less than 1.50. Mention may be made, as such, of processes for transformation by extrusion of pipes or sheets, by extrusion-blow molding of tubes, by injection molding, and also the abovementioned 3D printing processes.

There thus exists a continuous need to be able to reuse these compositions based on polyamides having a high inherent viscosity, in particular those already used in a manufacture but which have not been transformed into final products during the manufacturing process.

The object of the present invention is thus to provide a method for treating compositions based on polyamides having a high inherent viscosity, generally following a transformation process, so that they can be reused as starting materials in desired industrial applications.

More particularly, the aim of the present invention is to provide a method for treating a polyamide-based powder unused on conclusion of a 3D printing process, preferably a process of 3D printing by sintering, in order to be reused as starting material for industrial transformations, for example in an injection molding, extrusion or also 3D printing process.

Summary of the disclosure

According to a first aspect, a subject matter of the present disclosure is a process for the treatment of a composition (C1) based on polyamides (PA) which is intended to be recycled, comprising the following successive stages:

(i) a stage of supplying a mixture comprising the composition (C1) based on polyamides (PA), a polyamide chain-cutting agent, and optionally one or more filler(s) and/or additive(s);

(ii) a stage of kneading said mixture in the molten state, whereby a composition (C2) having a targeted inherent viscosity is obtained;

(iii) a stage of recovery of the composition (C2).

In the context of the present disclosure, the composition (C1) can be any type of industrial compositions based on polyamides, for example powders, granules, filaments, resins, fibers, films, pipes and/or their mixtures.

Within the meaning of the present disclosure, the term “a composition based on polyamides” is understood to mean a composition having a polyamide matrix,

which generally comprises more than 40% of polyamide by volume of the total composition.

According to a particularly advantageous example, the composition (C1) based on polyamides which is intended to be recycled is a powder based on polyamides, preferably that which has not been transformed on conclusion of a process of 3D printing by sintering.

When the composition (C1) is a powder based on polyamides, it generally comprises more than 50%, indeed even more than 60%, of polyamide by weight of the total composition.

The polyamide (PA) of the disclosure can be chosen from a homopolyamide, a copolyamide, a copolymer having polyamide blocks and polyether blocks, or their blends. It can also be a blend of one or more polyamides and at least one other polymer. The mixtures can be obtained by dry mixing of powders or by grinding the mixture in the form of granules. In the latter case, the polyamide preferably forms the matrix and the other polymer(s) form the dispersed phase.

Generally, the starting composition (C1) has an inherent viscosity of greater than or equal to 1.50, preferably of greater than or equal to 1.60.

Advantageously, the composition (C1) is a nontransformed material remaining on conclusion of a transformation process.

The "targeted" inherent viscosity of the composition (C2) is less than or equal to 1.50, preferably less than or equal to 1.40, 1.30, 1.25, 1.20, 1.15, 1.10, 1.05, or also less than or equal to 1.00.

The inherent viscosity of the composition (C2) is typically greater than or equal to 0.80.

For example, the inherent viscosity of the composition (C2) can be between 0.80 and 1.50, preferably between 0.90 and 1.40, between 0.90 and 1.30, between 0.90 and 1.20 (limits included).

The inherent viscosity of the recovered (or “recycled”) composition (C2) is typically reduced by at least 10%, preferably by at least 20%, with respect to that of the starting composition (C1).

According to one example, the inherent viscosity of the recovered composition (C2) is reduced by 0.30, preferably by 0.50, with respect to that of the starting composition (C1).

The recovered composition (C2) is typically in the form of granules.

The polyamide chain-cutting agent of the disclosure is a chemical agent which can react with the polyamides present in the composition which is intended to be recycled and which is capable of reducing the inherent viscosity of said composition.

The inventors have found that the use of the chain-cutting agent makes it possible to “cut” the chain of polyamides, thus making it possible to reduce the inherent viscosity of the polyamide, and also the inherent viscosity of the composition based on polyamides.

The present disclosure thus provides for the use of a specific chain-cutting agent to reduce the inherent viscosity of a composition based on polyamides in order to recover a composition which can be used in a subsequent transformation process.

According to one example, the chain-cutting agent is chosen from water, a carboxylic acid, an amino acid and/or their mixture.

According to one example, the chain-cutting agent is in the form of a solid (e.g., powder or granule) or in the form of a liquid (e.g., molten or in the form of an aqueous solution).

According to one example, the chain-cutting agent is a carboxylic acid. The carboxylic acid can be chosen from monocarboxylic acids, dicarboxylic acids or metal salts of mono- or dicarboxylic acids. Preferably, the carboxylic acid is chosen from adipic acid, azelaic acid, suberic acid, sebacic acid, dodecanedioic acid and/or their mixture.

