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(54) Title: PROCESS FOR PREPARING A POLYMERIC PRODUCT

(57) Abstract: The invention relates to a process for preparing a polymeric product from a polymeric starting material comprising at least one polymer, the process comprising the step of: a) subjecting the polymeric starting material to a temperature of at least 100°C, and to a pressure of at least 3000 bar; and b) subsequently reducing the temperature applied in step (a) while maintaining a pressure of at least 3000 bar; thereby obtaining a polymeric product.



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Process for preparing a polymeric product

Field of the invention

The present invention relates to a process for preparing a polymeric product. The present invention also relates to polymeric products and polymeric articles with a high thermal conductivity.

Background of the invention

Numerous applications require the transfer of heat across or through a thickness of solid material. Advances in the electronics industry have created a need for improved heat conducting materials. As electronic components, especially computers and similar devices, which rely on microprocessors, operate at faster and faster speeds and become smaller and smaller, the problem of managing the heat generated by such devices becomes critical. For instance, heat build-up in electronic products leads to reduced reliability ("mean-time-to-failure"), slower performance, and reduced power-handling capabilities. In addition, continued interest in increasing the number of electronic components on, and reducing the size of, semiconductor chips, notwithstanding the desire generally to reduce power consumption thereof, also contributes to the importance of thermal management. Also, chip-on-board technology, where semiconductor chips are mounted directly to printed circuit boards, creates further demands on thermal management because of the more efficient use of surface area thereon.

Electrically insulating polymeric products are often used for this purpose, their main downside being the fact that most polymers are thermal insulators as well.

Several methods exist to increase thermal conductivity of polymers. The polymer may be blended with appropriate additives to form a polymer compound. Ceramic fillers, such as boron nitride, aluminum nitride and aluminum oxide are examples of additives that enhance thermal conductivity while retaining, or only minimally modifying, the electrical insulation properties of the polymer.

Alternatively, polymer fibers may be stretched to obtain thermally conducting fibers. For example, Dyneema fibres from DSM, produced starting from a solution of UHMWPE have a thermal conductivity of the order of 20 W/m.K. Poulaert et al. (B. Poulaert, J.C. Chielens, C. Vandenhende, J.P. Issi, R. Legras, Polym. Commun. 31, 148, 1990) report the thermal conductivity of highly oriented polyethylene fibers. However, above-reported high thermal conductivities are associated with drawn or ultradrawn polyethylene fibers, and not with robust industrially produced polymeric articles.

There remains a need for improved polymeric articles with low electric conductivity and increased thermal conductivity.

Summary of the invention

It is therefore an object of the present invention to provide a polymeric product or article with improved thermal conduction properties. It is also an object of the present invention to provide a process for preparing a polymeric product or article with improved thermal conduction properties.

The inventors have surprisingly found these objects can be met either individually or in any combination by heating and compressing a polymeric starting material.

According to a first aspect, the invention provides a process for preparing a polymeric product from a polymeric starting material comprising at least one polymer, the process comprising the steps of:

subjecting the polymeric starting material to a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and to a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and

reducing the temperature while maintaining a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar;

thereby obtaining a polymeric product, wherein the thermal conductivity of the polymeric product is greater than the thermal conductivity of the polymeric starting material.

The present invention also encompasses a process for preparing a polymeric product from a polymeric starting material comprising at least one polymer, the process comprising the steps of:

a) subjecting the polymeric starting material to a temperature of at least 100°C, and to a pressure of at least 3000 bar; and

b) subsequently reducing the temperature applied in step (a) while maintaining a pressure of at least 3000 bar; thereby obtaining a polymeric product.

Preferably, said polymeric starting material has a thermal conductivity T_{c1} , and the polymeric product has a thermal conductivity T_{c2} , wherein $T_{c2} > T_{c1}$.

According to a second aspect, the invention provides a polymeric product obtained by the process according to the first aspect of the invention.

According to a third aspect, the invention provides an article comprising the polymeric product according to the second aspect of the invention.

- 5 According to a fourth aspect, the invention provides a polyolefin or polyolefin-based article, preferably comprising polyethylene, wherein the article has a thermal conductivity of at least 0.4 W/m.K, and wherein the smallest dimension of the article is at least 0.4 mm, preferably at least 0.5 mm, preferably at least 1.0 mm, preferably at least 2.0 mm.

10 The independent and dependent claims set out particular and preferred features of the invention. Features from the dependent claims may be combined with features of the independent or other dependent claims as appropriate.

In the following passages, different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or
15 advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

Brief description of the figures

Figure 1 represents a schematic representation of the thermal potentiometer used to measure the thermal conductivity of the samples.

20 Detailed description of the invention

Before the present aspects of the invention are described, it is to be understood that this invention is not limited to particular materials, products, articles or processes described, since such may, of course, vary. It is also to be understood that the terminology used herein is not intended to be limiting, since the scope of the present invention will be limited
25 only by the appended claims.

As used herein, the singular forms "a", "an", and "the" include both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a polyolefin" means one polyolefin or more than one polyolefin.

30 The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. It will be appreciated that the terms "comprising", "comprises" and "comprised of" as used herein comprise the terms "consisting of", "consists" and "consists of".

The recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of end points also includes the end point values themselves (e.g. from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

All references cited in the present specification are hereby incorporated by reference in their entirety. In particular, the teachings of all references herein specifically referred to are incorporated by reference.

According to the first aspect, the invention provides a process for preparing a polymeric product from a polymeric or polymeric-based starting material comprising at least one polymer, the process comprising the steps of:

a) subjecting the polymeric starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and

b) reducing the temperature while maintaining a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining the polymeric product. Preferably, the thermal conductivity of the polymeric product is higher than the thermal conductivity of the polymeric starting material.

Preferably, the process comprises the steps of:

a) subjecting the polymeric starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and

b) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably

at least 5000 bar, more preferably at least 8000 bar; thereby obtaining the polymeric product.

The temperature reduction in step (b) is preferably such that crystallization is induced in the polymeric material. In an embodiment the temperature can be reduced down to room temperature. In step b), the pressure is maintained on the polymeric starting material, thereby differentiating the above process from a typical injection moulding step. In an injection molding step, an "injection pressure" is used on a screw-like plunger to force material into a mould. However, once the material is in the mould, it does not undergo such a high pressure anymore.

- 10 The thermal conductivity of the polymeric starting material may be equal to the value reported e.g. in handbooks for said starting material. Preferably, the thermal conductivity of the polymeric product obtained by the present process is greater than the thermal conductivity reported in the handbooks for the polymeric starting material.

15 In a preferred embodiment of the invention, the process comprises a processing step prior to the heating step (a). In an embodiment, this processing step comprises the step of removing air from the polymeric starting material, for example removing the air from between polymer pellets or fluff. This step may be performed by various processes, including but not limited to vacuum imposition, compaction under high pressure, direct extrusion or injection of the melted polymeric starting material inside a mould. Any other step reducing the amount of air and/or air bubbles in the polymeric starting material may be suitable for this additional processing step. In a preferred embodiment, the process comprises the prior step of compacting the polymeric starting material under high pressure, for example at a pressure of at least 100 bars, and for example at a pressure of 100 to 1000 bars, for example at a pressure of 100 to 500 bars. This compaction step can be performed at a temperature below the melting temperature of the starting material, such as room temperature. In an embodiment said compaction is performed at a temperature of at least 20°C, for example at least 50°C, for example at least 100°C. Compaction time could be long but it is not required and short compaction times are preferred.

