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**PROCESS FOR THE PREPARATION OF A SHAPED PART OF AN ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE**

**VERFAHREN ZUR HERSTELLUNG EINES FORMTEILS AUS EINEM ULTRAHOCHMOLEKULAREN POLYETHYLEN**

**PROCEDE POUR PREPARER UNE PIECE FACONNEE CONSTITUEE D’UN POLYETHYLENE A POIDS MOLECULAIRE ULTRA ELEVE**

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<tr>
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<th>LIPPI, Dirk, Reinier</th>
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<td>Stichting Dutch Polymer Institute 5612 AB Eindhoven (NL)</td>
<td>WO-A-03/037590</td>
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Description

[0001] The present invention relates to a process for the preparation of a shaped part of an ultrahigh molecular weight polyethylene (UHMWPE) by heating the UHMWPE to a temperature above the melting temperature, shaping the resulting melt, and cooling the melt to a temperature below the melting temperature. The invention further relates to a shaped part obtainable with this process, and to the use thereof, especially in medical applications.

[0002] Such a process is known from WO 03/037590. In this publication a shaped part of UHMWPE is prepared wherein the UHMWPE is annealed for at least one hour at a temperature of between 130 and 160 °C in order to obtain a low chain entanglement and thus processability.

[0003] The processability of a synthetic polymer is often a compromise between the ease of processing and desired product properties. Processing routes conventionally applied in the polymer industry are injection moulding, extrusion and blow moulding. All these routes start from a melt of the polymer. Melt properties are mostly affected by the molecular mass of the polymer.

[0004] For a melt consisting of relatively low molecular mass polymer (Mw<Mc) there is a direct proportionality between zero-shear viscosity (η0) and molecular mass, whereas for a melt consisting of high molecular mass polymer (Mw>Mc) the viscosity depends much more strongly on the molecular mass (η0~(Mw)^3.4). Herein is Mw the weight averaged molecular mass and Mc the critical molecular mass, which is related to the shortest polymer chain length able to form an entanglement. This difference in viscosity of the two molecular mass regimes is due to the ability of long chains to entangle, which imposes a restriction on the flowability of a melt.

[0005] The motion of chains within a highly entangled melt is described by the reptation model introduced by De Gennes in J. Chem. Phys. 55, p. 572 (1971). In this model a chain within a melt moves in worm-like fashion through a virtual tube, which is delineated by entanglements formed by neighbouring chains. The time needed for a chain to renew its tube (reptation time), i.e. to change its position within the melt is also highly dependent on molecular mass (τ0~Mw^3). These fundamental restrictions make high molecular mass polymers rather intractable via conventional processing routes. On the other hand, final properties like tenacity, strength and wear improve with increasing molecular mass. Superior properties are necessary to meet the requirements of demanding applications.

[0006] The discrepancy between intrinsic properties related to high values of molecular mass and insufficient product performance due to difficulties in processing is encountered in UHMWPE as well as in other polymers of very high molecular mass. UHMWPE is a linear grade polyethylene, as is high-density polyethylene (HDPE), but possesses a weight average molecular mass (Mw) of at least 7.5 *10^5 g/mol (according to ASTM D4020). Preferably the UHMWPE has a weight average molecular mass of at least 3 *10^6 g/mol, because of excellent mechanical properties.

[0007] The density of the entanglements seems to play a prominent role in the process of forming a shaped part from the melt. The effect of entanglement density was confirmed by drawing experiments on single-crystal mats from UHMWPE, as reported by T. Ogita et al. in Macromolecules 26, p. 4646 (1993). In the case of melt crystallised UHMWPE, entanglements are trapped upon crystallisation and limit the extent to which the chains can be drawn. On the other hand, crystallisation of long molecular chains out of semi-dilute solutions leads to a much less entangled system and this enables these materials to be drawn below the melting temperature. It has always been believed that once a disentangled state of UHMWPE has been achieved, the formation of entanglements within the melt will be very slow, due to a long reptation time, and consequently one would be able to benefit from a disentangled state during processing. Experimental results however showed that highly disentangled solution crystallised films of UHMWPE, which are drawable below the melting temperature lose their drawability immediately upon melting. This phenomenon has been associated with that of “chain explosion”, as experimentally assessed by P. Barham and D. Sadler in Polymer 32, p. 393 (1991). With the help of in-situ neutron scattering experiments they observed that the chains of highly disentangled folded chain crystals of polyethylene increase the radius of gyration instantaneously upon melting. Consequently the chains entangle immediately upon melting, which causes the sudden loss in processability and drawability once the sample has been molten.

