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(54) Title: POLYPROPYLENE-BASED PARTICLES FOR ADDITIVE MANUFACTURING

(57) Abstract: Polypropylene-based powders are provided for use in the production of various articles by one or more additive manufacturing techniques. As described further herein, the polypropylene-based powders can exhibit particle morphologies, particle size distributions, and/or compositional parameters advantageous for production of articles having enhanced mechanical properties. In one aspect, a powder composition comprises particles of copolymer or terpolymer having a spherical shape, spheroidal shape, or a mixture of spherical and spheroidal shapes, the copolymer or terpolymer comprising one or more alkene monomeric species and the balance polypropylene.



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POLYPROPYLENE-BASED PARTICLES FOR ADDITIVE MANUFACTURING

RELATED APPLICATION DATA

The present application claims priority pursuant to Article 8 of the Patent
5 Cooperation Treaty to United States Provisional Patent Application Serial
Number 62/861,856 filed June 14, 2019, which is incorporated herein by
reference in its entirety.

FIELD

10 The present invention relates to polymeric powders and, in particular, to
polypropylene-based powders for use with one or more additive manufacturing
techniques.

BACKGROUND

15 Additive manufacturing generally encompasses processes in which digital
3-dimensional (3D) design data is employed to fabricate an article or
component in layers by material deposition and processing. Various techniques
have been developed falling under the umbrella of additive manufacturing.
Additive manufacturing offers an efficient and cost-effective alternative to
20 traditional article fabrication techniques based on molding processes. With
additive manufacturing, the significant time and expense of mold and/or die
construction and other tooling can be obviated. Further, additive
manufacturing techniques make an efficient use of materials by permitting
recycling in the process and precluding the requirement of mold lubricants and

coolant. Most importantly, additive manufacturing enables significant freedom in article design. Articles having highly complex shapes can be produced without significant expense allowing the development and evaluation of a series of article designs prior to final design selection.

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SUMMARY

Polypropylene-based powders are described herein for use in the production of various articles by one or more additive manufacturing techniques. The polypropylene-based powders can exhibit particle morphologies, particle size distributions, and/or compositional parameters advantageous for production of articles having enhanced mechanical properties. In one aspect, a powder composition comprises particles of copolymer or terpolymer having a spherical shape, spheroidal shape, or a mixture of spherical and spheroidal shapes, the copolymer or terpolymer comprising one or more alkene monomeric species and the balance polypropylene. In some embodiments, the alkene monomeric species is present in the copolymer or terpolymer in an amount of 3 to 9 molar percent. In some embodiments, the particles have an aspect ratio of 0.5–1. Moreover, the copolymer or terpolymer of the particles can have a random structure, including an isostatic random structure, and does not include formation of block copolymer or block terpolymer.

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In another aspect, articles produced by an additive manufacturing technique are described. An article produced by an additive manufacturing

technique comprises fused particles of copolymer or terpolymer comprising one or more alkene monomeric species and the balance polypropylene, wherein the article has a tensile strength of 18–23 MPa. In some embodiments, the article has an elongation at breakage greater than 70 percent.

5 In a further aspect, methods of forming articles are described. A method of forming an article comprises providing a powder composition including particles of copolymer or terpolymer having a spherical shape, spheroidal shape, or a mixture of spherical and spheroidal shapes, the copolymer or terpolymer comprising one or more alkene monomeric species and the balance
10 polypropylene. The powder is formed into the article via an additive manufacturing technique. In some embodiments, the additive manufacturing technique is a powder bed fusion technique. The article can exhibit tensile strength of 18–23 MPa and/or elongation at breakage greater than 70 percent, in some embodiments.

15 These and other embodiments are further described in the following detailed description.

DETAILED DESCRIPTION

Embodiments described herein can be understood more readily by
20 reference to the following detailed description and examples and their previous and following descriptions. Elements, apparatus and methods described herein, however, are not limited to the specific embodiments presented in the detailed description and examples. It should be recognized that these

embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations will be readily apparent to those of skill in the art without departing from the spirit and scope of the invention.