- 20
25
30 In some embodiment, step (a) comprises subjecting the polymeric starting material to a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and to a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least

4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; for at least 1 second, preferably for at least 5 seconds.

In some embodiments, the polymeric starting material is, prior, concomitant with the heating step (a) or subsequently, subjected to a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar.

In some embodiments, the polymeric starting material is subjected to a pressure of at least 1000 bar, preferably at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar, for at least 1 second, preferably for at least 5 seconds.

Step (b) of the process comprises a temperature reduction step at high pressure. During this step, crystallization of the polymeric starting material occurs. Preferably, the imposed pressure from the heating step (a) is maintained. All cooling rates can be considered but cooling rates inducing an industrially reasonable cycle time are preferred. In an embodiment, said cooling rate is for at most 10 minutes, preferably at most 5 minutes, preferably at most 1 minute, preferably at most 30 seconds, preferably at most 10 seconds, preferably at most 5 seconds, for all steps.

Optionally, an additional sample irradiation (e.g. by gamma-ray, irradiating between 1 and 200 kG, but typically 75 kG) can be imposed on the polymeric starting material. A non-limiting example of suitable irradiation includes gamma-ray irradiation, for example at 1 to 200 kG, for example at 75 kG. When applied, this irradiation step is preferably performed after crystallization at high pressure. The irradiation may thus increase the density of the molecules in the sample amorphous phase, potentially facilitating the phonon transfer between lamellae.

According to the invention, the polymeric starting material comprises at least one polymer. In some embodiments, the polymeric starting material comprises a blend of at least two polymers, or a blend of one or more polymers, optionally with additional charge. In some embodiments, the polymeric starting material comprises at least 80.0% by weight of the at least one polymer, preferably at least 90.0% by weight, preferably at least 95.0% by weight, preferably at least 98.0% by weight, preferably at least 99.0% by weight, preferably at least 99.5% by weight, preferably at least 99.8% by weight, preferably at least 99.9% by weight, with % by weight based on the total weight of the polymeric starting material. In some embodiments, the polymeric product comprises at least 80.0% by weight of the at least one polymer, preferably at least 90.0% by weight, preferably at

least 95.0% by weight, preferably at least 98.0% by weight, preferably at least 99.0% by weight, preferably at least 99.5% by weight, preferably at least 99.8% by weight, preferably at least 99.9% by weight, with % by weight based on the total weight of the polymeric product.

- 5 In a preferred embodiment, the at least one polymer is selected from the group comprising polyolefins, polystyrene, polylactic acid, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate, polyamides, poly(methyl methacrylate), polymethacrylate, polycarbonates, polyurethanes, and blends or mixtures thereof.

As used herein, the terms "olefin polymer" and "polyolefin" are used interchangeably.

- 10 Preferably, the at least one polymer is a polyolefin.

Preferably, the process comprises the steps of:

- a) subjecting a polyolefin starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for
15 example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and

- b) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining the polyolefin
20 product.

- In some embodiments, the polymeric starting material comprises at least 80.0% by weight of polyolefin, preferably at least 90.0% by weight, preferably at least 95.0% by weight, preferably at least 98.0% by weight, preferably at least 99.0% by weight, preferably at least 99.5% by weight, preferably at least 99.8% by weight, preferably at least 99.9% by
25 weight, with % by weight based on the total weight of the polymeric starting material. In some embodiments, the polymeric product comprises at least 80.0% by weight of polyolefin, preferably at least 90.0% by weight, preferably at least 95.0% by weight, preferably at least 98.0% by weight, preferably at least 99.0% by weight, preferably at least 99.5% by weight, preferably at least 99.8% by weight, preferably at least 99.9% by
30 weight, with % by weight based on the total weight of the polymeric product

The polyolefins suitable for use in the present invention may be any olefin homopolymer or any copolymer of an olefin and one or more comonomers. The polyolefins may be atactic, syndiotactic or isotactic. The olefin can for example be ethylene, propylene, 1-

butene, 1-pentene, 1-hexene, 4-methyl-1-pentene or 1-octene, but also cycloolefins such as for example cyclopentene, cyclohexene, cyclooctene or norbornene. The comonomer is different from the olefin and chosen such that it is suited for copolymerization with the olefin. The comonomer may also be an olefin as defined above. Further examples of suitable comonomers are vinyl acetate ($\text{H}_3\text{C}-\text{C}(=\text{O})\text{O}-\text{CH}=\text{CH}_2$) or vinyl alcohol ("HO-CH=CH₂", which as such is not stable and tends to polymerize). Examples of olefin copolymers suited for use in the present invention are random copolymers of propylene and ethylene, random copolymers of propylene and 1-butene, heterophasic copolymers of propylene and ethylene, ethylene-butene copolymers, ethylene-hexene copolymers, ethylene-octene copolymers, copolymers of ethylene and vinyl acetate (EVA), copolymers of ethylene and vinyl alcohol (EVOH).

Most preferred polyolefins for use in the present invention are olefin homopolymers and copolymers of an olefin and one or more comonomers, wherein said olefin and said one or more comonomer is different, and wherein said olefin is ethylene or propylene. The term "comonomer" refers to olefin comonomers which are suitable for being polymerized with olefin monomers, preferably ethylene or propylene monomers. Comonomers may comprise but are not limited to aliphatic C₂-C₂₀ alpha-olefins. Examples of suitable aliphatic C₂-C₂₀ alpha-olefins include ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. In an embodiment, the comonomer is vinyl acetate.

As used herein, the term "co-polymer" refers to a polymer, which is made by linking two different types of monomers in the same polymer chain. As used herein, the term "homopolymer" refers to a polymer which is made by linking olefin (preferably ethylene) monomers, in the absence of comonomers. The amount of comonomer can be from 0 to 12% by weight, based on the weight of the polyolefin, more preferably it can be from 0 to 9% by weight and most preferably it can be from 0 to 7% by weight. A copolymer can be a random or block (heterophasic) copolymer. Preferably, the copolymer is a random copolymer. Such olefin homopolymer and copolymers of an olefin and one or more comonomers are non-polar polymers. Preferred polyolefins for use in the present invention are propylene and ethylene polymers. Preferably, the polyolefin is selected from polyethylene and polypropylene homo- and copolymers. Preferably, the polyolefin is polyethylene or polypropylene, or a copolymer thereof. In an embodiment, the polyolefin is polypropylene. Preferably, the polyolefin is polyethylene. Even more preferably, the polyolefin is a homopolyethylene or a polyethylene copolymer with a low comonomer

content (preferably less than 1.0% by weight, more preferably less than 0.5% by weight, with % by weight based on the total weight of the polyolefin).

Preferably, the at least one polymer is polyethylene homo or copolymer.

Preferably, the process comprises the steps of:

- 5 a) subjecting a polyethylene starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and
- 10 b) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining a polyethylene product.

Preferably, the at least one polymer is a polyethylene with a weight average molecular weight M_w of at least 30 000 Da, for example of at least 50 000 Da, preferably of at least 100 000 Da, preferably of at least 200 000 Da.

