CF_2)_3OCHFCF_2COOH$, $CF_3O(CF_2)_3OCF_2COOH$, $CF_3(CF_2)_3(CH_2CF_2)_2CF_2CF_2CF_2COOH$, $CF_3(CF_2)_2CH_2(CF_2)_2COOH$, $CF_3(CF_2)_2COOH$, $CF_3(CF_2)_2(OCF(CF_3)CF_2)OCF(CF_3)COOH$, $CF_3(CF_2)_2(OCF_2CF_2)_4OCF(CF_3)COOH$, $CF_3CF_2O(CF_2CF_2O)_3CF_2COOH$, and their salts. Also contemplated for use in the preparation of the fluorinated polymers described herein are fluorinated polyether surfactants, such as described in U.S. Pat. No. 6,429,258.

Polymer particles produced with a fluorinated emulsifier typically have an average diameter, as determined by dynamic light scattering techniques, in range of about 10 nanometers (nm) to about 300 nm, and in some embodiments in range of about 50 nm to about 200 nm. If desired, the emulsifiers can be removed or recycled from the fluoropolymer latex as described in U.S. Pat. Nos. 5,442,097 to Obermeier et al., 6,613,941 to Felix et al., 6,794,550 to Hintzer et al., 6,706,193 to Burkard et al. and 7,018,541 to Hintzer et al. In some embodiments, the polymerization process may be conducted with no emulsifier (e.g., no fluorinated emulsifier). Polymer particles produced without an emulsifier typically have an average diameter, as determined by dynamic light scattering techniques, in a range of about 40 nm to about 500 nm, typically in range of about 100 nm and about 400 nm, and suspension polymerization will typically produce particles sizes up to several millimeters.

In some embodiments, a water soluble initiator can be useful to start the polymerization process. Salts of peroxy sulfuric acid, such as ammonium persulfate, are typically applied either alone or sometimes in the presence of a reducing agent, such as bisulfites or sulfinates (e.g., fluorinated sulfinates disclosed in U.S. Pat. Nos. 5,285,002 and 5,378,782 both to Grootaert) or the sodium salt of hydroxy methane sulfinic acid (sold under the trade designation “RONGALIT”, BASF Chemical Company, New Jersey, USA). Most of these initiators and emulsifiers have an optimum pH-range where they show most efficiency. For this reason, buffers are sometimes useful. Buffers include phosphate, acetate or carbonate buffers or any other acid or base, such as ammonia or alkali metal hydroxides. The concentration range for the initiators and buffers can vary from 0.01% to 5% by weight based on the aqueous polymerization medium.

Aqueous polymerization using the initiators described above will typically provide fluoropolymers with polar end groups; (see, e.g., Logothetis, Prog. Polym. Sci., Vol. 14, pp. 257-258 (1989)). If desired, such as for improved processing or increased chemical stability, the presence of strong polar end groups such as $SO_3^{(-)}$ and $COO^{(-)}$ in fluoropolymers can be reduced through known post treatments (e.g., decarboxylation, post-fluorination). Chain transfer agents of any kind can significantly reduce the number of ionic or polar end groups. The strong polar end groups can be reduced by these methods to any desired level. In some embodiments, the number of polar functional end groups (e.g.,

-COF, $-SO_2F$, $-SO_3M$, -COO-alkyl, –COOM, or $-O-SO_3M$, wherein alkyl is C_1-C_3 alkyl and M is hydrogen or a metal or ammonium cation), is reduced to less than or equal to 500, 400, 300, 200, or 100 per 10^6 carbon atoms. The number of polar end groups can be determined by known infrared spectroscopy techniques. In some embodiments, it may be useful to select initiators and polymerization conditions to achieve at least 1000 polar functional end groups (e.g., -COF, $-SO_2F$, $-SO_3M$, -COO-alkyl, –COOM, or $-O-SO_3M$, wherein alkyl is C_1-C_3 alkyl and M is hydrogen or a metal or ammonium cation) per 10^6 carbon atoms, 400 per 10^6 carbon atoms, or at least 500 per 10^6 carbon atoms. When a fluoropolymer has at least 1000, 2000, 3000, 4000, or 5000 polar functional end groups per 10^6 carbon atoms, the fluoropolymer may have increased interaction with the hollow ceramic microspheres and/or may have improved interlayer adhesion.

Chain transfer agents and any long-chain branching modifiers described above can be fed into the reactor by batch charge or continuously feeding. Because feed amount of chain transfer agent and/or long-chain branching modifier is relatively small compared to the monomer feeds, continuous feeding of small amounts of chain transfer agent and/or long-chain branching modifier into the reactor can be achieved by blending the long-chain branding modifier or chain transfer agent in one or more monomers.

Adjusting, for example, the concentration and activity of the initiator, the concentration of each of the reactive monomers, the temperature, the concentration of the chain transfer agent, and the solvent using techniques known in the art can control the molecular weight of the fluoropolymer Molecular weight of a fluoropolymer relates to the melt flow index. Fluoropolymers useful for practicing the present disclose may have melt flow indexes in a range from 0.01 grams per ten minutes to 10,000 grams per ten minutes (20 kg/372 °C), in a range from 0.5 grams per ten minutes to 1,000 grams per ten minutes (5 kg/372 °C), or in a range from 0.01 grams per ten minutes to 10,000 grams per ten minutes (5 kg/297 °C).

To coagulate the obtained fluoropolymer latex, any coagulant which is commonly used for coagulation of a fluoropolymer latex may be used, and it may, for example, be a water soluble salt (e.g., calcium chloride, magnesium chloride, aluminum chloride or aluminum nitrate), an acid (e.g., nitric acid, hydrochloric acid or sulfuric acid), or a water-soluble organic liquid (e.g., alcohol or acetone). The amount of the coagulant to be added may be in range of 0.001 to 20 parts by mass, for example, in a range of 0.01 to 10 parts by mass per 100 parts by mass of the fluoropolymer latex. Alternatively or additionally, the fluoropolymer latex may be frozen for coagulation. The coagulated fluoropolymer can be collected by filtration and washed with water. The washing water may, for example, be ion exchanged water, pure water or ultrapure water. The amount of the washing water may be from 1 to 5 times by mass to the fluoropolymer, whereby the amount of the emulsifier attached to the fluoropolymer can be sufficiently reduced by one washing.

Compositions (in some embodiments, filaments, pellets, or granules) according to the present disclosure and/or useful for practicing the methods and articles disclosed herein also include hollow ceramic microspheres. The hollow ceramic microspheres useful for practicing the present disclosure generally are those that are able to survive the extrusion process (e.g., without being crushed) and therefore are typically found in the three-dimensional article. A lower density in the three-dimensional article can provide evidence for the hollow ceramic microspheres surviving the process and being found in the three-dimensional article. Further evidence for the incorporation of hollow ceramic microspheres in the three-dimensional article can be obtained by cutting through the three-dimensional article and observing the cut surface with a microscope.

In some embodiments, the hollow microspheres useful for practicing the present disclosure are hollow glass microspheres. Hollow glass microspheres useful in the compositions and methods according to the present disclosure can be made by techniques known in the art (see, e.g., U. S. Pat. Nos. 2,978,340 (Veatch et al.); 3,030,215 (Veatch et al.); 3,129,086 (Veatch et al.); and 3,230,064 (Veatch et al.); 3,365,315 (Beck et al.); 4,391,646 (Howell); and 4,767,726 (Marshall); and U. S. Pat. App. Pub. No. 2006/0122049 (Marshall et. al). Techniques for preparing hollow glass microspheres typically include heating milled frit, commonly referred to as "feed", which contains a blowing agent (e.g., sulfur or a compound of oxygen and sulfur). Frit can be made by heating mineral components of glass at high temperatures until molten glass is formed.

Although the frit and/or the feed may have any composition that is capable of forming a glass, typically, on a total weight basis, the frit comprises from 50 to 90 percent of SiO_2, from 2 to 20 percent of alkali metal oxide, from 1 to 30 percent of B_2O_3, from 0.005-0.5 percent of sulfur (for example, as elemental sulfur, sulfate or sulfite), from 0 to 25 percent divalent metal oxides (for example, CaO, MgO, BaO, SrO, ZnO, or PbO), from 0 to 10 percent of tetravalent metal oxides other than SiO_2 (for example, TiO_2, MnO_2, or ZrO_2), from 0 to 20 percent of trivalent metal oxides (for example, Al_2O_3, Fe_2O_3, or Sb_2O_3), from 0 to 10 percent of oxides of pentavalent atoms (for example, P_2O_5 or V_2O_5), and from 0 to 5 percent fluorine (as fluoride) which may act as a fluxing agent to facilitate melting of the glass composition. Additional ingredients are useful in frit compositions and can be included in the frit, for example, to contribute particular properties or characteristics (for example, hardness or color) to the resultant hollow glass microspheres.

In some embodiments, the hollow glass microspheres useful in the compositions and methods according to the present disclosure have a glass composition comprising more alkaline earth metal oxide than alkali metal oxide. In some of these embodiments, the weight ratio of alkaline earth metal oxide to alkali metal oxide is in a range from 1.2:1 to 3:1. In some embodiments, the hollow glass microspheres have a glass composition comprising B_2O_3 in a range from 2 percent to 6 percent based on the total weight of the glass bubbles. In some embodiments, the hollow glass microspheres have a glass composition comprising up to 5 percent by weight Al_2O_3, based on the total weight of the hollow glass microspheres. In some embodiments, the glass composition is essentially free of Al_2O_3. "Essentially free of Al_2O_3" may mean up to 5, 4, 3, 2, 1, 0.75, 0.5, 0.25, or 0.1 percent by weight Al_2O_3. Glass compositions that are "essentially free of Al_2O_3" also include glass compositions having no Al_2O_3.

Hollow glass microspheres useful for practicing the present disclosure may have, in some embodiments, a chemical composition wherein at least 90%, 94%, or even at least 97% of the glass comprises at least 67% SiO_2, (e.g., a range of 70% to 80% SiO_2), a range of 8% to 15% of an alkaline earth metal oxide (e.g., CaO), a range of 3% to 8% of an alkali metal oxide (e.g., Na_2O), a range of 2% to 6% B_2O_3, and a range of 0.125% to 1.5% SO_3. In some embodiments, the glass comprises in a range from 30% to 40% Si, 3% to 8% Na, 5% to 11% Ca, 0.5% to 2% B, and 40% to 55% O, based on the total of the glass composition.

Hollow glass microspheres useful for practicing the present disclosure can be obtained commercially and include those marketed by 3M Company, St. Paul, MN, under the trade designation "3M GLASS BUBBLES" (e.g., grades K37, XLD-3000, S38, S38HS, S38XHS, K46, A16/500, A20/1000, D32/4500, H50/10000, S60, S60HS, iM30K, iM16K, S38HS, S38XHS, K42HS, K46, and H50/10000). Other suitable hollow glass microspheres can be obtained, for example, from Potters Industries, Valley Forge, PA, (an affiliate of PQ Corporation) under the trade designations "SPHERICEL HOLLOW GLASS SPHERES" (e.g., grades 110P8 and 60P18) and "Q-CEL HOLLOW SPHERES" (e.g., grades 30, 6014, 6019, 6028, 6036, 6042, 6048, 5019, 5023, and 5028), from Silbrico Corp., Hodgkins, IL under the trade designation "SIL-CELL" (e.g., grades SIL 35/34, SIL-32, SIL-42, and SIL-43), and from Sinosteel Maanshan Inst. of Mining Research Co., Maanshan, China, under the trade designation “Y8000”.

In some embodiments, the hollow microspheres useful for practicing the present disclosure are hollow ceramic microspheres other than the glass microspheres described above. In some embodiments, the hollow ceramic microspheres are aluminosilicate microspheres extracted from pulverized fuel ash collected from coal-fired power stations (i.e., cenospheres). Useful cenospheres include those marketed by Sphere One, Inc., Chattanooga, Tenn., under the trade designation "EXTENDOSPHERES HOLLOW SPHERES" (e.g., grades SG, MG, CG, TG, HA, SLG, SL-150, 300/600, 350 and FM-1); and those marketed by SphereServices, Inc., Oak Ridge, Tenn., under the trade designations "RECYCLOSPHERES", “SG500”, “Standard Grade 300”, “BIONIC BUBBLE XL-150”, and “BIONIC BUBBLE W-300”. Cenospheres typically have true average densities in a range from 0.25 grams per cubic centimeter (g/cc) to 0.8 g/cc, determined according to the method described below.

