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(54) "FIBRES AND FILMS OF ALIPHATIC POLYAMIDES"

(71) We, CONSIGLIO NAZIONALE DELLE RICERCHE, an Italian Body Corporate, of Piazzale delle Scienze, 7, Rome, Italy, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to fibres and films of aliphatic polyamides, in particular to fibres and films which exhibit a higher tensile strength than that of stretched fibres and biaxially stretched films of aliphatic polyamides prepared according to conventional processes.

It is known that the tensile strength or modulus of elasticity (M.E) of fibres constituted of synthetic linear polymers, in particular, polyamides, is considerably lower than that which could be theoretically expected, if the macromolecules were elongated and oriented parallel to the fibre axis. For instance, the modulus of elasticity of a typical fibre of nylon 6, prepared according to the conventional spinning process, is of the order of 200 kg/mm², while the value which can be theoretically expected is at least of the order of a higher magnitude. This difference can be attributed to the fact that in the conventional spinning process the complete parallelization and elongation of the single macromolecular chains cannot be attained along the fibre axis, but, on the contrary, only a partially elongated structure is obtained oriented along the axis of the fibre. If in the process of preparation of the fibre it were possible to elongate and orient all the macromolecules along the fibre axis, the fibre itself should attain the maximum value of the M.E. which could be theoretically expected on the basis of the stresses which are necessary for the deformation of the chemical linkages

formed along the macromolecular chain.

Attempts have been recently made to obtain unusual mechanical properties in polymeric solids. According to U.S. Patent No. 3, 671, 542 aromatic polyamides have been obtained which exhibit a modulus of elasticity up to about 9.000 kg/mm² (equivalent to about 1000 g/denier) by a wet spinning process, starting from anisotropic solutions. The possibility of preparing anisotropic solutions is, however, limited to polymers in which the presence of an aromatic ring ensures a rigid structure of the single molecules dispersed in the solution. In the case of non-aromatic polyamides, such as those formed by polycondensation of Epsilon-caprolactam (nylon 6) and of pyrrolidone (nylon 4), which cannot form anisotropic solutions, the method disclosed in U.S. Patent No. 3, 671, 542 cannot be applied.

Another approach aiming to provide unusual mechanical properties in polymeric solids has been disclosed in British Patent No. 1, 469, 526, which describes preparing a polyethylene having a modulus of elasticity which can reach the aforementioned value which has been reached by the aromatic polyamides by applying a cold extrusion and by controlling the molecular weight. However, this method does not relate to polyamides.

The present invention in one aspect provides a fibre or film of an aliphatic polyamide which is nylon 4 or nylon 6, the said fibre or film having a modulus of elasticity of at least 1000 kg/mm² and containing at least one halide of lithium or calcium in an amount of from 1 to 8% by weight.

The invention in another aspect provides a process for the manufacture of a fibre according to the invention, comprising:

adding to an aliphatic polyamide which is

nylon 4 or nylon 6 at least one halide of lithium or calcium in an amount of from 1 to 8% by weight and forming the resultant product into a fibre; mechanically orienting the obtained fibre
5 at a prevalently amorphous state, by means of a draft; and developing the crystallinity by heating the already oriented material, while maintaining the latter under a draft condition, at a temperature of at least 50°C below the melting
10 temperature of the polyamide.

The invention in a further aspect provides a process for the manufacture of a film according to the invention, comprising:

adding to an aliphatic polyamide which is
15 nylon 4 or nylon 6 at least one halide of lithium or calcium in an amount of from 1 to 8% by weight and subsequently forming the resultant product into a film;

mechanically orienting the obtained film at a
20 prevalently amorphous state by means of two drafts in two directions perpendicular to one another; and developing the crystallinity by heating the already oriented material while maintaining the latter under a draft condition,
25 at a temperature of at least 50°C below the melting temperature of the polyamide.

The halide is suitably lithium chloride or bromide or calcium chloride.

The addition of the halide to the polyamide
30 can be performed either by direct mixing of the already formed polyamide with the halide (occasionally in the presence of a solvent), or by polymerization of the monomer in the presence of the halide.