In an embodiment, the at least one polymer is Ultra High Molecular Weight Polyethylene.

Suitable Ultra High Molecular Weight Polyethylene comprises polyethylene having a weight average molecular weight M_w in the range of from 500 000 Da to 12 000 000 Da.

- 20 The polyolefin, such as polyethylene, can be prepared in the presence of any catalyst known in the art. As used herein, the term "catalyst" refers to a substance that causes a change in the rate of a polymerization reaction. In the present invention, it is especially applicable to catalysts suitable for the polymerization of ethylene to polyethylene. These catalysts will be referred to as ethylene polymerization catalysts or polymerization
- 25 catalysts. In some embodiments, the at least one polyolefin is prepared by a catalyst selected from the group comprising metallocene catalysts, chromium catalysts, and Ziegler-Natta catalysts.

The term "Ziegler-Natta catalyst" or "ZN catalyst" refers to catalysts having a general formula M^1X_v , wherein M^1 is a transition metal compound selected from group IV to VII from the periodic table of elements, wherein X is a halogen, and wherein v is the valence of the metal. Preferably, M^1 is a group IV, group V or group VI metal, more preferably titanium, chromium or vanadium and most preferably titanium. Preferably, X is chlorine or bromine, and most preferably, chlorine. Illustrative examples of the transition metal

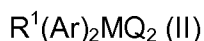
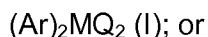
compounds comprise but are not limited to TiCl_3 and TiCl_4 . Suitable ZN catalysts for use in the invention are described in US6930071 and US6864207, which are incorporated herein by reference.

In some embodiments, the polyolefin is a polyolefin produced in the presence of small Ziegler-Natta catalyst particles. The polyolefin can be produced in the presence of a Ziegler-Natta catalyst with an average particle size (D50) of at most 15 μm , preferably at most 13 μm , preferably at most 10 μm , preferably at most 8 μm , for example at most 5 μm and preferably at least 3 μm . The D50 is defined as the particle size for which fifty percent by volume of the particles has a size lower than the D50. The D50 can be measured by laser diffraction analysis on a Malvern type analyzer after having put the catalyst in suspension in cyclohexane. Suitable Malvern systems include the Malvern 2000, Malvern 2600 and Malvern 3600 series. The Malvern MasterSizer may also be useful as it can more accurately measure the D50 towards the lower end of the range e.g. for average particle sizes of less 8 μm , by applying the theory of Mie, using appropriate optical means.

The term "metallocene catalyst" is used herein to describe any transition metal complexes consisting of metal atoms bonded to one or more ligands. The metallocene catalysts are compounds of Group 4 transition metals of the Periodic Table such as titanium, zirconium, hafnium, etc., and have a coordinated structure with a metal compound and ligands composed of one or two groups of cyclo-pentadienyl, indenyl, fluorenyl or their derivatives.

The structure and geometry of the metallocene can be varied to adapt to the specific need of the producer depending on the desired polymer. Metallocenes comprise a single metal site, which allows for more control of branching and molecular weight distribution of the polymer. Monomers are inserted between the metal and the growing chain of polymer.

In an embodiment, the metallocene catalyst has a general formula (I) or (II):



wherein the metallocenes according to formula (I) are non-bridged metallocenes and the metallocenes according to formula (II) are bridged metallocenes;

wherein said metallocene according to formula (I) or (II) has two Ar bound to M which can be the same or different from each other;

wherein Ar is an aromatic ring, group or moiety and wherein each Ar is independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, wherein each of said groups may be optionally substituted with one or more

substituents each independently selected from the group consisting of halogens, a hydrosilyl, a SiR^2_3 group wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms, wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl and P;

- 5 wherein M is a transition metal selected from the group consisting of titanium, zirconium, hafnium and vanadium; and preferably is zirconium;

wherein each Q is independently selected from the group consisting of halogens; a hydrocarboxy having 1 to 20 carbon atoms; and a hydrocarbyl having 1 to 20 carbon atoms, wherein said hydrocarbyl optionally contains one or more atoms selected from the
10 group comprising B, Si, S, O, F, Cl and P; and

wherein R^1 is a divalent group or moiety bridging the two Ar groups and selected from the group consisting of a $\text{C}_1\text{-C}_{20}$ alkylene, a germanium, a silicon, a siloxane, an alkylphosphine and an amine, and wherein said R^1 is optionally substituted with one or more substituents each independently selected from the group consisting of halogens, a
15 hydrosilyl, a SiR^3_3 group wherein R^3 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms, wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl and P.

The term "hydrocarbyl having 1 to 20 carbon atoms" as used herein is intended to refer to a moiety selected from the group comprising a linear or branched $\text{C}_1\text{-C}_{20}$ alkyl; $\text{C}_3\text{-C}_{20}$
20 cycloalkyl; $\text{C}_6\text{-C}_{20}$ aryl; $\text{C}_7\text{-C}_{20}$ alkylaryl and $\text{C}_7\text{-C}_{20}$ arylalkyl, or any combinations thereof. Exemplary hydrocarbyl groups are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, and phenyl. Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, fluorine and chlorine are preferred.

25 The term "hydrocarboxy having 1 to 20 carbon atoms" refers to a radical having the formula $-\text{O-R}_a$ wherein R_a is hydrocarbyl having 1 to 20 carbon atoms. Preferred hydrocarboxy groups are alkoxy groups. The term "alkoxy" or "alkyloxy" as used herein refers to a radical having the formula $-\text{O-R}_b$ wherein R_b is alkyl. Non-limiting examples of
30 suitable alkoxy groups include methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy, tert-butoxy, pentyloxy, amyloxy, hexyloxy, heptyloxy and octyloxy. Preferred hydrocarboxy groups are methoxy, ethoxy, propoxy, butoxy, and amyloxy.

As used herein, the term "alkyl" by itself or as part of another substituent, refers to a straight or branched saturated hydrocarbon radical group joined by single carbon-carbon bonds having 1 or more carbon atoms, for example 1 to 20 carbon atoms, for example 1

to 12 carbon atoms, for example 1 to 6 carbon atoms, for example 1 to 4 carbon atoms, for example 2 to 3 carbon atoms. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Thus, for example, C₁₋₁₂alkyl means an alkyl of 1 to 12 carbon atoms. Examples
5 of C₁₋₁₂alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *tert*-butyl, pentyl and its chain isomers, hexyl and its chain isomers, heptyl and its chain isomers, octyl and its chain isomers, nonyl and its chain isomers, decyl and its chain isomers, undecyl and its chain isomers, dodecyl and its chain isomers.

As used herein, the term "C₃₋₂₀cycloalkyl", by itself or as part of another substituent, refers
10 to a saturated or partially saturated cyclic alkyl radical containing from 3 to 20 carbon atoms. Examples of C₃₋₂₀cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

As used herein, the term "C₆₋₂₀aryl", by itself or as part of another substituent, refers to a
15 polyunsaturated, aromatic hydrocarbonyl group having a single ring (i.e. phenyl) or multiple aromatic rings fused together (e.g. naphthalene), or linked covalently, typically containing 6 to 20 carbon atoms; wherein at least one ring is aromatic. Examples of C₆₋₂₀aryl include phenyl, naphthyl, indanyl, biphenyl, or 1,2,3,4-tetrahydro-naphthyl.