In one aspect, a powder composition comprises particles of copolymer or
5 terpolymer having a spherical shape, spheroidal shape, or a mixture of
spherical and spheroidal shapes, the copolymer or terpolymer comprising one
or more alkene monomeric species and the balance polypropylene. In some
embodiments, for example, the particles have an aspect ratio of 0.5–1. The
spherical and/or spheroidal particles may also have an aspect ratio of 0.6–1,
10 0.7–1 or 0.8–1, in some embodiments.

The one or more alkene monomeric species of copolymer or terpolymer
forming the particles, in some embodiments, can be selected according to
various considerations including, but not limited to, altering the surface
energies of the particles and/or polymer chain structure to promote particle
15 coalescence in additive manufacturing techniques, including sintering. Any
alkene monomeric species consistent with the objectives of enhancing one or
more properties of articles produced by additive manufacturing can be
employed. In some embodiments, for example, the alkene monomeric species
for copolymerization with propylene monomer are selected from the group
20 consisting of ethylene, butene and 1–octene. Any combination of alkene
monomeric species with propylene monomer for particle formation is
contemplated. In some embodiments, the copolymer or terpolymer of the
particles has an isostatic random structure and does not include formation of

block copolymer or block terpolymer. Additionally, the copolymer or terpolymer can be linear or substantially linear. In being substantially linear, the copolymer or terpolymer has less than 1 percent branching.

Copolymer and terpolymer can comprise any amount of alkene monomer consistent with the objectives described herein. In some embodiments, the alkene monomeric species are present in the copolymer or terpolymer in an amount of 1 to 20 molar percent. Alternatively, the alkene monomeric species can be present in the copolymer or terpolymer an amount selected from Table I.

10 Table I – Molar % of alkene monomeric species

2.5-15
3-9
4-10
2.5-6
3-5.5

Specific amounts of alkene monomer can be selected according to several considerations including, but not limited to, identity of the alkene monomeric species, desired copolymer or terpolymer structure, and/or particle surface energy. Moreover, the copolymer or terpolymer can have a M_w/M_n ratio of 1.2 to 5, in some embodiments.

Particles comprising copolymer or terpolymer described herein can exhibit various thermal properties and/or phase transition properties facilitating formation of articles with advantageous mechanical properties via additive manufacturing techniques, including powder bed fusion techniques. In

some embodiments, copolymer or terpolymer of alkylene monomer and propylene forming the particles has a crystallization temperature less than 100°C. Crystallization temperature of the copolymer or terpolymer, for example, can range from 90–95°C. Additionally, in some embodiments, 5 copolymer or terpolymer of the particles can exhibit a difference between melting temperature and crystallization temperature ($T_m - T_c$) of less than 45°C or less than 40°C. In some embodiments, $T_m - T_c$ ranges from 30–45°C. Melting and crystallization temperature of the copolymer and terpolymer can be determined according to differential scanning calorimetry (DSC).

10 In addition to copolymer or terpolymer composition and structure, the spherical and/or spheroidal particles of the powder may also exhibit particle size distributions yielding additive manufactured articles having enhanced mechanical properties. The particles, for example, can have a D10 of 20–40 μm . In some embodiments, the particles have a D10 of at least (0.6)D50 or at 15 least (0.7)D50. D50 can range from 40–80 μm , in some embodiments. In conjunction with the foregoing D10 values, the particles can have a D90 of less than 150 μm or less than 120 μm . In some embodiments, less than 1 percent of the particles have size less than 10 μm .

20 In some embodiments, the powder composition has an apparent density of at least 0.4 g/cm³. Apparent density of the powder composition can be 0.4–0.6 g/cm³. The powder composition can also exhibit a tap density of at least 0.5 g/cm³. In some embodiments, the powder composition has a tap density of 0.45–0.65 g/cm³. Additionally, the ratio of tap density to apparent density

(Hausner ratio) of powder composition is 1.1 to 1.4, in some embodiments.

The Hausner ratio can be less than 1.25, such as 1.1–1.2, for example.

Apparent density and tap density of powder compositions described herein can be determined according to ASTM D1895–17.