In some embodiments, the hollow ceramic microspheres are perlite microspheres. Perlite is an amorphous volcanic glass that greatly expands and forms microspheres when it is sufficiently heated. The bulk density of perlite microspheres is typically in a range, for example, from 0.03 to 0.15 g/cm^3. A typical composition of perlite microspheres is 70% to 75% SiO_2, 12% to 15% Al_2O_3, 0.5% to 1.5% CaO, 3% to 4% Na_2O, 3% to 5% K_2O, 0.5% to 2% Fe_2O_3, and 0.2% to 0.7% MgO. Useful perlite microspheres include those available, for example, from Silbrico Corporation, Hodgkins, IL.

In some embodiments, the hollow ceramic microspheres are hollow aluminum oxide spheres. Hollow aluminum oxide spheres can be made by fusing high purity alumina. Compressed air is introduced to the melt to form bubbles. Suitable hollow aluminum oxide spheres of various sizes are commercially available, for example, from Imerys Fused Minerals, Villach, Austria, under the trade designation “ALODUR KKW”.

The "average true density" of hollow ceramic microspheres is the quotient obtained by dividing the mass of a sample of hollow ceramic microspheres by the true volume of that mass of hollow ceramic microspheres as measured by a gas pycnometer. The "true volume" is the aggregate total volume of the hollow ceramic microspheres, not the bulk volume. The average true density of the hollow ceramic microspheres useful for practicing the present disclosure is generally at least 0.20 grams per cubic centimeter (g/cc), 0.25 g/cc, or 0.30 g/cc. In some embodiments, the hollow ceramic microspheres useful for practicing the present disclosure have an average true density of up to about 0.65 g/cc. "About 0.65 g/cc" means 0.65 g/cc ± five percent. In some of these embodiments, the average true density of the hollow ceramic microspheres disclosed herein may be in a range from 0.2 g/cc to 0.65 g/cc, 0.2 g/cc to 0.5 g/cc, 0.3 g/cc to 0.65 g/cc, or 0.3 g/cc to 0.48 g/cc. Hollow ceramic microspheres having any of these densities can be useful for lowering the density of three-dimensional articles according to the present disclosure and/or made according to the methods disclosed herein.

In some embodiments of the compositions (including filaments, pellets, or granules) according to the present disclosure, the hollow ceramic microspheres in the composition are those described in U.S. Pat. No. 9,006,302 (Amos et al.).

For the purposes of this disclosure, average true density is measured using a pycnometer according to ASTM D2840- 69, "Average True Particle Density of Hollow Microspheres”. The pycnometer may be obtained, for example, under the trade designation "ACCUPYC 1330 PYCNOMETER" from Micromeritics, Norcross, Georgia, or under the trade designations “PENTAPYCNOMETER” or “ULTRAPYCNOMETER 1000” from Formanex, Inc., San Diego, CA. Average true density can typically be measured with an accuracy of 0.001 g/cc. Accordingly, each of the density values provided above can be ± five percent.

A variety of sizes of hollow ceramic microspheres may be useful in the methods, articles, compositions disclosed herein. As used herein, the term size is considered to be equivalent with the diameter and height of the hollow ceramic microspheres. In some embodiments, the hollow ceramic microspheres can have a median size by volume in a range from 14 to 70 micrometers (in some embodiments from 15 to 65 micrometers, 15 to 60 micrometers, or 20 to 50 micrometers). The median size is also called the D50 size, where 50 percent by volume of the hollow ceramic microspheres in the distribution are smaller than the indicated size. For the purposes of the present disclosure, the median size by volume is determined by laser light diffraction by dispersing the hollow ceramic microspheres in deaerated, deionized water. Laser light diffraction particle size analyzers are available, for example, under the trade designation "SATURN DIGISIZER” from Micromeritics. The size distribution of the hollow ceramic microspheres useful for practicing the present disclosure may be Gaussian, normal, or non-normal. Non-normal distributions may be unimodal or multi-modal (e.g., bimodal).

The hollow ceramic microspheres useful for practicing the present disclosure generally are those that are able to survive the extrusion process (e.g., without being crushed) in the method according to the present disclosure. A useful isostatic pressure at which ten percent by volume of hollow ceramic microspheres collapses is typically at least about 17 MPa. In some embodiments, an isostatic pressure at which ten percent by volume of the hollow ceramic microspheres collapses can be at least 17, 20, or 38 MPa, depending on the requirements of the final three-dimensional article. In some embodiments, an isostatic pressure at which ten percent, or twenty percent, by volume of the hollow ceramic microspheres collapses is up to 250 (in some embodiments, up to 210, 190, or 170) MPa. For the purposes of the present disclosure, the collapse strength of the hollow ceramic microspheres is measured on a dispersion of the hollow ceramic microspheres in glycerol using ASTM D3102 -72 "Hydrostatic Collapse Strength of Hollow Glass Microspheres"; with the exception that the sample size (in grams) is equal to 10 times the density of the ceramic bubbles. Collapse strength can typically be measured with an accuracy of ± about five percent. Accordingly, each of the collapse strength values provided above can be ± five percent. It should be understood by a person skilled in the art that not all hollow ceramic microspheres with the same density have the same collapse strength and that an increase in density does not always correlate with an increase in collapse strength.

In some embodiments, hollow ceramic microspheres useful for practicing the present disclosure are surface treated. In some embodiments, the hollow ceramic microspheres are surface treated with a coupling agent such as a zirconate, silane, or titanate. Typical titanate and zirconate coupling agents are known to those skilled in the art and a detailed overview of the uses and selection criteria for these materials can be found in Monte, S.J., Kenrich Petrochemicals, Inc., “Ken-React® Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents”, Third Revised Edition, March, 1995. Suitable silanes are coupled to ceramic (e.g., glass) surfaces through condensation reactions to form siloxane linkages with the siliceous surfaces. The treatment renders the microspheres more wet-able or promotes the adhesion of materials to the microsphere surface. This provides a mechanism to bring about covalent, ionic or dipole bonding between hollow ceramic microspheres and organic matrices. Silane coupling agents may be chosen based on the particular functionality desired. Suitable silane coupling strategies are outlined in Silane Coupling Agents: Connecting Across Boundaries, by Barry Arkles, pg 165 – 189, Gelest Catalog 3000-A Silanes and Silicones: Gelest Inc. Morrisville, PA. In some embodiments, useful silane coupling agents have amino functional groups (e.g., N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and (3-aminopropyl)trimethoxysilane). In compositions of the present disclosure, it may be useful to employ a combination of amino-functional silane and a maleic anhydride modified polyolefin (e.g., polyethylene or polypropylene) in a polyolefin based composition to enhance the coupling between the hollow ceramic microspheres and the polyolefin base resin. In some embodiments, it may be useful to use a coupling agent that contains a polymerizable moiety, thus incorporating the material directly into the polymer backbone. Examples of polymerizable moieties are materials that contain olefinic functionality such as styrenic, vinyl (e.g., vinyltriethoxysilane, vinyltri(2-

methoxyethoxy) silane), acrylic and methacrylic moieties (e.g., 3-metacrylroxypropyltrimethoxysilane). Other examples of useful silanes that may participate in crosslinking include 3-mercaptopropyltrimethoxysilane, bis(triethoxysilipropyl)tetrasulfane (e.g., available under the trade designation “SI-69” from Evonik Industries, Wesseling, Germany), and thiocyanatopropyltriethoxysilane. If used, coupling agents are commonly included in an amount of about 1 to 3% by weight, based on the total weight of the hollow ceramic microspheres.

In some embodiments, the hollow ceramic microspheres useful for practicing the present disclosure are provided with a polymeric coating as described in Int. Pat. Appl, Pub. Nos. WO2013/148307 (Barrios et al.), WO2014/100593 (Amos et al.), and WO2014/100614 (Amos et al.). The polymeric coating can include a cationic polymer, a nonionic polymer, a conductive polymer, a fluoropolymer (e.g., an amorphous fluoropolymer), an anionic polymer, or a hydrocarbon polymer. In some embodiments, the polymeric coating is a polyolefin (e.g., polyethylene, polypropylene, polybutylene, polystyrene, polyisoprene, paraffin waxes, EPDM copolymer, or polybutadiene) or an acrylic homopolymer or copolymer (e.g., polymethyl acrylate, polyethyl methacrylate, polyethyl acrylate, polyethyl methacrylate, polybutyl acrylate, or butyl methacrylate). In some embodiments, the polymeric coating is selected to be compatible with low-surface-energy polymer or polyolefin in the filament or composition disclosed herein. Polymeric coatings on hollow ceramic microspheres may be made, for example, by a process that includes combining a dispersion with a plurality of hollow ceramic microspheres such that a polymeric coating is disposed on at least a portion of the surfaces of the hollow ceramic microspheres. The dispersion can include a continuous aqueous phase and a dispersed phase. The continuous aqueous phase includes water and optionally one or more water-soluble organic solvents (e.g., glyme, ethylene glycol, propylene glycol, methanol, ethanol, N-methylpyrrolidone, and/or propanol). The dispersed phase includes any one or more of the polymers as described above. The polymer dispersion can be stabilized with a cationic emulsifier, for example. Cationically-stabilized polyolefin emulsions are readily available from commercial sources, for example, under the trade designation "MICHEM EMULSION' (e.g., grades 09730, 11226, 09625, 28640, 70350) from Michelman, Inc., Cincinnati, Ohio.

In some embodiments, the hollow ceramic microspheres useful for practicing the present disclosure are provided with an organic acid or mineral acid coating as described in U.S. Pat. No. 3,061,495 (Alford). In some embodiments, the hollow ceramic microspheres are treated with an aqueous solution of sulfuric acid, hydrochloric acid, or nitric acid at a concentration and for a time sufficient to reduce the alkali metal concentration of hollow ceramic microspheres. This can be useful, for example, when the composition including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres includes base-sensitive polymers such as PVDF, THV, and amorphous fluoropolymers comprising HFP and VDF.

In order to reduce the weight of the three-dimensional article, the hollow ceramic microspheres are typically present in the composition including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres (in some embodiments, the filament) disclosed herein in any of the above embodiments at a level of at least 0.5 percent by weight, based on the total weight of the composition. In some embodiments, the hollow ceramic microspheres are present in the composition at least at 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 percent by weight based on the total weight of the composition. In some embodiments, the hollow ceramic microspheres are present in the composition at a level of up to 20, 15, or 10 percent by weight, based on the total weight of the composition. In some embodiments, the hollow ceramic microspheres are present in the composition in a range from 0.5 to 20, 1 to 20, 5 to 20, or 5 to 15 percent by weight, based on the total weight of the composition.

Compositions including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres disclosed herein in any of the above embodiments may have at least 80 percent by weight of the low-surface-energy polymer or polyolefin, based on the total weight of the composition. In some embodiments, the composition includes greater than 80 percent by weight or at least 81, 82, 83, 84, 85, 89, 90, or 91 percent by weight of the low-surface-energy polymer or polyolefin, based on the total weight of the composition.

Compositions including a low-surface-energy polymer or polyolefin and hollow ceramic microspheres disclosed herein, including filaments, can include other ingredients. In some embodiments, the composition according to and/or useful in the method according to the present disclosure includes one or more stabilizers (e.g., UV stabilizers, antioxidants, or hindered amine light stabilizers (HALS)). Any class of UV stabilizer may be useful. Examples of useful classes of UV stabilizers include benzophenones, benzotriazoles, triazines, cinnamates, cyanoacrylates, dicyano ethylenes, salicylates, oxanilides, para-aminobenzoates, and carbon black. In some embodiments, the UV stabilizer has enhanced spectral coverage in the long-wave UV region (e.g., 315 nm to 400 nm), enabling it to block the high wavelength UV light that can cause yellowing in polymers. HALS are typically compounds that can scavenge free-radicals, which can result from photodegradation or other degradation processes. Suitable HALS include decanedioic acid, bis (2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl)ester. Suitable HALS include those available, for example, from BASF under the trade designations “TINUVIN” and “CHIMASSORB”. Such compounds, when used, can be present in an amount from about 0.001 to 1 percent by weight based on the total weight of the composition.

Examples of useful antioxidants include hindered phenol-based compounds and phosphoric acid ester-based compounds (e.g., those available from BASF, Florham Park, NJ, under the trade designations "IRGANOX" and "IRGAFOS" such as "IRGANOX 1076" and "IRGAFOS 168", those available from Songwon Ind. Co, Ulsan, Korea, under the trade designations “SONGNOX”, and butylated hydroxytoluene (BHT)). Antioxidants, when used, can be present in an amount from about 0.001 to 1 percent by weight based on the total weight of the composition. Antioxidants may quench oxy and peroxy radicals and can be useful, for example, for improving melt processing stability and long-term heat aging.

