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(54) Title: PROCESS FOR PRODUCING A THERMOPLASTIC POLYMER POWDER

(57) Abstract: Process for producing a thermoplastic polymer powder, which comprises the steps of: (i) compression-molding a powdery raw material of a thermoplastic polymer to form tablets, by means of a tablet press; and, (ii) comminuting the tablets to form the thermoplastic polymer powder. Further disclosed is a polymer powder obtained by said process, which typically has an average particle size ranging from 1 to 100 µm, and is further characterized by a combination of attributes which are in favour of powder coating application.



WO 2014/095676 A1

Description

PROCESS FOR PRODUCING A THERMOPLASTIC POLYMER POWDER

Cross-reference to related application

[0001] The present application claims priority to European application No. 12198855.4 filed on December 21, 2012, the whole content of this application being incorporated herein by reference. Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Technical Field

[0002] The present invention relates to a process for producing a thermoplastic polymer powder, and more particularly to a process for producing thermoplastic powders usable in powder coating application.

Background Art

[0003] The use of thermoplastic polymer powders in powder coating is well-known in the art. In a typical powder coating process, the polymer particles are electrostatically charged and deposited on a heated metal surface, and the thus-obtained coating is then heat cured to allow it to flow and form a hard finish. Unlike the conventional liquid paint, a powder coating does not require a solvent to keep the binder and fillers in a liquid suspension form and therefore produces less hazardous organic waste. As an additional advantage over the conventional liquid paint, powder coatings produce thicker coatings with a more homogenous appearance.

[0004] Nevertheless, the powdery raw material of a thermoplastic polymer, which is generally obtained after drying and cooling a polymerization product, has a low bulk density and thus causes significant inconveniences in storage and transportation for powder coating use. Moreover, the powdery raw materials are also found to suffer from poor powder fluidity and, as a result, cannot form an acceptable, smooth powder coating finish.

[0005] To alleviate these problems, EP 1120436 A (HOSOKAWA MICRON CORPORATION) 01.08.2001 proposes a process for producing thermal plastic resin granules. Said process comprises compression moulding a

powdery raw material of a thermoplastic resin, which is obtained by polymerizing a plurality of materials and then drying the obtained polymer, by passing the powdery raw material between two rolls arranged parallel with a minute gap there between at a temperature of 40°C or higher, and crushing the obtained compression-molded product into granules having grain diameters of 10mm or less. Nevertheless, the granules obtained by this process still do not have a desirably high bulk density, or a significantly improved surface roughness.

- [0006] Moreover, **US 6376647 B** (DAIKIN INDUSTRIES LTD.) 30.10.1997 and **EP 1398342 B** (DAIKIN INDUSTRIES, LTD.) 17.03.2004 both describe an identical process for treating the raw powders of fluorine-containing polymer for powder coating. Specifically, as detailed in US 6376647, said process comprises: densifying fluorine-containing polymer raw powder with rolls under conditions for permitting its specific gravity to achieve at least 90% of the true specific gravity; then comminuting the densified material; removing fine particles in the range of 3 to 40% by weight of the whole particle size distribution of the comminuted material by air classification; and further removing coarse particles in the range of 1 to 20% by weight of the whole particle size distribution of the comminuted material by classification. However, said process was proven ineffective when applied for obtaining a thicker film, e.g. a smooth coating with a thickness over 30 microns.
- [0007] Similarly, **US 7735759 B** (ELRINGKLINGER AG) 07.02.2008 and the related **US 2008/0033132 A** (ELRINGKLINGER AG) 07.02.2008 both disclose a method for production of a flowable powder of a fluoropolymer compound, which comprise pressing the powder into hand-shaped lump ("lumpy, hand-shaped intermediate product") and then crushing the lump, wherein the pressing step is carried out by means of at least one roller of a pressing device. This method, however, was not sufficiently effective in providing the polymer powders with uniform grain size within a narrow range.
- [0008] **US 6518349 B** (E. I. DU PONT NEMOURS AND COMPANY) 29.05.2000 discloses yet another method for preparing a sprayable powder of

fluoropolymer, which involves spray drying a liquid dispersion of primary particles of non-fibrillatable fluoropolymer and densifying the granules formed by spray drying, preferably by mechanical compaction rollers. Nevertheless, such a method requires enormous facilities and high costs, and its productivity is low.

