

(43) International Publication Date
15 October 2015 (15.10.2015)

- (51) **International Patent Classification:**
B29C 67/00 (2006.01) **C08J 3/12** (2006.01)
B33Y 70/00 (2015.01)
- (21) **International Application Number:**
PCT/US2015/024452
- (22) **International Filing Date:**
6 April 2015 (06.04.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/976,110 7 April 2014 (07.04.2014) US
- (71) **Applicant:** SABIC GLOBAL TECHNOLOGIES B.V.
[NL/NL]; Plasticslaan 1, NL-4612 PX Bergen op Zoom
(NL).
- (72) **Inventor; and**
- (71) **Applicant (for BZ only):** COX, Keith E. [US/US]; 1 Lex-
an Lane, Mt. Vernon, Indiana 47620 (US).
- (72) **Inventors:** HUIJS, Franciscus Maria; Plasticslaan 1, NL-
4612 PX Bergen op Zoom (NL). KALYANARAMAN,
Viswanathan; 1 Lexan Lane, Mt. Vernon, Indiana 47620
(US).
- (74) **Agent:** SIMONS, William A.; Cantor Colburn LLP, 20
Church Street, 22nd Floor, Hartford, Connecticut 06103
(US).

(81) **Designated States** (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
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.

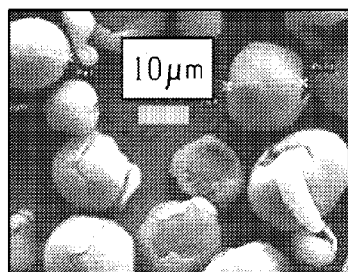
(84) **Designated States** (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, 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).

Declarations under Rule 4.17:

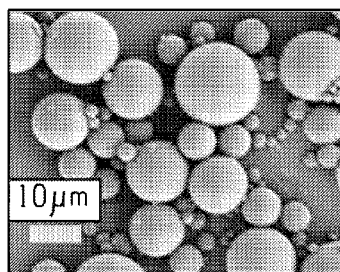
- as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) **Title:** POWDER BED FUSING THERMOPLASTIC POLYMERS

POWDER A

Fig. 1A

POWDER B

Fig. 1B

(57) **Abstract:** A method comprising: providing a powder composition including at least one ultrafine, spherical thermoplastic polymer powder having a glass transition temperature (T_g) of at least 150 degrees C; and powder bed fusing the powder composition to form a three-dimensional article.

POWDER BED FUSING THERMOPLASTIC POLYMERS

BACKGROUND

[0001] Additive Manufacturing (AM) is a production technology that is transforming the way all sorts of things are made. AM makes three-dimensional (3D) solid objects of virtually any shape from a digital model. Generally, this is achieved by creating a digital blueprint of a desired solid object with computer-aided design (CAD) modeling software and then slicing that virtual blueprint into very small digital cross-sections. These cross-sections are formed or deposited in a sequential layering process in an AM machine to create the 3D object. AM has many advantages, including dramatically reducing the time from design to prototyping to commercial product. Running design changes are possible. Multiple parts can be built in a single assembly. No tooling is required. Minimal energy is needed to make these 3D solid objects. It also decreases the amount waste and raw materials. AM also facilitates production of extremely complex geometrical parts. AM also reduces the parts inventory for a business since parts can be quickly made on-demand and on-site.

[0002] Several different techniques that use polymers have been developed for AM. These include material extrusion processes such as fused filament fabrication as well as powder bed fusing processes such as laser sintering.

[0003] Laser sintering is a process by which a three dimensional article may be formed in a layer-wise fashion by selectively projecting a laser beam having the desired energy onto a bed of resin particles. Prototype or production parts may be efficiently and economically produced by this process, which is often times referred to as selective laser sintering. This process has been described in U.S. Pat. Nos. 4,944,817; 5,516,697 and 5,382,308 to Bourell, et al.; 5,304,329 and 5,342,919 to Dickens, Jr. et al. and 5,385,780 to Lee.

[0004] In the laser sintering process, a high power laser is used to fuse polymer powders of the required material type together into the desired three-dimensional shape. SLS processes require a polymer powder of well-defined shape, size and composition in order to make high quality part. The preferred size of the particles is usually below 100 μm (Ref: Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications July 1, 2004 vol. 218 no. 3 247-252) and a narrow distribution of particle sizes is also preferred to get optimum precision and density of the sintered part. In addition, for good stacking of the powder particles, it is important that they have a regular,

reproducible shape, like spherical morphology. However, the preparation of such powders from thermoplastic resins on an economic, large scale is not straightforward.

[0005] Most of the thermoplastic powders used for powder bed fusion processes such as laser sintering are made by (cryogenic) milling and subsequent sieving. This method has the disadvantage that the distribution in particle size is relatively high and that it is difficult to control the exact size of the powder. Also, fines are generated that cannot be used in the SLS process. Finally, the shape of the powder particles is very irregular.

[0006] Recently, Sumika Enviro Science has published a patent (Japanese published patent No. JP05288361B2) that describes a method to make spherical polyamide particles for laser sintering. The spherical polyamide particles are polymerized in an aqueous medium maintaining the shape of the spherical particles. Disadvantage of this method is that it seems not possible to add additives such as colorants, flow agents and the like into the particles. However, this reference does not teach or suggest this process would be useful with any thermoplastic polymers that have high glass transition temperatures (T_g). Also, polyamides have low glass transition temperatures (i.e., below 100 degrees C)

[0007] There is still a need to provide suitable thermoplastic polyetherimide powder that can be used in powder bed fusion processes. The present invention offers a solution to that problem.

BRIEF DESCRIPTION

[0008] Some embodiments are directed to a method comprising: providing a powder composition including at least one ultrafine, spherical thermoplastic powder having a glass transition temperature (T_g) of at least 150 degrees C; and powder bed fusing the powder composition to form a three-dimensional article.

[0009] Another embodiment is directed to a method comprising: providing a powder composition including at least one ultrafine, spherical thermoplastic powder having a glass transition temperature (T_g) of at least 150 degrees C wherein the thermoplastic powder is chosen from polyetherimides, polysulfones, and polyarylsulfones and combinations thereof; and powder bed fusing the powder composition to form a three-dimensional article.

[0010] Still another embodiment is directed to a method comprising providing a powder composition including at least one ultrafine, high T_g, spherical polyetherimide powder; and powder bed fusing the powder composition to form a three-dimensional article.

[0011] Another embodiment is directed to the method of manufacturing a three dimensional article may comprise the steps of: (1) depositing a quantity of a powder

composition including at least one ultrafine, high Tg, spherical thermoplastic powder on a support surface; (2) leveling the composition to form a smooth layer on the support surface; (3) then directing an energy beam over a predetermined target area on the support surface causing the composition to form an integral layer; and (d) repeating steps (1) to (3) to form additional layers that are integrally bonded to adjacent layers to form a three-dimensional article, wherein the thermoplastic composition includes at least one ultrafine, high Tg, spherical thermoplastic powder. The energy beam may be a laser.

[0012] And still another embodiment is directed to the use of powders made with the emulsion process as described in US Patent Application Serial No. 13/841802, filed on 15-03-2013, (Assignee Docket No. 12PLAS0295-US-NP) in powder bed fusing processes.

[0013] Still another embodiment is directed to three dimensional articles of manufacture made by the powder bed fusing processes as described herein

[0014] The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring to the Figures, which are exemplary embodiments:

[0015] Figure 1 is two microphotographs showing the particle size morphology of two different Selective Laser Sintering (SLS) powders.

[0016] Figure 2 is two microphotographs showing the difference build platform surfaces using the two different SLS powders shown in Figure 1.