[0008] These results showed that the fundamental restrictions resulting from the strong dependence of the zero-shear viscosity on molecular mass cannot be easily overcome. Simple disentanglement of the chains prior to melting will not lead to a less entangled melt and accordingly it cannot be used to improve the melt processability of UHMWPE.

[0009] The objective of the present invention is to provide a process for the manufacture of a shaped part of ultra high molecular weight polyethylene (UHMWPE) comprising melt processing, which part shows good processability below its melting point, and wherein the state of disentanglement is maintained long enough in the melt to process it as an only partly entangled melt.

[0010] According to the present invention this objective is achieved with a process wherein:

a) the UHMWPE has a weight average molecular weight (Mw) of at least 1 * 10^6 g/mol,

b) during the shaping the storage plateau modulus (G*) of the UHMWPE is kept at a value of at most 1.5 MPa,

c) whereafter, before the cooling, the G* is raised to its final value.
The invention also relates to a shaped part that is obtainable with the process of the present invention, as well between 1.2 and 2.5.

fulfilling the above stipulated criteria. Preferably, the MWD of the UHMWPE lies between 1.2 and 3.0, more preferred in a processing window between the initial G* and the highly entangled stage (having a G* of around 2.0 MPa). Preferably

An additional annealing step, as taught in WO 03/037590, will increase that build-up time and therefore enlarge the processing window between the initial G* and the highly entangled stage (having a G* of around 2.0 MPa). Preferably

The G* build-up time can be extended or reduced by polymerization temperature and/or processing heating rate. In fact, the slower the build up of the G* value during the shaping, the better it is for the processability of the UHMWPE, as it retards the increase in entanglement. Therefore it is preferred that the speed (ψ) at which the G* builds up during shaping, is less than 3 MPa/hour, more preferred even less than 0.5 MPa/hour.

After the shaping, the value of the then achieved G* is raised to its final value of around 2.0 MPa. The speed at which this is done, can be as high as the situation allows. This can be achieved by increasing the heating rate. The final temperature should preferably not exceed 450 K.

An additional annealing step, as taught in WO 03/037590, will increase that build-up time and therefore enlarge the processing window between the initial G* and the highly entangled stage (having a G* of around 2.0 MPa). Preferably

This requires specific conditions for the polymerization process in which the UHMWPE is made:

- the temperature at which the polymerization takes place is between 225 and 325 K, more preferably between 260 and 305 K. The higher the temperature, the higher the G*-value of the resulting UHMWPE;
- The catalyst is an unsupported single-site catalyst or a mixture of unsupported single-site catalysts, known for the polymerization of ethylene to UHMWPE;
- The catalyst concentration is low: less than 1*10^-4 mol/l, more preferred less than 1*10^-5 mol/l.
- The polymerization temperature is lower than 325 K and preferably lower than 300 K.
- As of this nature, the polymerization takes place initially in solution and after formation and precipitation of polymer in suspension.

The UHMWPE that is used in the process of the present invention has to fulfill at least the following criteria:

- the weight average molecular weight (Mw) is at least 1*10^6,
- the storage plateau modulus (G*) is kept at a value of at most 1.5 MPa during the shaping.

The G* is determined under nitrogen with a rotational viscometer (rheometer), using a parallel plate geometry (diameter 12 mm). Samples for rotational viscometry were made using compression moulding. The circular preforms having a diameter of about 8 mm and a thickness of 1 mm were moulded at a temperature of 50°C. Each two minutes the pressing force was increased in seven steps to a maximum of 50 kN. Oscillatory shear measurements were performed in a frequency range of 0.1 - 100 Hz at 180 °C.

With the process according to the invention a shaped part can be made by melt processing out of ultra high molecular weight polyethylene. The part thus formed is still highly drawable below its melting point, which indicates that, even though the UHMWPE under the specified conditions is processed in the melt, it still has a low entanglement density.

Surprisingly it has been found that when using the specified UHMWPE, under the specified conditions, a separate annealing step can be omitted. The process of increasing entanglement is under the conditions of the present invention so much retarded, that a disentangled thermodynamically metastable melt is present for a sufficient large time to process the material.

The time during which the entanglement increases, resulting in a build-up of the storage plateau modulus G* to a final value of around 2.0 MPa (which is indicative for a highly entangled UHMWPE), is in most cases depending on the heating rate (Θ) of the polymer. When a dependence is observed, the build-up time increases with a decreasing Θ.