[0009] Therefore, there remains a need to provide a process for producing a thermoplastic polymer powder with improved properties tailored for powder coating application. Particularly, it would be advantageous to have a process to produce thermoplastic polymer powders having uniform size distribution and a higher bulk density, in combination with better flowability and minimized surface roughness.

Summary of invention

[0010] To meet the above need, the present invention provides a process for producing a thermoplastic polymer powder, which comprises the steps of:
(i) compression-molding a powdery raw material of a thermoplastic polymer to form tablets, by means of a tablet press; and,
(ii) comminuting the tablets to form the thermoplastic polymer powder.

[0011] The Applicant has found that, using the process of the present invention, it is possible to obtain thermoplastic polymer powder having a particle size of 100 μm or less. Advantageously, comparing with the powdery raw material of a thermoplastic polymer, the powder obtained by the invented process has a more uniform particle size distribution, a notably higher bulk density, as well as a better flowability and reduced surface roughness. Moreover, using the polymer powders obtained by the invented process, one skilled in the art can easily obtain a thicker coating in a standard electrostatic powder coating procedure.

[0012] For the purpose of the present invention, the term "thermoplastic" refers to polymers which exist at room temperature and below their glass transition temperature if they are amorphous or, if they are semi-crystalline, exist below their melting point. The thermoplastic polymers have the property of becoming soft when they are heated and of becoming rigid again when they are cooled, without there being an appreciable chemical change.

[0013] The "powdery raw material" of a thermoplastic polymer, as used in the

present invention, can be obtained by drying a thermoplastic resin after polymerization. Alternatively, said powder raw material may be obtained by drying and then cooling a thermoplastic resin after polymerization.

[0014] Accordingly, in one embodiment of the present invention, the invented process optionally contains an additional step prior to the compression-molding step (i), that is, providing a powdery raw material of a thermoplastic polymer by drying a thermoplastic resin after polymerization.

[0015] The “tablet press” used in step (i) of the invented process can be any device used in the art to manufacture tablet product, and generally refers to a mechanical device that compresses a powder or granular material into tablets in at least one cavity formed by two punches and a die, wherein the punches are pressed together with great force to fuse the material together.

[0016] Specifically, the tablet press used in the invented process may be a single punch tablet press or a rotary tablet press, both well known in the chemistry art.

[0017] In an exemplified embodiment of the present invention, a single punch tablet press is used to form the tablets in step (i) and the tablet formation process is described below. Firstly, the powdery raw material is filled in a feed shoe, which is then emptied into a die cavity of the single punch table press. Subsequently, the feed shoe is retracted and scrapes all excess powder away from the die cavity. An upper punch then compresses the powders within the die cavity. After compression, the upper punch retracts and a low punch raises and ejects the tablet. As the feed shoe returns to fill the die cavity, it pushes the compressed tablet from the die.

[0018] Preferably, a rotary tablet press is used to form the tablets in step (i). One classic example of rotary tablet press is described in **US 3255716** (E. L. KNOECHEL ET AL) , which was issued on June 14, 1966. Such rotary tablet press essentially comprises a main operating unit with a central rotary turret designed to enable the powdery product to be volumetrically dosed into a plurality of dies located in a first rotating disc and equally distributed around the circumference of the disc. In a standard tablet

formation procedure using such rotary press, a pair of opposed cam operated punches compress the powder in each die into an individual tablet. The rotary turret arrangement allows a plurality of punch and die sets to continuously produce tablets around the circular path followed by the rotary press by sequentially contacting an arrangement of cam above and below the turret that lift and lower the punches.