[0017] Figure 3 is a microphotograph showing a 3D laser sintered part manufactured with powder B shown in Figures 1 and 2

DETAILED DESCRIPTION

[0018] The present process has several advantages. This method employs spherical particles of well-defined particle size in the range that is optimum for powder bed fusing processes such as laser sintering and with a narrow size distribution. Also, with this process, the powder compositions that contain additives like stabilizers, colorants and flow agents, or even specific additives that can help in the laser sintering process (e.g. specific absorbers for laser wavelength, curable resin to post crosslink, and the like.). Another advantage of the good particle size control with this method is that it gives the advantage of mixing 2 or more powders with different particle sizes. This may lead to better layer formation due to

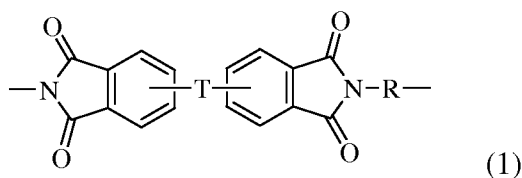
improved particle stacking, similar to the use of latexes with different particle sizes in waterborne emulsion paints.

[0019] The phrase “thermoplastic powder having a glass transition temperature (T_g) of at least 150 degrees C” as used herein includes at least one thermoplastic polymer powder that have a glass transition temperature of at least 150 degrees C. Examples of these powders can include polyetherimides, polysulfones, and polyarylsulfones and combinations thereof. Suitable polyarylsulfones include polyphenylsulfones. Specific embodiments include ULTEM polyetherimide polymers (including such grades such as 1000 and 1040), SILTEM poly(siloxane-etherimide) polymers (including such grades such as STM1700, STM1500 as well as XH6050).

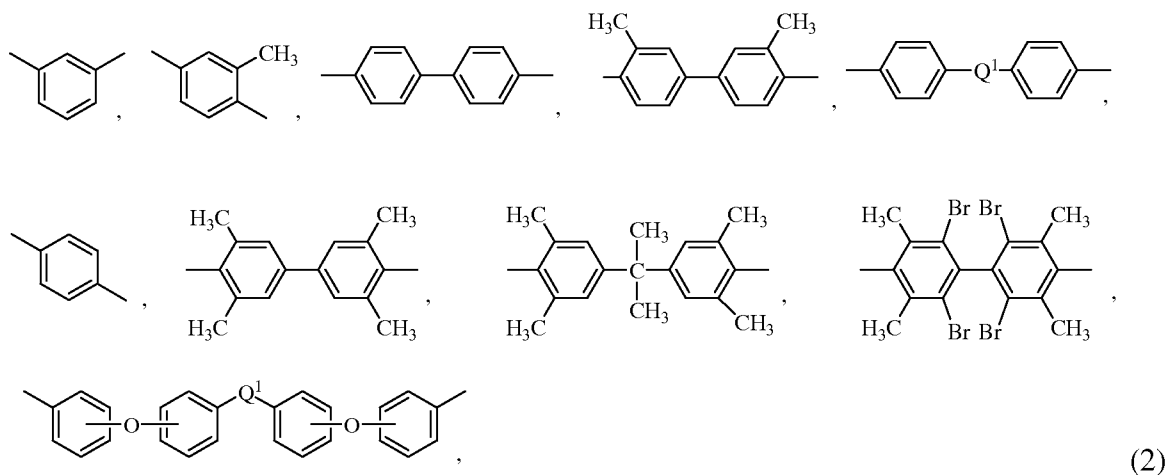
[0020] The term “ultrafine” as used herein means thermoplastic powdered particles that a mean particle size of about 10 to about 100 microns wherein the amount of powder particles less than 10 microns is less than 2 percent by volume. In some embodiments, the powder can be monomodal and have a mean particle of about 10 to about 100 microns. In another embodiment, at least two powder compositions may employed wherein each powder composition has a different mean particle size from about 10 to about 100 microns, thereby forming a polymodal powder composition. The powder may also have a bulk density of greater than 0.5 grams per cubic centimeter (g/cc).

[0021] The term “spherical” as used herein means the thermoplastic powder particles are substantially spherical in shape. These spherical particles can be made by the emulsion process as described in US Patent Application, Serial No. 13/841802 filed on 15-03-2013

[0022] The term “polyetherimide” is used herein to mean a compound comprising more than 1, for example 10 to 1000, or 10 to 500, structural units of formula (1)

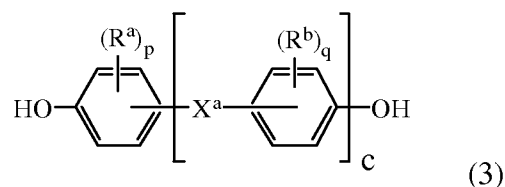


wherein each R is the same or different, and is a substituted or unsubstituted divalent organic group, such as a C₆₋₂₀ aromatic hydrocarbon group or a halogenated derivative thereof, a straight or branched chain C₂₋₂₀ alkylene group or a halogenated derivative thereof, a C₃₋₈ cycloalkylene group or halogenated derivative thereof, in particular a divalent group of formula (2)



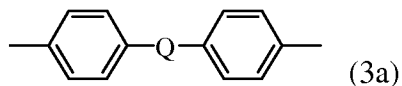
wherein Q^1 is -O-, -S-, -C(O)-, -SO₂-, -SO-, -C_yH_{2y}- wherein y is an integer from 1 to 5 or a halogenated derivative thereof (which includes perfluoroalkylene groups), or -(C₆H₁₀)_z- wherein z is an integer from 1 to 4. In an embodiment R is m-phenylene, p-phenylene, or a diaryl sulfone.

[0023] Further in formula (1), T is -O- or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions. The group Z in -O-Z-O- of formula (1) is also a substituted or unsubstituted divalent organic group, and can be an aromatic C₆₋₂₄ monocyclic or polycyclic moiety optionally substituted with 1 to 6 C₁₋₈ alkyl groups, 1 to 8 halogen atoms, or a combination thereof, provided that the valence of Z is not exceeded. Exemplary groups Z include groups derived from a dihydroxy compound of formula (3)



wherein R^a and R^b can be the same or different and are a halogen atom or a monovalent C₁₋₆ alkyl group, for example; p and q are each independently integers of 0 to 4; c is 0 to 4; and X^a is a bridging group connecting the hydroxy-substituted aromatic groups, where the bridging group and the hydroxy substituent of each C₆ arylene group are disposed ortho, meta, or para (specifically para) to each other on the C₆ arylene group. The bridging group X^a can be a single bond, -O-, -S-, -S(O)-, -S(O)₂-, -C(O)-, or a C₁₋₁₈ organic bridging group. The C₁₋₁₈ organic bridging group can be cyclic or acyclic, aromatic or non-aromatic, and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous. The C₁₋₁₈ organic group can be disposed such that the C₆ arylene groups connected thereto

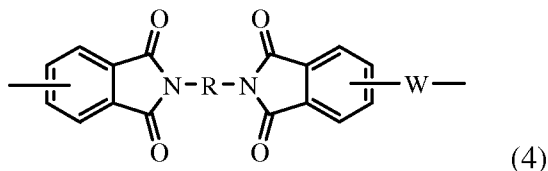
are each connected to a common alkylidene carbon or to different carbons of the C₁₋₁₈ organic bridging group. A specific example of a group Z is a divalent group of formula (3a)



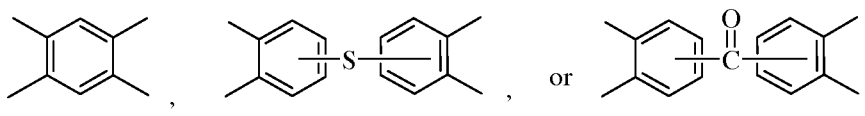
wherein Q is -O-, -S-, -C(O)-, -SO₂-, -SO-, or -C_yH_{2y}- wherein y is an integer from 1 to 5 or a halogenated derivative thereof (including a perfluoroalkylene group). In a specific embodiment Z is derived from bisphenol A, such that Q in formula (3a) is 2,2-isopropylidene.

[0024] In an embodiment in formula (1), R is m-phenylene or p-phenylene and T is -O-Z-O- wherein Z is a divalent group of formula (3a). Alternatively, R is m-phenylene or p-phenylene and T is -O-Z-O wherein Z is a divalent group of formula (3a) and Q is 2,2-isopropylidene.