The term "arylalkyl", as a group or part of a group, refers to an alkyl as defined herein,
wherein one or more hydrogen atoms are replaced by an aryl as defined herein.
20 Examples of arylalkyl radicals include benzyl, phenethyl, dibenzylmethyl, methylphenylmethyl, 3-(2-naphthyl)-butyl, and the like.

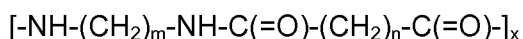
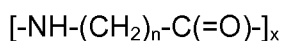
As used herein, the term "alkylaryl", by itself or as part of another substituent, refers to an
aryl group as defined herein, wherein one or more hydrogen atoms are replaced by an
alkyl as defined herein.

25 Illustrative examples of metallocene catalysts comprise but are not limited to bis(cyclopentadienyl) zirconium dichloride (Cp₂ZrCl₂), bis(cyclopentadienyl) titanium dichloride (Cp₂TiCl₂), bis(cyclopentadienyl) hafnium dichloride (Cp₂HfCl₂); bis(tetrahydroindenyl) zirconium dichloride, bis(indenyl) zirconium dichloride, and bis(*n*-butyl-cyclopentadienyl) zirconium dichloride, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)
30 zirconium dichloride, ethylenebis(1-indenyl) zirconium dichloride, dimethylsilylene bis(2-methyl-4-phenyl-inden-1-yl) zirconium dichloride, diphenylmethylenecyclopentadienyl)(fluoren-9-yl) zirconium dichloride, and dimethylmethylenecyclopentadienyl)[1-(4-*tert*-butyl-2-methyl-cyclopentadienyl)](fluoren-9-yl) zirconium dichloride.

The metallocene catalysts can be provided on a solid support. The support can be an inert solid, organic or inorganic, which is chemically unreactive with any of the components of the conventional metallocene catalyst. Suitable support materials for the supported catalyst of the present invention include solid inorganic oxides, such as silica, alumina, magnesium oxide, titanium oxide, thorium oxide, as well as mixed oxides of silica and one or more Group 2 or 13 metal oxides, such as silica-magnesia and silica-alumina mixed oxides. Silica, alumina, and mixed oxides of silica and one or more Group 2 or 13 metal oxides are preferred support materials. Preferred examples of such mixed oxides are the silica-aluminas. Most preferred is silica. The silica may be in granular, agglomerated, fumed or other form. The support is preferably a silica compound. In a preferred embodiment, the metallocene catalyst is provided on a solid support, preferably a silica support. In an embodiment, the catalyst used for preparing the polyolefin is a supported metallocene-alumoxane catalyst comprising a metallocene and an alumoxane which are bound on a porous silica support.

The term "chromium catalysts" refers to catalysts obtained by deposition of chromium oxide on a support, e.g. a silica or aluminum support. Illustrative examples of chromium catalysts comprise but are not limited to CrSiO_2 or CrAl_2O_3 .

In an embodiment, the at least one polymer is a polyamide. Polyamides are characterized in that the polymer chain comprises amide groups ($-\text{NH}-\text{C}(=\text{O})-$). Polyamides useful in the present invention are preferably characterized by one of the following two chemical structures



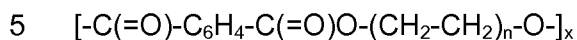
wherein m and n may be independently chosen from one another and be an integer from 1 to 20.

Specific examples of suitable polyamides are polyamides 4, 6, 7, 8, 9, 10, 11, 12, 46, 66, 610, 612 and 613.

In an embodiment, the polymer is a polystyrene. The polystyrenes used in the present invention may be any styrene homopolymer or copolymer. They may be atactic, syndiotactic or isotactic. Styrene copolymers comprise one or more suitable comonomers, i.e. polymerizable compounds different from styrene. Examples of suitable comonomers are butadiene, acrylonitrile, acrylic acid or methacrylic acid. Examples of styrene copolymers that may be used in the present invention are butadiene-styrene copolymers,

which are also referred to as high-impact polystyrene (HIPS), acrylonitrile-butadiene-styrene copolymers (ABS) or styrene-acrylonitrile copolymers (SAN).

In an embodiment, the polymer is a polyester. Polyesters that may be used in the present invention are preferably characterized by the following chemical structure



wherein n is an integer from 1 to 10, with preferred values being 1 or 2.

Specific examples of suitable polyesters are polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

Furthermore, preferred polyesters are poly(hydroxy carboxylic acid)s. From a standpoint
10 of availability and transparency, the poly(hydroxy carboxylic acid) is preferably a polylactic acid (PLA). Preferably the polylactic acid is a homopolymer obtained either directly from lactic acid or from lactide, preferably from lactide.

In an embodiment, the at least one polymer is a polycarbonate. Polycarbonates are polymers comprising carbonate groups $(-O-(C=O)-O-)$.

15 In an embodiment, the at least one polymer is a polyurethane. Polyurethanes are copolymers of an isocyanate, preferably a di-isocyanate, and an alcohol, preferably a polyol. Polyurethanes comprise carbamate links.

In a preferred embodiment, the at least one polymer has a weight average molecular weight M_w of at least 30 000 Da, preferably at least 50 000 Da, preferably at least 100 000
20 Da, preferably at least 200 000 Da. Molecular weights can be determined by Size Exclusion Chromatography (SEC), or from intrinsic viscosity measurements.

In some embodiments, the polyolefin has a weight average molecular weight M_w of at least 30 000 Da, for example at least 50 000 Da, preferably at least 100 000 Da, preferably at least 200 000 Da

25 In some embodiments, the polyethylene has a weight average molecular weight M_w of at least 30 000 Da, for example at least 50 000 Da, preferably at least 100 000 Da, preferably at least 200 000 Da

In some embodiments, the at least one polymer has monomodal or multimodal, for example bimodal molecular weight distribution. As used herein, the term "monomodal
30 polymers" refers to polymers having one maximum in their molecular weight distribution curve, which is also defined as a unimodal distribution curve. As used herein, the term "polymers with a bimodal molecular weight distribution" or "bimodal polymers" it is meant,

polymers having a distribution curve being the sum of two unimodal molecular weight distribution curves. By the term “polymers with a multimodal molecular weight distribution” or “multimodal polymers” it is meant polymers with a distribution curve being the sum of at least two, preferably more than two unimodal distribution curves.

- 5 In an embodiment, the at least one polymer is polyethylene, and the polymeric starting material has a density of from 0.900 to 0.970 g/cm³, preferably from 0.940 to 0.970 g/cm³, as determined with the ASTM D 1895 standard.

In some embodiments, the polymeric starting material can be in the form of fluff or pellets.

- 10 As used herein, the term “fluff” refers to the polymer material that is prepared in a loop reactor with the hard catalyst particle at the core of each grain of the powder. As used herein the term “resin” encompasses both the fluff prepared in the loop reactor as well as the subsequently melted and/or pelletized polymer.