- [0019] In step (i) of the invented process, the tablets are preferably produced at a temperature of 0 to 150°C, preferably 5°C to 80°C, more preferably 10°C to 50°C.
- [0020] Generally, the tablets obtained in step (i) of the invented process are of a cylinder shape, with a diameter of from 3 mm to 25 mm, preferably 5 mm to 15 mm, and more preferably between 8 mm to 12 mm. The height of the cylindrical tablets is variable by adjusting the compressing force and loading in each die of the tablet press, and is typically ranging from 1 mm to 25 mm, preferably from 2 mm to 15 mm, and more preferably from 3 mm to 10 mm.
- [0021] In the comminuting step (ii) of the invented process, the tablets obtained from step (i) may be formed into a thermoplastic polymer powder by a mill or a grinding machine.
- [0022] In a specific embodiment of the invented process, the comminuting step (ii) includes crushing the tablets with a crusher and then milling the crushed tablets by a mill or a grinding machine.
- [0023] Alternatively, the comminuting step (ii) of the invented process only includes milling the tablets. The milling is usually carried out with a mechanical mill. Examples of the mechanical mill include impact type mills such as a cutter mill, a hammer mill, a pin mill, a jet mill, etc., and grinding type mills which mill a material with a shear force generated by a rotating blade and a peripheral stator. To obtain a high milling efficiency, the millers of a high shear type are preferable. The milling temperature is from -200 to +100°C. In the freeze milling, the temperature is usually from -200 to -100°C, for which liquid nitrogen is often used. However, given the huge facilities and high cost of freeze milling, the milling of the tablets of the invented process is usually carried out at room temperature (10 to 30°C),

to keep the whole process simple and economical.

[0024] Typically, the thermoplastic polymer powder obtained from step (ii) of the invented process has a particle size of 100 μm or less, with a uniform particle size distribution.

[0025] Optionally, subsequent to the comminuting step (ii), the invented process includes a classification step (iii) below:

(iii) classifying the thermoplastic polymer powder to remove particles with a size in a predetermined range and obtain a classified powder.

[0026] Specifically, said classification step (iii) may include the following step(s):

(iii-a) Removing fine particles with a size of less than 1 μm by classification, and/or

(iii-b) Removing coarse particles with a size of more than 100 μm by classification,

wherein the sequence of step (iii-a) and step (iii-b) is exchangeable.

[0027] Preferably, step (iii-a) is a step of removing fine particles with a size of less than 5 μm . More preferably, step (iii-a) is a step of removing fine particles with a size of less than 10 μm .

[0028] Also preferably, step (iii-b) is a step of removing coarse particles with a size of more than 80 μm . More preferably, step (iii-b) is a step of removing coarse particles with a size of more than 60 μm .

[0029] As said, if step (iii-a) and step (iii-b) are both present in the process invention, the sequence thereof is exchangeable. In one embodiment of the process invention, step (iii-a) is performed after step (iii-b).

[0030] In general, for the classification of fine particles in step (iii-a), air classification is used. In such air classification, the milled particles are supplied in a cylindrical classifying room with air under reduced pressure, and dispersed with whirling air in the room while the fine particles are being classified by centrifugal force. The fine particles are collected from the center of the room to a cyclone and a bag filter, and again sheeted. In the classifying room, a rotating member such as a cone or a rotor is set for uniformly whirling the particles and the air. When classification cones are used, the classification is controlled by adjusting the flow of secondary air and a gap between the classification cones. When a rotor is used, the

classification is controlled by adjusting the flow of air in the classifying room and the rotation speed of the rotor.

- [0031] The air pressure of a blower is usually from 0.001 to 1 MPa, preferably from 0.01 to 0.5 MPa. The range of classification is usually from 1 to 50% by weight, preferably 3 to 40% by weight, and thus the fine particles and fibrous particles are removed in a percentage of 3 to 40% by weight based on the whole particles. When the amount of the fine particles removed is less than 3% by weight, the flowability of the powder is not improved, and the remaining particles have a very wide particle size distribution so that the leveling property of the coated film deteriorates. When the amount of the particles removed exceeds 40% by weight, the powder becomes less attractive from the viewpoint of costs.
- [0032] For the classification of coarse particles in step (iii-b), an air classifier or a vibration sieve based on meshes can be used, with the former being preferable. The range of classification based on particle sizes can be adjusted by the operation speed of the employed classifier, which is usually from 1 to 20% by weight, and preferably from 2 to 10% by weight of the whole particle size distribution, to remove the undesired coarse particles.
- [0033] Preferably, the fine particles recovered in the classification of step (iii-a) are again compression-molded like the powdery raw material in step (i). Likewise, the coarse particles recovered in the classification of step (iii-b) are preferably recycled to be again comminuted like the tables in step (ii).
- [0034] According to yet another embodiment of the present invention, the process further includes the following step after step (iii):
(iv) contacting the classified powder with an air stream at a temperature higher than the melting-initiation temperature of the thermoplastic polymer.
- [0035] For instance, the aforementioned step (iv) can be carried out using a continuous airflow type heating drier. A contact temperature in the continuous airflow type heating drier is usually 1000°C or less, preferably from 200 to 800°C, and a contact time is typically from 0.1 to 10 seconds. A heat source is preferably gas heating for energy saving purpose. The heat-treated powder may be further classified with the air classifier or

