PRODUCTION OF RESILIENT, HIGH DENIER, FLAME-RESISTANT FELTAMENTS

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ABSTRACT OF THE DISCLOSURE

Wet spinning process for manufacture of polybenzimidazole monofilaments of at least 100 denier per filament which are particularly useful as non-flammable elements for fibrous closures. The spinning solution is extruded and coagulated, then water washed to reduce the solvent level to about 5 to 35 by weight, heated at about 80 to 110° C., heated to about 120 to 200° C., re-washed to reduce the solvent level to less than 1% by weight, dried and finally hot drawn. Drawing may be followed by a hot relaxation.

Fibrous closures represent an important advance in the closure art. One member of the closure contains pile or loops and the other member contains inter-engageable stiff, resilient hooks generally made by cutting suitable looped yarn. Separation requires a force of a considerable magnitude when release of a large number of hooks at once is attempted, but separation may be quite readily effected by progressively peeling the layers apart. In special applications, they are preferable to conventional closures such as metal zippers since they (1) can be quickly opened, (2) can be quickly closed, i.e., no special orientation is required, (3) cannot get “stuck” or easily break, and (4) are invisible.

Air and sea craft represent an important area where such advantages are highly desirable. These closures have heretofore been used in such environments as a means of quick, easy and reliable attachment and detachment. For example, they are widely used in the interior of commercial aircraft to permit easy and non-destructive stripping for periodic examination of the aircraft frame and structure. Additionally they are invaluable in space and underwater vehicles. Materials which are resistant to flames and high temperatures are preferred for the closure devices, but such materials have, heretofore, not been available. As the Apollo capsule tragedy of Jan. 27, 1967 unfortunately dramatized, materials which may be regarded as flame-resistant in a normal atmosphere may be extremely flammable, or even explosive, in oxygen rich atmospheres.

Moreover, asphyxiation or other incidents of fire are surprisingly high causes of death in vehicular accidents in general. A material for the above fasteners which would inhibit the start and limit the spread of fire is much to be desired. Although truly non-flammable substances as glass and mineral fibers can be used to some extent as loop or pile material and as backing fabrics, they cannot be fabricated into hooking elements having suitable mechanical properties.

It is an object of the invention to provide a filamentary material which is resistant to flames and high temperatures even in oxygen rich atmosphere and which possesses good tensile properties. It is a more specific object to provide stiff and resilient hooking elements for fibrous closures which are substantially self-extinguishing and which can be heat set. We have found that polybenzimidazoles represent such materials. Polybenzimidazoles are a known class of heterocyclic polymers. They are described, for example in U.S. Pat. Nos. 2,895,948 and 3,174,947. Polybenzimidazoles are characterized by a high degree of thermal stability. They may be spun to form fibers which show great resistance to degradation by heat, hydrolytic media and oxidizing media. Such fibers heretofore available however were not suitable as closure hooks. Polybenzimidazole fibers have generally been produced by dry spinning techniques, however the filaments produced thereby are of relative low denier. These filaments cannot sustain the total load required of hooking elements. Plying and twisting the low denier filaments is unsatisfactory since the individual filaments fibrillate or separate when woven. It has not been possible to produce suitable high denier monofilaments by dry-spinning. A wet-spinning method suitable for producing low denier polybenzimidazoles is disclosed in a pending application Ser. No. 416,593, now U.S. Pat. No. 3,441,640. In this method polybenzimidazole dissolved in sulfuric acid is spun into an aqueous sulfuric acid bath. Attempts to prepare acceptable high denier polybenzimidazoles by this method failed because the filaments were too cracked and brittle.

It is thus a further object of this invention to produce high denier polybenzimidazole filaments. More specifically, it is an object that these polybenzimidazole filaments be heat settable and possess tensile properties suitable for fibrous closure hooks.

These objects have now been realized by the method of this invention which broadly comprises wet spinning an organic solution of polybenzimidazole into an aqueous coagulating bath to produce high denier filaments followed by a series of controlled thermal treatments to heal radial incursions and to increase tensile properties. To produce the closure member, the high denier polybenzimidazole filaments is fabricated into a looped pile fabric. The loops are then set by heat treatment and certain of the loops are cut.

