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SHAPED ARTICLES FROM POLYMERIC MATERIALS

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This invention relates to fiber-forming synthetic polymers and more particularly to an improved method for cold drawing filaments derived from synthetic linear condensation polyamides.

This application is a continuation-in-part of my Patents Nos. 2,071,250 and 2,071,253 and applications Serial Number 91,617, filed July 20, 1936 which has been refiled as application Serial No. 136,031, filed April 9, 1937. In these applications there is described a new class of fiber-forming materials referred to as synthetic linear condensation polyamides. These fiber-forming polyamides are made by subjecting bifunctional polyamide-forming reactants, which may be either a polymerizable amino acid or a suitable mixture of diamine and dibasic acid, to polymerizing conditions until the polyamide formed is capable of being drawn into filaments which possess the unusual property of being capable of being cold drawn, that is drawn or elongated under application of stress in the solid state, into fibers showing upon X-ray examination orientation along the fiber axis.

The oriented fibers, preferably made by extruding the molten polymer through a suitable orifice and cold drawing the resultant filaments, are for most purposes more useful than the unoriented filaments from which they are prepared because the oriented fibers are more pliable, tough, and elastic. However, when it is desired to prepare large cold drawn filaments of the type to be used as bristles, horse hair substitutes, tennis strings, musical instrument strings, fish line leaders, surgical sutures, dental floss, and the like, the force required to draw the large filaments at ordinary speeds of drawing is often sufficient to break the filaments rather than cold draw them.

This invention is particularly concerned with a process by means of which the filaments may be cold drawn upon the application of considerably less drawing force, thus making possible the ready production of oriented large filaments such as the bristles mentioned in the first mentioned application without resorting to the use of extremely high viscosity polyamides or the use of organic plasticizers which decrease the softening temperature and affect the solubility of the bristle.

An object of this invention is to improve the properties of filaments derived from synthetic linear condensation polymers. A further object is to provide an improved process for preparing oriented synthetic linear condensation polyamide filaments. A further object is to improve the drawability of polyamide filaments. A still further object is the manufacture of oriented large diameter filaments or bristles. Other objects will appear hereinafter.

The term "filament" as used herein refers to both the oriented and unoriented filaments or threads which are prepared from these polymers regardless of whether the filaments or threads are long (continuous) or short (staple), while the term "fiber" refers more specifically to the oriented filaments or threads. The filaments may be prepared by the processes of dry or wet spinning or they may be prepared directly from the molten polymer.

I have found that when the undrawn polyamide filaments are first moistened with or soaked in water or other hydroxylated non-solvent, particularly one having molecular weight below 125, that the filaments are much more easily cold drawn into oriented products. Similar soaking of partially cold drawn filaments also facilitates their further cold drawing.

This pre-treatment of the filaments which materially decreases the force required to cold draw them is particularly advantageous in the case of large filaments which would otherwise break. but it is also useful in the cold drawing of smaller filaments of the type to be used in the preparation of yarns and fabrics, since it decreases the force required to cold draw the filaments and destroys the electrostatic charges on the filaments. The cold drawing of wet filaments is also an important feature in the preparation of crimped or wool-like polyamide fibers by the process described in application Serial Number 125,939, filed on even date herewith by V. R. Hardy and J. B. Miles, Jr. The hydroxylated non-solvent with which the filaments are moistened or soaked before cold drawing is preferably water but may be one of various other liquid non-solvents which contain an hydroxyl group. The term "non-solvent" as applied to these agents indicates that they do not dissolve the polyamide under the conditions of operation. These liquid non-solvents include alcohols, particularly the lower aliphatic alcohols, glycols, hydroxy esters, hydroxy ketones, and the like. These liquids may be used alone, in admixture, or diluted with water. They may also be used with non-hydroxylated compounds such as acetone, dioxan, ethyl acetate, and ether. Small amounts of polyamide solvents, e. g., phenols, and formic acids, may also be added. Furthermore, the non-solvent employed may contain foreign materials, such as wetting agents, salts, dyes, dye assistants, etc.

The most pronounced effects are obtained by treating the polyamide filament with the hydroxylated non-solvent until the latter has penetrated throughout the entire filament, i. e., until the filament is substantially saturated. The time required for this purpose is dependent among other things upon the diameter of the filament and the nature of the liquid non-solvent. In the case of small filaments, e. g., those to be used in making fabrics, where the diameter of the final product (cold drawn fiber) will usually be in the neighborhood of 0.00015–0.0015 inch, corresponding roughly to 0.1–10 denier, the time required for saturation is very short. Thus, the desired effect can be obtained by spraying a filament with water and drawing immediately. In the case of larger filaments, for example, those to be used in making bristles and the like, where the diameter of the final product will usually be in the neighborhood of 0.003 to 0.06 inch, much longer treatment is necessary. In some instances, several days' soaking in water or the like is required to secure the maximum effect. In general, the soaking time can be shortened by using the liquid at a somewhat elevated temperature. For example, water at 75 to 100° C. acts more rapidly than cold water. When elevated temperatures are used it is desirable not to prolong the soaking after saturation has been attained. It is important that the filament be drawn while wet. This does not mean that the filament must be drawn immediately upon removal from the liquid in which it has been soaked. If the filament is removed from the liquid and then kept in a moist atmosphere, i. e., in air of high relative humidity, it can be kept almost indefinitely without losing its improved drawing qualities. The drawing may also be applied while the filament is drying. It is within the scope of this invention to cold draw filaments which have been only partly saturated with the liquid medium. If desired, the filaments can be drawn while in the liquid medium.