If an extended processing time window is required, it is preferred that Θ is at most 5 K/minute; even more preferred at most 1 K/minute.

Also the starting value of G* is therefore of importance. The lower the G* of the used UHMWPE, the longer it takes to achieve the G* = 2.0 MPa value. Therefore it is preferred that the initial value of the G* of the used UHMWPE is at most 0.75 MPa. For a given polymerization with a specific catalyst system, the resulting G* starting value is typically lower with lower polymerization temperature. Although from a mechanical properties point of view, the desired G* end-value is 2.0 (fully entangled material), for processing the UHMWPE the G* must be below 1.5 MPa, more preferably below 1.2 MPa.

The UHMWPE that is used in the process of the present invention has to fulfill at least the following criteria:

This invention also relates to a shaped part that is obtainable with the process of the present invention, as well...
as to the use of the shaped part. The shaped part can be in the form of a filament, a film, a moulded or extruded article. The processes to obtain such a shaped part from the polymer meet are known to the skilled artisan.

[0022] As the shaped parts according to the present invention have enhanced toughness, wear and abrasion resistance, reduced oxygen permeability, and are essentially grain boundary free, they are very well suited for the use in a medical application. Preferably the shaped part can thus be used as an element of a hip or knee prosthesis.

[0023] Also other uses, wherein the improved physical and mechanical properties of the shaped are applicable, can be referred to, like the use of the UHMWPE-based shaped part in bearings.

[0024] The invention is elucidated with the following non-limiting Examples and comparative experiments.

Examples I - IV and comparative experiment A

[0025] An UHMWPE was prepared according to Example XXV of EP-A-1,057,837. The product had an initial $G^*$ of 0.6 MPa, an MWD of 2 and an Mw of $4 \times 10^6$ (according to ASTM D4020).

[0026] A sample thereof was molten in a rheometer (Ares 3LS-4A, Rheometrics Inc.) and heated with different heating rates from 398 to 418 K. The increase of the storage plateau modulus $G^*$ (recorded at 10 rad/s) was followed in relation to different heating rates $\Theta$.

[0027] The results are given in Table 1.

<table>
<thead>
<tr>
<th>Example</th>
<th>$\Theta$ (K/min)</th>
<th>$G^*$ after 8,000 sec. (MPa)</th>
<th>$G^*$ after 16,000 sec. (MPa)</th>
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<tbody>
<tr>
<td>I</td>
<td>0.25</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>II</td>
<td>1.00</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>III</td>
<td>5.00</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>A</td>
<td>20.00</td>
<td>1.7</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Example IV and comparative experiment B

[0028] The UHMWPE of Example I was heated to a temperature of 453 K at different heating rates $\Theta$. The $G^*$-value was recorded (at 10 rad/s) vs. time. The results are given in Table 2.

<table>
<thead>
<tr>
<th>Example</th>
<th>$\Theta$ (K/min)</th>
<th>$G^*$ after 10,000 sec. (MPa)</th>
<th>$G^*$ after 80,000 sec. (MPa)</th>
</tr>
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<tbody>
<tr>
<td>IV</td>
<td>0.25</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>B</td>
<td>20.00</td>
<td>1.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>

[0029] The products from comparative experiments A and B had a poor drawability, resulting from their high $G^*$-value. The products from the Examples I-IV were very well drawable, due to their low $G^*$-value ($\leq 1.5$ MPa).
Examples V to VIII

Experimental:

[0030] All air- and/or water-sensitive activities were performed under an argon atmosphere using Schlenk techniques or in a conventional nitrogen-filled glove box (Braun MB-150 GI). Methylalumoxane was purchased from WITCO GmbH as a 10 wt% toluene solution. Ethylene was obtained from Air Liquide. Petroleum-ether (40-60), used as the polymerization solvent, was dried over Al₂O₃. The catalysts [3-tBu-2-O-C₆H₅CH=N(C₆F₅)]₂TiCl₂ and (C₅Me₅)₂Sm(THF)₂ were synthesized according to the literature. The molecular weight and molecular weight distribution was measured at 135°C by gel-permeation chromatography (GPC; GPC210, Polymer Labs) using 1,2,4-trichlorobenzene as solvent.