More specifically the process of this invention comprises the steps of (1) extruding a solution of polybenzimidazole in a water-miscible organic solvent into an aqueous coagulating bath containing 0 to 60% by weight of a water-miscible organic solvent, (2) washing the coagulated filament with water to reduce the solvent level to 5 to 35% by weight of the total filamentary weight, (3) drying and heating the filament at a temperature of about 80 to 110° C. until it turns a translucent dark brown, (4) heating the filament at a temperature of about 120 to 200° C., (5) washing the filament to reduce the solvent level to less than about 1% by weight, (6) drying the filament and (7) heating the filament at a temperature of about 400 and 550° C. while simultaneously stretching said filament to about 1.5 to 5 its length.

For end uses which require that these filaments be looped, the process should also include step (8)—relaxing said filament at a temperature of about 350 to 525° C.

The spinning solution should consist of the polybenzimidazole in about 20—30% by weight dissolved in a water-miscible liquid. The viscosity should be within the range of 500 to 8000 poises. Exemplary of such water-compatible solvents are dimethyl acetamide, dimethyl formamide and dimethyl sulfoxide. The dope can additionally contain additives, e.g., stabilizers such as lithium chloride.

The temperature of the spinning solution during extrusion should be within the range of 10 to 180° C. and preferably 25 to 80° C. The spinneret should contain holes of a diameter of between 80 and 600 microns. The extrusion pressure should be between 100 and 750 p.s.i.

The coagulation bath can be water containing 0 to 60% by weight, and preferably 0 to 40%, of a water-
miscible solvent such as the aforementioned dimethyl formamide or dimethyl acetamide. If more than 60% of the water-miscible organic solvent is present coagulation is poor, resulting in little or no fiber formation at practical spinning speeds. The bath temperature should be between 10 and 80°C.

The coagulated polybenzimidazole monofilament is passed to a wash roll where the level of the residual organic solvent is reduced to about 5 to 35 weight percent and preferably 15 to 25% of the total filamentary weight by washing with water. It is essential to the success of this process that the washing does not remove all residual solvent. If this precaution is not observed, healing will not occur as evidenced by the absence of the indicated color change, resulting in a weak fiber which is difficult to even package.

The filament is then passed to a drying element such as steam heated rolls at a temperature of about 80 to 110°C. During this procedure the filament dries and turns from an opaque whitish color to a characteristic translucent brown. This color change and change in clarity is indicative of an internal change in void structure.

The filament is then passed to a heating element such as a hot shoe, a heated roll, or a muffle furnace at a temperature of about 120 to 200°C to complete healing. In a preferred embodiment, this step is conducted employing two hot shoes in series (one face up, the other face down) to effect healing around the entire periphery. This procedure greatly increases the elongation of the fiber throughout the subsequent processing steps.

The filament is then washed exhaustively with water to reduce the residual solvent level to less than 1% by weight of the total filamentary weight. Following this, the filament is dried at about 150 to 250°C. Drying is maintained for a substantial period of time, e.g., 16 hours, and can be facilitated by multi-stage drying. The filament is then passed over a heating element such as a hot shoe or heated roll at a temperature of about 400 to 350°C, and preferably 450 to 500°C, and simultaneously stretched to about 1.5 to 5 times its length, and preferably 3 to 4 times. The yarn can then be relaxed over a similar heating element at a temperature of 350 to 525°C, and preferably about 450 to 300°C, to achieve about 30-60% relaxation. This relaxation step is critical for end uses of the polybenzimidazole filaments which involves looping, such as in the fibrous closures. This step increases the elongation and hence reduces brittleness which may manifest itself by fibrillation when closed knots are tied in the filaments.

The resultant monofilament is then ready to be woven into a backing or otherwise connected thereto as further discussed below. The final denier per filament should be at least 100, and preferably at least 200, and can be as high as 500 denier. The filaments have a predominantly circular cross-section.

A small loop can be tied in the monofilament and contacted with a hot metal surface, e.g., a hot shoe at about 350 to 550°C for several seconds. Upon cooling and being untied, the loops will have a permanently set configuration in the filament and can be repeatedly straightened under tension without apparent loss of resiliency. This heat-setting operation is preferably effected in situ, i.e., while an integral part of the closure member. It may be effected before adhesion, however.