The force required to draw the wet filaments is much less than that required to draw dry filaments, often ⅓ to ⅔ less. That water should have such a remarkable effect on the drawing qualities of the polyamide filaments is very surprising, for water does not dissolve or noticeably swell the filaments. The amount of water absorbed on complete saturation is generally in the neighborhood of 6% based on the weight of the dry filaments. However, marked improvements in drawing qualities are obtained even though the filament is not completely saturated. For this reason the present invention, as previously mentioned, is particularly advantageous in working with large filaments. Thus, filaments having a diameter above 0.025 inch cannot generally be drawn at ordinary speeds due to breakage unless they have been penetrated with a liquid of the type described above. The size of filaments which can be drawn without pretreatment is dependent among other things upon the method by which they are prepared and upon the nature of the polymer, particularly its intrinsic viscosity, where intrinsic viscosity is defined as

$$\frac{\log_e \eta_r}{C}$$

where η_r is the viscosity of a dilute m-cresol solution of the polyamide divided by the viscosity of m-cresol in the same units and at the same temperature, and C is the concentration in grams of polyamide per 100 cc. of solution. In general, the strength of the filaments increases with the intrinsic viscosity. Polyamides having intrinsic viscosities above 0.8 are most suitable for the preparation of large filaments of the bristle type.

Filaments of diameter as high as 0.025 can be but seldom cold drawn without breakage unless pretreated with an hydroxylated non-solvent, and in the absence of this treatment filaments of the mentioned diameter can be drawn only under especially favorable conditions, e. g., when modified with plasticizers. In fact, filaments having a diameter as low as 0.015 inch frequently give trouble in cold drawing unless they are pretreated with water. This fact is illustrated in Example III below.

The following examples in which the parts are by weight illustrate the invention more specifically:

Example I

Filaments of 0.032 inch diameter were prepared by melt spinning a fiber-forming synthetic linear condensation polyamide of intrinsic viscosity 0.91 prepared from hexamethylenediamine and adipic acid. It was impossible to cold draw these large filaments successfully due to breakage. When the filaments were first soaked in hot water for an hour, they were readily cold drawn without breakage. This was true even when the filaments were removed from the hot water and allowed to cool in a moist atmosphere before cold drawing.

Example II

An undrawn filament of 0.024 inch diameter obtained from polyhexamethylene adipamide of intrinsic viscosity 0.83 was cut in samples 12 inches long. After soaking in various hydroxylated non-solvents for 36 hours at approximately 25° C., the samples were tested on a Scott tester with the results indicated below:

Treatment	Force required to effect cold drawing
	Pounds
None (i. e., aged in air)	3.3
Water	1.2
Ethyl alcohol	1.2
Propyl alcohol	2.0
Isopropyl alcohol	1.6
Furfuryl alcohol	1.0
Ethyl lactate	1.7
Ethyl glycollate	2.9
Ethylene glycol	2.9
Benzyl alcohol	1.1

Example III

A portion of a filament having a diameter of 0.016 inch prepared from polyhexamethylene adipamide of intrinsic viscosity 0.98 was soaked in cold water for 72 hours and then cold drawn with the aid of a Scott tester. The force required to cold draw the filament was about 0.45 lb. Another sample of the same filament, which had been soaked in ethyl alcohol for 72 hours, was found to cold draw under a force of about 0.7 lb. On the other hand, untreated samples of the same filament usually broke without drawing when subjected to stress in the Scott tester, generally at a force in the neighborhood of 1.5 lb.

Although this invention has been described with particular reference to polyamides because of their particularly valuable fiber-forming properties, it is applicable broadly to fiber-forming synthetic linear condensation polymers. As examples of such polymers might be mentioned polyesters, polyacetals, polyethers, polyesterpolyamides, and other co-polymers.

This invention is not limited to the use of filaments, but is applicable broadly to shaped articles or products capable of undergoing cold drawing, regardless of whether the drawing is to be applied in one direction or in more than one direction. As additional examples of such products might be mentioned ribbons, bands, foils, and films. As in the case of filaments, cold drawing is facilitated by pretreating the products with water or some other hydroxylated non-solvent. The oriented products in general have more desirable properties than the unoriented products from which they are derived.