It should be noted that the conditions for
35 the formation of polyamide salt mixtures and some characteristics of such mixtures have been already described. In Italian Patent No. 943, 553 a process has been described for directly mixing
40 already polymerized polyamides with inorganic salts, while there is also known a polyamide polymerization in presence of inorganic salts. As can be well understood from the above, some properties of polyamide-salt mixtures are
45 different from the corresponding properties of the pure polyamides. In particular, the presence of the salt decreases either the melting temperature or the crystallinity of the pure polyamide. Thus owing to the presence of the salt,
50 the polyamides can be worked (by spinning, extrusion, etc.) at temperatures lower than the temperatures conventionally used for the polyamides, also reducing either the energy consumptions or the difficulties due to the phenomenon
55 of thermal degradation which takes place at the high working temperatures which are conventionally used. From the above prior art it can also be learned that if the polyamide which is
60 subjected to water washing (or to a prolonged baking in some cases) there is complete recovery of the properties of the pure polyamides, in particular of the melting temperature and crystallinity.

65 As far as the recovery of the mechanical

properties of the pure polyamides are concerned, as a result of the salt washing (or prolonged baking in some cases) the above prior art does not give sufficient details, since it is only
70 known that such mechanical properties can be restored (in some cases there has been noted a modest improvement in the properties of the pure polyamides as a result of washing the salt). It should be noted that the nature of the
75 mechanical properties to which reference has been made in the above prior art is that which has been exhibited by samples of non-oriented polyamides (isotropic films) or only lightly oriented (extruded fibres in the absence of
80 tensile stress).

Subsequent studies have now shown that orientation of polyamide-halide mixtures, followed by prolonged heating while maintaining the material under the acquired draft
85 condition, results in highly oriented fibres or films having mechanical properties much higher than those of polyamides which have been not treated with halides as described in the present invention.

As will be better explained in the following
90 examples, an orientation can be imparted to the polyamide halide mixture in various manners. For instance, a mechanically prepared polyamide halide mixture can be extruded in the absence
95 of solvent at a temperature higher than the melting temperature of the mixture (much lower than that of the pure polyamide) and the fibre can be drawn in a spinning line, controlling the fibre cooling. Alternatively a solution
100 of pure polyamide and halide can be spun in a co-solvent, coagulating the fibre into a liquid which must be a solvent for the halide but which does not dissolve the polyamide and
105 which contains a halide having the same activity as the gel. In this case the halide remains in the coagulated fibre and the orientation will be controlled, varying the tensile stress on the spinning line and the other parameters of the working process. Alternatively biaxially
110 stretched film can be prepared, starting from an isotropic film of the polyamide-halide mixture, by subjecting it to consecutive drafts along two perpendicular directions using a machine of the
115 "Instron" type at a suitable temperature. "Instron" is a Registered Trade Mark.

In all these cases the working is managed in
such a manner as to reduce the crystallinity of the polyamide owing to the presence of the
120 halide (in comparison with the crystallinity of the pure polyamide), thus enabling a more efficient orientation and elongation of the molecular chains to be obtained, which, owing
125 to the fact that they are situated in non-crystalline zones, are more easily deformable and orientable. The subsequent prolonged heating is carried out in such a way as not to eliminate such orientation, but, on the contrary, so as to allow the crystallinity to develop in
130 the oriented state, thus producing a highly oriented and crystalline polyamide having

surprising mechanical properties.

Particularly advantageous results have been obtained using nylon 6 and nylon 4 to which halides such as lithium halides and calcium chloride have been added. The invention will be further described with reference to the following illustrative Examples, which illustrate the possibility of producing stretched fibres and biaxially stretched films of polyamides having mechanical properties much higher than those of conventionally treated polyamides.

Such materials according to the invention have many uses the polyamides attain mechanical properties similar to those of metallic materials, while still exhibiting a density which is twice or three times lower.

EXAMPLE 1

A sample of pure nylon 6 having a melting temperature of 235°C is used for the preparation of a mixture containing 4% (by weight) of LiCl by means homogenizing two finely subdivided components in a tube under vacuum at a temperature of 250°C for 5 hours. The melting point of the mixture is 187°C.

The sample of pure nylon 6 and the mixture with LiCl are used for the preparation of fibres by means of a conventional extruder under a pressure of 260°C. The extrusion takes place in air at ambient temperature and the fibre is collected by a revolving cylinder so as to obtain a draft ratio of about 5%. The fibres are then dried for at least two days and are then subjected to resistance tests to tensile stress in an Instron machine. The value of the modulus of elasticity, either of the fibres obtained from pure nylon 6 or from the mixture with LiCl, is about 220-240 kg/mm². The measure of the degree of crystallinity in a differential calorimeter indicates a value of about 40% in the case of the pure nylon 6 and of about 5% in the case of the nylon 6-LiCl mixture. The fibres are then maintained at a constant length in a stove for 17 days and are then dried. The value of the M.E. in the case of pure nylon 6 (and its crystallinity) remain unvaried, while the M.E. value of the fibres which are obtained starting from the nylon 6-LiCl mixture is increased up to about 1000 kg/mm² and the crystallinity is increased up to about 40%.