[0025] In some embodiments, the polyetherimide can be a copolymer, for example, a polyetherimide sulfone copolymer comprising structural units of formula (1) wherein at least 50 mole% of the R groups are of formula (2) wherein Q¹ is -SO₂- and the remaining R groups are independently p-phenylene or m-phenylene or a combination comprising at least one of the foregoing; and Z is 2,2'-(4-phenylene)isopropylidene. Alternatively, the polyetherimide optionally comprises additional structural imide units, for example imide units of formula (4)

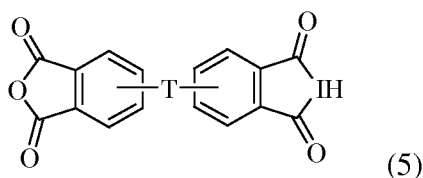


wherein R is as described in formula (1) and W is a linker of the formulas

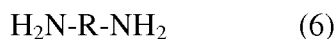


These additional structural imide units can be present in amounts from 0 to 10 mole % of the total number of units, specifically 0 to 5 mole %, more specifically 0 to 2 mole %. In an embodiment no additional imide units are present in the polyetherimide.

[0026] The polyetherimide can be prepared by any of the methods well known to those skilled in the art, including the reaction of an aromatic bis(ether anhydride) of formula (5)



with an organic diamine of formula (6)



wherein T and R are defined as described above. Copolymers of the polyetherimides can be manufactured using a combination of an aromatic bis(ether anhydride) of formula (5) and a different bis(anhydride), for example a bis(anhydride) wherein T does not contain an ether functionality, for example T is a sulfone.

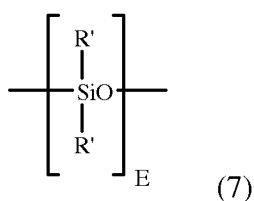
[0027] Illustrative examples of bis(anhydride)s include 3,3-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride; 2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl ether dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride; and, 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride, as well as various combinations thereof.

[0028] Examples of organic diamines include ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylene tetramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2,2-dimethylpropylenediamine, N-methyl-bis (3-aminopropyl) amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy) ethane, bis(3-aminopropyl) sulfide, 1,4-cyclohexanediamine, bis-(4-aminocyclohexyl) methane, m-phenylenediamine, p-

phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, m-xylylenediamine, p-xylylenediamine, 2-methyl-4,6-diethyl-1,3-phenylene-diamine, 5-methyl-4,6-diethyl-1,3-phenylene-diamine, benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, 1,5-diaminonaphthalene, bis(4-aminophenyl) methane, bis(2-chloro-4-amino-3,5-diethylphenyl) methane, bis(4-aminophenyl) propane, 2,4-bis(p-amino-t-butyl) toluene, bis(p-amino-t-butylphenyl) ether, bis(p-methyl-o-aminophenyl) benzene, bis(p-methyl-o-aminopentyl) benzene, 1, 3-diamino-4-isopropylbenzene, bis(4-aminophenyl) sulfide, bis-(4-aminophenyl) sulfone, and bis(4-aminophenyl) ether. Combinations of these compounds can also be used. In some embodiments the organic diamine is m-phenylenediamine, p-phenylenediamine, sulfonyl dianiline, or a combination comprising one or more of the foregoing.

[0029] The polyetherimides can have a melt index of 0.1 to 10 grams per minute (g/min), as measured by American Society for Testing Materials (ASTM) D1238 at 340 to 370 °C, using a 6.7 kilogram (kg) weight. In some embodiments, the polyetherimide polymer has a weight average molecular weight (Mw) of 1,000 to 150,000 grams/mole (Dalton), as measured by gel permeation chromatography, using polystyrene standards. In some embodiments the polyetherimide has an Mw of 10,000 to 80,000 Daltons. Such polyetherimide polymers typically have an intrinsic viscosity greater than 0.2 deciliters per gram (dl/g), or, more specifically, 0.35 to 0.7 dl/g as measured in m-cresol at 25 °C.

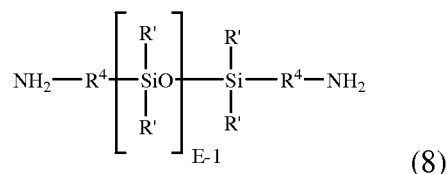
[0030] The thermoplastic "polyetherimide" composition as used in the present specification and claims can also comprise a poly(siloxane-etherimide) copolymer comprising polyetherimide units of formula (1) and siloxane blocks of formula (7).



wherein each R' is independently a C₁₋₁₃ monovalent hydrocarbyl group. For example, each R' can independently be a C₁₋₁₃ alkyl group, C₁₋₁₃ alkoxy group, C₂₋₁₃ alkenyl group, C₂₋₁₃ alkenyloxy group, C₃₋₆ cycloalkyl group, C₃₋₆ cycloalkoxy group, C₆₋₁₄ aryl group, C₆₋₁₀ aryloxy group, C₇₋₁₃ arylalkyl group, C₇₋₁₃ arylalkoxy group, C₇₋₁₃ alkylaryl group, or C₇₋₁₃ alkylaryloxy group. The foregoing groups can be fully or partially halogenated with fluorine, chlorine, bromine, or iodine, or a combination comprising at least one of the foregoing. In an embodiment no halogens are present. Combinations of the foregoing R groups can be used in the same copolymer. In an embodiment, the polysiloxane blocks comprises R' groups that

have minimal hydrocarbon content. In a specific embodiment, an R' group with a minimal hydrocarbon content is a methyl group

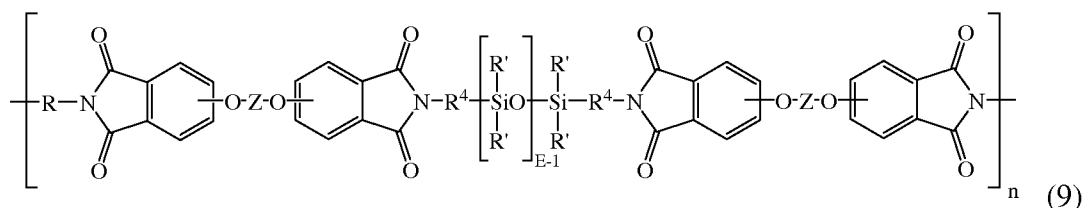
[0031] The poly (siloxane-etherimide)s can be formed by polymerization of an aromatic bisanhydride (4) and a diamine component comprising an organic diamine (6) as described above or mixture of diamines, and a polysiloxane diamine of formula (7)



wherein R' and E are as described in formula (7), and R⁴ is each independently a C₂-C₂₀ hydrocarbon, in particular a C₂-C₂₀ arylene, alkylene, or arylenealkylene group. In an embodiment R⁴ is a C₂-C₂₀ alkyl group, specifically a C₂-C₂₀ alkyl group such as propylene, and E has an average value of 5 to 100, 5 to 75, 5 to 60, 5 to 15, or 15 to 40. Procedures for making the polysiloxane diamines of formula (8) are well known in the art.

[0032] In some poly(siloxane-etherimide)s the diamine component can contain 10 to 90 mole percent (mol %), or 20 to 50 mol%, or 25 to 40 mol% of polysiloxane diamine (8) and 10 to 90 mol%, or 50 to 80 mol%, or 60 to 75 mol% of diamine (6), for example as described in US Patent 4,404,350. The diamine components can be physically mixed prior to reaction with the bisanhydride(s), thus forming a substantially random copolymer. Alternatively, block or alternating copolymers can be formed by selective reaction of (6) and (8) with aromatic bis(ether anhydrides) (5), to make polyimide blocks that are subsequently reacted together. Thus, the poly(siloxane-imide) copolymer can be a block, random, or graft copolymer.