Reinforcing filler may be useful in the composition according to and/or useful in the method according to the present disclosure. Reinforcing filler can be useful, for example, for enhancing the tensile, flexural, and/or impact strength of the composition. Examples of useful reinforcing fillers include silica (including nanosilica), other metal oxides, metal hydroxides, and carbon black. Other useful fillers include glass fiber, carbon fiber, wollastonite, talc, mica, calcium carbonate, titanium dioxide (including nano-titanium dioxide), wood flour, other natural fillers and fibers (e.g., walnut shells, hemp, cellulosic fibers, and corn silks), and clay (including nano-clay). However, in some embodiments, the presence of such reinforcing fillers in the composition according to the present disclosure can lead to an undesirable increase in the density of the composition. Accordingly, in some embodiments, the composition is free of reinforcing filler or contains up to 5, 4, 3, 2, or 1 percent by weight reinforcing filler, based on the total weight of the composition. More specifically, in some embodiments, the composition is free of reinforcing fibers or contains up to 5, 4, 3, 2, or 1 percent by weight reinforcing fibers, based on the total weight of the composition. More specifically, in some embodiments, the composition is free of cellulosic fibers (in some embodiments, wood fibers) or contains up to 5, 4, 3, 2, or 1 percent by weight cellulosic fibers (in some embodiments, wood fibers), based on the total weight of the composition. In some embodiments, the composition is free of glass fibers or contains up to 5, 4, 3, 2, or 1 percent by weight glass fibers, based on the total weight of the composition. Such fibers and other fillers having high aspect ratios may line up in the flow direction during bead extrusion, which can exacerbate the differential shrinkage problem described above.

In some embodiments of the composition according to and/or useful in the method according to the present disclosure, the composition includes a microwave-absorbing material. The three-dimensional article made by the method according to the present disclosure be subjected to microwave heating to improve adhesion between at least the second layer and the first layer of the three-dimensional article. The microwave-absorbing material can be included, for example, within the bulk of the low-surface-energy polymer or polyolefin, on the surface of the extruded first and second layer portions, on the surface of the hollow ceramic microspheres, or a combination of these. The microwave-absorbing material can comprise at least one of carbon nanotubes, carbon black, buckyballs, graphene, superparamagnetic nanoparticles, magnetic nanoparticles, metallic nanowires, semiconducting nanowires, quantum dots, polyaniline (PANI), and poly3,4-ethylenedioxythiophene polystyrenesulfonate. Coating the surfaces of the hollow ceramic microspheres and/or first and second layer portions of the three-dimensional article can be carried out, for example, by spraying a dispersion of the microwave-absorbing material onto the desired surface. Dip coating the hollow ceramic microspheres and/or input filaments, pellets, or granules for the melt extrusion manufacturing process in a bath of the dispersion may also be useful. Filaments coated with a microwave absorbing material can be made by simultaneous co-extrusion of a polymer and microwave-absorbing material sheath and pure low-surface-energy polymer or polyolefin core coaxial filament using the method described, for example, in U.S. Pat. No. 5,219,508 (Collier et al.). The three-dimensional article can be irradiated with microwaves during or after it is extruded. In these embodiments, the melt extrusion additive manufacturing device useful for practicing the present disclosure further includes a microwave source operable for irradiating the three-dimensional article or one or more layers thereof after extrusion through the extruder as described in U.S. Pat. Appl. No. 2016/0324491 (Sweeney et al.).

Other additives may be incorporated into the composition disclosed herein in any of the embodiments described above. Examples of other additives that may be useful, depending on the intended use of the three-dimensional article, include compatibilizers, impact modifiers, preservatives, mixing agents, colorants (e.g., pigments or dyes), dispersants, floating or anti-setting agents, flow or processing agents, wetting agents, anti-ozonant, odor scavengers, acid neutralizer, antistatic agent, and adhesion promoters (e.g., a coupling agent described above).

In some embodiments, for example, when the low-surface-energy polymer is a polyolefin, the compatibilizer is a polyolefin modified with polar functional groups. In some embodiments, the polar functional groups include maleic anhydride, carboxylic acid groups, and hydroxyl groups. In some embodiments, the compatibilizer is a maleic anhydride-modified polyolefin. The level of grafting of the polar functional groups (e.g., the level of grafting of maleic anhydride in the modified polyolefin may be in a range from about 0.5-3%, 0.5-2%, 0.8-1.2%, or about 1%). The compatibilizer can added to the composition in an amount sufficient to improve a mechanical property of the composition. In some embodiments, compatibilizer is present in the composition in amount of at least 1, 1.5, 2, or 2.5 percent, based on the total weight of the composition. In some embodiments, compatibilizer is present in the composition in amount of up to 3, 4, or 5 percent, based on the total weight of the composition. In some embodiments, compatibilizer is present in the composition in amount in a range from 1.5 percent to 4 percent or 2 percent to 4 percent, based on the total weight of the composition. In some embodiments, the composition includes a compatibilizer as described in any of these embodiments and a surface treated hollow ceramic microsphere, such as any of those described above. In some of these embodiments, the compatibilizer is a maleic anhydride-modified polyolefin, and the hollow ceramic microspheres are modified with a silane coupling agent having amino functional groups.

Useful impact modifiers for the compositions described herein include elastomers. In some embodiments, for example, when the low-surface-energy polymer is a polyolefin, the impact modifier may be a polyolefin and may be chemically non-crosslinked. In some embodiments, the impact modifier is free of any of the polar functional groups described above in connection with the compatibilizer. In some embodiments, the impact modifier includes only carbon-carbon and carbon-hydrogen bonds. In some embodiments, the impact modifier is an ethylene propylene elastomer, an ethylene octene elastomer, an ethylene propylene diene elastomer, an ethylene propylene octene elastomer, polybutadiene, a butadiene copolymer, polybutene, or a combination thereof. In some embodiments, the impact modifier is an ethylene octene elastomer.

The method according to the present disclosure includes heating the composition to provide the composition in molten form. Heating may be carried out, for example, in the extrusion head. It should be understood that the low-surface-energy polymer or polyolefin other components of the composition described above may melt when the composition is heated. However, not every component of the composition needs to melt or be a liquid for it to be considered to be in molten form. For example, the hollow ceramic microspheres do not melt. In other examples, reinforcing fillers and certain stabilizers and pigments also would not typically melt when the composition is in molten form.

In some embodiments, the low-surface-energy polymer or polyolefin in compositions and methods disclosed herein is crosslinkable, forming a thermoset in the three-dimensional article. For example, polyethylene may be crosslinkable in the presence of a peroxide or sulfonyl hydrazide crosslinking agent, which can be added to the composition when the hollow ceramic microspheres are added. Examples of suitable crosslinking agents include dicumyl peroxide, benzoyl peroxide, 1,10-decane-bis(sulfonyl hydrazide), 1,1-di-tert-butyl peroxy-3,3,5-trimethyl cyclohexane, 2,5-dimethyl-2,5-di(tert-butyl peroxy) hexane, tert-butyl-cumyl peroxide, α,α'-di(butyl peroxy)-diisoproyl benzene, and 2,5-dimethyl-2,5-di(tert-butyl peroxy) hexyne. When the composition is heated, the crosslinking agents decompose to form free-radical species, which can abstract a hydrogen from the polyethylene chain to form a crosslinking sight. The term "crosslinked" refers to joining polymer chains together by covalent chemical bonds, usually via crosslinking molecules or groups, to form a network polymer. Therefore, a chemically non-crosslinked polymer is a polymer that lacks polymer chains joined together by covalent chemical bonds to form a network polymer. A crosslinked polymer is generally characterized by insolubility, but may be swellable in the presence of an appropriate solvent. A non-crosslinked polymer is typically soluble in certain solvents and is typically melt-processable. A polymer that is chemically non-crosslinked may also be referred to as a linear polymer. A melt-processable polymer that is chemically non-crosslinked may also be referred to as a thermoplastic.

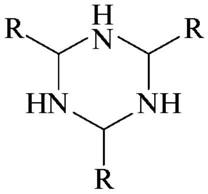
In some low-surface-energy polymers or polyolefins (e.g., polypropylene) addition of peroxide and the resulting free-radical formation can cause chain scission or “vis-breaking”. Due to the statistical probability that a peroxide moiety will encounter a longer polymer chain than a shorter polymer chain, chain scission generally has the effect of narrowing the molecular weight distribution. Narrowing the molecular weight distribution of the polymer changes the polymer rheology and melt flow properties and can be useful, for example, for polypropylene fiber extrusion. Chain scission using this method may be useful, for example, for making low-diameter filaments.

A fluoropolymer described above including at least one cure site monomer is crosslinkable, and the three-dimensional object formed from such a fluoropolymer can be a fluoroelastomer. A commonly used cure system is based on a peroxide cure reaction using appropriate curing compounds having or creating peroxides. It is generally believed that the bromine or iodine atoms are abstracted in the free radical peroxide cure reaction, thereby causing the fluoropolymer molecules to cross-link and to form a network. Suitable organic peroxides are those which generate free radicals at curing temperatures. A dialkyl peroxide or a bis(dialkyl peroxide) which decomposes at a temperature above the extrusion temperature may be useful. A di-tertiarybutyl peroxide having a tertiary carbon atom attached to the peroxy oxygen, for example, may be useful. Among the peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexane. Other peroxides useful for making fluoroelastomers can be selected from compounds such as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl perbenzoate, alpha,alpha'-bis(t-butylperoxy-diisopropylbenzene), and di[1,3-dimethyl-3-(t-butylperoxy)-butyl]carbonate. A tertiary butyl peroxide having a tertiary carbon atom attached to a peroxy oxygen may be a useful class of peroxides. Further examples of peroxides include 2,5-dimethyl-2,5-di(t-butylperoxy)hexane; dicumyl peroxide; di(2-t-butylperoxyisopropyl)benzene; dialkyl peroxide; bis (dialkyl peroxide); 2,5-dimethyl-2,5-di(tertiarybutylperoxy)3-hexyne; dibenzoyl peroxide; 2,4-dichlorobenzoyl peroxide; tertiarybutyl perbenzoate; di(t-butylperoxy-isopropyl)benzene; t-butyl peroxy isopropylcarbonate, t-butyl peroxy 2-ethylhexyl carbonate, t-amyl peroxy 2-ethylhexyl carbonate, t-hexylperoxy isopropyl carbonate, di[1,3-dimethyl-3-(t-butylperoxy)butyl] carbonate, carbonoperoxoic acid, O,O'-1,3-propanediyl OO,OO'-bis(1,1-dimethylethyl) ester, and combinations thereof. The amount of peroxide curing agent used generally will be at least 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.2, or even 1.5; at most 2, 2.25, 2.5, 2.75, 3, 3.5, 4, 4.5, 5, or even 5.5 parts by weight per 100 parts of the fluoropolymer may be used.

The curing agents may be present on carriers, for example silica containing carriers.

A peroxide cure system may also include one or more coagent. Typically, the coagent includes a polyunsaturated compound which is capable of cooperating with the peroxide to provide a useful cure. These coagents can be added in an amount between 0.1 and 10 parts per hundred parts fluoropolymer, in some embodiments between 2 and 5 parts per hundred parts fluoropolymer. Examples of useful coagents include tri(methyl)allyl isocyanurate (TMAIC), triallyl isocyanurate (TAIC), tri(methyl)allyl cyanurate, poly-triallyl isocyanurate (poly-TAIC), triallyl cyanurate (TAC), xylylene-bis(diallyl isocyanurate) (XBD), N,N'-m-phenylene bismaleimide, diallyl phthalate, tris(diallylamine)-s-triazine, triallyl phosphite, 1,2-polybutadiene, ethyleneglycol diacrylate, diethyleneglycol diacrylate, and combinations thereof. Another useful coagent may be represented by the formula CH2=CH-Rf1-CH=CH2 wherein Rf1 may be a perfluoroalkylene having from 1 to 8 carbon atoms. Such coagents can provide enhanced mechanical strength to the final cured elastomer.