5 Powder compositions having the foregoing compositions and/or properties can be produced according to various techniques including, but not limited to, solvent precipitation, spray forming, and/or pulverization, milling and shaping.

As described herein, the foregoing properties of the powder composition
10 can be advantageous for producing articles having enhanced mechanical properties via additive manufacturing techniques. An article manufactured by an additive manufacturing technique, for example, comprises fused particles of copolymer or terpolymer comprising the one or more alkene monomeric species and the balance polypropylene. In some embodiments, the additively
15 manufactured article has a tensile strength of 17–25 MPa or 18–23 MPa. Additionally, the article can exhibit a tensile modulus of at least 700 MPa. The article, for example, can exhibit a tensile modulus of 700–1100 MPa. The article can also exhibit an elongation at break greater than 50 percent or greater than 70 percent according to ASTM D638. In some embodiments, the
20 article exhibits an elongation at break of at least 90 percent. Elongation at break of the article can also range from 95–110 percent, in some embodiments. Additionally, the article can have a heat deflection temperature of 30–90°C.

Moreover, the article can have a notched impact strength greater than 35 J/m according to ASTM D256, in some embodiments. For example, the article can have a notched impact strength of 40 to 70 J/m. The article can also exhibit less than 5 vol.% porosity or less than 3 vol.% porosity, in some
 5 embodiments.

Enhancements to particle coalescence in the additive manufacturing process provided by the composition and properties of the copolymer or terpolymer described herein can assist in producing one or more of the foregoing mechanical properties of the article. The article can be manufactured
 10 by any desired additive manufacturing technique. In some embodiments, the article is manufactured by a powder bed technique, such as selective laser sintering (SLS) or selected laser melting (SLM). Table II provides a summary of the foregoing properties an article can exhibit when formed from powder compositions described herein via an additive manufacturing technique,
 15 according to some embodiments.

Table II – AM Article Properties

Property	Value
Tensile Strength	18–25 MPa
Tensile Modulus	700–1100 MPa
Elongation at break	70 to >100%
Notched impact strength	35–70 J/m
Porosity	< 5 vol.%

In a further aspect, methods of forming articles are described. A method
 20 of forming an article comprises providing a powder composition including

particles of copolymer or terpolymer, the copolymer or terpolymer comprising one or more alkene monomeric species and the balance polypropylene. The powder is formed into the article via an additive manufacturing technique.

Powder compositions and the resultant articles of methods described herein

5 can have any composition, architecture and/or properties described above, including the compositions and properties of Tables I and II. In some embodiments, the particles of copolymer or terpolymer have a spherical shape, spheroidal shape, or a mixture of spherical and spheroidal shapes.

Alternatively, the particles of copolymer or terpolymer described herein are

10 non-spherical or irregular shape, but exhibit bulk and/or tap density values disclosed above. Additionally, the additive manufacturing technique can be a powder bed technique, such as selective laser sintering (SLS) or selected laser melting (SLM).

These and other embodiments are further illustrated in the following

15 examples.

EXAMPLE 1 - *Powder Composition*

Random copolymer described herein comprising about 5 molar percent ethylene and the balance isotactic polypropylene was synthesized and formed

20 into a powder composition via solvent pulverization. The random copolymer did not exhibit branching. The powder composition displayed the properties in Table III.

Table III – Copolymer Powder Properties

Property	Value
D10	26 μm
D50	55 μm
D90	110 μm
T _c	95°C
T _m	129°C

Individual copolymer particles exhibiting the properties of Table III had a spherical and/or spheroidal morphology.

5

EXAMPLE 2 – *Powder Composition*

Random terpolymer described herein comprising about 3 molar percent ethylene, 3 molar percent butane, and the balance isotactic polypropylene was synthesized and formed into a powder composition via solvent pulverization.