[0033] Examples of specific poly(siloxane-etherimide) are described in US Pat. Nos. 4,404,350, 4,808,686 and 4,690,997. In an embodiment, the poly(siloxane-etherimide) has units of formula (9)



wherein R' and E of the siloxane are as in formula (5), the R and Z of the imide are as in formula (1), R⁴ is the same as R⁴ as in formula (8), and n is an integer from 5 to 100. In a specific embodiment, the R of the etherimide is a phenylene, Z is a residue of bisphenol A, R⁴

is n-propylene, E is 2 to 50, 5, to 30, or 10 to 40, n is 5 to 100, and each R' of the siloxane is methyl.

[0034] The relative amount of polysiloxane units and etherimide units in the poly(siloxane-etherimide) depends on the desired properties, and are selected using the guidelines provided herein. In particular, as mentioned above, the block or graft poly(siloxane-etherimide) copolymer is selected to have a certain average value of E, and is selected and used in amount effective to provide the desired wt% of polysiloxane units in the composition. In an embodiment the poly(siloxane-etherimide) comprises 10 to 50 wt%, 10 to 40 wt%, or 20 to 35 wt% polysiloxane units, based on the total weight of the poly(siloxane-etherimide).

[0035] The term "alkyl" includes branched or straight chain, unsaturated aliphatic C₁₋₃₀ hydrocarbon groups e.g., methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, n- and s-hexyl, n- and s-heptyl, and, n- and s-octyl. "Alkenyl" means a straight or branched chain, monovalent hydrocarbon group having at least one carbon-carbon double bond (e.g., ethenyl (-HC=CH₂)). "Alkoxy" means an alkyl group that is linked via an oxygen (i.e., alkyl-O-), for example methoxy, ethoxy, and sec-butyloxy groups.

[0036] "Alkylene" means a straight or branched chain, saturated, divalent aliphatic hydrocarbon group (e.g., methylene (-CH₂-) or, propylene (-CH₂)₃-).

[0037] "Cycloalkylene" means a divalent cyclic alkylene group, -C_nH_{2n-x}, wherein x represents the number of hydrogens replaced by cyclization(s). "Cycloalkenyl" means a monovalent group having one or more rings and one or more carbon-carbon double bond in the ring, wherein all ring members are carbon (e.g., cyclopentyl and cyclohexyl).

[0038] The term "aryl" means an aromatic hydrocarbon group containing the specified number of carbon atoms, such as to phenyl, tropone, indanyl, or naphthyl. The prefix "hetero" means that the compound or group includes at least one ring member that is a heteroatom (e.g., 1, 2, or 3 heteroatom(s)), wherein the heteroatom(s) is each independently N, O, S, or P.

[0039] "Substituted" means that the compound or group is substituted with at least one (e.g., 1, 2, 3, or 4) substituents independently selected from, a C₁₋₉ alkoxy, a C₁₋₉ haloalkoxy, a nitro (-NO₂), a cyano (-CN), a C₁₋₆ alkyl sulfonyl (-S(=O)₂-alkyl), a C₆₋₁₂ aryl sulfonyl (-S(=O)₂-aryl), a thiol (-SH), a thiocyno (-SCN), a tosyl (CH₃C₆H₄SO₂-), a C₃₋₁₂ cycloalkyl, a C₂₋₁₂ alkenyl, a C₅₋₁₂ cycloalkenyl, a C₆₋₁₂ aryl, a C₇₋₁₃ arylalkylene, a C₄₋₁₂

heterocycloalkyl, and a C₃₋₁₂ heteroaryl instead of hydrogen, provided that the substituted atom's normal valence is not exceeded.

[0040] The at least one ultrafine, high Tg, spherical polyetherimide powder used in the present processes can be made by the methods disclosed in US Patent Application Serial No. 13/841,802 filed on March 15, 2013, which is incorporated herein by reference in its entirety.

[0041] In some embodiments, the at least one ultrafine, high Tg, spherical thermoplastic powder such as polyetherimide powder is made by a process comprising (a) dissolving high Tg thermoplastic material such as polyetherimide polymer in an organic solvent capable of dissolving the thermoplastic material to form a solution; (b) emulsifying the solution by combining the solution with water and a surfactant to form an emulsion; (c) transferring the emulsion into a receiving water containing a surfactant to remove the organic solvent and form a slurry; and (d) recovering thermoplastic particles of less than 75 micron diameter. This process may further include heating the emulsion up to or below the boiling point of the emulsion before transferring the emulsion into the receiving water.

Alternatively, this process may include heating the emulsion above the boiling point of the emulsion before transferring the emulsion into the receiving water. The solvent may be a member selected from the group of methylene chloride, chloroform, and combinations thereof. The surfactant may be an anionic surfactant including sodium dodecyl benzene sulfonate (SDBS), sodium lauryl sulfate, and combinations thereof. This process may further comprise filtering the slurry to form a wet cake. And, this process may further comprise drying the wet cake under heat and vacuum.

[0042] In other embodiment, the at least one ultrafine, high Tg, spherical thermoplastic powder such as polyetherimide polymer powder is made by the steps of: (a) dissolving a thermoplastic material such as polyetherimide polymer in a solvent to form a solution, wherein the thermoplastic material is soluble in the solvent, the solvent has a boiling point that is less than 100 C and the solvent is immiscible with water; (b) emulsifying the solution by combining the solution with de-ionized water and a surfactant under agitation conditions sufficient to form an emulsion; (c) transferring the emulsion into a de-ionized receiving water, the receiving water also containing a surfactant and removing the solvent and form a slurry; (d) pre-filtering the slurry to remove any macro particles or contaminants; (e) filtering the slurry to form a wet cake; (f) filtering the slurry to form a wet cake; (g)

drying the washed wet cake under heat and vacuum; and (h) recovering particles of thermoplastic material such as polyetherimide (PEI) of less than 75 micron diameter.

[0043] The powder composition comprises between 50 to 100 weight percent of the at least one ultrafine, high T_g, spherical thermoplastic polymer powder such as polyetherimide powder, based on the weight of polymeric materials in the powder. Besides the spherical polyetherimide powder, the powder composition can contain a colorant or a process aid.

[0044] In some embodiments, the powder composition may optionally contain a flow agent. In particular, a thermoplastic composition of the present invention contains 0%, preferably 0.05%, to about 5%, and more preferably about 0.075% to about 1%, by weight of a particulate flow agent. Particularly, the powder composition contains about 0.1% to about 0.25%, by weight, of the flow agent.

[0045] This optional flow agent included in the powder composition is a particulate inorganic material having a median particle size of 10 microns or less, and is chosen from the group consisting of a hydrated silica, amorphous alumina, a glassy silica, a glassy phosphate, a glassy borate, a glassy oxide, titania, talc, mica, a fumed silica, kaolin, attapulgite, calcium silicate, alumina, and magnesium silicate. The flow agent preferably is present in an amount sufficient to allow the polyetherimide to flow and level on the build surface of the laser sintering device. One useful flow agent is a fumed silica.

[0046] A powder composition also can contain other optional ingredients. These optional ingredients are particulate materials and include organic and inorganic materials, such as fillers and coloring agents. An optional ingredient is present in a sufficient amount to perform its intended function, without adversely affecting the thermoplastic composition or an article prepared therefrom. Optional ingredients have a particle size in the range of the particle sizes of the polyetherimide and/or optional flow agent. Each optional ingredient is milled, if necessary, to the desired median particle size and particle size distribution.

[0047] Each individual optional ingredient, if present at all, typically is present in the powder composition in an amount of about 0.1% to about 30%, by weight, of the composition. The total amount of optional ingredients in the powder composition ranges from 0% up to about 30%, by weight.

[0048] It is not necessary for each optional ingredient to melt during the laser sintering process. However, each optional ingredient must be compatible with the polyetherimide in order to provide a strong and durable article of manufacture. The optional

ingredient, therefore, can be inorganic, filler that imparts additional strength to the article of manufacture.