Curing of composition including a fluoropolymer and hollow ceramic microspheres, wherein the fluoropolymer has nitrogen-containing cure sites, can also be modified by using yet other types of curatives to achieve a dual cure system. Examples of such curatives for fluoropolymers with nitrile cure sites include fluoroalkoxy organophosphohium, organoammonium, or organosulfonium compounds (e.g., Int. Pat. Appl. Pub. No. WO 2010/151610 (Grootaert et al.), bis-aminophenols (e.g., U.S. Pat. Nos. 5,767,204 (Iwa et al.) and 5,700,879 (Yamamoto et al.)), bis-amidooximes (e.g., U.S. Pat . No. 5,621,145 (Saito et al.)), and ammonium salts (e.g., U.S. Pat . No. 5,565,512 (Saito et al.)). In addition, organometallic compounds of arsenic, antimony, and tin (e.g., allyl-, propargyl-, triphenyl- allenyl-, and tetraphenyltin and triphenyltin hydroxide) as described in U.S. Pat. Nos. 4,281,092 (Breazeale) and 5,554,680 (Ojakaar) and ammonia-generating compounds may be useful. "Ammonia-generating compounds" include compounds that are solid or liquid at ambient conditions but that generate ammonia under conditions of cure. Examples of such compounds include hexamethylenetetramine (urotropin), dicyandiamide, and metal-containing compounds of the formula $A^{w+}(NH_3)_xY^{w-}$, wherein A^{w+} is a metal cation such as Cu^{2+}, Co^{2+}, Co^{3+}, Cu^{+}, and Ni^{2+}; w is equal to the valance of the metal cation; Y^{w-} is a counterion (e.g., a halide, sulfate, nitrate, acetate); and x is an integer from 1 to about 7. Further examples include substituted and unsubstituted triazine derivatives such as those of the formula:



wherein R is a hydrogen atom or a substituted or unsubstituted alkyl, aryl, or arylalkylene group having from 1 to about 20 carbon atoms. Specific useful triazine derivatives include hexahydro-1,3,5-s-triazine and acetaldehyde ammonia trimer.

The curable composition may further contain acid acceptors. Acid acceptors may be added to improve the fluoroelastomers steam and water resistance. Such acid acceptors can be inorganic or blends of inorganic and organic acid acceptors. Examples of inorganic acceptors include magnesium oxide, lead oxide, calcium oxide, calcium hydroxide, dibasic lead phosphate, zinc oxide, barium carbonate, strontium hydroxide, calcium carbonate, hydrotalcite, etc. Organic acceptors include epoxies, sodium stearate, and magnesium oxalate. Particularly suitable acid acceptors include magnesium oxide and zinc oxide. Blends of acid acceptors may be used as well. The amount of acid acceptor will generally depend on the nature of the acid acceptor used. However, some applications like fuel cell sealants or gaskets for the semi-conductor industry require low metal content. Accordingly, in some embodiments, the composition is free of such acid acceptors or includes an amount of these acid acceptors such that the composition has less than 1 ppm total metal ion content.

In some embodiments, an acid acceptor is used between 0.5 and 5 parts per 100 parts of the curable composition. In other embodiments, an acid acceptor is not needed and the composition is essentially free an acid acceptor. As used herein, essentially free of an acid acceptor or essentially free of a metal-containing acid acceptor means less than 0.01, 0.005, or even 0.001 parts per 100 parts of the composition according to the present disclosure and includes being free of an acid acceptor.

Curing is typically achieved by heat-treating the curable composition. The heat-treatment is carried out at an effective temperature and effective time to create a cured fluoroelastomer. Optimum conditions can be tested by examining the cured highly fluorinated elastomer for its mechanical and physical properties. Typically, curing is carried out at temperatures greater than 120°C or greater than 150°C. Typical curing conditions include curing at temperatures between 160°C and 210°C or between 160°C and 190°C. Typical curing periods include from 3 to 90 minutes. Curing may be carried out under pressure. For example pressures from 10 to 100 bar may be applied. A post curing cycle may be applied to ensure the curing process is fully completed. Post curing may be carried out at a temperature between 170°C and 250°C for a period of 1 to 24 hours.

Filaments, or strands, according to the present disclosure and/or useful for practicing some embodiments of the method of the present disclosure can generally be made using techniques known in the art for making filaments. Filaments, or strands, can be made by extrusion through a strand die.

In some embodiments, filaments, or strands, according to the present disclosure and/or useful for practicing some embodiments of the method of the present disclosure are made by extrusion through a strand die. Hollow ceramic microspheres can be added to a low-surface-energy polymer or polyolefin composition in an extruder (e.g., a twin-screw extruder) equipped with a side stuffer that allows for the hollow ceramic microsphere addition. The composition comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres can be extruded through a strand die having an appropriate diameter. Optionally, the strand can be cooled upon extrusion using a water bath. The filament can be lengthened using a belt puller. The speed of the belt puller can be adjusted to achieve a desired filament diameter.

An embodiment of a strand die useful for making a filament 50 according to the present disclosure and/or useful for practicing the present disclosure is shown in the sectional view of FIG. 2. Strand die 20 includes a strand die body 21 that is surrounded by a heater band 23. The composition comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres can be extruded through cavity 29 in the strand die body 21. In the illustrated embodiment, the strand die 20 is equipped with a strand die screw-in insert 25. Die swell 27 can occur as the strand 50 exits the strand die body 21. The screw-in insert 25 allows for quickly changing the land length and diameter during extrusion to accommodate different resins, which exhibit, for example, different die swell characteristics, to obtain a strand 50 having a desired diameter and ovality.

The aspect ratio (that is, length to diameter or width) of filaments useful in some embodiments of the method of the present disclosure may be, for example, at least 10:1, 25:1, 50:1, 100:1, 150:1, 200:1, 250:1, 500:1, 1000:1, or more; or in a range from 200:1 to 10,000:1. Filaments can have any desired length and can be provided in a coil, for example. Filaments having a length of at least about 20 feet (6 meters) can be useful in a method according to the present disclosure. Filaments having a length of up to about 100 feet (30.5 meters) can also be useful. Typically, the filaments disclosed herein have a maximum cross-sectional dimension up to 3 (in some embodiments, up to 2.5, 2, 1.75, or 1.5) millimeters (mm). For example, the filament may have a circular cross-section with an average diameter in a range from 1 micrometer to 3 mm, 1.5 to 3 mm, or 1.5 to 2 mm.

The incorporation of hollow ceramic microspheres into three-dimensional articles made by the method of the present disclosure provides an advantageous weight reduction. Thus, compositions and methods disclosed herein are useful, for example, for lowering the specific gravity of a three-dimensional article made by melt extrusion additive manufacturing in comparison to a three-dimensional article comprising the low-surface-energy polymer or polyolefin but no hollow ceramic microspheres. Specific gravity refers to the density of the substance making up the three-dimensional object, and not the bulk of the three-dimensional object, which can include void spaces. The hollow ceramic microspheres also provide useful mechanical properties to the three-dimensional article, for example, higher rigidity and higher modulus. Typically and unexpectedly, when hollow ceramic microspheres are present in the composition, adhesion between the first layer and second layer is better than in a comparative three-dimensional article. The comparative three-dimensional article is prepared according to the method of making the three-dimension article except that the composition does not comprise hollow ceramic microspheres. Also, typically and advantageously, the layers in the three-dimensional article made by the method of the present disclosure are more dimensionally stable than in the comparative three-dimensional article. Also, typically and advantageously, the layers in the three-dimensional article made by the method of the present disclosure can cool faster than in the comparative three-dimensional article because of the presence of the hollow ceramic microspheres. Faster cooler can reduce the time required to make the three-dimensional article. The interlayer adhesion and dimensional stability can be seen in the photomicrograph of the three-dimensional article of Example 4 shown in FIG. 3. By comparison, the comparative three-dimensional article of Comparative Example C is shown in FIG. 4. Poor flow during extrusion and interlayer adhesion results in the non-uniform appearance of the three-dimensional article shown in FIG. 4. Upon closer inspection under microscope, air pockets or voids can be seen in the layers themselves.

The incorporation of hollow ceramic microspheres into a filament, or strand, for use in fused filament fabrication according to the present disclosure can also provide advantages. Typically and advantageously, a filament that is made from a composition including hollow ceramic microspheres and a low-surface-energy polymer or polyolefin can be made with better ovality than a filament made from a composition that does not contain hollow ceramic microspheres. As used herein, ovality refers to the distortion of the cross-section of the filament from a round shape. Ovality can be expressed as a percentage and is calculated by taking twice the difference between the major and minor axes of the filament divided by the sum of the major and minor axes and multiplying by 100 as shown in the equation below:

$$[2(\text{major axis} - \text{minor axis})]/(\text{major axis} + \text{minor axis}) \times 100.$$

Major and minor axes can be measured with a caliper, for example.

In some embodiments, the ovality of the filament for used in fused filament fabrication is up to 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, or 2%. Accordingly, the present disclosure provides a filament comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres having an ovality of up to up to 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, or 2%. In some of these embodiments, the aspect ratio (that is, length to diameter or major axis) of the filament is at least 10:1, 25:1, 50:1, 100:1, 150:1, 200:1, 250:1, 500:1, 1000:1, or more; or in a range from 100:1 to 10,000:1. As shown in Example 3 and Comparative Example B, below, filaments having dimensions suitable for evaluation in a 3D printer were prepared by extruding a composition including high density polyethylene and hollow glass microspheres. However, in the absence of hollow glass microspheres, it was difficult to get a consistent feed of the high density polyethylene through the extruder, which resulted in poor diameter control and unacceptable ovality. A filament of high density polyethylene suitable for evaluation in a 3D printer could not be prepared in the absence of hollow glass microspheres.

Some Embodiments of the Disclosure

In a first embodiment, the present disclosure provides a method of making a three-dimensional article, the method comprising:

heating a composition comprising a low-surface-energy polymer and hollow ceramic microspheres;

extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three-dimensional article; and

extruding at least a second layer of the composition in molten form onto at least the portion of the first layer to make at least a portion of the three-dimensional article.

In a second embodiment, the present disclosure provides the method of the first embodiment, further comprising at least partially melting the low-surface-energy polymer in the extrusion head to provide the composition in molten form.

In a third embodiment, the present disclosure provides the method of the second embodiment, wherein the low-surface-energy polymer comprises at least one of a polyolefin or fluoropolymer.

In a fourth embodiment, the present disclosure provides the method of the third embodiment, wherein the polyolefin comprises at least one of polypropylene or polyethylene. The polyolefin may be polypropylene.

In a fifth embodiment, the present disclosure provides the method of the third embodiment, wherein the fluoropolymer comprises interpolymerized units from at least one partially fluorinated or perfluorinated ethylenically unsaturated monomer represented by formula $RCF=CR_2$, wherein each R is independently fluoro, chloro, bromo, hydrogen, a fluoroalkyl group having up to 8 carbon atoms and optionally interrupted by one or more oxygen atoms, a fluoroalkoxy group having up to 8 carbon atoms and optionally interrupted by one or more oxygen atoms, alkyl having up to 10 carbon atoms, alkoxy having up to 8 carbon atoms, or aryl having up to 8 carbon atoms.

In a sixth embodiment, the present disclosure provides the method of the fifth embodiment, wherein the fluoropolymer is an amorphous fluoropolymer.

In a seventh embodiment, the present disclosure provides the method of the sixth embodiment, wherein the fluoropolymer further comprises a cure site, and wherein composition further comprises a curing agent.

In an eighth embodiment, the present disclosure provides the method of the fifth embodiment, wherein the fluoropolymer is a semi-crystalline thermoplastic.

In a ninth embodiment, the present disclosure provides the method of any one of the first to eighth embodiments, wherein the composition comprises greater than 80 percent by weight of the low-surface-energy polymer.

In a tenth embodiment, the present disclosure provides the method of any one of the first to ninth embodiments, wherein the composition comprises at least 85 percent by weight of the low-surface-energy polymer.

In an eleventh embodiment, the present disclosure provides the method of any one of the first to tenth embodiments, wherein the hollow ceramic microspheres are present in the composition in a range from 0.5 percent to 20 percent by weight, based on the total weight of the composition.

In a twelfth embodiment, the present disclosure provides the method of the eleventh embodiment, wherein the hollow ceramic microspheres are present in the composition in a range from 5 percent to 15 percent by weight, based on the total weight of the composition.

In a thirteenth embodiment, the present disclosure provides the method of any one of the first to twelfth embodiments, further comprising providing the composition as a filament comprising the low-surface-energy polymer and the hollow ceramic microspheres before heating.

In a fourteenth embodiment, the present disclosure provides the method of the thirteenth embodiment, wherein the filament has lower ovality in comparison to a filament comprising the low-surface-energy polymer but not including the hollow ceramic microspheres.