10 The terpolymer did not exhibit branching. The powder composition displayed the properties in Table IV.

Table IV – Terpolymer Powder Properties

Property	Value
D10	28 μm
D50	62 μm
D90	112 μm
T _c	95°C
T _m	129°C

15 Individual terpolymer particles exhibiting the properties of Table IV had a spherical and/or spheroidal morphology.

EXAMPLE 3 - *AM Articles*

Tensile test bars and impact samples (notched and un-notched) were printed from powder compositions of Examples 1 and 2 on a sPro60 HD-HS SLS machine commercially available from 3D Systems of Rock Hill, SC. Tensile test bars and impact samples were also printed from comparative powder compositions 3-5 on the sPro60 HD-HS SLS machine. Compositional parameters of comparative powder compositions were as follows:

Comparative powder 3 - solvent pulverized isotactic polypropylene

Comparative powder 4 - solvent pulverized block copolymer comprising 6-10 molar percent ethylene and the balance polypropylene

Comparative powder 5 - solvent pulverized copolymer of less than 2 molar percent ethylene with the balance polypropylene

Additional parameters of Comparative powders 3-5 are provided in Table V.

Table V - Comparative powders 3-5

Property	Comparative Powder 3	Comparative Powder 4	Comparative Powder 5
D10	23 μm	22 μm	25 μm
D50	55 μm	52 μm	65 μm
D90	112 μm	102 μm	115 μm
T _c	116°C	115°C	104°C
T _m	166°C	168°C	150°C

Comparative powders 3-5 exhibited a spherical and/or spheroidal morphology.

Print temperature and laser parameters of the sPro60 HD-HS SLS machine were optimized for each powder composition of Examples 1-2 and Comparative

powders 3–5. Optimization was administered to achieve the highest mechanical properties for each printed article. All articles were printed in the XY plane and in accordance with the specifications set forth in the related ASTM. Results of the mechanical testing of the articles printed with each powder composition are provided in Table VI.

Table VI – Article Mechanical Properties

Property	Ex. 1	Ex. 2	Comp. 3	Comp. 4	Comp. 5
Tensile Modulus (MPa)	900	1000	1200	1000	850
Tensile Strength (MPa)	20	21	12	12	16
Elongation at Breakage (%)	>100	>100	2	3	18
Notched Impact (J/m)	43	60	29	30	60

As provided in Table VI, the articles made from powder compositions described herein embodied in Examples 1 and 2 exhibited superior elongation at break, and impact and tensile strengths, while maintaining comparable tensile modulus values.

Various embodiments of the invention have been described in fulfillment of the various objects of the invention. It should be recognized that these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations thereof will be readily apparent to

those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

1. A powder composition comprising:
particles of copolymer or terpolymer having a spherical shape, spheroidal
shape, or a mixture of spherical and spheroidal shapes, the copolymer or
5 terpolymer comprising one or more alkene monomeric species in an amount of
3 to 9 molar percent, and the balance polypropylene.
2. The powder composition of claim 1, wherein the particles have an aspect
ratio of 0.7 to 1.
- 10 3. The powder composition of claim 1, wherein the copolymer or terpolymer
has a crystallization temperature less than 100°C.
4. The powder composition of claim 1, wherein a difference between
15 melting temperature and crystallization temperature of the copolymer or
terpolymer is less than 45°C.
5. The powder composition of claim 1, wherein the copolymer or terpolymer
is not substantially branched.
- 20 6. The powder composition of claim 1, wherein the monomeric alkene
species are selected from the group consisting of ethylene, butene and 1-
octene.

7. The powder composition of claim 1, wherein the copolymer or terpolymer has an isotactic random structure.
8. The powder composition of claim 1, wherein the copolymer or terpolymer
5 has M_w/M_n ratio of 1.2 to 5.
9. The powder composition of claim 1, wherein the particles have a D10 of at least (0.6)D50.
- 10 10. The powder composition of claim 9, wherein the particles have a D90 of less than 150 μm .
11. The powder composition of claim 1 having an apparent density greater than 0.4 g/cm^3 .
- 15 12. The powder composition of claim 1 having an apparent density of 0.4–0.6 g/cm^3 .
13. The powder composition of claim 1 having a tap density greater than 0.5
20 g/cm^3 .
14. The powder composition of claim 1 having a Hausner ratio of 1.1 to 1.4.