Polymerizations:

Examples V and VI: Catalyst is (C₅Me₅)₂Sm(THF)₂

[0031] The polymerizations were carried out at -10 and 0°C, respectively, under atmospheric pressure using a 2000 ml round bottom flask, equipped with a thermocouple and a mechanical stirrer. Petroleum ether (1000 ml) was introduced to the argon-purged reactor after which the solvent was saturated by bubbling ethylene into the solution for 45 minutes at -10°C and 0°C, resp. The polymerization was initiated by addition of a toluene solution of catalyst (2.8 μmol) into the reactor while stirring vigorously. The same amount of catalyst was added ten times at an interval of one minute. The polymerization was quenched after 15 min with methanol. The solid UHMWPE was recovered by filtration, washed with water and acetone and dried (vacuum oven 60°C, overnight).

Examples VII and VIII: Catalyst is [3-tBu-2-O-C₆H₅CH=N(C₆F₅)]₂TiCl₂

[0032] The polymerizations were carried out under atmospheric pressure using a 2000 ml round bottom flask, equipped with a thermocouple and a mechanical stirrer. Petroleum ether (1000 ml) was introduced to the argon-purged reactor after which the solvent was saturated by bubbling ethylene into the solution for 30 minutes at -10°C and +20°C, respectively. The polymerization was initiated by addition of a toluene solution of methylalumoxane (20 ml) after which a toluene solution of the catalyst (1 μmol) was introduced into the reactor while stirring vigorously. After 20 minutes the ethylene feed was stopped and isobutyl alcohol was added to terminate the polymerization. HCl and water were added to the resulting mixture. The solid UHMWPE was recovered by filtration, washed with water and acetone and dried (vacuum oven 60°C, overnight).

<table>
<thead>
<tr>
<th>Example</th>
<th>Catalyst</th>
<th>Synthesis temp (°C)</th>
<th>Mw</th>
<th>Mn</th>
<th>MWD 10</th>
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<tr>
<td>V</td>
<td>Sm</td>
<td>-10</td>
<td>1,225,500</td>
<td>607,700</td>
<td>2.0</td>
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<tr>
<td>VI</td>
<td></td>
<td>0</td>
<td>2,040,500</td>
<td>832,856</td>
<td>2.5</td>
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<tr>
<td>VII</td>
<td>Ti</td>
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<td>840,600</td>
<td>1.3</td>
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<td>+20</td>
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<td>794,800</td>
<td>1.4</td>
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[0033] The results of the G* measurements are given in Figure 1 at page 12 (determined at a heating rate Θ of 20 K/minute).

Claims

1. Process for the preparation of a shaped part of an ultrahigh molecular weight polyethylene (UHMWPE) by heating the UHMWPE to a temperature above the melting temperature, shaping the resulting melt, and cooling the melt to a temperature below the melting temperature, wherein

   a) the UHMWPE has a weight average molecular weight (Mw) of at least 1 * 10⁶ g/mol,
   b) during the shaping the storage plateau modulus (G*) of the UHMWPE is kept at a value of at most 1.5 MPa,
   c) whereafter, before the cooling, the G* is raised to its final value.

2. Process according to claim 1, wherein the heating rate Θ is at most 5 K/minute.
3. Process according to claim 2, wherein θ is at most 1 K/minute.

4. Process according to claim 1, wherein the MWD is between and inclusive 1.2 - 3.0.

5. Process according to anyone of claims 1-3, wherein the initial value of G* is at most 0.75 MPa.

6. Process according to anyone of claims 1-5, wherein G* builds up to a value of 1.5 MPa at a speed (Ψ) less than 3 MPa/hour.

7. Process according to claim 6, wherein Ψ is less than 0.5 MPa/hour.

8. Process according to anyone of claims 1-7, wherein the UHMWPE is obtained through a solution or suspension polymerization at a temperature of between 225 and 325 K. using an unsupported catalyst in a concentration of less than 1*10^-4 mol/L.

9. Process according to anyone of claims 1-8, wherein the UHMWPE is either a homopolymer of ethylene, or a copolymer of ethylene with another α-olefin or cyclic olefin.

10. Process according to claim 8, wherein the polymerisation takes place at a temperature between and inclusive 260 and 305 K.

11. Process according to anyone of claims 1-10, wherein the UHMWPE is annealed during the heating, at a temperature of not less than 398K and not more than 410K.

12. Essentially grain boundary free shaped part, obtainable with a process according to anyone of claims 1-11.

13. Use of a shaped part according to claim 12, or prepared according to anyone of claims 1-11, in a medical application.