In a fifteenth embodiment, the present disclosure provides a method of making a three-dimensional article, the method comprising:

heating a composition comprising a polyolefin and hollow ceramic microspheres;

extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three-dimensional article; and

extruding at least a second layer of the composition in molten form onto at least the portion of the first layer to make at least a portion of the three-dimensional article.

In a sixteenth embodiment, the present disclosure provides the method of the fifteenth embodiment, further comprising at least partially melting the polyolefin in the extrusion head to provide the composition in molten form.

In a seventeenth embodiment, the present disclosure provides the method of the sixteenth embodiment, wherein the polyolefin comprises at least one of polypropylene or polyethylene.

In an eighteenth embodiments, the present disclosure provides the method of the seventeenth embodiment, wherein the polyolefin comprises polypropylene.

In a nineteenth embodiment, the present disclosure provides the method of any one of the fifteenth to eighteenth embodiments, wherein the composition comprises greater than 80 percent by weight of the polyolefin.

In a twentieth embodiment, the present disclosure provides the method of any one of the fifteenth to nineteenth embodiments, wherein the composition comprises at least 85 percent by weight of the polyolefin.

In a twenty-first embodiment, the present disclosure provides the method of any one of the fifteenth to twentieth embodiments, wherein the hollow ceramic microspheres are present in the composition in a range from 0.5 percent to 20 percent by weight, based on the total weight of the composition.

In a twenty-second embodiment, the present disclosure provides the method of the twenty-first embodiment, wherein the hollow ceramic microspheres are present in the composition in a range from 5 percent to 15 percent by weight, based on the total weight of the composition.

In a twenty-third embodiment, the present disclosure provides the method of any one of the fifteenth to twenty-second embodiments, wherein providing the composition comprises providing a filament comprising the polyolefin and the hollow ceramic microspheres.

In a twenty-fourth embodiment, the present disclosure provides the method of the twenty-third embodiment, wherein the filament has lower ovality in comparison to a filament comprising the polyolefin but not including the hollow ceramic microspheres.

In a twenty-fifth embodiment, the present disclosure provides the method of any one of the fifteenth to twenty-fourth embodiments, wherein at least some of the polyolefin is modified with maleic anhydride.

In a twenty-sixth embodiment, the present disclosure provides the method of any one of the first to twenty-fifth embodiments, wherein an isostatic pressure at which ten percent by volume of hollow ceramic microspheres collapses is at least 17 MPa, at least 34 MPa, or at least 51 MPa.

In a twenty-seventh embodiment, the present disclosure provides the method of any one of the first to twenty-sixth embodiments, wherein the hollow ceramic microspheres have a median size by volume in a range from 14 to 70 micrometers.

In a twenty-eighth embodiment, the present disclosure provides the method of any one of the first to twenty-seventh embodiments, wherein the hollow ceramic microspheres have an average true density of at least 0.2 grams per cubic centimeter.

In a twenty-ninth embodiment, the present disclosure provides the method of any one of the first to twenty-eighth embodiments, wherein the hollow ceramic microspheres are hollow glass microspheres.

In a thirtieth embodiment, the present disclosure provides the method of any one of the first to twenty-ninth embodiments, wherein the hollow ceramic microspheres are surface treated with a coupling agent.

In a thirty-first embodiment, the present disclosure provides the method of any one of the first to thirtieth embodiments, wherein the composition further comprises at least one of a compatibilizer, impact modifier, UV stabilizer, hindered amine light stabilizer, anti-oxidant, colorant, dispersant, floating or anti-settling agent, flow or processing agent, wetting agent, anti-ozonant, adhesion promoter, odor scavengers, acid neutralizer, antistatic agent, or inorganic filler.

In a thirty-second embodiment, the present disclosure provides the method of any one of the first to thirty-first embodiments, wherein the composition further comprises at least one of carbon black, glass fiber, carbon fiber, talc, or mica.

In a thirty-third embodiment, the present disclosure provides the method of any one of the first to thirty-first embodiments, wherein the composition is substantially free of cellulosic fibers. The cellulosic fibers may be wood fibers.

In a thirty-fourth embodiment, the present disclosure provides the method of any one of the first to thirty-first embodiments, wherein the composition is substantially free of glass fibers.

In a thirty-fifth embodiment, the present disclosure provides the method of any one of the first to thirty-first, thirty-third, and thirty-fourth embodiments, wherein the composition is substantially free of reinforcing fibers.

In a thirty-sixth embodiment, the present disclosure provides the method of any one of the first to thirty-fifth embodiments, wherein in the three-dimensional article, adhesion between the first layer and second layer is better than in a comparative three-dimensional article, wherein the comparative three-dimensional article is prepared according to the method of making the three-dimension article except that the composition does not comprise hollow ceramic microspheres.

In a thirty-seventh embodiment, the present disclosure provides the method of any one of the first to thirty-sixth embodiments, wherein the three-dimensional article has a lower specific gravity than a comparative three-dimensional article, wherein the comparative three-dimensional article is prepared according to the method of making the three-dimension article except that the composition does not comprise hollow ceramic microspheres.

In a thirty-eighth embodiment, the present disclosure provides the method of any one of the first to thirty-seventh embodiments, wherein making the three-dimensional article is faster than making a comparative three-dimensional article, wherein the comparative three-dimensional article is prepared according to the method of making the three-dimension article except that the composition does not comprise hollow ceramic microspheres.

In a thirty-ninth embodiment, the present disclosure provides the method of any one of the first to thirty-eighth embodiments, further comprising:

retrieving, from a non-transitory machine readable medium, data representing a model of the three-dimensional article; and

executing, by one or more processors interfacing with a manufacturing device, manufacturing instructions using the data.

In a fortieth embodiment, the present disclosure provides the method of the thirty-ninth embodiment, further comprising generating, by the manufacturing device, the three-dimensional article.

In a forty-first embodiment, the present disclosure provides a three-dimensional article made by the method of any one of the first to fortieth embodiments.

In a forty-second embodiment, the present disclosure provides a filament for use in fused filament fabrication, the filament comprising a low-surface-energy polymer and hollow ceramic microspheres.

In a forty-third embodiment, the present disclosure provides the filament of the forty-second embodiment, having an ovality of up to ten percent.

In a forty-fourth embodiment, the present disclosure provides a filament comprising a low-surface-energy polymer and hollow ceramic microspheres, wherein the filament has an ovality of up to ten percent.

In a forty-fifth embodiment, the present disclosure provides the filament of any one of the forty-second embodiment to forty-fourth embodiment, wherein the low-surface-energy polymer comprises at least one of a polyolefin or a fluoropolymer.

In a forty-sixth embodiment, the present disclosure provides the filament of the forty-fifth embodiment, wherein the polyolefin comprises at least one of polypropylene or polyethylene. The polyolefin may be polypropylene.

In a forty-seventh embodiment, the present disclosure provides the filament of the forty-fifth embodiment, wherein the fluoropolymer comprises interpolymerized units from at least one partially fluorinated or perfluorinated ethylenically unsaturated monomer represented by formula $RCF=CR_2$, wherein each R is independently fluoro, chloro, bromo, hydrogen, a fluoroalkyl group having up to 8 carbon atoms and optionally interrupted by one or more oxygen atoms, a fluoroalkoxy group having up to 8 carbon atoms and optionally interrupted by one or more oxygen atoms, alkyl having up to 10 carbon atoms, alkoxy having up to 8 carbon atoms, or aryl having up to 8 carbon atoms.

In a forty-eighth embodiment, the present disclosure provides the filament of the forty-fifth or forty-seventh embodiment, wherein the fluoropolymer is an amorphous fluoropolymer.

In a forty-ninth embodiment, the present disclosure provides the filament of the forty-eighth embodiment, wherein the fluoropolymer further comprises a cure site, and wherein composition further comprises a curing agent.

In a fiftieth embodiment, the present disclosure provides the filament of the forty-fifth or forty-seventh embodiment, wherein the fluoropolymer is a semi-crystalline thermoplastic.

In a fifty-first embodiment, the present disclosure provides the filament of any one of the forty-second to fiftieth embodiments, wherein the filament comprises greater than 80 percent by weight of the low-surface-energy polymer.

In a fifty-second embodiment, the present disclosure provides the filament of any one of the forty-second to fifty-first embodiments, wherein the filament comprises at least 85 percent by weight of the low-surface-energy polymer.

In a fifty-third embodiment, the present disclosure provides a filament for use in fused filament fabrication, the filament comprising a polyolefin and hollow ceramic microspheres.

In a fifty-fourth embodiment, the present disclosure provides the filament of the fifty-third embodiment, having an ovality of up to ten percent.

In a fifty-fifth embodiment, the present disclosure provides a filament comprising a polyolefin and hollow ceramic microspheres, wherein the filament has an ovality of up to ten percent.

In a fifty-sixth embodiment, the present disclosure provides the filament of any one of the fifty-third embodiment to fifty-fifth embodiment, wherein the polyolefin comprises at least one of polypropylene or polyethylene.

In a fifty-seventh embodiment, the present disclosure provides the filament of the fifty-sixth embodiment, wherein the polyolefin comprises polypropylene.

In a fifty-eighth embodiment, the present disclosure provides the filament of any one of the fifty-third to fifty-seventh embodiments, wherein the filament comprises greater than 80 percent by weight of the polyolefin.

In a fifty-ninth embodiment, the present disclosure provides the filament of any one of the fifty-third to fifty-eighth embodiments, wherein the filament comprises at least 85 percent by weight of the polyolefin.

In a sixtieth embodiment, the present disclosure provides the filament of any one of the fifty-third to fifty-ninth embodiments, wherein at least some of the polyolefin is modified with maleic anhydride.

In a sixty-first embodiment, the present disclosure provides the filament of any one of the forty-second to sixtieth embodiments, wherein the hollow ceramic microspheres are present in the filament in a range from 0.5 percent to 20 percent by weight, based on the total weight of the filament.

In a sixty-second embodiment, the present disclosure provides the filament of the sixty-first embodiment, wherein the hollow ceramic microspheres are present in the filament in a range from 5 percent to 15 percent by weight, based on the total weight of the filament.

In a sixty-third embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-second embodiments, wherein an isostatic pressure at which ten percent by volume of hollow ceramic microspheres collapses is at least 17 MPa, at least 34 MPa, or at least 51 MPa.

In a sixty-fourth embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-third embodiments, wherein the hollow ceramic microspheres have a median size by volume in a range from 14 to 70 micrometers.

In a sixty-fifth embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-fourth embodiments, wherein the hollow ceramic microspheres have an average true density of at least 0.2 grams per cubic centimeter.

In a sixty-sixth embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-fifth embodiments, wherein the hollow ceramic microspheres are hollow glass microspheres.

In a sixty-seventh embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-sixth embodiments, wherein the hollow ceramic microspheres are surface treated with a coupling agent.

In a sixty-eighth embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-seventh embodiments, wherein the filament further comprises at least one of a compatibilizer, impact modifier, UV stabilizer, hindered amine light stabilizer, anti-oxidant, colorant, dispersant, floating or anti-settling agent, flow or processing agent, wetting agent, anti-ozonant, adhesion promoter, odor scavengers, acid neutralizer, antistatic agent, or inorganic filler.

In a sixty-ninth embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-eighth embodiments, wherein the filament further comprises at least one of carbon black, glass fiber, carbon fiber, talc, or mica.

In a seventieth embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-ninth embodiments, wherein the filament is substantially free of cellulosic fibers. The cellulosic fibers may be wood fibers.

In a seventy-first embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-eighth embodiments, wherein the filament is substantially free of glass fibers.

In a seventy-second embodiment, the present disclosure provides the filament of any one of the forty-second to sixty-eighth and seventy-first embodiments, wherein the filament is substantially free of reinforcing fibers.

In a seventy-third embodiment, the present disclosure provides the filament of any one of the forty-second to seventy-second embodiments, wherein the filament has an aspect ratio of at least 10:1, 25:1, 50:1, 100:1, 150:1, or 200:1.

In a seventy-fourth embodiment, the present disclosure provides a composition comprising a low-surface-energy polymer and hollow ceramic microspheres for use in melt extrusion additive manufacturing.

In a seventy-fifth embodiment, the present disclosure provides the composition of the seventy-fourth embodiment, for lowering the specific gravity of a three-dimensional article made by melt extrusion additive manufacturing in comparison to a three-dimensional article comprising the low-surface-energy polymer but no hollow ceramic microspheres.

