advantageous to recycle these powders so as to limit the energy and resource consumption. Processes for recycling polyamides contained in used compositions, notably derived from 3D printing waste, have been described.

Thus, CN110483986 describes a process for recycling residual polyamide 12 powder after selective laser sintering. This process involves dissolving the powder to be recycled in an acidic solution and then neutralizing and atomizing this solution to obtain a recycled polyamide powder. This process, which is specific to the treatment of 3D printing waste, thus involves treatment in an acidic medium, which is very aggressive toward the polyamide. It also does not allow the polyamide to be separated from the other products present in the composition, and does not allow the physicochemical features of the recycled polyamide powder to be controlled, notably its viscosity, particle size or thermal characteristics. Also, it requires specific equipment and the management of the acidic solution streams makes it particularly cumbersome to implement.

CN109810284 describes a process for dissolving polyamide 12 waste from 3D printing, by means of a composite solvent system comprising a mixture of hydrochloric, formic and acetic acid. A solid/liquid separation step is performed at elevated temperature before precipitating the polyamide by adding water as a non-solvent. However, this dissolution/precipitation process in an acidic medium is very aggressive toward the polyamide and does not allow control of the physicochemical features of the recycled powder either. Moreover, the management of the acidic solution streams also makes this process cumbersome to implement.

There is thus a real need for a process for recycling used polyamide compositions into a recycled polyamide powder, which is notably useful for technologies of powder agglomeration via electromagnetic radiation-mediated fusion, allowing these drawbacks to be overcome.

Summary

The inventors have now developed a dissolution/precipitation process which allows used polyamide compositions to be recycled and which also effectively increases the difference $T_{f1} - T_c$ of the recycled polyamides, by obtaining a monomodal melting endotherm.

More particularly, it was found that by introducing, at the end of the polyamide precipitation phase, a temperature steady stage of sufficient duration, it was possible to convert a precipitated polyamide powder characterized by a non-monomodal melting endotherm and more than one melting temperature (T_{f1}), (T_{f1}^{max}) being the highest melting temperature, into a polyamide powder characterized by a monomodal melting endotherm and a single melting temperature (Tf_1) equal to (T_{f1}^{max}), and thus to increase the temperature difference ($T_{f1} - T_c$). The inventors were notably able to demonstrate that this temperature steady stage allowed crystal refinement to take place, and thus a single crystal phase to be obtained.

The polyamide powders obtained are thus particularly advantageous for use in a process of powder agglomeration via electromagnetic radiation-mediated fusion, notably in that they allow the working window to be widened and thus the quality and/or definition of the objects manufactured from these powders to be improved.

According to yet other advantages, the recycling process according to the disclosure is easy to perform and does not require the use of acidic conditions. It also allows the particle size of the powder to be controlled, notably its span factor, and the polyamide to be separated, at least partially, from the other compounds present in the used composition, such as additives and fillers. The recycling process thus allows a recycled polyamide powder to be obtained with a high degree of purity, the thermal features of which are improved relative to those of the used polyamide.

In one aspect, the present disclosure refers to a process for recycling a used polyamide composition into a recycled polyamide powder having a monomodal melting endotherm and a single melting temperature (T_{f1}^{max}), said process comprising the steps of:

i. placing a used polyamide composition in contact with a solvent so as to obtain a mixture;

ii. heating the mixture so as to dissolve the polyamide in the solvent;

iii. cooling the mixture to the precipitation temperature (T_p) of the polyamide in said solvent, thereby obtaining a precipitated polyamide powder characterized by a non-monomodal melting endotherm and more than one melting temperature, (T_{f1}^{max}) being the highest melting temperature; and

iv. maintaining the temperature of the mixture at a temperature at most equal to T_p, notably in the range from T_p - 0.1°C to T_p -15°C, until the precipitated polyamide powder is characterized by a monomodal melting endotherm and a melting temperature (T_{f1}^{max}); and

v. recovery of the recycled polyamide powder obtained.

In another aspect, the disclosure refers to a polyamide powder with a monomodal melting endotherm and a single melting temperature (T_{f1}^{max}) which may be obtained via the recycling process as defined above.

In another aspect, the disclosure refers to a composition in powder form for 3D printing, notably by laser sintering, comprising:

- a polyamide powder as defined above; and
- at least one filler or additive.

In another aspect, the disclosure refers to a process for manufacturing polyamide objects by powder agglomeration via electromagnetic radiation-mediated fusion, the powder being as defined above.

In another aspect, the disclosure refers to a manufactured article obtained by electromagnetic radiation-mediated fusion of a powder as defined above or of a composition as defined above.

In another aspect, the disclosure refers to a mineral filler which may be obtained according to the recycling process as defined above.

Thus, according to a first example, the object of the disclosure is thus to provide a process for recycling a used polyamide composition into a recycled polyamide powder having a monomodal melting endotherm and a single melting temperature (T_{f1}^{max}), said process comprising the steps of:

i. placing a used polyamide composition in contact with a solvent so as to obtain a mixture;

ii. heating the mixture so as to dissolve the polyamide in the solvent;

iii. cooling the mixture to the precipitation temperature (T_p) of the polyamide in said solvent, thereby obtaining a precipitated polyamide powder characterized by a non-monomodal melting endotherm and more than one melting temperature, (T_{f1}^{max}) being the highest melting temperature; and

iv. maintaining the temperature of the mixture at a temperature at most equal to T_p, notably in the range from T_p - 0.1°C to T_p -15°C, until the precipitated polyamide powder is characterized by a monomodal melting endotherm and a melting temperature (T_{f1}^{max}); and

v. recovery of the recycled polyamide powder obtained.