vibration sieve to remove the coarse particles. Thereby, a powder having a narrower particle size distribution can be obtained.

[0036] As a result of step (iv), generally, the surfaces of the powder particles are rounded so that the bulk density and flowability of the powder are further increased, and thus could provide an even better powder coating on the applied articles.

[0037] The thermoplastic polymer powder resulted from the invented process, by virtue of its combined attributes of high bulk density, uniform particle size and good flowability, can be advantageously used for powder coating and form a smooth film with a thickness of 30 to 110 μm in only one pass. Moreover, in the films formed by these polymer powders, no pinholes or orange-peel surfaces were observed.

[0038] Furthermore, the present invention provides a thermoplastic polymer powder produced by any one of the above processes. The thermoplastic polymer powder has an average particle size of 1 to 100 μm , preferably 3 to 80 μm , and more preferably 5 to 60 μm .

[0039] The thermoplastic polymer used in the present invention may be of any kind, for example but not limited to: fluoropolymers, polyethylene, polyethylene terephthalate, polystyrene, acrylonitrile butadiene styrene (ABS), metacrylate polymer, polyamide, polycarbonate, polyacetal, polyphenylene ether, polyphenylene sulphide, polyether ether ketone, polysulfone, polybutylene terephthalate, polyvinylidene chloride, and the like.

[0040] Preferably, the thermoplastic polymer used in the present invention is a fluoropolymer, i.e. a polymer comprising recurring units derived from at least one fluorinated monomer. To the purpose of the present invention, the fluoropolymer comprises preferably more than 20 % moles, more preferably more than 30 % moles of recurring units derived from the fluorinated monomer.

[0041] In particular, while various fluoropolymers are historically utilized for powder coating application, their powdery raw materials generally do not provide desired uniform particle size and often give poor yield and surface roughness upon coating. The process of the present invention, notably,

provides an easy and convenient procedure for improving the physical properties of various fluoropolymer powders, making them well tailored for powder coating application.

[0042] Fluoropolymers which have been found particularly suitable for the process of the present invention are per(halo)fluoropolymers. For the purpose of the invention, the term “per(halo)fluoropolymer” is intended to denote a fluoropolymer substantially free of hydrogen atoms. The per(halo)fluoropolymer can comprise one or more halogen atoms (Cl, Br, I) different from fluorine. The term “substantially free of hydrogen atom” is understood to mean that the per(halo)fluoropolymer consists essentially of recurring units derived from ethylenically unsaturated monomers comprising at least one fluorine atom and free of hydrogen atoms [per(halo)fluoromonomer (PFM)]. The per(halo)fluoropolymer can be a homopolymer of a per(halo)fluoromonomer (PFM) or a copolymer comprising recurring units derived from more than one per(halo)fluoromonomer (PFM).

[0043] Non limitative examples of suitable per(halo)fluoromonomers (PFM) are notably :

C₂-C₈ perfluoroolefins, such as tetrafluoroethylene (TFE) and hexafluoropropene (HFP);