In a seventy-sixth embodiment, the present disclosure provides the composition of the seventy-fourth or seventy-fifth embodiment, for improving adhesion between layers of a three-dimensional article made by melt extrusion additive manufacturing in comparison to a three-dimensional article comprising the low-surface-energy polymer but no hollow ceramic microspheres.

In a seventy-seventh embodiment, the present disclosure provides the composition of any one of the seventy-fourth embodiment to seventy-sixth embodiment, for increasing the speed of making a three-dimensional article by melt extrusion additive manufacturing in comparison to making a three-dimensional article by melt extrusion additive manufacturing with the low-surface-energy polymer but no hollow ceramic microspheres.

In a seventy-eighth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to seventy-seventh embodiments, wherein the low-surface-energy polymer comprises at least one of a polyolefin or a fluoropolymer.

In a seventy-ninth embodiment, the present disclosure provides the composition of the seventy-eighth embodiment, wherein the polyolefin comprises at least one of polypropylene or polyethylene. The polyolefin may be polypropylene.

In an eightieth embodiment, the present disclosure provides the composition of the seventy-eighth embodiment, wherein the fluoropolymer comprises interpolymerized units from at least one partially fluorinated or perfluorinated ethylenically unsaturated monomer represented by formula $RCF=CR_2$, wherein each R is independently fluoro, chloro, bromo, hydrogen, a fluoroalkyl group having up to 8 carbon atoms and optionally interrupted by one or more oxygen atoms, a fluoroalkoxy group having up to 8 carbon atoms and optionally interrupted by one or more oxygen atoms, alkyl having up to 10 carbon atoms, alkoxy having up to 8 carbon atoms, or aryl having up to 8 carbon atoms.

In an eighty-first embodiment, the present disclosure provides the composition of the seventy-eighth or eightieth embodiment, wherein the fluoropolymer is an amorphous fluoropolymer.

In an eighty-second embodiment, the present disclosure provides the composition of the eighty-first embodiment, wherein the fluoropolymer further comprises a cure site, and wherein composition further comprises a curing agent.

In an eighty-third embodiment, the present disclosure provides the composition of the seventy-eighth or eightieth embodiment, wherein the fluoropolymer is a semi-crystalline thermoplastic.

In an eighty-fourth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to eighty-third embodiments, wherein the composition comprises greater than 80 percent by weight of the low-surface-energy polymer.

In an eighty-fifth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to eighty-fourth embodiments, wherein the composition comprises at least 85 percent by weight of the low-surface-energy polymer.

In an eighty-sixth embodiment, the present disclosure provides a composition comprising a polyolefin and hollow ceramic microspheres for use in melt extrusion additive manufacturing.

In an eighty-seventh embodiment, the present disclosure provides the composition of the eighty-sixth embodiment, for lowering the specific gravity of a three-dimensional article made by melt extrusion additive manufacturing in comparison to a three-dimensional article comprising the polyolefin but no hollow ceramic microspheres.

In an eighty-eighth embodiment, the present disclosure provides the composition of the eighty-sixth or eighty-seventh embodiment, for improving adhesion between layers of a three-dimensional article made by melt extrusion additive manufacturing in comparison to a three-dimensional article comprising the polyolefin but no hollow ceramic microspheres.

In an eighty-ninth embodiment, the present disclosure provides the composition of any one of the eighty-sixth to eighty-eighth embodiment, for increasing the speed of making a three-dimensional article by melt extrusion additive manufacturing in comparison to making a three-dimensional article by melt extrusion additive manufacturing with the polyolefin but no hollow ceramic microspheres.

In a ninetieth embodiment, the present disclosure provides the composition of any one of the eighty-sixth to eighty-ninth embodiments, wherein the polyolefin comprises at least one of polypropylene or polyethylene.

In a ninety-first embodiment, the present disclosure provides the composition of the ninetieth embodiment, wherein the polyolefin comprises polypropylene.

In a ninety-second embodiment, the present disclosure provides the composition of any one of the eighty-sixth to ninety-first embodiments, wherein the composition comprises greater than 80 percent by weight of the polyolefin.

In a ninety-third embodiment, the present disclosure provides the composition of any one of the eighty-sixth to ninety-second embodiments, wherein the composition comprises at least 85 percent by weight of the polyolefin.

In a ninety-fourth embodiment, the present disclosure provides the composition of any one of the eighty-sixth to ninety-third embodiments, wherein at least some of the polyolefin is modified with maleic anhydride.

In a ninety-fifth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to ninety-fourth embodiments, wherein the hollow ceramic microspheres are present in the composition in a range from 0.5 percent to 20 percent by weight, based on the total weight of the composition.

In a ninety-sixth embodiment, the present disclosure provides the composition of the ninety-fifth embodiment, wherein the hollow ceramic microspheres are present in the composition in a range from 5 percent to 15 percent by weight, based on the total weight of the composition.

In a ninety-seventh embodiment, the present disclosure provides the composition of any one of the seventy-fourth to ninety-sixth embodiments, wherein an isostatic pressure at which ten percent by volume of hollow ceramic microspheres collapses is at least 17 MPa, at least 34 MPa, or at least 51 MPa.

In a ninety-eighth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to ninety-seventh embodiments, wherein the hollow ceramic microspheres have a median size by volume in a range from 14 to 70 micrometers.

In a ninety-ninth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to ninety-eighth embodiments, wherein the hollow ceramic microspheres have an average true density of at least 0.2 grams per cubic centimeter.

In a hundredth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to ninety-ninth embodiments, wherein the hollow ceramic microspheres are hollow glass microspheres.

In a hundred-and-first embodiment, the present disclosure provides the composition of any one of the seventy-fourth to hundredth embodiments, wherein the hollow ceramic microspheres are surface treated with a coupling agent.

In a hundred-and-second embodiment, the present disclosure provides the composition of any one of the seventy-fourth to hundred-and-first embodiments, wherein the composition further comprises at least one of a compatibilizer, impact modifier, UV stabilizer, hindered amine light stabilizer, anti-oxidant, colorant, dispersant, floating or anti-settling agent, flow or processing agent, wetting agent, anti-ozonant, adhesion promoter, odor scavengers, acid neutralizer, antistatic agent, or inorganic filler.

In a hundred-and-third embodiment, the present disclosure provides the composition of any one of the seventy-fourth to hundred-and-second embodiments, wherein the composition further comprises at least one of carbon black, glass fiber, carbon fiber, talc, or mica.

In a hundred-and-fourth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to hundred-and-second embodiments, wherein the composition is substantially free of cellulosic fibers. The cellulosic fibers may be wood fibers.

In a hundred-and-fifth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to hundred-and-second embodiments, wherein the composition is substantially free of glass fibers.

In a hundred-and-sixth embodiment, the present disclosure provides the composition of any one of the seventy-fourth to hundred-and-second and hundred-and-fourth embodiments, wherein the composition is substantially free of reinforcing fibers.

EXAMPLES

The following specific, but non-limiting, examples will serve to illustrate the present disclosure. Unless otherwise noted, all parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight.

Examples 1 and 2 and Comparative Example A

Examples 1 and 2 and Comparative Example A filaments were prepared using a co-rotating, 25 mm-diameter, twin screw extruder (obtained from Thermo Fisher Scientific, Waltham, MA). The base polyolefin used was Lyondell Basell 6523 PP (a general purpose polypropylene homopolymer resin in pellet form, obtained from Lyondell Basel Industries, Wilmington, DE, under trade designation “PRO-FAX 6523”).

To prepare Examples 1 and 2, “iM16K” glass bubbles (hollow glass microspheres with isostatic crush strength of 16,000 psi (110.3 MPa), and true density of 0.46 g/cc, obtained from 3M Company, St. Paul, MN, under trade designation “3M GLASS BUBBLES iM16K”) were introduced into the polyolefin using a side stuffer unit. The amount of glass bubbles fed into the polyolefin was sufficient to result in 5 wt. % and 10 wt. % glass bubbles with respect to the total weight of polyolefin and glass bubbles, respectively, for Examples 1 and 2. The “iM16K” glass bubbles and polyolefin were allowed to blend via the twin screw process.

The resulting polyolefin-glass bubble blend was extruded through a strand die, shown in FIG. 2, with about a 0.165 inch (0.42 cm) diameter into a water bath. The temperature of the water bath was about 40 °C. The extruder screw speed was 150 RPM. The extruder temperature profile used to produce the filaments was:

Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Die
180 °C	210 °C	210 °C	210 °C	210 °C	210 °C	210 °C

The filament was conveyed down the line using a belt puller (manufactured by CDS, Lachine, Quebec, Canada). The speed of the belt puller was adjusted (27 to 33 feet per minute (about 8-10 meters per minute) to attain the target diameter of about 1.75+/- 0.10 mm. Long sections of filaments were coiled by hand at the exit of the belt puller. This process was able to produce sections of filaments of the proper dimensions to allow for evaluation in a 3-D printer.

Comparative Example A filament was prepared in the same manner as Examples 1 and 2 above except that no glass bubbles was added to the polyolefin.

Example 3 and Comparative Example B

Example 3 filaments were prepared using a 1" (2.5 cm) diameter, single screw extruder (manufactured by Harrel Inc., E. Norwalk, CT) and a Guill Extrusion Head with a 5.0 mm, inside diameter strand die (obtained from Guill Tool & Engineering Co. Inc., West Warrick, RI). The base polyolefin used to prepare Example 3 filaments was Braskem "IE59U3" HDPE (a polyethylene homo polymer with a melt flow rate of 5.0 g/10 minutes at 190 °C/2.16 kg test condition, obtained from Braskem USA, Philadelphia, PA, under trade designation "IE59U3"). To the polyolefin sufficient amount of "iM16K" glass bubbles was added to prepare a blend containing 10 wt. % of glass bubbles with respect to the total weight of polyolefin and glass bubbles. The extruder temperature used for processing is in the table below:

Barrel #1	Barrel #2	Barrel #3	Head	Adapter 1	Adapter 2	Die #1	Die #2
185 °C	210 °C	210 °C	210 °C	210 °C	220 °C	220 °C	220 °C

The resulting polyolefin-glass bubble blend was extruded through a strand die described above in Examples 1 and 2. The resulting extruded polyolefin-glass bubble filament was fed into a water bath. The temperature of the water bath was about 40 °C. Then, the filament was conveyed down the line using a belt puller (manufactured by CDS). The speed of the belt puller was adjusted to attain the target diameter of about 2.88 mm +/- 0.10 mm. Long sections of filaments were coiled by hand at the exit of the belt puller. This process was able to produce sections of filaments of the proper dimensions to allow for evaluation in a 3-D printer.

Comparative Example B filaments was prepared in the same manner as Example 3 filaments except that no "iM16K" glass bubble was added to the base polyolefin. . In the absence of "iM16K" glass bubbles, it was difficult to get a consistent feed through the extruder, which resulted in poor diameter control and unacceptable ovality. A filament from this material would not have been dimensionally acceptable for the 3-D printer.

Example 4 and Comparative Example C

MakerBot Replicator 2X experimental 3D printer (obtained from MakerBot Industries, Brooklyn, N.Y., equipped with software version 3.8.0.168) was used to fabricate calibration cubes using Example 2 and Comparative Example A thermoplastic filament prepared as described above.

Calibration cube had dimensions of 19 mm x 19 mm x 10 mm.

To prepare 3D-printed Example 4 sample, a filament prepared as described above in Example 2 was successfully printed using a heating block temperature of 230 °C and a platform temperature of 110 °C. FIG. 3 shows a photograph of the 3D-printed calibration cube of Example 4.

To prepare 3D-printed Comparative Example C sample, a filament prepared as described above in Comparative Example A was used. Initial attempts to 3D print using a heating block temperature of 230 °C and a platform temperature of 110 °C were not successful. Then another attempt was made to 3D print Comparative Example C calibration cube using a heating block temperature of 255 °C and a platform temperature of 130 °C (maximum capability of the 3D printer used). Under these conditions only four layers were successfully formed due to poor flow of the filament and interlayer adhesion. FIG. 4 shows a photograph of the 3D-printed calibration cube of Comparative Example C.