[0049] Another optional ingredient is a coloring agent, for example a pigment or a dye, like carbon black, to impart a desired color to the article of manufacture. The coloring agent is not limited, as long as the coloring agent does not adversely affect the composition or an article prepared therefrom, and is sufficiently stable to retain its color under conditions of the laser sintering process and during exposure to the laser.

[0050] Still other additional optional ingredients may also include, for example, toners, extenders, fillers, colorants (e.g., pigments and dyes), lubricants, anticorrosion agents, thixotropic agents, dispersing agents, antioxidants, adhesion promoters, light stabilizers, organic solvents, surfactants, flame retardants, and mixtures thereof.

[0051] Still another optional ingredient also can be a second polymer that modifies the properties of the polyetherimide.

[0052] The spherical polyetherimide powder used herein may have certain characteristics. It may have a glass transition temperature of more than 150° C. and less than 350° C., more particular, it may have a glass transition temperature of more than 200° C. and less than 300° C. In some embodiments, the commercially available ULTEM polyetherimide has a T_g of 215 degrees C. It may have comprises at least 5 weight percent of one or more amorphous polyetherimide powder. It may have has a weight average molecular weight of between 1,000 and 150,000 Daltons. Each powder may be monomodal and have a mean particle of about 10 to about 75 microns. The powder may have a bulk density of greater than 0.5 grams per cubic centimeter (g/cc). In another embodiment, at least two powder compositions may employed wherein each powder composition has a different mean particle size, thereby forming a polymodal powder composition. In some embodiments, the method of manufacturing a three dimensional article may comprise the steps of: (1) depositing a quantity of a powder composition including at least one ultrafine, high T_g , spherical polyetherimide powder on a support surface; (2) leveling the composition to form a smooth layer on the support surface; (3) then directing an energy beam over a predetermined target area on the support surface causing the composition to form an integral layer; and (d) repeating steps (1) to (3) to form additional layers that are integrally bonded to adjacent layers to form a three-dimensional article, wherein the thermoplastic composition includes at least one ultrafine, high T_g , spherical polyetherimide powder. The energy beam may be a laser.

[0053] The term “powder bed fusing” is used herein to mean all laser sintering and all selective laser sintering processes as well as other powder bed fusion processes. For example, sintering of the powder composition may be accomplished via application of electromagnetic radiation other than that produced by a laser, with the selectivity of the sintering achieved, for example, through selective application of inhibitors, absorbers, susceptors, or the electromagnetic radiation (e.g., through use of masks or directed laser beams). Any other suitable source of electromagnetic radiation may be used, including, for example, infrared radiation sources, microwave generators, lasers, radiative heaters, lamps, or a combination thereof. In some embodiments, selective mask sintering (“SMS”) techniques may be used to produce three-dimensional articles of the invention. For further discussion of SMS processes, see for example U.S. Pat. No. 6,531,086 which describes an SMS machine in which a shielding mask is used to selectively block infrared radiation, resulting in the selective irradiation of a portion of a powder layer. If using an SMS process to produce articles from powder compositions of the invention, it may be desirable to include one or more materials in the powder composition that enhance the infrared absorption properties of the powder composition. For example, the powder composition may include one or more heat absorbers and/or dark-colored materials (e.g., carbon black, carbon nanotubes, or carbon fibers).

[0054] The present invention also includes all three dimensional products made by powder bed fusing these powder compositions. After a layer-by-layer manufacture of an article of manufacture, the article may exhibit excellent resolution, durability, and strength. These articles of manufacture may have a wide variety of uses, including as prototypes and as end products as well as molds for end products.

[0055] In particular, powder bed fused (e.g., laser sintered) articles may be produced from the powder compositions using any suitable powder bed fusing processes including laser sintering processes. These articles can include a plurality of overlying and adherent sintered layers that include a polymeric matrix which, in some embodiments, have reinforcement particles dispersed throughout the polymeric matrix. Laser sintering processes are sufficiently well known, and are based on the selective sintering of polymer particles, where layers of polymer particles are briefly exposed to laser light and the polymer particles exposed to the laser light are thus bonded to one another. Successive sintering of layers of polymer particles produces three-dimensional objects. Details concerning the selective laser sintering process are found, by way of example, in the specifications U.S. Pat. No. 6,136,948

and WO 96/06881. However, the powder described herein may also be used in other rapid prototyping or rapid manufacturing processing of the prior art, in particular in those described above. For example, the inventive powder may in particular be used for producing moldings from powders via the SLS (selective laser sintering) process, as described in U.S. Pat. No. 6,136,948 or WO 96/06881, via the SIB process (selective inhibition of bonding of powder), as described in WO 01/38061, via 3D printing, as described in EP 0 431 924, or via a microwave process, as described in DE 103 11 438. The specifications cited, and in particular the processes described therein, are expressly incorporated into the disclosure content of the present description of the invention by way of reference.

[0056] The sintered layers of laser sintered articles of the present invention may be of any thickness suitable for laser sintered processing. The plurality of sintered layers may be each, on average, preferably at least about 50 microns thick, more preferably at least about 80 microns thick, and even more preferably at least about 100 microns thick. In a preferred embodiment, the plurality of sintered layers are each, on average, preferably less than about 200 microns thick, more preferably less than about 150 microns thick, and even more preferably less than about 120 microns thick. Three-dimensional articles produced from powder compositions of the invention using a layer-by-layer sintering other than laser sintering may have layer thicknesses that are the same or different from those described above.

[0057] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention.

EXAMPLES

[0058] To evaluate the advantages of the spherical morphology in the SLS process a comparative study was conducted. Two powders with comparable mean particle size were manufactured. Powder A was manufactured through jet milling while powder B was manufactured via the emulsion process described herein. The difference in particle surface morphology is apparent from the SEM images shown in Figure 1.

[0059] Powder A has a rough, cracked surface and potato-like morphology while the powder B consists of dense spheres. The mean particle size for both powder A and B where

between 10-15 micron. The particle size distribution for powder A was much narrower than that of powder B as can be seen from the tabulated data below. Powder B contains a larger percentage of submicron particles.

Table 1

PSD	D10 [micron]	D50 [micron]	D90 [micron]
Powder A	5.98	10.45	17.01
Powder B	4.07	14.66	45.97

[0060] Several methods have been developed in the past to quantitatively characterize powder flow, including Angle of Repose, Hausner Ratio, bulk/tap density, and the like. However a reliable means of correlating these powder properties and actual powder handling within the SLS process is still under development. Therefore a qualitative scale from 1-4 is used to distinguish between the performance of the two powders, as given in Table 2:

Table 2

Ranking#	Description
1	Poor powder flow: powder tends to stick together, tumbles in large pieces or needs to be dragged to the build platform. Impossible to create a smooth powder bed.
2	Usable powder flow: powder still tends to stick and amalgamate and is difficult to move to the build platform, but with some effort a usable power bed can be created.
3	Sufficient powder flow: powder tumbles freely and tends not to amalgamate. and can transported to create a smooth surface on the build platform
4	Good powder flow: powder flows freely and can easily be transported to the build platform to form a smooth surface

[0061] Ultrafine powders typically exhibit poor powder flow, even with the addition of large quantities flow promoters. Powder A exhibited poor powder flow behavior as indicated in Table 3. Even with the addition of 2% (by weight) of fumed silica flow promoter, it was impossible to create a smooth powder bed from which 3D parts could be manufactured. A sample of the powder bed is shown in Figure 2 (a).

[0062] Table 3: Powder flow behavior of polyetherimide made from jet milling process versus emulsion based process. The flow behavior was quantified from poor (ranked as 1) to good (ranked as 4).

Sample	Description	Additive	Powder flow ranking	
A		Jet milled powder	None	1
A		Jet milled powder	2% fumed silica	1
B		Powder from emulsion process	None	2
B		Powder from emulsion process	0.1% fumed silica	4

[0063] The advantages of the spherical powder, powder B, is clearly apparent when processing the powders within an SLS machine. Even with a significant amount of submicron particles, adding 0.1% (by weight) of fumed silica flow promotor, powder B exhibits good powder flow behavior as shown in Table 3. A smooth surface on the build platform is easily created as shown in Figure 2 (b).