EXAMPLE 2

A nylon 6-LiCl mixture is prepared as described in Example 1; fibre extrusion is also carried out as described in Example 1. The obtained fibres, having a draft ratio of 5:1, have a M.E. of about 230 kg/mm² (before that the crystallinity is developed by baking at 160°C). The fibres are drawn by means of an Instron machine in a thermostatically controlled room maintained at the temperature of vitreous transition (about 60°C). The thus imparted draft ratio is about 3:1. The crystallinity is then developed by heating at 160°C for 17 days under the conditions stated in Example 1. The thus obtained M.E. values are about 5000 kg/mm².

EXAMPLE 3

To a sample of anhydrous pyrrolidone is added 8% of LiCl and metallic sodium to obtain a 0.4 molar sodium-pyrrolidone mixture (catalyst). 600-700 ml of dehydrated CO₂ are then added. The polymerization takes place rapidly at about 50°C.

The nylon 4-LiCl mixture is then spun at 210°C, as described in Example 1, and then oriented at 80°C in an Instron machine so as to obtain a total draft ratio of 20:1. The development takes place as described in Example 1. The corresponding M.E. is about 3000 kg/mm².

EXAMPLE 4

A nylon 6-5% CaCl₂ mixture is prepared in the form of a film of about 2 mm by means of compression into a mould under a pressure of 150 kg/cm² for 40 seconds at 200°C. The film is then subjected to drafts along two perpendicular directions set at right angles to each other, at 80°C in an Instron machine. The draft ratios in the two directions are about 3:1. When the crystallinity is developed by extraction of the salt with boiling H₂O, the M.E. in the two directions are about 1000 kg/mm².

EXAMPLE 5

To a homogeneous solution of nylon 6 (40% by weight) in formic acid is added LiBr so as to obtain a salt/nylon 6 ratio of 6% by weight. This homogeneous solution is spun at ambient temperature through a nozzle having a diameter of 75 µm at a linear speed of about 50m/min in water containing 6% of LiBr. The fibre is collected from the coagulation bath at a speed of about 20m/min. After the coagulation process the fibre is caused to pass through pure water, while applying a draft ratio of 1.26:1, and is then drawn again with a draft ratio of about 5.2:1.

The thus prepared fibre is conditioned in a stove under vacuum at 25°C for 3 days and then is caused to crystallize at a constant length while still in the stove under vacuum at 160°C for 17 days. The M.E. values exhibited by the thus prepared fibres are about 1500 kg/mm².

WHAT WE CLAIM IS:-

1. A fibre or film of an aliphatic polyamide which is nylon 4 or nylon 6, the said fibre or film having a modulus of elasticity of at least 1,000 kg/mm² and containing at least one halide of lithium or calcium in an amount of from 1 to 8% by weight.
2. A fibre or film as claimed in Claim 1, wherein the said halide is lithium chloride or bromide or calcium chloride.
3. A fibre or film according to Claim 1, substantially as herein described in any of the foregoing Examples.
4. A process for the manufacture of a fibre as claimed in Claim 1, comprising:
 - adding to an aliphatic polyamide which is nylon 4 or nylon 6 at least one halide of lithium or calcium in an amount of from 1 to 8% by weight and forming the resultant product into a fibre; mechanically orienting the obtained

- fibre at a prevalently amorphous state, by means of a draft; and developing the crystallinity by heating the already oriented material, while maintaining the latter under a draft condition,
- 5 at a temperature of at least 50°C below the melting temperature of the polyamide.
5. A process for the manufacture of a film as claimed in Claim 1, comprising:
- 10 adding to an aliphatic which is nylon 4 or nylon 6 at least one halide of lithium or calcium in an amount of from 1 to 8% by weight and subsequently forming the resultant product into a film;
- 15 mechanically orienting the obtained film at a prevalently amorphous state by means of two drafts in two directions perpendicular to one another; and developing the crystallinity by heating the already oriented material while maintaining the latter under a draft condition, at a temperature of at least 50° below the melting temperature of the polyamide.
6. A process as claimed in Claim 4 or 5, wherein the said halide is lithium chloride or bromide or calcium chloride.
7. A process according to Claim 4 or 5 for the manufacture of a fibre or film substantially as herein described with reference to any of the foregoing Examples.
8. A fibre of film when obtained by the process as claimed in any of Claims 4 to 7.
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