A valuable class of fiber-forming polyamides for the preparation of filaments, ribbons, bands, foils, and other products with which this invention is concerned, are those derived from diamines of formula $NH_2CH_2RCH_2NH_2$ and dicarboxylic acids of formula $HOOCCH_2R'CH_2COOH$ or amide-forming derivatives thereof, in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms. An especially valuable group of polyamides within this class are those in which R is $(CH_2)_x$ and R' is $(CH_2)_y$, wherein x and y are integers and x is at least two. As examples of polyamides which fall within one or both of these groups might be mentioned in addition to polyhexamethylene adipamide cited in the foregoing examples, polytetramethylene adipamide, polytetramethylene suberamide, polytetramethylene sebacamide, polypentamethylene sebacamide, polyhexamethylene sebacamide, polyhexamethylene β-methyl adipamide, polyoctamethylene adipamide, polydecamethylene adipamide, polydecamethylene p-phenylenediacetamide, and poly-p-xylylene sebacamide. As already indicated, this invention is applicable also to fiber-forming polyamides derived from polymerizable monoaminomonocarboxylic acids and their amide-forming derivatives. As examples of such polyamides might be mentioned the polymers derived from 6-aminocaproic acid, 9-aminononoanoic acid, and 11-aminoundecanoic acid. It is also within the scope of this invention to draw wet filaments and the like derived from a mixture of fiber-forming polyamides or from interpolyamides, i. e., polyamides prepared from a mixture of polyamide-forming reactants, e. g., a mixture of two or more diamines with one or more dicarboxylic acids, or a mixture of a diamine, a dicarboxylic acid, and an amino acid.

This invention is not limited to the cold drawing of filaments, etc., consisting solely of synthetic polymers. Other materials such as plasticizers, e. g., orthohydroxydiphenyl, delusterants, pigments, extenders, fillers, dyes, resins, oils, cellulose derivatives, and the like may be present in addition to the synthetic polymer. Thus, a polyamide filament containing 3% titanium dioxide as delusterant is more readily drawn when wet than when dry. The foreign material, when present in moderate amounts, does not interfere with the cold drawing operation or the beneficial effect of the water thereon.

It will be evident from the foregoing discussion that this invention provides a simple and economical process for improving the drawing qualities of synthetic linear condensation polymer filaments, foils, ribbons, films, and the like. It is especially useful in the preparation of large oriented polyamide filaments, e. g., bristles, since such large filaments cannot ordinarily be cold drawn by the methods heretofore described.

As many apparently different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. An improved method for cold drawing shaped articles derived from fiber-forming synthetic polymers which comprises wetting the article with an hydroxylated non-solvent for the polymer, and then applying sufficient stress to the article to effect cold drawing.

2. A process for manufacturing shaped articles which comprises forming such articles from fiber-forming synthetic polyamides, substantially saturating the article with an hydroxylated non-solvent for the polyamide, and then applying sufficient stress to the article to effect cold drawing.

3. A process for manufacturing artificial fibers which comprises forming a filament from a fiber-forming synthetic polyamide, wetting the filament with an hydroxylated non-solvent for the polyamide, and then cold drawing the filament.

4. A process for manufacturing artificial bristles which comprises forming from a fiber-forming synthetic polyamide a filament having a diameter such that when cold drawn the resulting diameter will be from 0.003 to 0.06 inch, substantially saturating the filament with an hydroxylated non-solvent for the polyamide, and then cold drawing the filament.

5. The process set forth in claim 2 in which said polyamide is the reaction product of a diamine and a substance of the class consisting of dicarboxylic acids and amide-forming derivatives thereof.

6. The process set forth in claim 2 in which said polyamide is obtainable from a diamine of the formula $NH_2CH_2RCH_2NH_2$ and a dicarboxylic acid of the formula $HOOCCH_2R'CH_2COOH$, R and R' being divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation, and R having a chain length of at least two carbon atoms.

7. The process set forth in claim 2 in which said non-solvent is water.

8. The process set forth in claim 2 in which said non-solvent is an alcohol.

9. The process set forth in claim 3 in which said non-solvent is water and in which said polyamide is the reaction product of a diamine and a dicarboxylic acid.

10. The process set forth in claim 4 in which said non-solvent is water and in which said polyamide is the reaction product of a diamine and a dicarboxylic acid.

11. The process set forth in claim 2 in which said polyamide is polyhexamethylene adipamide.

12. The process set forth in claim 4 in which said polyamide is polyhexamethylene adipamide and in which said non-solvent is water.

13. The process set forth in claim 2 in which said non-solvent is ethyl alcohol.

14. An improved method for cold drawing fiber-forming synthetic linear condensation polyamides in the form of filaments, foils, ribbons, films and the like which comprises wetting said polyamide in such form with an hydroxylated non-solvent therefor and subjecting it to cold drawing.

15. A process for preparing fibers exhibiting orientation along the fiber axis which comprises cold drawing synthetic linear condensation polyamide filaments substantially saturated with water.

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