A preferred subclass of polybenzimidazole for production of the monofilament of this invention consists of recurring units of the formula:

\[
\text{CH}_2 - \text{C} = \text{N} - \text{R} - \text{C} = \text{N} - \text{CH}_2
\]

wherein \( R \) is an aromatic nucleus having each of the two depicted pairs of nitrogen atoms substituted upon adjacent carbon atoms of the said aromatic nucleus and \( R' \) is a carbocyclic ring. Examples of such heterocyclic rings include pyridine, pyrazine, furan, quinoline, thiophene and pyran. Preferred \( R \) groups are 3,3', 4,4'-bisphenylene and 1,2,4,5-phenylene-

and 1,2,4,5-phenylene-

and

wherein \( R' \) is

Examples of such polybenzimidazoles include poly-2,2'-(pyridylene-3',5')-5,5'-benzimidazole; poly-2,2'-(furylene-2',3')-benzimidazole; poly-2,2'-(naphthalene-1',6')-5,5'-benzimidazole; poly-2,2'-(biphenylene-4',4')-5,5'-benzimidazole; poly-2,2'-amylene-5,5'-benzimidazole; poly-2,2'-octylene-5,5'-benzimidazole; poly-2,2'-octylene-5,5'-benzimidazole; poly-2,2'-cyclohexenylene-5,5'-benzimidazole.

Another type of polybenzimidazole within the purview of the instant invention consists of recurring units of the formula:

\[
\text{CH}_2 - \text{C} = \text{N} - \text{R} \quad -\text{CH}_2
\]

wherein \( Z \) is an aromatic nucleus having the two depicted nitrogen atoms substituted on adjacent carbon atoms of said aromatic nucleus. Exemplary of such polybenzimidazole is poly-2,5(6)-benzimidazole.

The most important and preferred polybenzimidazole is poly 2,2'-m-phenylene-5,5'-benzimidazole which consists of recurring units of the formula:

This species is commonly referred to as simply PBI. A preparation of PBI is described in Example II of Patent No. 3,174,947.

The following examples illustrate the operation of the process of this invention and its critical features.

**EXAMPLE I**

A spinning solution having a viscosity at 30°C of 1500 poise is prepared containing dimethylacetamide, 22.5% by weight of PBI based on the weight of dimethylacetamide and 2% by weight of lithium chloride based on the weight of dimethylacetamide. This solution is extruded at the rate of 10 meters per minute through a spinneret having a single hole of 414 micron diameter into a bath containing only water at 60°C. The coagulated filament is then wrapped around a wash roll and repeatedly passed through water at a temperature of 17°C and a speed of 10.2 meters/minute to reduce the residual solvent level to about 18%. The filament is then passed around a steam heated roll at a speed of 10.3 meters/minute until the color turns from an opaque whitish color to a translucent dark brown. The resultant
brown filament is passed over a hot shoe at 150° C. and wound on a bobbin.

The bobbin is washed in a circulating hot water (50–70° C.) tank for 65 hours. The residual dimethylacetamide residue is less than 1%. The bobbin is then sequentially dried under room conditions for 4 hours at 100° C. in a circulating air oven for 2.5 hours, and at 200° C. in a circulating air oven for 16.5 hours. The dried filament is then drawn at a ratio of 2.6:1 at a supply speed of 2.5 meters per minute over a 1-foot hot shoe having a surface temperature of 445–450° C. The filament is then relaxed about 40% (rolls at a ratio of 5/3) at a supply speed of 5 meters per minute over a 1-foot hot shoe having a surface temperature of 445–450° C.

The physical properties of the resultant filament compares to those of the undrawn and unraveled filaments as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Washed and dried</th>
<th>Drawn and relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity, g/d.</td>
<td>1.28</td>
<td>2.81</td>
</tr>
<tr>
<td>Elongation, percent</td>
<td>34.8</td>
<td>39.7</td>
</tr>
<tr>
<td>Initial modulus, g/d.</td>
<td>46.1</td>
<td>59.7</td>
</tr>
<tr>
<td>DPF</td>
<td>402</td>
<td>278</td>
</tr>
</tbody>
</table>

EXAMPLE II

The PBI dope is extruded and treated in a similar manner as in Example I except that two hot shoes in series, both at 150° C., are employed after the steam roll and the drawing and relaxing processing speeds are increased. The resultant filament has the following physical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Washed and dried</th>
<th>Drawn and relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity, g/d.</td>
<td>1.4</td>
<td>3.24</td>
</tr>
<tr>
<td>Elongation, percent</td>
<td>60.4</td>
<td>34.2</td>
</tr>
<tr>
<td>Initial modulus, g/d.</td>
<td>43.3</td>
<td>78.0</td>
</tr>
<tr>
<td>DPF</td>
<td>438</td>
<td>225</td>
</tr>
</tbody>
</table>

EXAMPLE III

The procedure of Example I is repeated except that the filament is thoroughly washed after exiting from the water bath with using two hot-water washes at 50–60° C. The filament is quite white after the second wash. The residual solvent level is about 4%. Passage over the steam roll does not change the color to a translucent brown. The resultant filament is extremely weak such that it cannot even be packaged.