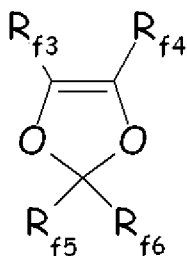
chloro- and/or bromo- and/or iodo- C₂-C₆ per(halo)fluoroolefins, like chlorotrifluoroethylene;

per(halo)fluoroalkylvinylethers complying with general formula CF₂=CFOR_{f1} in which R_{f1} is a C₁-C₆ per(halo)fluoroalkyl, such as -CF₃, -C₂F₅, -C₃F₇ ;

per(halo)fluoro-oxyalkylvinylethers complying with general formula CF₂=CFOX₀₁, in which X₀₁ is a C₁-C₁₂ per(halo)fluorooxyalkyl having one or more ether groups, like perfluoro-2-propoxy-propyl group;

per(halo)fluoro-methoxy-alkylvinylethers complying with general formula CF₂=CFOCF₂OR_{f2} in which R_{f2} is a C₁-C₆ per(halo)fluoroalkyl, such as -CF₃, -C₂F₅, -C₃F₇ or a C₁-C₆ per(halo)fluorooxyalkyl having one or more ether groups, such as -C₂F₅-O-CF₃;

per(halo)fluorodioxoles of formula :



wherein each of R_{f3} , R_{f4} , R_{f5} , R_{f6} , equal or different each other, is independently a fluorine atom, a C_1 - C_6 perfluoroalkyl group, optionally comprising one or more oxygen atom, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-OCF_3$, $-OCF_2CF_2OCF_3$; preferably a per(halo)fluorodioxole complying with formula here above, wherein R_{f3} and R_{f4} are fluorine atoms and R_{f5} and R_{f6} are perfluoromethyl groups ($-CF_3$) [perfluoro-2,2-dimethyl-1,3-dioxole (PDD)], or a per(halo)fluorodioxole complying with formula here above, wherein R_{f3} , R_{f5} and R_{f6} are fluorine atoms and R_{f4} is a perfluoromethoxy group ($-OCF_3$) [2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole or perfluoromethoxydioxole (MDO)].

- [0044] The per(halo)fluoropolymer is advantageously chosen among tetrafluoroethylene (TFE) homopolymers and copolymers of TFE with at least one per(halo)fluoromonomer (PFM) different from TFE.
- [0045] According to one embodiment of the invention, the thermoplastic polymer is chosen among TFE copolymers comprising recurring units derived from at least one per(halo)fluoroalkylvinylether, as above defined, preferably from at least one perfluoroalkylvinylether, as above defined and optionally further comprising recurring units derived from C_3 - C_8 perfluoroolefins. Good results within this embodiment have been obtained with TFE copolymers comprising recurring units derived from one or more than one perfluoroalkylvinylether as above specified; particularly good results have been achieved with TFE copolymers wherein the perfluoroalkylvinylether is perfluoromethylvinylether (of formula $CF_2=CFOCF_3$), perfluoroethylvinylether (of formula $CF_2=CFOC_2F_5$), perfluoropropylvinylether (of formula $CF_2=CFOC_3F_7$) and mixtures thereof.
- [0046] Examples of TFE polymer suitable to be used to produce the thermoplastic

polymer powder of the present invention include MFA and PFA which are commercially available from Solvay Solexis Inc. under the trade name of HYFLON® PFA P and M series and HYFLON® MFA.

- [0047] Furthermore, the present invention is also related to the use of a thermoplastic polymer powder produced by one of the aforementioned processes for powder coating. Specifically, the thermoplastic polymer powder can be coated by a coating method such as spray coating, electrostatic spray coating, fluidized bed coating, electrostatic fluidized bed coating, etc. An aqueous dispersion paint or a dispersion paint in an organic solvent may also be used.

Description of embodiments

- [0048] The invention will now be described in more detail with reference to the following examples, whose purpose is merely illustrative and not limitative of the scope of the invention.

Example

[0049] Materials

The polymer powder used in the following Example and comparative Example is HYFLON® PFA powder obtained from Solvay Specialty Polymers Italy, SPA, which is a copolymer of tetrafluoroethylene and perfluoropropylvinylether.

[0050] Determination of Bulk Density

The bulk density (BD) measurement was carried out according to the ASTM D1895-96 (2003) standard test.

[0051] Measurement of Average Particle Diameter

The average particle diameter of the polymer powder particles was on a Beckman Coulter laser analyzer, model LS 13 320.

[0052] General Procedure of Electrostatic Powder Coating

To test the powder coating efficiency of the polymer powders obtained in the following Example and comparative Example, a carbon steel plate was first sand blasted with 60 mesh sand and then treated with a liquid primer. On the wet primer a layer of polymer powder was applied as top coat with an electrostatic gun (Optiflex system from ITW Gema), under the following conditions: 40 kV Voltage, 15mA Current, 20% Q powder and a total air

volume of 3.5 Nm³/h. The coated plate was then placed in an air ventilated oven at 380°C for 20 minutes, and subsequently cooled down at the room temperature.