Examples 5 to 11 and Comparative Examples D to G

The filament for Example 5 was made as described for Example 1 except for the modification that the extruder used to prepare Example 3 was used. The speed of the belt puller was adjusted to attain the target diameter of about 2.75 mm +/- 0.10 mm. The filament for Examples 6 to 9 was made as described for Example 2 except for the modification that the extruder used to prepare Example 3 was used. The speed of the belt puller was adjusted to attain the target diameter of about 2.75 mm +/- 0.10 mm. The filament for Examples 10 to 11 was made as described for Example 3 except for the modification that the speed of the belt puller was adjusted to attain the target diameter of about 2.75 mm +/- 0.10 mm. The filament for Comparative Examples D to F were made as described for Comparative Example A except for the modification that the extruder used to prepare Example 3 was used. The speed of the belt puller was adjusted to attain the target diameter of about 2.75 mm +/- 0.10 mm. The filament for Comparative Example G was made as described for Comparative Example B except for the modification that the speed of the belt puller was adjusted to attain the target diameter of about 2.75 mm +/- 0.10 mm.

An “AW3D AXIOM” Dual Desktop 3D Printer, obtained from “AIRWOLF3D”, Costa Mesa, Cal., was used to print 300% scale cones having a 20-mm base diameter and a 30-mm height. The printer was controlled with Repetier-Host V1.6.2, dividing the CAD “.stl” file into slices with Slic3r V.1.2.9. The interface software was from Repetier.com, a project of Hot-World GmbH & Co., KG, Willich, Germany, and the slicer software was from Slic3r.org. To prepare the cones, an extruder temperature of 200 °C and a platform temperature of 100 °C were used. All fans were turned off during printing of the cones.

Cones were printed at 25mm/sec, 50mm/sec, 75mm/sec, and 100mm/sec, with the speed used for each Example and Comparative Example shown in Table 1, below. For each of these speeds, the time it takes to make each successive ring decreases because the diameter is successively smaller. The cones were quantitatively evaluated by measuring the first two defects in each cone by distance from base, then averaging them. The higher the measurement without defects, the better the inter-layer adhesion, cooling, and solidification of the previous layer and or bottom surface of each layer. The cone with the lowest number was considered the poorest performer. The cones were ranked qualitatively by placing them next to each other and ranking them based on surface quality, amount of noticeable defects, dimensional acuity and the height of any extreme failure. Extreme failure is the point where the printer no longer deposits the material or the next layer does not adhere to the previous layer. Comparative Example G, made from HDPE, could not be printed at 25mm/sec or 50mm/sec, due to poor feeding characteristics of the strand. The poor feeding was due to poor ovality. An attempt to print the filament of C.E. D to F at 100 mm/sec was also not successful.

Table 1: Filament Formulations and Performance in Cone Printing

Example	Speed (mm/sec)	polymer	Loading of microspheres (wt. %)	Height of Defect (mm, Ave of 1st two from base)	Qualitative Ranking of Cones (1 to 5, 5 being best)
C.E. D	25	PP	0	24.2	1
C.E. E	50	PP	0	1.5	1
C.E. F	75	PP	0	6.2	1
Ex. 5	75	PP	5	33.3	2
Ex. 6	25	PP	10	36.8	5
Ex. 7	50	PP	10	53.2	4
Ex. 8	75	PP	10	36.4	2
Ex. 9	100	PP	10	28.2	1
Ex. 10	25	HDPE	10	37.2	4
Ex. 11	50	HDPE	10	28.5	3

Examples 12 and 13

Examples 12 and 13 were prepared using a ZE 25A twin screw extruder with a 25 mm diameter screw (manufactured by KraussMaffei Berstorff, Munich, Germany). The base fluoroplastic was obtained from 3M Company under the designation "3M™ Dyneon™ Fluoroplastic THV 610AZ".

To prepare Example 12, "iM16K" glass bubbles were introduced into the fluoroplastic. The amount of glass bubbles fed into the fluoroplastic was sufficient to result in 4 wt. % glass bubbles with respect to the total weight of fluoroplastic and glass bubbles. The "iM16K" glass bubbles and fluoroplastic were allowed to blend via the twin screw process.

The resulting fluoroplastic-glass bubble blend was extruded through a strand die, with an approximately 5 mm diameter into a water bath. The temperature of the water bath was about 20 °C. The extruder screw speed was 150 rpm. The extruder temperature profile used to produce filaments (strands) was:

Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Die
210 °C	230 °C	240 °C	250 °C	260 °C	260 °C	270 °C

To prepare Example 13, "iM16K" glass bubbles were introduced into the fluoroplastic. The amount of glass bubbles fed into the fluoroplastic was sufficient to result in 13 wt. % glass bubbles with respect to the total weight of fluoroplastic and glass bubbles. The "iM16K" glass bubbles and fluoroplastic were allowed to blend via the twin screw process.

The resulting fluoroplastic-glass bubble blend was extruded through a strand die, with an approximately 5 mm diameter into a water bath. The temperature of the water bath was about 20 °C. The extruder screw speed was 200 rpm. The extruder temperature profile used to produce filaments (strands) was:

Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Die
200 °C	210 °C	220 °C	230 °C	235 °C	240 °C	250 °C

The strands were cut into pellets using a GS25 E4 pelletizer (manufactured by Reduction Engineering Scheer, Kent, OH) at a rotor speed of 22 rpm.

Examples 14 and 15

Examples 14 and 15 were prepared using the ZE 25A twin screw extruder with a 25 mm diameter screw. The base fluoroplastic was obtained from 3M Company, but no longer available, under the trade designation "3M™Dyneon™ Fluoroplastic HTE 1705Z".

To prepare Examples 14 and 15 "iM16K" glass bubbles were introduced into the fluoroplastic. The amount of glass bubbles fed into the fluoroplastic was sufficient to result in 4.5 wt. % and 15 wt. %

glass bubbles with respect to the total weight of fluoroplastic and glass bubbles, respectively, for Examples 14 and 15. The "iM16K" glass bubbles and fluoroplastic were allowed to blend via the twin screw process.

The resulting fluoroplastic-glass bubble blend was extruded through a strand die, with an approximately 5 mm diameter into a water bath. The temperature of the water bath was about 20 °C. The extruder screw speed was 200 rpm. The extruder temperature profile used to produce filaments was:

Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Die
200 °C	230 °C	240 °C	250 °C	255 °C	260 °C	260 °C

The strands were cut into pellets using a GS25 E4 pelletizer (manufactured by Reduction Engineering Scheer, Kent, OH).

The resulting pellets of Example 14 above (4.5 wt. % glass bubbles) were extruded using a ME 30/4X25D single screw extruder with a 30 mm screw diameter, (manufactured by Bernhard Ide GMBH & Co. KG, Ostfildern, Germany).

A 2.5 mm die was used to form monofilaments with a diameter of about 1.65 mm. The extruder screw speed was 6.3 rpm. The extruder temperature profile used to produce monofilaments was:

Zone 1	Zone 2	Zone 3	Zone 4	Flange	Head	Die
200 °C	230 °C	245 °C	255 °C	260 °C	270 °C	280 °C

The resulting pellets of Example 15 above (15 wt. % glass bubbles) were extruded using a ME 30/4X25D single screw extruder with a 30 mm screw diameter, (manufactured by Bernhard Ide GMBH & Co. KG, Ostfildern, Germany).

A 3.7 mm die was used to form monofilaments with a diameter of about 1.65 mm. The extruder screw speed was 5.8 rpm. The extruder temperature profile used to produce monofilaments was:

Zone 1	Zone 2	Zone 3	Zone 4	Flange	Head	Die
220 °C	230 °C	245 °C	255 °C	270 °C	280 °C	295 °C

The monofilaments were wound up on a spool using a PW400 rewinder (manufactured by Peter Khu Sondermaschinenbau GmbH, Hagenbrunn, Austria).

This disclosure is not limited to the above-described embodiments but is to be controlled by the limitations set forth in the following claims and any equivalents thereof. This disclosure may be suitably practiced in the absence of any element not specifically disclosed herein.

What is claimed is:

1. A method of making a three-dimensional article, the method comprising:

heating a composition comprising a low-surface-energy polymer and hollow ceramic microspheres;

extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three dimensional article; and

extruding at least a second layer of the composition in molten form from the extrusion head onto at least the portion of the first layer to make at least a portion of the three dimensional article.

2. The method of claim 1, wherein the low-surface-energy polymer comprises at least one of a polyolefin or fluoropolymer.

3. A method of making a three-dimensional article, the method comprising:

heating a composition comprising a polyolefin and hollow ceramic microspheres;

extruding the composition in molten form from an extrusion head to provide at least a portion of a first layer of the three dimensional article; and

extruding at least a second layer of the composition in molten form onto at least the portion of the first layer to make at least a portion of the three dimensional article.

4. The method of claim 2 or 3, wherein the polyolefin comprises at least one of polypropylene or polyethylene.

5. The method of any one of claims 2 to 4, further comprising a maleic-anhydride modified polyolefin.

6. The method of any one of claims 2 to 5, wherein the composition comprises greater than 80 percent by weight of the polyolefin.

7. The method of any one of claims 1 to 6, wherein the composition comprises at least 5 percent by weight of the hollow ceramic microspheres.

8. The method of any one of claims 1 to 7, wherein the composition is substantially free of cellulosic fibers and glass fibers.

9. The method of any one of claims 2 to 8, further comprising providing the composition as a filament comprising the polyolefin and the hollow ceramic microspheres before heating.

10. The method of any one of claims 1 to 9, wherein an isostatic pressure at which ten percent by volume of hollow ceramic microspheres collapses is at least about 17 MPa.

11. The method of any one of claims 1 to 10, wherein the hollow ceramic microspheres are surface treated with a coupling agent.

12. A three-dimensional article made by the method of any one of claims 1 to 11.

13. A filament for use in fused filament fabrication, the filament comprising a low-surface-energy polymer or polyolefin and hollow ceramic microspheres.

14. The filament of claim 13, wherein the polyolefin comprises at least one of polyethylene or polypropylene.

15. A composition for increasing the speed of making a three-dimensional article by melt extrusion additive manufacturing, the composition comprising a low-surface-energy polymer or a polyolefin and hollow ceramic microspheres.