[0064] Proof of concept was demonstrated with powder B by manufacturing four square parts. Each part consisted of twenty subsequently sintered powder layers. A sample of the manufactured parts are shown in Figure 3. The parts made by the SLS process using powder B, showed good mechanical integrity whereas it was not possible to manufacture a part using powder A, as summarized in Table 4.

[0065] Table X4:

Sample	Additive	SLS process can be used to make parts with integrity
Powder A	2% fumed silica	No
Powder B	0.1% fumed silica	Yes

[0066] The present invention is further illustrated by the following Embodiments.

[0067] Embodiment 1: A method comprising: providing a powder composition including at least one ultrafine, spherical thermoplastic polymer powder having a glass transition temperature (T_g) of at least 150 degrees C; and powder bed fusing the powder composition to form a three-dimensional article.

[0068] Embodiment 2: The method of Embodiment 1, wherein the powder composition comprises between 50 to 100 weight percent of the at least one ultrafine, high T_g, spherical thermoplastic polymer powder, based on the weight of polymeric materials in the powder.

[0069] Embodiment 3: The method of any of Embodiments 1-2, wherein the spherical thermoplastic polymer powder has a glass transition temperature of more than 150° C. and less than 350° C.

[0070] Embodiment 4: The method of any of Embodiments 1-3, wherein the spherical thermoplastic polymer powder has a glass transition temperature of more than 200° C. and less than 300° C.

[0071] Embodiment 5: The method of any of Embodiments 1-4, wherein the thermoplastic polymer powder has a weight average molecular weight of between 1,000 and 150,000 Daltons.

[0072] Embodiment 6: The method of any of Embodiments 1-5, wherein each ultrafine, high Tg, spherical thermoplastic polymer powder is monomodal and has a mean particle of about 10 to about 75 microns and the amount of powder particles smaller than 10 microns is less than 2 percent by volume.

[0073] Embodiment 7: The method of any of Embodiments 1-6, further comprising adding a flow agent or to the powder composition.

[0074] Embodiment 8: The method of Embodiment 7, wherein the flow agent chosen from the group consisting of a hydrated silica, amorphous alumina, a glassy silica, a glassy phosphate, a glassy borate, a glassy oxide, titania, talc, mica, a fumed silica, kaolin, attapulgite, calcium silicate, alumina, and magnesium silicate and combinations thereof.

[0075] Embodiment 9: The method of any of Embodiments 7-8, wherein the amount of flow agent is from about 0.05% to about 5% of the powder composition.

[0076] Embodiment 10: The method of any of Embodiments 1-9, wherein the polyetherimide powder has a bulk density of greater than 0.5 grams per cubic centimeter.

[0077] Embodiment 11: The method of any of Embodiments 1-10, wherein at least two powder compositions are employed and each powder composition has a different mean particle size, thereby forming a polymodal powder composition.

[0078] Embodiment 12: A method comprising: providing a powder composition including at least one ultrafine, spherical thermoplastic polymer powder having a glass transition temperature (Tg) of at least 150 degrees C wherein the thermoplastic polymer powder is chosen from polyetherimides, polysulfones, and polyarylsulfones and combinations thereof; and powder bed fusing the powder composition to form a three-dimensional article.

[0079] Embodiment 13: The method of Embodiment 12, wherein the powder composition comprises between 50 to 100 weight percent of the at least one ultrafine, high Tg, spherical thermoplastic polymer powder, based on the weight of polymeric materials in the powder.

[0080] Embodiment 14: The method of any of Embodiments 12-13, wherein the spherical thermoplastic polymer powder has a glass transition temperature of more than 150° C. and less than 350° C.

[0081] Embodiment 15: The method of any of Embodiments 12-14, wherein the spherical thermoplastic polymer powder has a glass transition temperature of more than 200° C. and less than 300° C.

[0082] Embodiment 16: The method of any of Embodiments 12-15, wherein the thermoplastic polymer powder has a weight average molecular weight of between 1,000 and 150,000 Daltons.

[0083] Embodiment 17: The method of any of Embodiments 12-16, wherein each ultrafine, high Tg, spherical thermoplastic polymer powder is monomodal and has a mean particle of about 10 to about 75 microns and the amount of powder particles smaller than 10 microns is less than 2 percent by volume.

[0084] Embodiment 18: The method of any of Embodiments 12-17, further comprising adding a flow agent or to the powder composition.

[0085] Embodiment 19: The method of Embodiment 18, wherein the flow agent chosen from the group consisting of a hydrated silica, amorphous alumina, a glassy silica, a glassy phosphate, a glassy borate, a glassy oxide, titania, talc, mica, a fumed silica, kaolin, attapulgite, calcium silicate, alumina, and magnesium silicate and combinations thereof.

[0086] Embodiment 20: The method of any of Embodiments 18-19, wherein the amount of flow agent is from about 0.05% to about 5% of the powder composition.

[0087] Embodiment 21: The method of any of Embodiments 1-20, wherein the polyetherimide powder has a bulk density of greater than 0.5 grams per cubic centimeter.

[0088] Embodiment 22: The method of any of Embodiments 1-21, wherein at least two powder compositions are employed and each powder composition has a different mean particle size, thereby forming a polymodal powder composition.

[0089] Embodiment 23: A method comprising: providing a powder composition including at least one ultrafine, high Tg, spherical polyetherimide powder; and powder bed fusing the powder composition to form a three-dimensional article.

[0090] Embodiment 24: The method of Embodiment 23, wherein the powder composition comprises between 50 to 100 weight percent of the at least one ultrafine, high Tg, spherical polyetherimide powder, based on the weight of polymeric materials in the powder.

[0091] Embodiment 25: The method of any of Embodiments 23-24, wherein the spherical polyetherimide powder has a glass transition temperature of more than 150° C. and less than 350° C.

[0092] Embodiment 26: The method of any of Embodiments 23-25, wherein the spherical polyetherimide powder has a glass transition temperature of more than 200° C. and less than 300° C.

[0093] Embodiment 27: The method of any of Embodiments 23-26, wherein the powder composition comprises at least 5 weight percent of one or more amorphous polyetherimide powder.

[0094] Embodiment 28: The method of any of Embodiments 23-27, wherein the polyetherimide powder has a weight average molecular weight of between 1,000 and 150,000 Daltons.

[0095] Embodiment 29: The method of any of Embodiments 23-24, wherein each ultrafine, high Tg, spherical polyetherimide powder is monomodal and has a mean particle of about 10 to about 75 microns.

[0096] Embodiment 30: The method of any of Embodiments 23-29, wherein at least one ultrafine, high Tg, spherical polyetherimide powder is made by a process comprising (a) dissolving polyetherimide in an organic solvent capable of dissolving the polyetherimide to form a solution; (b) emulsifying the solution by combining the solution with water and a surfactant to form an emulsion; (c) transferring the emulsion into a receiving water containing a surfactant to remove the organic solvent and form a slurry; and (d) recovering polyetherimide particles of less than 75 micron diameter.

[0097] Embodiment 31: The method of Embodiment 30, further comprising heating the emulsion up to or below the boiling point of the emulsion before transferring the emulsion into the receiving water.

[0098] Embodiment 32: The method of any of Embodiments 30-31, further comprising heating the emulsion above the boiling point of the emulsion before transferring the emulsion into the receiving water.

[0099] Embodiment 33: The method of any of Embodiments 30-32, wherein the solvent is a member selected from the group of methylene chloride, chloroform, and combinations thereof.

[0100] Embodiment 34: The method of any of Embodiments 30-33, wherein the surfactant is anionic, cationic or non-ionic surfactant or combinations thereof.

[0101] Embodiment 35: The method of any of Embodiments 30-34, wherein the surfactant is a surfactant selected from the group of sodium dodecyl benzene sulfonate (SDBS), sodium lauryl sulfate, and combinations thereof.