- As used herein, the term “pellet” is defined as polymer material that is prepared through compounding and homogenizing of the resin, for instance with mixing and/or extruder equipment. Preferably, the polymer particles have an average diameter (D50) of at most 2mm, more preferably at most 1mm, more preferably at most 100µm. The D50 is defined as the particle size for which fifty percent by volume of the particles has a size lower than the D50. The average size of the particles is preferably assessed by particle sieving. Alternatively, the size may be measured by using optical measurements, preferably with a Camsizer.
- 15
20

Preferably, the process comprises the steps of:

- a) providing a polyolefin starting material having a thermal conductivity T_{c1}
- b) subjecting said polyolefin starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and
- 25
- c) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining a polyolefin product, having a thermal conductivity T_{c2} , wherein $T_{c2} > T_{c1}$.
- 30

According to the invention, the thermal conductivity of the polymeric product is greater than the thermal conductivity of the polymeric starting material. In a preferred

embodiment, the polymeric product has a thermal conductivity of at least 0.4 W/m.K. The thermal conductivity is determined using the method described in B. Poulaert, et al., Polym. Commun. 31, 148 (1990)

5 In some embodiments, the polymeric product has a thermal conductivity of at least 0.5 W/m.K, preferably at least 0.6 W/m.K, preferably at least 0.8 W/m.K, preferably at least 1.0 W/m.K, preferably at least 1.2 W/m.K, preferably at least 1.4 W/m.K, preferably at least 1.6 W/m.K, preferably at least 1.8 W/m.K, preferably at least 2.0 W/m.K.

10 In some embodiments, the ratio of the thermal conductivity of the polymeric product to the thermal conductivity of the starting material is at least 2, preferably at least 5, preferably at least 10.

Preferably, the process comprises the steps of:

- a) providing a polyolefin starting material,
- b) subjecting said polyolefin starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and
- c) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining a polyolefin product having a thermal conductivity T_{c2} of at least 0.4 W/m.K. Preferably, T_{c2} is at least 0.5 W/m.K, preferably at least 0.6 W/m.K, preferably at least 0.8 W/m.K, preferably at least 1.0 W/m.K, preferably at least 1.2 W/m.K, preferably at least 1.4 W/m.K, preferably at least 1.6 W/m.K, preferably at least 1.8 W/m.K, preferably at least 2.0 W/m.K.

25 Preferably, the process comprises the steps of:

- a) providing a polyethylene starting material,
- b) subjecting said polyethylene starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and
- c) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably

at least 5000 bar, more preferably at least 8000 bar; thereby obtaining a polyethylene product having a thermal conductivity T_{c2} of at least 0.4 W/m.K. Preferably, T_{c2} is at least 0.5 W/m.K, preferably at least 0.6 W/m.K, preferably at least 0.8 W/m.K, preferably at least 1.0 W/m.K, preferably at least 1.2 W/m.K, preferably at least 1.4 W/m.K, preferably at least 1.6 W/m.K, preferably at least 1.8 W/m.K, preferably at least 2.0 W/m.K.

Preferably, the process comprises the steps of:

a) providing a polyolefin starting material having a thermal conductivity T_{c1} ,

b) subjecting said polyolefin starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and

c) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining a polyolefin product having a thermal conductivity T_{c2} , wherein the ratio of the thermal conductivity of the polyolefin product to the thermal conductivity of the polyolefin starting material (T_{c2}/T_{c1}) is at least 2, preferably at least 5, preferably at least 10.

Preferably, the process comprises the steps of:

a) providing a polyethylene starting material having a thermal conductivity T_{c1} ,

b) subjecting said polyolefin starting material to (i) a temperature of at least 100°C, preferably at least 150°C, preferably at least 200°C, preferably at least 220°C, more preferably at least 240°C, and (ii) to a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; and

c) reducing the temperature while maintaining a pressure of at least 3000 bar, for example at least 3500 bar, for example at least 4000 bar, for example at least 4500 bar, preferably at least 5000 bar, more preferably at least 8000 bar; thereby obtaining a polyethylene product having a thermal conductivity T_{c2} , wherein the ratio of the thermal conductivity of the polyethylene product to the thermal conductivity of the polyethylene starting material (T_{c2}/T_{c1}) is at least 2, preferably at least 5, preferably at least 10.

In a preferred embodiment, the polymeric product remains electrically insulating. The electrical resistance, is preferably at least 1000 ohm, preferably at least 1 000 000 ohm,

more preferably at least 10^{12} ohm; with the electrical resistance being measured between the two bases of a cylinder with a diameter of 16 mm and a height of 40 mm.

In a preferred embodiment, the polymeric product comprises polyethylene and has a density increase of at least 1%, preferably at least 2%, preferably at least 5% compared to the starting material.

In an embodiment, the polymeric product comprises polyethylene and has a density of at least 0.965 g/cm^3 , preferably at least 0.970 g/cm^3 , preferably at least 0.975 g/cm^3 , preferably at least 0.980 g/cm^3 , with the density being measured using a Accupyc 1330 pycnometer (commercialized by micromeritics).

10 The polymeric starting material and the polymeric product may comprise additives. Preferably, the amount of additives is limited. In some embodiments, the polymeric product comprises at most 20.0% by weight of additives, preferably at most 10.0% by weight, preferably at most 5.0% by weight, preferably at most 2.0% by weight, preferably at most 1.0% by weight, with % by weight based on the total weight of the polymer product.

In some embodiments, the additives are selected from the group comprising metal oxides, nitrides, carbon nanotubes, graphite and graphene. In some embodiments, the additives are selected from the group comprising antioxidants, antiacids, pigments and peroxides. In some embodiments, the additives are selected from the group comprising metal oxides, nitrides, carbon nanotubes, graphite, graphene, antioxidants, antiacids, pigments and peroxides.

Preferably, the additive is a metal oxide. In a preferred embodiment, the polymeric product comprises at most 20.0% by volume of metal oxide, preferably at most 10.0% by volume, preferably at most 5.0% by volume, preferably at most 2.0% by volume, preferably at most 1.0% by volume, preferably at most 0.5% by volume, preferably at most 0.2% by volume, preferably at most 0.1% by volume, with % by volume based on the total volume of the polymer product.

In some embodiments, the metal oxide is selected from magnesium oxide and aluminium oxide or a combination thereof. Preferably the metal oxide is magnesium oxide.