[0053] Measurement of Coating thickness

For each coated plate prepared as described above, the coating thickness was measured at nine different positions of the plate with an Elcometer 456 coating thickness gauge, and the average value was reported.

[0054] Measurement of Surface Roughness (Ra)

Surface roughness R_a (μm) of each coated plate was measured using a MITUTOYO SURFTEST SJ-201.

[0055] Example 1

The HYFLON® PFA powder as received (having a bulk density of 0.483 g/cm³ and a particle size distribution as shown in Table 1) was compressed in a rotary tablet press (PR200 manufactured by B&D Italia), at a processing temperature between 10°C to 50°C, to obtain cylindrical tablets each characterized by a diameter of 10 cm and a density of 1.889 g/cm³. Subsequently, the polymer tablets were crushed in an ACM 10 mill manufactured by Alphine Hosokawa, and the crushed tablets were then classified by a classifier attached to the mechanical mill, to remove coarse particles having at least 100 micron in size. The remaining polymer powder was then delivered to a second classifier (Mikro Classifier CC manufactured by Alphine Hosokawa), to remove fine particles with a size of 5 micron or less (the amount of removed fine particles: 32.7% by weight). The resulting polymer powder (densified powder) had an average bulk density of 0.848 g/cm³ and a particle size distribution as shown in Table 1.

[0056] The densified powder was then applied on metallic substrate using electrostatic powder coating. The results of its final coating thickness and roughness (R_a) are shown in Table 1.

[0057] Comparative Example 1

The HYFLON® PFA powder as received (having a bulk density of 0.483 g/cm³ and a particle size distribution as shown in Table 1) was directly applied on metallic substrate using electrostatic powder coating. The

results of its final coating thickness and roughness (R_a) are also shown in Table 1.

Table 1

Sample	PSD* (μm)			BD (g/cm^3)	Coating thickness (μm)	R_a (μm)
	$d_{10}\%$	$d_{50}\%$	$d_{90}\%$			
Ex. 1	10.7	24.1	43.7	0.848	89	0.9
Comp. Ex. 1	2.3	17.3	74.9	0.483	40	3.7

** PSD = particle size distribution, for which $d_{10}\%$, $d_{50}\%$, and $d_{90}\%$ respectively represents a particle diameter corresponding to a point of 10%, 50% and 90% in the cumulative curve of the polymer particle size distribution.*

[0058] Clearly, compared to the raw polymer powder material, the densified polymer powder produced by the invented process has a more uniform particle size distribution and a notably higher bulk density, which in turn offer a better mechanical strength and efficiency in transportation and storage. Moreover, compared to the unprocessed raw powder, said densified polymer powder advantageously provided a thicker and smoother top coat using a same electrostatic powder coating procedure.

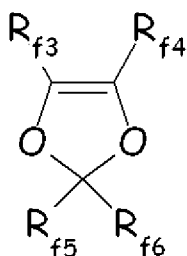
[0059] Additionally, the fine particles and coarse particles recovered in the optional classification steps of the invented process can be readily recycled, respectively, to join raw polymer powders in the compression-molding treatment and subsequent classification, to provide better yield of densified polymers with improved performance in electrostatic powder coating.