[0102] Embodiment 36: The method of any of Embodiments 30-35, further comprising filtering the slurry to form a wet cake.

[0103] Embodiment 37: The method of any of Embodiments 30-36, further comprising drying the wet cake under heat and vacuum.

[0104] Embodiment 38: The method of any of Embodiments 23-37, further comprising adding a flow agent or to the powder composition.

[0105] Embodiment 39: The method of Embodiment 38, wherein the flow agent chosen from the group consisting of a hydrated silica, amorphous alumina, a glassy silica, a glassy phosphate, a glassy borate, a glassy oxide, titania, talc, mica, a fumed silica, kaolin, attapulgite, calcium silicate, alumina, and magnesium silicate and combinations thereof.

[0106] Embodiment 40: The method of any of Embodiments 38-39, wherein the amount of flow agent is from about 0.05% to about 5% of the powder composition.

[0107] Embodiment 41: The method of any of Embodiments 23-40, wherein the polyetherimide powder has a bulk density of greater than 0.5 grams per cubic centimeter.

[0108] Embodiment 42: The method of any of Embodiments 23-41, wherein at least two powder compositions are employed and each powder composition has a different mean particle size, thereby forming a polymodal powder composition.

[0109] Embodiment 43: A method of manufacturing a three dimensional article comprising the steps of: (1) depositing a quantity of a powder composition including at least one ultrafine, high Tg, spherical thermoplastic polymer powder on a support surface; (2) leveling the composition to form a smooth layer on the support surface; (3) then directing an energy beam over a predetermined target area on the support surface causing the composition to form an integral layer; and (d) repeating steps (1) to (3) to form additional layers that are integrally bonded to adjacent layers to form a three-dimensional article, wherein the thermoplastic composition includes at least one ultrafine, high Tg, spherical thermoplastic powder.

[0110] Embodiment 44: The method of claim of the Embodiment 43 wherein the energy beam is a laser.

[0111] Embodiment 45: The method of any of the Embodiments 43-44, wherein the at least one ultrafine, high Tg, spherical thermoplastic powder is made by the steps of: (a)

dissolving a thermoplastic polymer material in a solvent to form a solution, wherein the thermoplastic polymer is soluble in the solvent, the solvent has a boiling point that is less than 100 C and the solvent is immiscible with water; (b) emulsifying the solution by combining the solution with de-ionized water and a surfactant under agitation conditions sufficient to form an emulsion; (c) transferring the emulsion into a de-ionized receiving water, the receiving water also containing a surfactant and removing the solvent and form a slurry; (d) pre-filtering the slurry to remove any macro particles or contaminants; (e) filtering the slurry to form a wet cake; (f) filtering the slurry to form a wet cake; (g) drying the washed wet cake under heat and vacuum; and (h) recovering particles of thermoplastic polymer powder of less than 75 micron diameter.

[0112] Embodiment 46: The method of any of the Embodiments 43-45, wherein the thermoplastic polymer is chosen from polyetherimide, polysulfone, polyarylsulfones, and combinations thereof.

[0113] Embodiment 47: A three-dimensional sintered article resulting from the method of any of the Embodiments 1-46.

[0114] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. "Combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms "a" and "an" and "the" herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to "some embodiments", "another embodiment", "an embodiment", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least some embodiments described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0115] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the

appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

[0116] I/we claim:

CLAIMS:

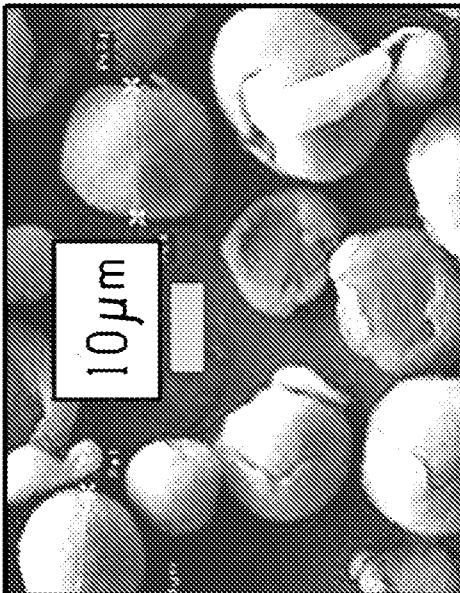
1. A method comprising: providing a powder composition including at least one ultrafine, spherical thermoplastic polymer powder having a glass transition temperature (T_g) of at least 150 degrees C; and powder bed fusing the powder composition to form a three-dimensional article.
2. The method of claim 1, wherein the powder composition comprises between 50 to 100 weight percent of the at least one ultrafine, high T_g, spherical thermoplastic polymer powder, based on the weight of polymeric materials in the powder.
3. The method of any of claims 1-2, wherein the spherical thermoplastic polymer powder has a glass transition temperature of more than 150° C. and less than 350° C.
4. The method of any of claims 1-3, wherein the thermoplastic polymer powder has a weight average molecular weight of between 1,000 and 150,000 Daltons.
5. The method of any of claims 1-4, wherein each ultrafine, high T_g, spherical thermoplastic polymer powder is monomodal and has a mean particle of about 10 to about 75 microns and the amount of powder particles smaller than 10 microns is less than 2 percent by volume.
6. The method of any of claims 1-5, further comprising adding a flow agent or to the powder composition.
7. The method of claim 6, wherein the flow agent chosen from the group consisting of a hydrated silica, amorphous alumina, a glassy silica, a glassy phosphate, a glassy borate, a glassy oxide, titania, talc, mica, a fumed silica, kaolin, attapulgite, calcium silicate, alumina, and magnesium silicate and combinations thereof.
8. The method of any of claims 6-7, wherein the amount of flow agent is from about 0.05% to about 5% of the powder composition.
9. The method of any of claims 1-8, wherein the thermoplastic polymer powder is chosen from polyetherimides, polysulfones, and polyarylsulfones and combinations thereof; and powder bed fusing the powder composition to form a three-dimensional article.

10. The method of any of claims 1-9, wherein at least two powder compositions are employed and each powder composition has a different mean particle size, thereby forming a polymodal powder composition.
11. A method comprising: providing a powder composition including at least one ultrafine, high Tg, spherical polyetherimide powder; and powder bed fusing the powder composition to form a three-dimensional article.
12. The method of claim 11, wherein the powder composition comprises between 50 to 100 weight percent of the at least one ultrafine, high Tg, spherical polyetherimide powder, based on the weight of polymeric materials in the powder.
13. The method of any of claims 11-12, wherein the spherical polyetherimide powder has a glass transition temperature of more than 150° C. and less than 350° C.
14. The method of any of claims 11-13, wherein the spherical polyetherimide powder has a glass transition temperature of more than 200° C. and less than 300° C.
15. The method of any of claims 11-14, wherein at least one ultrafine, high Tg, spherical polyetherimide powder is made by a process comprising (a) dissolving polyetherimide in an organic solvent capable of dissolving the polyetherimide to form a solution; (b) emulsifying the solution by combining the solution with water and a surfactant to form an emulsion; (c) transferring the emulsion into a receiving water containing a surfactant to remove the organic solvent and form a slurry; and (d) recovering polyetherimide particles of less than 75 micron diameter.
16. The method of claim 15, wherein the solvent is a member selected from the group of methylene chloride, chloroform, and combinations thereof.
17. The method of any of claims 15-16, wherein the surfactant is anionic, cationic or non-ionic surfactant or combinations thereof.
18. A method of manufacturing a three dimensional article comprising the steps of: (1) depositing a quantity of a powder composition including at least one ultrafine, high Tg, spherical thermoplastic polymer powder on a support surface; (2) leveling the composition to form a smooth layer on the support surface; (3) then directing an energy beam over a predetermined target area on the support surface causing the composition to

form an integral layer; and (d) repeating steps (1) to (3) to form additional layers that are integrally bonded to adjacent layers to form a three-dimensional article, wherein the thermoplastic composition includes at least one ultrafine, high Tg, spherical thermoplastic powder.