30 Preferably, the nitrides are selected from boron nitride and aluminium nitride.

The polymeric product may comprise an antioxidant. Preferably, the antioxidant is selected from phenolic antioxidants such as pentaerythritol tetrakis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] (herein referred to as Irganox 1010), tris(2,4-ditert-butylphenyl)

phosphite (herein referred to as Irgafos 168), 3DL-alpha-tocopherol, 2,6-di-tert-butyl-4-methylphenol, dibutylhydroxyphenylpropionic acid stearyl ester, 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, 2,2'-methylenebis(6-tert-butyl-4-methyl-phenol), hexamethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate],

5 benzenepropanamide,N,N'-1,6-hexanediyl bis[3,5-bis(1,1-dimethylethyl)-4-hydroxy] (Antioxidant 1098), Diethyl 3,5-Di-Tert-Butyl-4-Hydroxybenzyl Phosphonate, Calcium bis[monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate], Triethylene glycol bis(3-tert-butyl-4-hydroxy-5-methylphenyl)propionate (Antioxidant 245), 6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol, 3,9-bis(2-(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy-

10 1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-triyl)triethylene tris[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, Tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, ethylene

15 bis[3,3-bis(3-tert-butyl-4-hydroxyphenyl)butyrate], and 2,6-bis[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl] octahydro-4,7-methano-1H-indenyl]-4-methyl-phenol. Suitable antioxidants also include, for example, phenolic antioxidants with dual functionality such 4,4'-Thio-bis(6-tert-butyl-m-methyl phenol) (Antioxidant 300), 2,2'-Sulfanediylbis(6-tert-butyl-4-methylphenol) (Antioxidant 2246-S), 2-Methyl-4,6-bis(octylsulfanylmethyl)phenol,

20 thiodiethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol, N-(4-hydroxyphenyl)stearamide, bis(1,2,2,6,6-pentamethyl-4-piperidyl) [[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxy-benzoate, 2-(1,1-dimethylethyl)-6-

25 [[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl] methyl]-4-methylphenyl acrylate, and Cas nr. 128961-68-2 (Sumilizer GS). Suitable antioxidants also include, for example, aminic antioxidants such as N-phenyl-2-naphthylamine, poly(1,2-dihydro-2,2,4-trimethyl-quinoline), N-isopropyl-N'-phenyl-p-phenylenediamine, N-Phenyl-1-naphthylamine, CAS nr. 68411-46-1 (Antioxidant 5057), and 4,4-bis(alpha,alpha-dimethylbenzyl)diphenylamine

30 (Antioxidant KY 405).

Preferably, the antioxidant is present in an amount of at least 500 ppm.

The polymeric product may comprise an antiacid. Preferably, the antiacid is calcium stearate. Preferably, the antiacid is present in an amount of at least 100 ppm. Preferably, the antiacid is present in an amount of at least 500 ppm.

35 The polymeric product may comprise a pigment.

The polymeric product may comprise a peroxide. Preferably, the polymeric product comprises at least 50 ppm and at most 500 ppm of peroxide. Non-limiting examples of suitable peroxides are 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (for example > 92 % , commercialized by AKZO Nobel under the name Trigonox 101) or 3,6,9-triethyl-3,6,9,-
5 trimethyl-1,4,7-triperoxonane (for example commercialized, in a solution at 41 % in isoparaffinic hydrocarbons, by AKZO Nobel under the name Trigonox 301).

In a preferred embodiment, the process is for making a thermally conductive polymeric product.

According to a second aspect, the invention encompasses the polymeric product obtained
10 by the process according to the first aspect of the invention.

According to a third aspect, the invention provides an article comprising the polymeric product of the second aspect of the invention. Preferably, the article is a molded article.

The present invention also encompasses a polyolefin article, preferably polyethylene, wherein the polyolefin article has a thermal conductivity of at least 0.4 W/m.K, and
15 wherein the smallest dimension of the article can be for example at least 0.05 mm, for example at least 0.10 mm, for example at least 0.2 mm, preferably at least 0.4 mm, preferably at least 0.5 mm, preferably at least 1.0 mm, preferably at least 2.0 mm.

Preferably, the polyolefin article, preferably polyethylene, has a thermal conductivity of at least 0.4 W/m.K, and wherein the smallest dimension of the article is at least 0.4 mm,
20 preferably at least 0.5 mm, preferably at least 1.0 mm, preferably at least 2.0 mm.

Preferably, the article or polyolefin article is a macroscopically three-dimensional article. As used herein, the term "macroscopically three-dimensional article" refers to an article wherein the main dimensions of the article are all of the same order of magnitude. These main dimensions are preferably at least 400 μm , preferably at least 1000 μm .

25 In some embodiments, the article or polyolefin article is a macroscopically two-dimensional article. As used herein, the term "macroscopically two-dimensional article" refers to an article wherein the two of the three main dimensions of the article are of the same order of magnitude, while a third dimension is several orders of magnitude smaller. The two main dimensions are preferably at least 400 μm , preferably at least 1000 μm ,
30 whereas a third dimension is smaller than said threshold. Examples of "macroscopically two-dimensional articles" are films or sheets.

Preferably, the article is not a macroscopically one-dimensional article. As used herein, the term "macroscopically one-dimensional article" refers to an article wherein the two of

the three main dimensions of the article are of the same order of magnitude, while a third dimension is several orders of magnitude larger. The two main dimensions are preferably at most 400 μm , preferably at most 1000 μm , whereas a third dimension is larger than said threshold. Examples of "macroscopically one-dimensional articles" are fibers.

- 5 In a preferred embodiment, the two largest dimensions of the article or polyolefin article are at least 0.4 mm, preferably at least 0.5 mm, preferably at least 1.0 mm, preferably at least 2.0 mm.

The products and articles according to the invention are particularly useful as a heat conductor. The products and articles according to the invention are particularly suitable
10 useful as an electrical insulator.

The articles may be formed, by example, while forming the polymeric product, machining the product onto other articles, such as polymeric articles or articles made from other materials. If, after crystallization under high pressure, a production process must be used to produce the final object, it is preferred that such a production process avoids any
15 melting of the polymer, even locally.

The articles may include housings for electronic parts, heat sinks, fans, and other devices used to convey heat away from electronic components. The articles may include optical pickup bases, which are heat-radiating bodies enclosing semiconductor lasers in optical pickups; packaging and heat sink materials for semiconductor elements; casings of fan
20 motors; motor core housings; secondary battery casings; personal computer and mobile telephone housings, etc.

In a preferred embodiment, the article or polyolefin article is in the form of a housing for electronic parts, a heat sink, an optical pickup base, or a fan.

In a preferred embodiment, the article or polyolefin article is in the form of a battery casing, a fan motor housing, a motor core housing, a personal computer housing, or a
25 mobile telephone housing.

The polymeric products and articles of the present invention have been surprisingly been discovered to have good thermal conductivity and high electrical resistivity. The invention also encompasses the use of the polymeric products and articles as a heat conductor. In
30 a preferred embodiment, this use is to dissipate heat from a battery, preferably from a Li-ion battery.

Similar properties are requested in applications such as lighting applications, e.g. LED board and automotive headlamp reflectors, substrates, electronic packaging or to encapsulate small motors and motor bobbins.

Examples

5 Test methods

The density of the polyolefin was measured by hydrostatic balance, according to ASTM D 1895.

10 The He pycnometry density of the polymeric product was measured using a Micromeritics Accupyc 1330. The way to operate this equipment is described in the notice provided by the constructor.

Molecular weights (weight average and number average) were determined on Waters Alliance 2000 GPCV instruments with refractive index detection by size exclusion chromatography (SEC). Prior to analysis, the samples were kept at a temperature of 160°C for a period of 1 hour without stirring. 300 µl of filtered sample was injected in the
15 apparatus. Two Shodex AT-806MS (Showa Denko) and one Styragel HT6E (Waters) columns were used with a flow rate of 1 ml/min. Analyses were carried out at a temperature of 145 C in 1,2,4-trichlorobenzene (TCB), BAKER 8430 (minimum 99 %), stabilized with 1 g/l of butylated hydroxytoluene (BHT). The polymer solution concentration, measured at room temperature, was of 1 mg/ml.