According to a preferential example, the carboxylic acid is adipic acid.

According to one example, stage (i) is provided with from 0.1% to 2%, preferably from 0.2% to 1.8%, for example from 0.2% to 1.0%, from 0.2% to 0.8%, by weight of carboxylic acid, with respect to the weight of the composition (C1).

The carboxylic acid employed as chain-cutting agent is to be distinguished from those which may be present in the composition (C1) as residues of polymerization monomers, which are present in trace form, generally at less than 0.1%, in the composition.

According to one example, the chain-cutting agent is an amino acid. The amino acid can be chosen from aminocaproic acid, 7-aminoheptanoic acid, 11-aminoundecanoic acid, 12-aminododecanoic acid and/or their mixture.

This constitutes a particularly advantageous example. This is because, surprisingly, it has been observed that the use of an amino acid in the process of the disclosure makes it possible to rapidly reduce the inherent viscosity of the composition based on polyamides which is intended to be recycled (namely, generally in less than 10 minutes), thus making possible their reuse as starting material in transformation processes.

It has also been observed that this reduction in the inherent viscosity is reversible, that is to say that the inherent viscosity can increase again during its subsequent use. This property is particularly valuable for reapplication of the polyamides in 3D printing, a process which requires an increase in the inherent viscosity of the starting material during its implementation.

According to one example, an amino acid is chosen which corresponds to the monomer unit of the polyamide (PA) in the composition (C1) to be recycled. For example, an 11-aminoundecanoic acid can be chosen in the process for recycling a polyamide 11. Alternatively, for example, a 12-aminododecanoic acid can be chosen in a process for recycling a polyamide 12.

According to one example, the amino acid is an 11-aminoundecanoic acid.

According to one example, the amino acid is a 12-aminododecanoic acid.

According to one example, stage (i) is provided with from 0.1% to 10%, preferably from 0.2% to 8%, for example from 1% to 7%, by weight of amino acid, with respect to the weight of the composition (C1).

The amino acid employed as chain-cutting agent is to be distinguished from those which may be present in the composition (C1) as residues of polymerization monomers, which are present in trace form, generally at less than 0.1%, in the composition.

According to one example, the chain-cutting agent is water.

According to one example, stage (i) is provided with from 0.05% to 10%, preferably from 0.1% to 8%, for example from 0.5% to 7%, by weight of water, with respect to the weight of the composition (C1).

The inherent viscosity targeted for the composition recovered on conclusion of the transformation process can be easily achieved, in particular by adjusting the amount of the chain-cutting agent employed. Typically, if, during the process, the final inherent viscosity reached is too high, the amount of chain-cutting agent can be increased in increments of 10% (in relative value) without changing the amount of starting composition, until the targeted inherent viscosity is obtained. In the contrary case, if the final viscosity is too low, the amount of chain-cutting agent can be reduced in increments of 10% (in relative value) without changing the amount of starting composition, until the targeted inherent viscosity is obtained.

According to one example, one or more fillers and/or additives can be introduced in stage (i) of the process of the present disclosure. These fillers and/or additives make it possible to improve the properties of the polyamide according to its final use and/or to improve the mechanical properties (for example the Young's modulus, the elongation at break, the impact strength) or also the esthetic properties, such as the color.

According to one example, the fillers and/or the additives may already be present in the composition (C1) based on polyamides (PA) which is intended to be recycled, or also be added to the composition (C2) after the recovery stage (iii).

The conditions applied in the kneading stage (ii) are chosen in order to make possible intimate mixing of the compounds in the molten state.

According to one example, a temperature greater by at least 5°C, preferably greater by at least 10°C, with respect to the melting point of the polyamide (PA), is applied in the kneading stage (ii). This temperature should generally remain below 330°C, so as to avoid thermal degradation of the composition based on polyamides according to the disclosure.

In the context of the present disclosure, the composition (C1) can comprise one or more polyamides. When the composition (C1) comprises a polyamide, the temperature applied is greater by at least 5°C, preferably greater by at least 10°C, with respect to the melting point of the polyamide. When the composition (C1) comprises several polyamides, the temperature applied is greater by at

least 5°C, preferably greater by at least 10°C, with respect to the highest melting point of the polyamides.

According to one example, the temperature applied in stage (ii) is greater than 200°C and less than 330°C, preferably greater than 220°C and less than 320°C, for example of between 220°C and 310°C, or for example of between 230°C and 300°C.

The stage of the recovery (iii) can be carried out with methods known to a person skilled in the art.