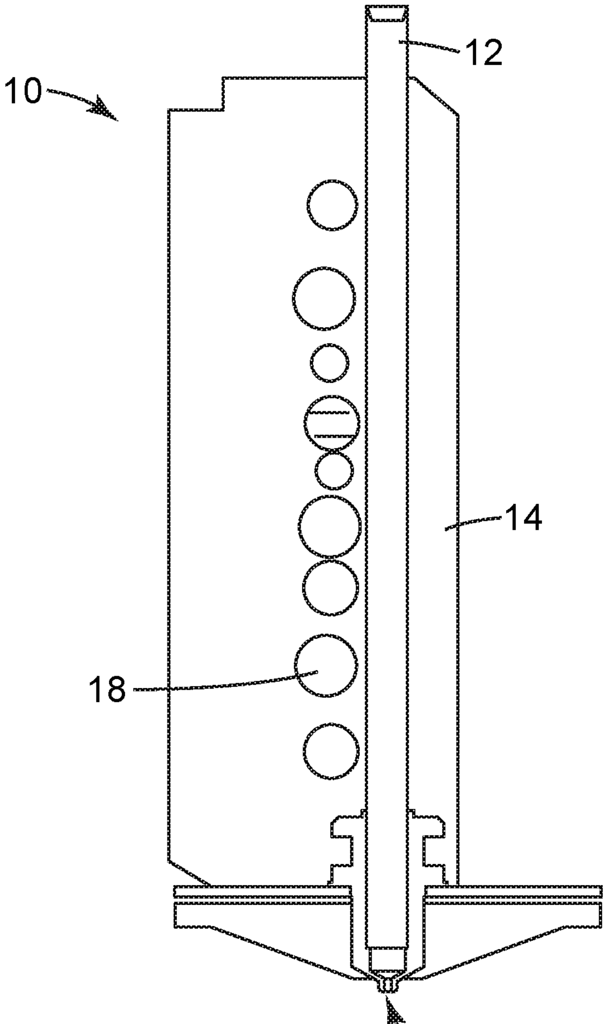


Fig. 1

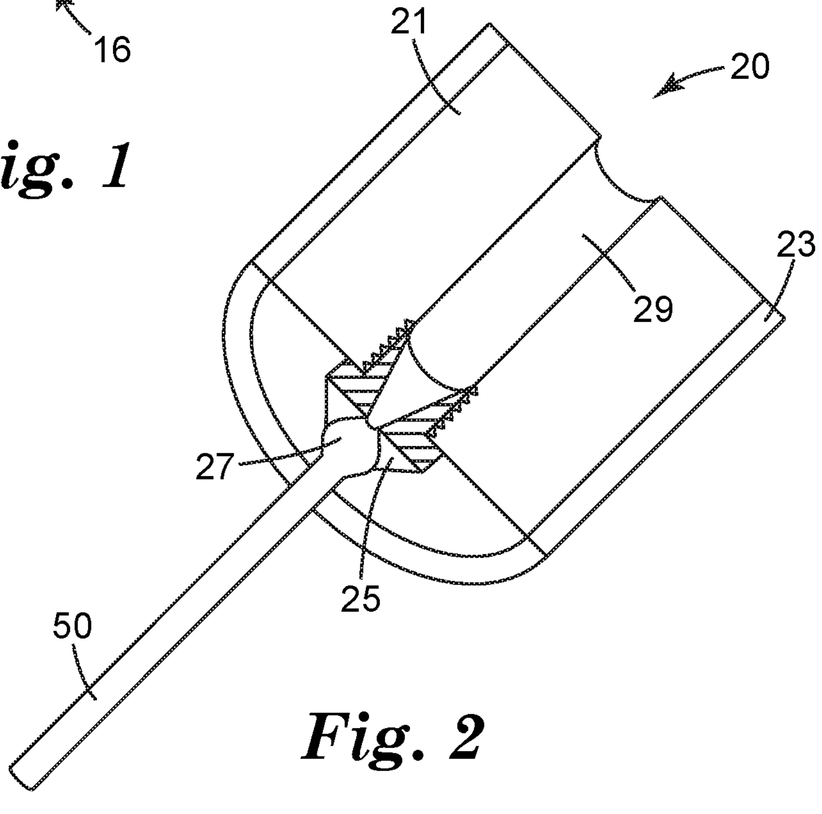


Fig. 2

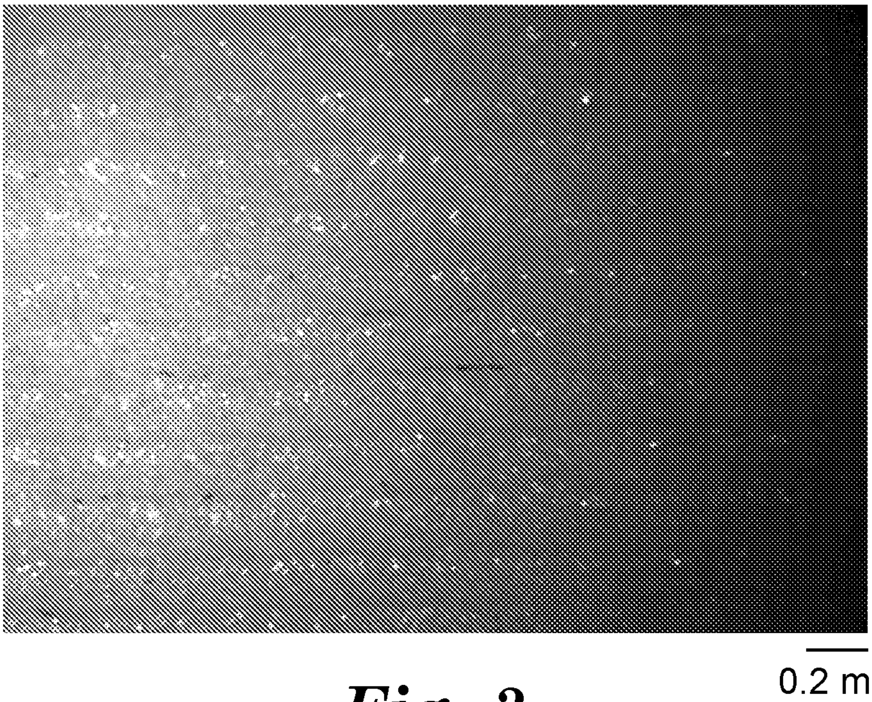


Fig. 3

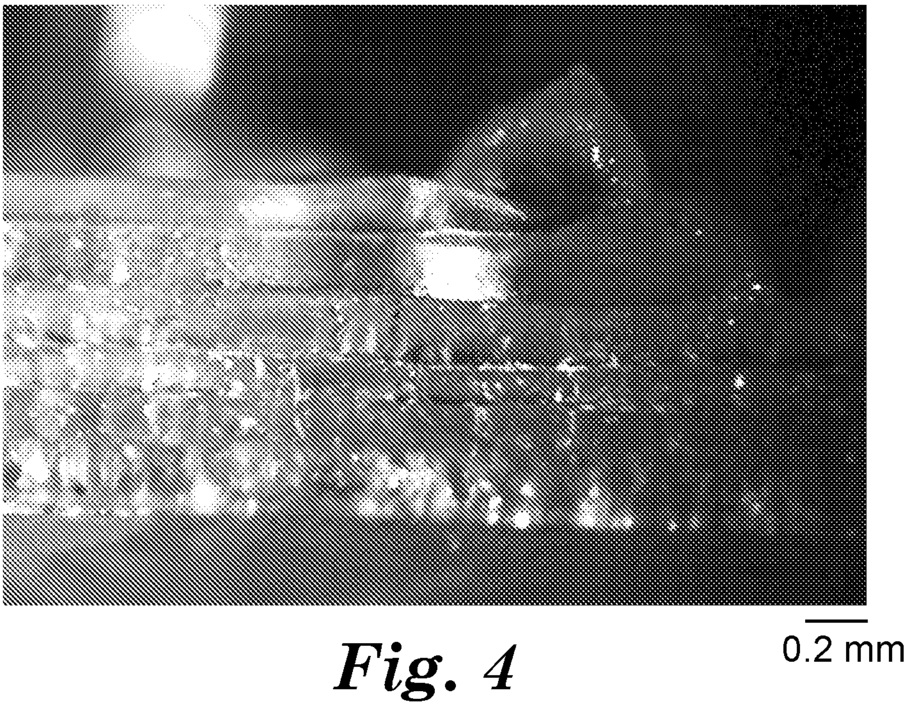
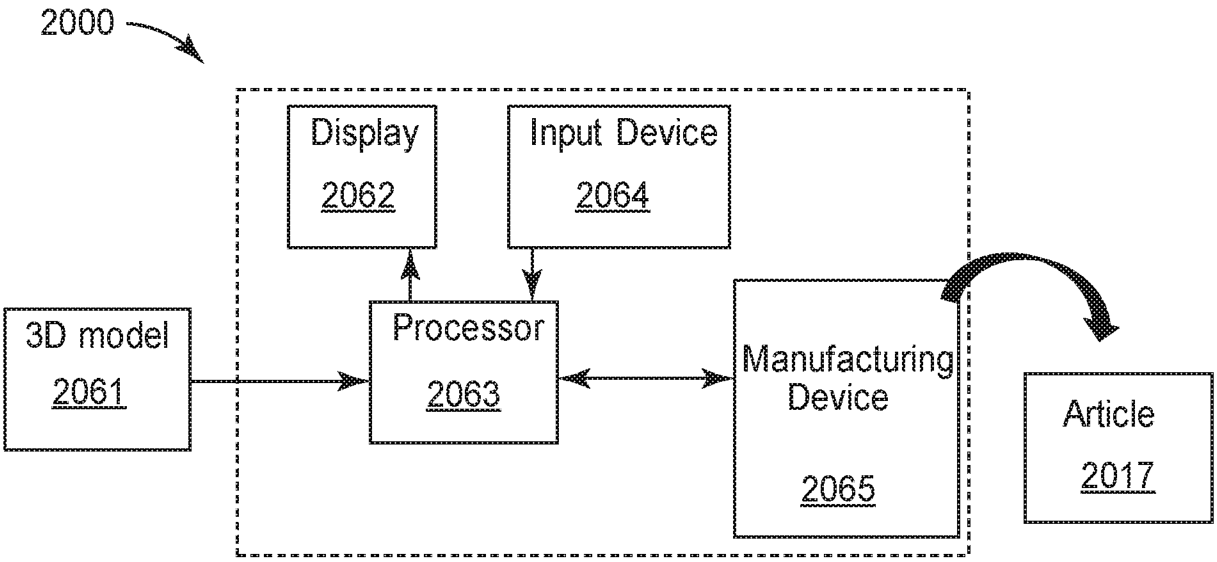


Fig. 4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2062
Input Device
2064
3D model
2061
Processor
2063
Manufacturing Device
2065
Article
2017

Fig. 5

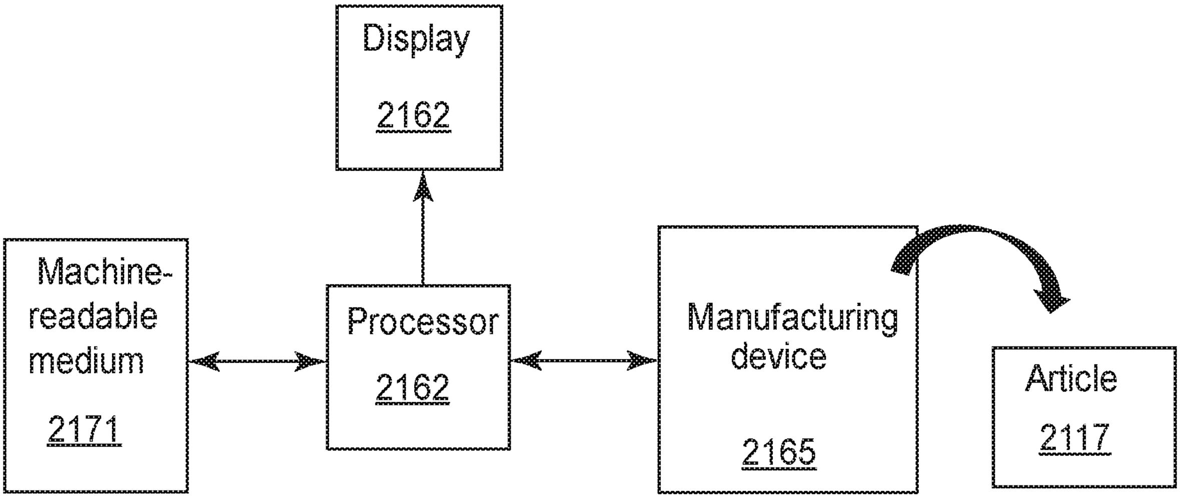
Display
2162
Machine-readable medium
2171
Processor
2162
Manufacturing device
2165
Article
2117

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/062251

A. CLASSIFICATION OF SUBJECT MATTER

B33Y 70/00 (2015.01) C08K 7/24 (2006.01) B29C 64/118 (2017.01)

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)

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)

Database: PATENW, Google Patents
IPC/CPC Symbols: C08F, C08K7/24, C08L23, C08L27, B29C47/00, B29B9/06, B29C64/00, B33Y, B28B1/001, B29K23/00, B29K223/00, B29K423/00, B29K2105/165, B29K2509/02, B29K2509/08, B29K2023/00, B29K2223/00, B29K2423/00, B32B27/32, B32B2264/101, B32B2264/107, C04B2111/0018, C04B38/009, C04B20/002, C04B2235/528, C03C12/00, C03C11/002 *and subsets thereof*
Keywords: hollow glass microsphere, extrusion, fused filament fabrication, additive manufacturing *and similar terms thereof*
Database: Google Scholar
Keywords: hollow glass microsphere, extrusion, fused filament fabrication, additive manufacturing *and similar terms thereof*

Inventor names searched in PATENW and internal databases provided by IP Australia.
Applicant names searched in Espacenet, AusPat and internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ 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 application or patent 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 6 February 2018	Date of mailing of the international search report 06 February 2018
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	**Authorised officer** Joel Parraga AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832839

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT	International application No. **PCT/US2017/062251**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 102015003378 A1 (BECKMANN JÖRG) 22 September 2016, machine translation obtained from Espacenet abstract, paragraphs [0005]-[0007], [0019], claims 1-10	1-4, 6, 8-9,12-15
X	CN 105645840 A (CHENGDU NEW KELI CHEM SCI CO) 08 June 2016, machine translation obtained from Espacenet abstract, example 1, claims 1-5	1-4, 7-9, 12-15
X	WO 2014/160362 A1 (TUNDRA COMPOSITES, LLC) 02 October 2014 abstract, pages 27, 32-44, claims 1, 23	1-5, 7, 9-15

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/US2017/062251**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
DE 102015003378 A1	22 September 2016	DE 102015003378 A1	22 Sep 2016
CN 105645840 A	08 June 2016	CN 105645840 A	08 Jun 2016
WO 2014/160362 A1	02 October 2014	WO 2014160362 A1	02 Oct 2014
		CA 2903076 A1	02 Oct 2014
		GB 2528599 A	27 Jan 2016
		GB 2528599 B	06 Dec 2017
		US 2016002468 A1	07 Jan 2016

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.