20 The calibration was based on narrow polystyrene standards.

The calibration curve was fitted using a third order polynomial:

$$\log M_p = A t^3 + B t^2 + C t + D$$

Wherein M_p is the molecular weight at the distribution peak as announced in the certificate and t is the time expressed in seconds.

25 Using this calibration curve, the molecular weights obtained after integration were based on polystyrene. Each measured data point was converted from PS to other polymer using the relationship:

$$\log M_p (PE) = A \log (M_p (PS)) + B$$

The calculation for polypropylene was based on the Mark-Houwink relation ($\log_{10}(M_{PP}) =$
30 $\log_{10}(M_{PS}) - 0.25323$); cut off on the low molecular weight end at $M_{PP} = 1000$.

The calculation for polyethylene was based on the Mark-Houwink relation ($\log_{10}(M_{PE}) = 0.965909 - \log_{10}(M_{PS}) - 0.28264$) (or $K_{PE}M_{PE}^{(\alpha_{PE}+1)} = K_{PS}M_{PS}^{(\alpha_{PS}+1)}$, with $K_{PS} = 0.000167$, $K_{PE} = 0.000525$, $\alpha_{PS} = 0.7$ and $\alpha_{PE} = 0.76$); cut off on the low molecular weight end at $M_{PE} = 1000$. Values for other polymers than PE and PP can be found in the literature.

- 5 Data treatment was performed using the Empower software (Waters).

The molecular weight distribution (MWD) (polydispersity) was then calculated as M_w/M_n .

- For polyethylene, for weight average molecular weight M_w higher than 1 000 000 dalton, M_v molecular weight is determined starting from the intrinsic viscosity measurement determined in agreement with ASTM D2857, ASTM D4020 and ISO 1628-3 norms. M_v is
10 then calculated using the following relation:

$$M_v = 53700 IV^{1.37}$$

wherein IV is the measured intrinsic viscosity (in ml/g).

- The thermal conductivity was measured using a potentiometer (schematically illustrated in Figure 1), and the method as described in B. Poulaert, et al., Polym. Commun. 31, 148
15 (1990), which is hereby incorporated in its entirety by reference. Briefly, and with reference to figure 1, the method of Poulaert et al. comprises energizing a sample heater H_s in order to establish a temperature difference between the heater H_s and a heat sink S. Then, currents in three guard heaters H_0 , H_1 , H_2 are adjusted to reduce to insignificance the temperature differences read on thermocouples ΔT_0 , ΔT_1 and ΔT_2 , which sense,
20 respectively, the temperature difference between the a guard G and the sample heater H_1 , between C_1 and the copper post on which H_1 is wound, and between C_2 and the copper post on which H_2 is wound, wherein C_1 and C_2 are two points on the sample. A thermocouple T_{diff} reads the exact image of the temperature difference along the sample between the points C_1 and C_2 when the zeroing of ΔT_1 and ΔT_2 is achieved. S_1 , S_2 , S_1'
25 and S_2' are small diameter, thin-walled stainless steel tubes, and the Ris are electrically insulated supports.

Example 1

- 20 grams of a UHMWPE powder having bimodal molecular weight distribution was prepared by blending a 50/50 mixture of two polyethylene powders characterized,
30 respectively, by $M_w = 2\,800\,000$ Da and $M_w = 4\,400\,000$ Da, based on intrinsic viscosity measurements.

The blend was introduced in the central part of a steel cylinder with thick walls. The cylindrical internal chamber was 90 mm height and had a diameter of 16 mm. A piston

was introduced in the cylindrical chamber and the whole system was installed in a press (trade mark: Fontijne Holland) able to impose a maximum force of 350 kN on the piston. The pressure imposed on the polymer was controlled by the force applied on the piston, following the formula as below:

5 Pressure (Pa) = Applied force (N)/ $[\pi * (8 * 10^{-3})^2]$

Thanks to an external electrical device, the temperature of the whole cylinder could be controlled.

To induce the crystallization at high temperature, the following "temperature/pressure" history was used:

- 10 - applying a temperature of 260°C and a pressure of 500 bars during 1 hour;
- compressing at 8000 bars during 15 minutes;
- decreasing the temperature to 240°C and holding the pressure during 7 hours; and
- stopping the heating and lowering the temperature to 50°C, maintaining 8000 bars.

The whole device was then removed from the press and the polyethylene sample was
15 recovered for subsequent analysis.

The thermal conductivity was measured as described in B. Poulaert, J-C. Chielens, C. Vandenhende, J-P. Issi and R. Legras, Polym. Commun. 31, 148 (1990). However, to adjust the sample to fit the analysis device, a cylinder (diameter = 16 mm) with 3.3 mm height was extracted from the whole polyethylene sample and inserted in the centre of a
20 "normal" polyethylene cylinder with 3.3 mm height and 30 mm diameter. By "normal" polyethylene, we refer to a polyethylene which was not crystallized at high pressure. Great care was made to obtain a very flat surface for the final cylinder and thus to allow a good contact inside the thermal conductivity apparatus. The device was developed for the thermal conductivity measurement in the central part, so no significant error was induced
25 by the above-described extension of the diameter of the sample from 16 to 30 mm. This procedure was required for the geometrical insertion of the sample in the analytical apparatus. The measured thermal conductivity of the sample was 1.5 W/m.K.

The density of the sample increased from 0.916 (according to the ASTM D1895 norm) to 0.973 g/cm³, as measured at room temperature using the Accupyc 1330 pycnometer, after
30 treating at 8000 bars.

Example 2

17 grams of a homopolyethylene was treated at 4300 bar and a temperature of 240°C in the device as described above. The measured thermal conductivity of the sample was 1.38 W/m.K.

5 Example 3

17 grams of a UHMWPE with 2% by weight NC700 carbon nanotubes was treated at 8000 bar and a temperature of 280°C in the device as described above. The measured thermal conductivity of the sample was 0.42 W/m.K.

Example 4

10 17 grams of a homopolyethylene was treated at 4300 bar and a temperature of 240°C in the device as described above. The measured thermal conductivity of the sample was 1.07 W/m.K.

It is to be understood that although preferred embodiments have been discussed for providing embodiments according to the present invention, various modifications or
15 changes may be made without departing from the scope and spirit of this invention.

Claims

1. A process for preparing a polymeric product from a polymeric starting material comprising at least one polymer, the process comprising the steps of:
 - a) subjecting the polymeric starting material to a temperature of at least 100°C, and to
5 a pressure of at least 3000 bar; and
 - b) subsequently reducing the temperature applied in step (a) while maintaining a pressure of at least 3000 bar; thereby obtaining a polymeric product.
2. The process according to claim 1, wherein the at least one polymer is selected from the group comprising polyolefins, polystyrene, polylactic acid, polyvinyl chloride,
10 polyethylene terephthalate, polybutylene terephthalate, polyamides, poly(methyl methacrylate), polymethacrylate, polycarbonates, polyurethanes, and blends or mixtures thereof.
3. The process according to claim 1 or 2, wherein the at least one polymer has a weight average molecular weight M_w as measured by SEC of at least 30 000 Da, preferably
15 at least 100 000 Da, preferably at least 200 000 Da.
4. The process according to any of the preceding claims, wherein the polymeric product has a thermal conductivity of at least 0.4 W/m.K.
5. The process according to any of the preceding claims, wherein the polymeric product is characterized by an electrical resistance of at least 1000 ohm, with the electrical
20 resistance being measured between the two bases of a cylinder with a diameter of 16 mm and a height of 40 mm.
6. The process according to any of the preceding claims, wherein the polymeric product comprises polyethylene and has a density increase of at least 1%, preferably at least 2%, preferably at least 5% compared to the starting material.
- 25 7. The process according to any of the preceding claims, wherein the polymeric product comprises at most 20.0% by volume of additive, with % by volume based on the total volume of the polymer product.
8. The process according to any of the preceding claims, wherein the polymeric product comprises polyethylene and has a density of at least 0.960 g/cm³, as measured using
30 a Accupyc 1330 pycnometer.
9. The process according to any of the preceding claims, for making a thermally conductive polymeric product.