Typically, the stage of the recovery consists of an extrusion stage, a stage of cooling the composition in the molten state using a water-containing cooling liquid, a stage of cutting the composition in the form of granules, and a stage of separation of the cooling liquid and the cooled composition.

The cutting stage can be carried out during the cooling stage, or after the cooling stage, and before the separation stage or after the separation stage.

The process of the disclosure can be a batch process.

The process of the disclosure can preferably be a continuous process.

In order to recover a composition having an inherent viscosity of less than 1.50, for example of less than 1.40, the residence time of the mixture in stage (ii) is typically equal to or less than 10 minutes, in particular less than 5 minutes, or less than 3 minutes, indeed even less.

The process of the present disclosure thus makes it possible to carry out a recycling of a composition based on polyamides in a simple and very effective manner: the composition intended to be recycled is treated in less than 10 minutes, indeed even in less than 5 minutes, or 3 minutes, indeed even less, so that a composition based on polyamides which can be reused as starting material can be recovered.

The present disclosure thus provides a simple and effective solution for recycling a composition based on polyamides, in particular such a composition in the powder form, such as that which has not been transformed on conclusion of a 3D printing process using a powder (e.g. process of 3D printing by sintering).

According to another example, a subject matter of the present disclosure is an installation for the implementation of the process of the disclosure. According to

one example, the process of the disclosure is carried out by means of a “reactive” extruder (with external heating) known to a person skilled in the art. Preferably, the process is carried out in an extruder comprising two conveying screws rotating in a corotating manner.

In another aspect, a subject matter of the present disclosure is a recycled composition based on polyamides, which is capable of being obtained by the process as defined above, having an inherent viscosity of less than or equal to 1.50, preferably of less than or equal to 1.40, 1.30, 1.25, 1.20, 1.15, 1.10, 1.05, or also less than or equal to 1.00.

The recycled composition on conclusion of the transformation process can be in the form of granules, in the form of a powder, filament, resin, fiber, films or pipe, preferably in the form of granules.

One of the advantages of the present disclosure is that the recycled composition on conclusion of the process according to the disclosure can be usable directly and/or can be easily transformed with the technologies known to a person skilled in the art.

In another aspect, the disclosure relates to the use of the recycled composition as defined above, preferably in the form of granules, in a transformation process.

According to another example, the disclosure relates to a process of transformation by employing a recycled composition based on polyamides, preferably in the form of granules, as starting material.

The disclosure also relates to an article manufactured according to a process of transformation by employing a recycled composition based on polyamides as is defined above.

In another aspect, the disclosure relates to a manufactured article obtained by the transformation process as defined above.

By way of example, the composition recovered on conclusion of the process according to the disclosure can be used in coatings, paints, corrosion-resistant compositions, additives for paper, electrophoresis gels, multilayer composite materials, the packaging industry, toys, the textile industry, the automotive industry and/or the electronics industry.

The present disclosure also relates to the use of the recycled composition based on polyamides which is obtained according to the process of the disclosure in a 3D printing process, preferably a process of 3D printing by sintering.

According to one example, the 3D printing process is a process using a powder.

Alternatively, the 3D printing process can be other types of 3D printing process other than those using a powder. For example, mention may be made of techniques such as FDM (Fused Deposition Modeling), or else FFF (Fused Filament Fabrication), using filaments.

The present disclosure also relates to a manufactured article obtained by the 3D printing processes as mentioned above.

This manufactured item can be chosen from prototypes, models and parts, in particular in the automotive, nautical, aeronautical, aerospace or medical (prostheses, hearing systems, cell tissues, and the like) fields, design, housings for electronics, telephony, home automation, computing, lighting, sports or industrial appliances.

The disclosure will now be described in more detail.

Detailed description

DEFINITION

"Inherent Viscosity"

The inherent viscosity in solution of the composition based on polyamides is preferably measured according to the standard ISO 307:2007 modified in that the solvent is m-cresol rather than sulfuric acid, in that the concentration is 0.5% by weight and in that the temperature is 20°C.

POLYAMIDES

The nomenclature used to define polyamides is described in the standard ISO 1874-1:1992 “Plastics - Polyamide (PA) moulding and extrusion materials - Part 1: Designation”, in particular on page 3 (tables 1 and 2), and is well known to a person skilled in the art.

The composition (C1) based on polyamides which is intended to be recycled of the present invention can be provided in all its forms in any industrial application, such as powder, granules, filament, resin, fiber, films or pipe.

The composition (C1) preferably has an inherent viscosity of greater than or equal to 1.50, preferably of greater than or equal to 1.60.