EXAMPLE IV

The procedure of Example I is repeated except that the wash roll is bypassed, i.e. the filament exiting from the coagulating bath is directly passed to the steam roll without an intervening washing step. The residual solvent level is about 38%. On the steam roll the filament turns color more rapidly resulting in a somewhat lighter color than the pre-washed filament. The resultant filament is much softer than that of Example I and tends to stick to the roll.

EXAMPLE V

The procedure of Example I is followed except that no hot shoe treatment is employed after the steam roll treatment. The resultant filament has the following physical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity, g/d.</td>
<td>2.50</td>
</tr>
<tr>
<td>Elongation, percent</td>
<td>13.5</td>
</tr>
<tr>
<td>Initial modulus, g/d.</td>
<td>67.1</td>
</tr>
<tr>
<td>DPF</td>
<td>243</td>
</tr>
</tbody>
</table>

This filament is too brittle to be fabricated into closure hooks.

The above examples show that by the process of this invention one can produce high denier polypenbenzimidazole filaments having good tensile properties. They also illustrate the critical importance of the washing and heat treating steps.

The fibrous closure containing the high denier polybenzimidazole monofilaments of this invention can be fabricated in known manner, as for example that disclosed by De Mestral in U.S. Pat. Nos. 2,717,437; 3,009,235; 3,154,837 and 3,136,026. For example they can be woven into the supporting material in the conventional manner of making a pile fabric and then cut. In still another method hooking members can be applied to a plastic support by electrostatic dispersion and glueing. In a preferred embodiment one member has all the hooks and they are randomly arranged while the other member has all the hooks and they are oriented. It is of course possible for each member to have hooks and loops.

Aside from their use in the aforesaid closures, the monofilaments can also advantageously replace other fibrous materials in such uses as high-speed, heat-generating machinery, firemen's clothing and the like. In view of their stiffness and resiliency they may also be used in cleaning, scouring and/or brushing means such as in clothes brushes and shoe brushes.

In standard laboratory tests the high denier polybenzimidazole filaments of this invention burn very slowly in an oxygen rich atmosphere compared to the burning of nylon, Nomex, cotton, steel wire and similar materials. Moreover, the kindling temperature is very high. Thus a static spark will not ignite the monofilament.

Numerous variations of the above process will be apparent to one skilled in the art within the spirit of the present invention.

What is claimed is:

1. A process for the production of polybenzimidazole monofilaments of at least 100 denier per filament comprising (1) extruding a spinning solution comprising polybenzimidazole dissolved in a water-miscible organic solvent selected from the group consisting of dimethyl acetamide, dimethyl formamide and dimethyl sulfoxide into an aqueous coagulation bath containing 0% and 60% by weight of a water-miscible organic solvent selected from the group consisting of dimethyl acetamide, dimethyl formamide and dimethyl sulfoxide, (2) washing the coagulated filament with water to reduce the solvent level to between 5% and 35% by weight of the total filamentary weight, (3) drying and heating the filament at a temperature of about 80 to 110° C. until it turns a translucent brown (4) heating the filament at a temperature of about 120 to 200° C., (5) washing the filament to reduce the solvent level to less than about 1% by weight, (6) drying the filament, (7) heating the filament at a temperature of about 400 and 550° C., while simultaneously stretching said filament to about 1.5 to 5 its length.

2. A process according to claim 1 wherein the solvent of said spinning solution is dimethylacetamide.

3. A process according to claim 1 wherein said coagulation bath consists essentially of water.

4. A process according to claim 1 wherein said solvent level is reduced to between 15 and 25% in step (2).

5. A process according to claim 1 wherein step (3) is effected by serially contacting two hot surfaces, each at a temperature of about 120 to 180° C.

6. A process according to claim 1 followed by step (8) relaxing said filament at a temperature of 350 to 525° C.

7. A process according to claim 6 wherein the stretched filament is relaxed in step (8) about 30 to 60%.

8. A process according to claim 1 wherein所述 polybenzimidazole is poly-2,2'-m-phenylene-5',5'-bibenzimidazole.

9. A process according to claim 7 wherein the mono filament is fabricated into a loop configuration and heat set.

10. A process according to claim 5 wherein the poly-
benzimidazole is poly-2,2'-m-phenylene-5,5'-bibenzimidazole, the coagulation bath consists essentially of water and the stretched filament is relaxed about 30 to 60%.

References Cited

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DONALD J. ARNOLD, Primary Examiner
H. MINTZ, Assistant Examiner
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