Advantageously, the process also has one or more of the following features. Thus, in certain examples, the process according to the disclosure is a process:

- in which the solvent which is placed in contact with the polyamide is an alcohol, in particular a C_1-C_4 aliphatic alcohol, preferably ethanol;
- in which the heating of the mixture is performed at a temperature of from 100°C to 200°C, and preferably from 120°C to 160°C; and/or in which the heating of the mixture has a duration of from 1 to 6 hours, and preferably from 1 to 3 hours;
- in which the cooling of the mixture in step iii) is performed at a rate of from 1°C to 100°C per hour and preferably from 10°C to 60°C per hour;
- in which the polyamide is polyamide 11, polyamide 6, or polyamide 10.10, or polyamide 10.12, or polyamide 6.10;
- in which the precipitation temperature T_p of the polyamide is between 80°C and 130°C, notably between 100 and 120°C;
- in which, in step iv), the mixture is maintained at a temperature close to the precipitation temperature for a period of at least 2 hours, notably between 3 and 12 hours, with effect from the start of precipitation of the polyamide;
- also comprising a step vi) of drying the precipitated polyamide powder recovered in step v) or obtained on conclusion of step iv), notably at a temperature of between 10°C and 150°C, more particularly between 50 and 100°C;
- in which the drying of the precipitated polyamide powder is performed at a pressure ranging from 10 mbar to atmospheric pressure;
- in which the composition also comprises volatile organic compounds (VOCs);
- in which the composition comprises mineral fillers, notably fibers, in particular glass and/or carbon fibers; and/or
- also comprising a step vii) of separating and recovering the mineral fillers that may be present in the precipitated polyamide powder, notably after step iv), v) or vi).

According to a second example, an object of the present disclosure is also to provide a polyamide powder having a monomodal melting endotherm and a single melting temperature (T_{f1}^{max}) that can be obtained via the recycling process according to the disclosure.

Advantageously, the powder has one or more of the following features. Thus, in certain examples, the powder according to the disclosure is a polyamide powder:

- characterized in that it has a volume-mean diameter of between 10 and 200 µm, notably between 20 and 100 µm, and preferentially between 40 and 80 µm;
- characterized in that it has a diameter Dv10 of greater than 5 µm, notably between 10 and 70 µm, and preferentially between 20 and 60 µm;
- characterized in that it has a diameter Dv90 of less than 350 µm, notably between 30 and 200 µm, and preferentially between 50 and 150 µm;
- characterized in that it has a median diameter Dv50 of between 10 and 200 µm, notably between 20 and 100 µm, and preferentially between 30 and 90 µm;
- characterized in that it has a span factor of between 0.1 and 1.5; preferably between 0.1 and 1.0 and more preferentially between 0.5 and 1.0;
- in which the polyamide is polyamide 11;
- characterized in that it has a melting temperature (T_{f1}^{max}) of between 195 and 205°C; and/or
- in which the difference between the melting temperature (T_{f1}^{max}) and the crystallization temperature (T_c) is between 35 and 45°C.

According to a third example, the disclosure relates to a polyamide 11 powder having a monomodal melting endotherm and a single melting temperature (T_{f1}^{max}) of between 195°C and 205°C, also having at least one of the following features:

- a volume-mean diameter of between 10 and 200 µm, notably between 20 and 100 µm, and preferentially between 40 and 80 µm;
- a diameter Dv10 of greater than 5 µm, notably between 10 and 70 µm, and preferentially between 20 and 60 µm;
- a volume-median diameter Dv50 of between 10 and 200 µm, notably between 20 and 100 µm, and preferentially between 30 and 90 µm;
- a diameter Dv90 of less than 350 µm, notably between 30 and 200 µm, and preferentially between 50 and 150 µm;

- a span factor of between 0.1 and 1.5; preferably between 0.1 and 1 and more preferentially between 0.5 and 1.0;
- an enthalpy of fusion of greater than 100 J/g; and preferentially between 110 and 160 J/g; and/or
- an inherent viscosity of between 0.8 and 1.8, and preferentially between 1.0 and 1.5.

According to a fourth example, a subject of the disclosure is a composition in powder form for 3D printing, notably by laser sintering, comprising:

- a polyamide powder according to the disclosure; and
- at least one filler or additive.

According to a fifth example, the disclosure relates to a process for manufacturing polyamide objects by powder agglomeration via electromagnetic radiation-mediated fusion, the powder being as defined previously.

According to a sixth example, the disclosure relates to a manufactured article obtained by electromagnetic radiation-mediated fusion of a powder or a composition according to the disclosure.

According to a seventh example, a subject of the disclosure is the use of a process according to the disclosure for increasing the difference (T_{f1} -T_c) between the melting temperature (T_{f1}) and the crystallization temperature (T_c) of a polyamide.

According to an eighth example, the disclosure relates to recycled mineral fillers which may be obtained according to the recycling process according to the disclosure.

According to one example, the recycled mineral fillers are precoated with a polyamide powder having a monomodal melting endotherm and a single melting temperature, which may be obtained via the recycling process according to the disclosure.

Figures

[Fig. 1] represents an image obtained by scanning electron microscopy (SEM) (magnification x 120) of glass fibers, precoated with PA11, obtained on conclusion of the process according to inventive example 1.