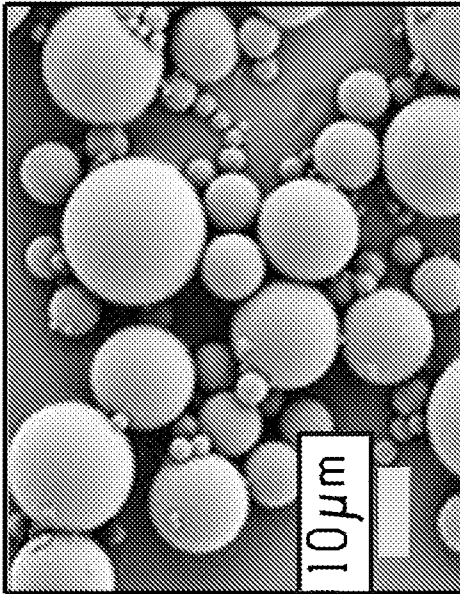
19 The method of claim 18, wherein the at least one ultrafine, high Tg, spherical thermoplastic powder is made by the steps of: (a) dissolving a thermoplastic polymer material in a solvent to form a solution, wherein the thermoplastic polymer is soluble in the solvent, the solvent has a boiling point that is less than 100 C and the solvent is immiscible with water; (b) emulsifying the solution by combining the solution with de-ionized water and a surfactant under agitation conditions sufficient to form an emulsion; (c) transferring the emulsion into a de-ionized receiving water, the receiving water also containing a surfactant and removing the solvent and form a slurry; (d) pre-filtering the slurry to remove any macro particles or contaminates; (e) filtering the slurry to form a wet cake; (f) filtering the slurry to form a wet cake; (g) drying the washed wet cake under heat and vacuum; and (h) recovering particles of thermoplastic polymer powder of less than 75 micron diameter.

20 A three-dimensional sintered article resulting from the method of any of the claims 1-19.



POWDER A

Fig. 1A



POWDER B

Fig. 1B

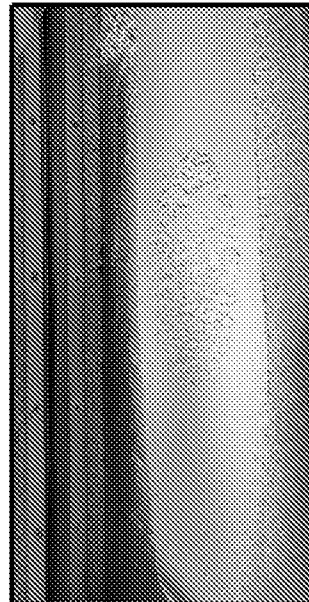


Fig. 2A

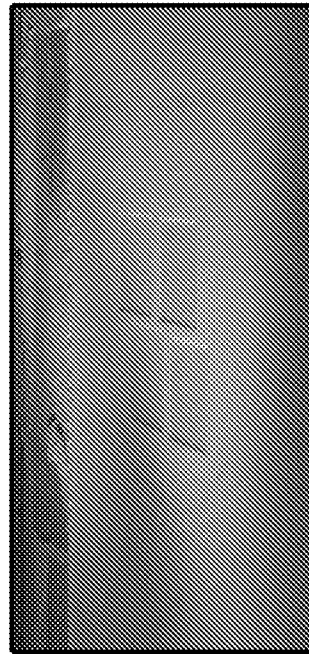


Fig. 2B

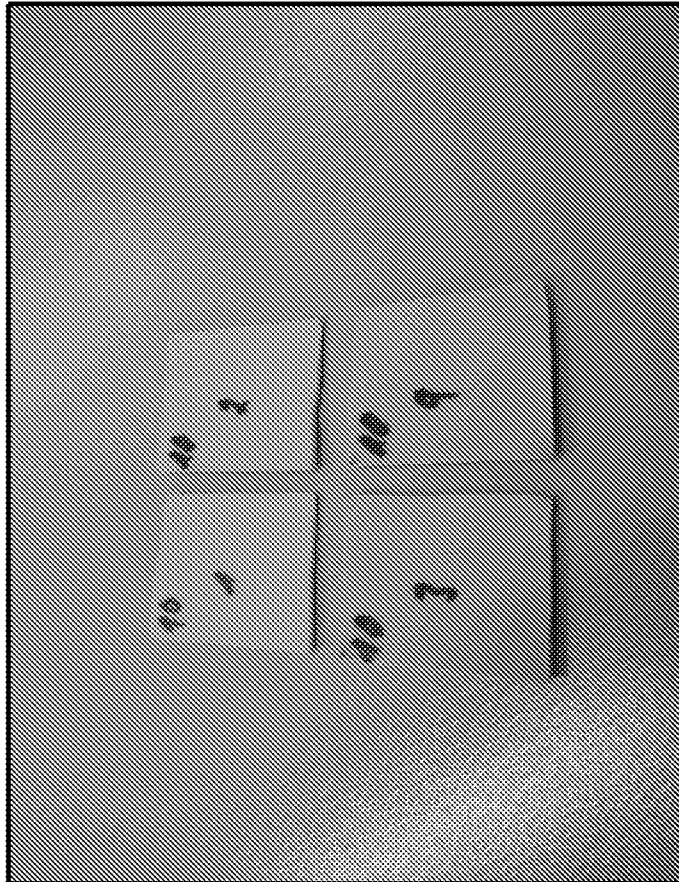


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/024452

A. CLASSIFICATION OF SUBJECT MATTER

INV. B29C67/00 B33Y70/00
 ADD. C08J3/12

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)

B29C C08J B33Y

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/033548 A1 (BRODKIN DMITRI [US] ET AL) 21 March 2002 (2002-03-21)	1,3,4,9,18,20
Y	paragraph [0015]; claims 1,3,4,7,8,10,11,22	2,5-8,10-17,19
X	US 2008/122141 A1 (BEDAL BRYAN [US] ET AL) 29 May 2008 (2008-05-29)	18,20
Y	abstract claims 1, 2, 7, 8, 15 - 23, 48	2,6-8
X	US 5 817 206 A (MCALEA KEVIN P [US] ET AL) 6 October 1998 (1998-10-06)	18,20
Y	abstract figures 1a, 1b, 4a, 4b column 5, line 62 - column 6, line 41 claim 1	5,10
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"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)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 June 2015

Date of mailing of the international search report

06/07/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Lozza, Monica

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/024452

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/070442 A1 (ASANO ITARU [JP] ET AL) 24 March 2011 (2011-03-24) abstract paragraph [0227] paragraph [0241] claims 1, 14 -----	11-17,19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/024452

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002033548 A1	21-03-2002	US 6322728 B1 US 2002033548 A1	27-11-2001 21-03-2002
US 2008122141 A1	29-05-2008	US 2008122141 A1 WO 2008067496 A2	29-05-2008 05-06-2008
US 5817206 A	06-10-1998	AU 2262297 A CA 2244754 A1 EP 0879261 A1 JP 3989552 B2 JP 2000504642 A US 5817206 A WO 9729148 A1	28-08-1997 14-08-1997 25-11-1998 10-10-2007 18-04-2000 06-10-1998 14-08-1997
US 2011070442 A1	24-03-2011	AU 2009250453 A1 CN 102099400 A CN 104109250 A EP 2287236 A1 JP 5099135 B2 JP 5223989 B2 JP 5324698 B2 JP 5338957 B2 JP 5387796 B2 JP 2012197460 A JP 2012197461 A JP 2013076085 A JP 2013237857 A KR 20110029126 A TW 201011062 A US 2011070442 A1 US 2013337263 A1 WO 2009142231 A1	26-11-2009 15-06-2011 22-10-2014 23-02-2011 12-12-2012 26-06-2013 23-10-2013 13-11-2013 15-01-2014 18-10-2012 18-10-2012 25-04-2013 28-11-2013 22-03-2011 16-03-2010 24-03-2011 19-12-2013 26-11-2009