15. An article manufactured by an additive manufacturing technique comprising:

fused particles of copolymer or terpolymer comprising one or more alkene monomeric species and the balance polypropylene, wherein the article
5 has a tensile strength of 18–23 MPa.

16. The article of claim 15, wherein the alkene monomeric species are present in the copolymer or terpolymer in an amount of 1 to 20 molar percent.

10 17. The article of claim 15, wherein the alkene monomeric species are present in the copolymer of terpolymer in an amount of 3 to 9 molar percent.

18. The article of claim 15, wherein the monomeric alkene species are selected from the group consisting of ethylene, butene and 1-octene.

15

19. The article of claim 15 having a tensile modulus of at least 700 MPa.

20. The article of claim 15 having an elongation at break greater than 70 percent according to ASTM D638.

20

21. The article of claim 15 having a notched impact strength greater than 40 J/m according to ASTM D256.

22. A method of forming an article comprising:
providing a powder composition including particles of copolymer or terpolymer having a spherical shape, spheroidal shape, or a mixture of spherical and spheroidal shapes, the copolymer or terpolymer comprising one
5 or more alkene monomeric species and the balance polypropylene; and
forming the powder composition into the article via an additive manufacturing technique, wherein the article has a tensile strength greater than 18–23 MPa.
- 10 23. The method of claim 22, wherein the additive manufacturing technique is a powder bed fusion technique.
24. The method of claim 23, wherein the powder bed fusion technique is selective laser sintering or selective laser melting.
- 15 25. The method of claim 23, wherein the particles have an aspect ratio of 0.5 to 1.
26. The method of claim 23, wherein the alkene monomeric species are
20 present in the copolymer or terpolymer in an amount of 3 to 9 molar percent.
27. The method of claim 23, wherein the monomeric alkene species are selected from the group consisting of ethylene, butene and 1–octene.

28. The method of claim 23, wherein the article has an elongation at break greater than 70 percent according to ASTM D638.

5 29. The method of claim 23, wherein the article has a notched impact strength greater than 40 J/m according to ASTM D256.

30. The method of claim 23, wherein the article has less than 5 vol.% porosity.

10

31. The method of claim 23, wherein the powder composition has an apparent density of 0.4–0.6 g/cm³.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/037366

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F210/06 B29C64/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08F B29C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103 980 401 A (CHINESE ACAD INST CHEMISTRY) 13 August 2014 (2014-08-13) paragraph [0047]; claims 1-10; example 2 -----	1-6,8, 13,14
X	CN 106 279 476 A (INST CHEMISTRY CAS) 4 January 2017 (2017-01-04) claims 1-9 -----	1-10,13, 14
X	JP 2008 162857 A (JAPAN POLYPROPYLENE CORP) 17 July 2008 (2008-07-17) examples 5, 6; table 2 -----	1-6, 11-14

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 22 September 2020	Date of mailing of the international search report 25/11/2020
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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 Bernhardt, Max
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/037366

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-14

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/037366

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 103980401	A	13-08-2014	NONE	

CN 106279476	A	04-01-2017	NONE	

JP 2008162857	A	17-07-2008	JP 5508660 B2	04-06-2014
			JP 2008162857 A	17-07-2008

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-14

a powder composition comprising spherical or spheroidal shaped particles of propylene copolymers comprising 3-9 mol-% of an alkene monomeric species (claim 1), wherein further parameters are defined in claims 2-14

2. claims: 15-21

An article which comprises a propylene co- or terpolymer comprising alkene monomeric species having a tensile strength of 18-23 MPa. (claim 15). The articles is further defined in claims 16-21.

3. claims: 22-31

A method of forming an article comprising:
providing a powder composition including particles of copolymer or terpolymer having a spherical shape, spheroidal shape, or a mixture of spherical and spheroidal shapes, the copolymer or terpolymer comprising one or more alkene monomeric species and the balance polypropylene; and forming the powder composition into the article via an additive manufacturing technique, wherein the article has a tensile strength greater than 18-23 MPa (claim 22). The method is further defined in claims 23-31.