Claims

1. A process for producing a thermoplastic polymer powder, which comprises the steps of:
 - (i) compression-molding a powdery raw material of a thermoplastic polymer to form tablets, by means of a tablet press; and,
 - (ii) comminuting the tablets to form the thermoplastic polymer powder.
2. The process of claim 1, wherein the tablet press is a rotary tablet press.
3. The process of claim 1, wherein the tablet press is a single punch tablet press.
4. The process of any one of the preceding claims, wherein the step (ii) only includes milling the tablets.
5. The process of any one of the preceding claims, further comprising the step of:
 - (iii) classifying the thermoplastic polymer powder to remove particles with a size in a predetermined range and obtain a classified powder.
6. The process of claim 5, wherein the step (iii) comprises:
 - (iii-a) Removing fine particles with a size of less than 1 μm by classification, and/or
 - (iii-b) Removing coarse particles with a size of more than 100 μm by classification,wherein the sequence of step (iii-a) and step (iii-b) is exchangeable.
7. The process of claim 6, wherein step (iii-a) is performed after step (iii-b).
8. The process of claim 6 or 7, wherein step (iii-a) is performed by an air classifier.
9. The process of any one of claims 6-8, further comprising: recycling the fine particles removed from step (iii-a) to the compression-molding step (i), and/or recycling the coarse particles removed from step (iii-b) to the comminuting step (ii).
10. The process of any one of claims 5-9, further comprising the step of:
 - (iv) contacting the classified powder with an air stream at a temperature higher than the melting-initiation temperature of the thermoplastic polymer.
11. The process of any of the preceding claims, wherein the thermoplastic polymer is selected from a group consisting of: fluoropolymers, polyethylene, polyethylene terephthalate, polystyrene, acrylonitrile butadiene styrene (ABS), metacrylate polymer, polyamide, polycarbonate, polyacetal, polyphenylene

ether, polyphenylene sulphide, polyether ether ketone, polysulfone, polybutylene terephthalate, and polyvinylidene chloride.

12. The process of any of the preceding claims, wherein the thermoplastic polymer is a fluoropolymer.
13. The process of any of the preceding claims, wherein the thermoplastic polymer is a per(halo)fluoromonomers (PFM) selected from a group consisting of:
 - C₂-C₈ perfluoroolefins, such as tetrafluoroethylene (TFE) and hexafluoropropene (HFP);
 - chloro- and/or bromo- and/or iodo- C₂-C₆ per(halo)fluoroolefins, like chlorotrifluoroethylene;
 - per(halo)fluoroalkylvinylethers complying with general formula $\text{CF}_2=\text{CFOR}_{f1}$ in which R_{f1} is a C₁-C₆ per(halo)fluoroalkyl, such as -CF₃, -C₂F₅, -C₃F₇;
 - per(halo)fluoro-oxyalkylvinylethers complying with general formula $\text{CF}_2=\text{CFOX}_{01}$, in which X_{01} is a C₁-C₁₂ per(halo)fluorooxyalkyl having one or more ether groups, like perfluoro-2-propoxy-propyl group;
 - per(halo)fluoro-methoxy-alkylvinylethers complying with general formula $\text{CF}_2=\text{CFOCF}_2\text{OR}_{f2}$ in which R_{f2} is a C₁-C₆ per(halo)fluoroalkyl, such as -CF₃, -C₂F₅, -C₃F₇ or a C₁-C₆ per(halo)fluorooxyalkyl having one or more ether groups, such as -C₂F₅-O-CF₃;
 - per(halo)fluorodioxoles of formula :



wherein each of R_{f3} , R_{f4} , R_{f5} , R_{f6} , equal or different each other, is independently a fluorine atom, a C₁-C₆ perfluoroalkyl group, optionally comprising one or more oxygen atom, e.g. -CF₃, -C₂F₅, -C₃F₇, -OCF₃, -OCF₂CF₂OCF₃; preferably a per(halo)fluorodioxole complying with formula here above, wherein R_{f3} and R_{f4} are fluorine atoms and R_{f5} and R_{f6} are perfluoromethyl groups (-CF₃) [perfluoro-2,2-dimethyl-1,3-dioxole (PDD)], or a

per(halo)fluorodioxole complying with formula here above, wherein R_{f3} , R_{f5} and R_{f6} are fluorine atoms and R_{f4} is a perfluoromethoxy group (-OCF₃) [2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole or perfluoromethoxydioxole (MDO)].

14. A thermoplastic polymer powder obtained from a process of any of the preceding claims, having a particle size ranging between 1 to 100 μm .
15. The use of the thermoplastic polymer powder of claim 14 for powder coating.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/076637

A. CLASSIFICATION OF SUBJECT MATTER

INV. B29B9/08 B29B9/16 B07B7/08 B07B7/083 B07B7/10
C08J3/12

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)

B29B B07B C08J

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

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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

7 March 2014

Date of mailing of the international search report

20/03/2014

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/076637

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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