14. Use according to claim 13, wherein the shaped part is an element of a hip or knee prosthesis.

Patentansprüche

1. Verfahren zur Herstellung eines Formteils aus ultrahochmolekularem Polyethylen (UHMWPE) durch Erhitzen des UHMWPE auf eine Temperatur oberhalb der Schmelztemperatur, Formen der erhaltenen Schmelze und Abkühlen der Schmelze auf eine Temperatur unterhalb der Schmelztemperatur, wobei
   a) das UHMWPE ein gewichtsmitteles Molekulargewicht (Mw) von mindestens 1*10^6 g/mol aufweist,
   b) man während des Formens den Plateau-Speichermodul (G*) des UHMWPE bei einem Wert von höchstens 1,5 MPa hält
   c) und dann vor dem Abkühlen den G* auf seinen Endwert erhöht.

2. Verfahren nach Anspruch 1, bei dem die Aufheizrate θ höchstens 5 K/min beträgt.

3. Verfahren nach Anspruch 2, bei dem θ höchstens 1 K/min beträgt.

4. Verfahren nach Anspruch 1, bei dem die MWD zwischen und einschließlich 1,2 - 3,0 liegt.

5. Verfahren nach einem der Ansprüche 1-3, bei dem der Anfangswert von G* höchstens 0,75 MPa beträgt.

6. Verfahren nach einem der Ansprüche 1-5, bei dem sich G* mit einer Geschwindigkeit (Ψ) von weniger als 3 MPa/Stunde bis zu einem Wert von 1,5 MPa aufbaut.

7. Verfahren nach Anspruch 6, bei dem Ψ weniger als 0,5 MPa/Stunde beträgt.


10. Verfahren nach Anspruch 8, bei dem die Polymerisation bei einer Temperatur zwischen und einschließlich 260 und 305 K erfolgt.


12. Im wesentlichen korngrenzenfreier Formkörper, der nach einem Verfahren gemäß einem der Ansprüche 1-11 er-hältlich ist.


Revendications

1. Procédé pour la préparation d’une pièce façonnée constituée d’un polyéthylène à poids moléculaire ultra élevé (UHMWPE) par chauffage de l’UHMWPE à une température supérieure à la température de fusion, façonnage de la matière fondue résultante et refroidissement de la matière fondue à une température inférieure au point de fusion, dans lequel :

   a) l’UHMWPE possède un poids moléculaire moyen en poids (Mw) d’au moins 1 * 10^6 g/mole,
   b) pendant le façonnage, le module de conservation au plateau (G*) de l’UHMWPE est maintenu à une valeur d’au plus 1,5 MPa,
   c) après quoi, avant le refroidissement, le G* est augmenté à sa valeur finale.

2. Procédé selon la revendication 1, dans lequel la vitesse d’élévation de la température θ est d’au plus 5 K/minute.

3. Procédé selon la revendication 2, dans lequel θ est d’au plus 1 K/minute.

4. Procédé selon la revendication 1, dans lequel la répartition du poids moléculaire varie de 1,2 à 3,0.

5. Procédé selon l’une quelconque des revendications 1 à 3, dans lequel la valeur initiale de G* est d’au plus 0,75 MPa.

6. Procédé selon l’une quelconque des revendications 1 à 5, dans lequel G* augmente jusqu’à une valeur de 1,5 MPa à une vitesse (ψ) inférieure à 3 MPa/h.

7. Procédé selon la revendication 6, dans lequel ψ est inférieure à 0,5 MPa/h.

8. Procédé selon l’une quelconque des revendications 1 à 7, dans lequel l’UHMWPE est obtenu par polymérisation en solution ou en suspension à une température comprise entre 225 et 325 K, en utilisant un catalyseur non supporté dans une concentration inférieure à 1 * 10^-4 mole/l.

9. Procédé selon l’une quelconque des revendications 1 à 8, dans lequel l’UHMWPE est soit un homopolymère d’éthy-lène, ou un copolymère d’éthylène avec une autre α-oléfine ou une oléfine cyclique.

10. Procédé selon la revendication 8, dans lequel la polymérisation se déroule à une température qui varie de 260 à 305 K.

11. Procédé selon l’une quelconque des revendications 1 à 10, dans lequel l’UHMWPE est recuit pendant le chauffage, à une température d’au moins 398 K et d’au plus 410 K.

13. Utilisation d’une pièce façonnée selon la revendication 12, ou préparée selon l’une quelconque des revendications 1 à 11, dans une application médicale.

14. Utilisation selon la revendication 13, dans laquelle la pièce façonnée est un élément d’une prothèse de la hanche ou du genou.
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 03037590 A [0002] [0018]
- EP 1057837 A [0025]