10. A polymeric product obtained by the process according to any of claims 1 to 9.
11. An article comprising the polymeric product of claim 10.
12. A polyolefin article, preferably polyethylene, wherein the polyolefin article has a thermal conductivity of at least 0.4 W/m.K, and wherein the smallest dimension of the article is at least 0.4 mm, preferably at least 0.5 mm, preferably at least 1.0 mm, preferably at least 2.0 mm.
13. The polyolefin article of claim 12, wherein the two largest dimensions of the article are at least 0.4 mm, preferably at least 0.5 mm, preferably at least 1.0 mm, preferably at least 2.0 mm.
14. The article of any of claims 11 to 13, in the form of a housing for electronic parts, a heat sink, an optical pickup base, or a fan.
15. The article of any of claims 11 to 13 in the form of a battery casing, a fan motor housing, a motor core housing, a personal computer housing, or a mobile telephone housing.

AMENDED CLAIMS

received by the International Bureau on 25 October 2013 (25.10.13)

1. A process for preparing a thermally conductive polymeric product from a polymeric starting material comprising at least one polymer, the process comprising the steps of:
 - a) subjecting the polymeric starting material to a temperature of at least 100°C, and to
5 a pressure of at least 3000 bar; and
 - b) subsequently reducing the temperature applied in step (a) while maintaining a pressure of at least 3000 bar; thereby obtaining a thermally conductive polymeric product, wherein the polymeric product has a thermal conductivity of at least 0.4 W/m.K.
- 10 2. The process according to claim 1, wherein the at least one polymer is selected from the group comprising polyolefins, polystyrene, polylactic acid, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate, polyamides, poly(methyl methacrylate), polymethacrylate, polycarbonates, polyurethanes, and blends or mixtures thereof.
- 15 3. The process according to claim 1 or 2, wherein the at least one polymer has a weight average molecular weight M_w as measured by SEC of at least 30 000 Da, preferably at least 100 000 Da, preferably at least 200 000 Da.
4. The process according to any of the preceding claims, wherein the polymeric product is characterized by an electrical resistance of at least 1000 ohm, with the electrical
20 resistance being measured between the two bases of a cylinder with a diameter of 16 mm and a height of 40 mm.
5. The process according to any of the preceding claims, wherein the polymeric product comprises polyethylene and has a density increase of at least 1%, preferably at least 2%, preferably at least 5% compared to the starting material.
- 25 6. The process according to any of the preceding claims, wherein the polymeric product comprises at most 20.0% by volume of additive, with % by volume based on the total volume of the polymer product.
7. The process according to any of the preceding claims, wherein the polymeric product comprises polyethylene and has a density of at least 0.960 g/cm³, as measured using
30 a Accupyc 1330 pycnometer.
8. A polymeric product obtained by the process according to any of claims 1 to 7.
9. An article comprising the polymeric product of claim 8.

10. The article of claim 9, in the form of a housing for electronic parts, a heat sink, an optical pickup base, or a fan.
11. The article of any of claims 9 or 10 in the form of a battery casing, a fan motor housing, a motor core housing, a personal computer housing, or a mobile telephone housing.

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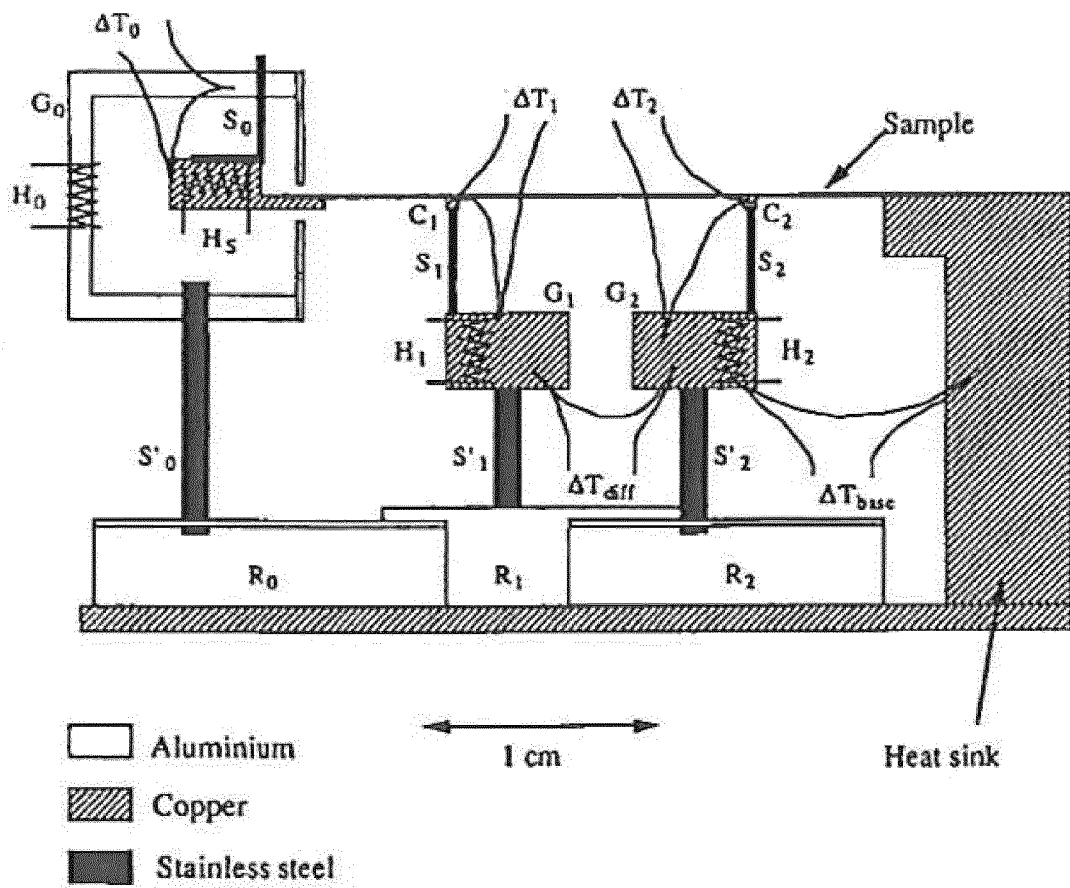


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/060353

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F6/26 C08G63/88 C08G64/40 C08G77/32 C08J5/00
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 C08G 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)

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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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INTERNATIONAL SEARCH REPORT

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