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SYNTHETIC POLYMER

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This invention relates to synthetic fibers and more particularly to the manufacture and spinning of such fibers from polyamides.

Fiber-forming synthetic linear condensation polyamides known as superpolyamides capable of yielding excellent fibers can be prepared from polymerizable amino acids and their equivalents and from suitable diamine-dibasic acid mixtures and their equivalents. These polyamides and their conversion into fibers are described by W. H. Carothers in Patents 2,071,253 and 2,130,523, and in the applications there referred to. While the properties of these polyamide fibers will of course vary considerably with the nature of the reactants used in their preparation, common characteristics of the fibers are high tenacity, high orientation, lack of sensitivity toward conditions of humidity, extraordinary resistance to solvents and chemical reagents, exceptionally good elastic recovery, good dyeing properties, and good aging characteristics in air even at elevated temperatures. In addition, many of these fibers have high melting points which add to their utility as textile fibers. It was pointed out that the fibers could be prepared by spinning the polyamides from melt, that is, by extruding the molten polyamide through an orifice and cold-drawing (applying stress) to the resultant filaments to produce orientation therein. This is a particularly desirable method of preparing fibers, since it is simpler and more economical than the conventional methods of spinning from solution. However, some difficulty has been encountered in spinning certain of the superpolyamides, particularly those of high melting point, by this process, because the products tend to undergo thermal decomposition (form bubbles) at the high temperatures required to spin them from melt. The formation of bubbles prevents smooth spinning and causes defects in the fibers.

An object of this invention is to overcome the above described tendency of superpolyamides to decompose when spun from melt. A further object is to decrease the temperatures required for the melt spinning of polyamides. A further object is to provide a convenient and economical method for the preparation of fibers, ribbons, films, and the like from polyamides. A still further object is the preparation of new and valuable fibers. Other objects will appear hereinafter.

The above objects are accomplished by adding to a molten fiber-forming polyamide an agent, referred to herein as a melting point depressor, which lowers the melting point of the polyamide, and then forming the molten mixture into fibers,

ribbons, bands, foils, films, and rods, and the like, by introducing the molten mixture in the desired shape into a medium which causes it to congeal without substantially removing the melting point depressor therefrom. More specifically, these objects are accomplished by extruding a molten mixture of polyamide and a melting point depressor therefor through an orifice into air at ordinary temperature and subjecting the filaments thus formed to stress (cold-drawing) to produce fiber orientation therein. The melting point depressor may be retained in the product or be removed therefrom either before or after cold-drawing.

The tendency of the polyamide to form bubbles during melt spinning is overcome, or at least greatly diminished through the addition to the molten polyamide of the above mentioned melting point depressors which for the purpose of this invention are organic, chemically inert, high boiling materials (boiling above 225° C. and preferably above 275° C.), stable above the spinning temperature and solvents for the polyamide at that temperature. For the present purpose the agent is regarded as being a solvent for the polyamide if it is miscible and forms a homogeneous mixture with the molten polyamide.

As an example of the lowered melting point caused by these agents it may be noted that polyhexamethylene adipamide (derived from hexamethylenediamine and adipic acid) has a melting point of 248° C. and in the absence of a melting point depressor requires a temperature of about 285° C. for spinning from a melt. At this temperature the polymer develops gaseous decomposition products at the rate of about 0.05 cc. per minute per gram of polymer. At 275° C., the rate of decomposition is approximately one-half as fast, while at 255–260° C., at which temperature spinning is possible in the presence of 17% of hydroxydiphenyl as melting point depressor, almost no decomposition occurs. In addition to decreasing the melting point of the polyamide, the depressor lowers the viscosity of the molten mixture so that any bubbles which form rise to the surface of the molten mass and do not enter the spinneret orifices.

The most valuable melting point depressors are nonpolymeric materials, particularly the high boiling phenols, such as the o-hydroxydiphenyl, naphthols, and the bis-(hydroxyphenyl) dimethylmethanes. Other materials useful for the purpose of this invention include ketones, ethers, and amides. The boiling point of the depressor must be above the temperature at which the

polyamide-mixture is spun. It is desirable that the boiling point of the depressor be at least 5° C. higher than the spinning temperature.

The spinning of the molten polyamide-depressor mixture can be carried out in essentially the same manner as the spinning of pure polyamides from melt. The molten mass is extruded through an orifice or through a spinneret containing a plurality of orifices. The extruded portion congeals as it leaves the spinneret and comes in contact with the air. The filaments obtained under such conditions that no stress is applied very closely resemble the mixture from which they are obtained. However, if moderate stress is applied to these filaments, they can be elongated or cold-drawn as much as 200 to 700%. This cold-drawing, that is, stretching below the melting point of the filaments, is accompanied by a progressive increase in tensile strength until a definite limit is reached beyond which the application of additional stress causes the filaments to break.

The cold-drawn filaments remain permanently extended, they are much stronger than the material from which they are drawn, more pliable and elastic, and when examined by X-rays they furnish a sharp fiber diffraction pattern. This evidence of fiber orientation shows that the cold-drawn filaments are true fibers. In practice, the formation of continuous oriented fibers from the extruded filaments is easily conducted as an integral part of the spinning operation. Thus, the filaments as they leave the spinneret may be collected on a drum or bobbin and then transferred continuously to a second drum driven at a higher rate of speed, so as to produce the desired degree of stretching or cold-drawing. If desired, the cold-drawing operation may be carried out as a separate and distinct operation.

It is desirable to apply the cold-drawing and other operations to which the filaments are subjected in an atmosphere of high moisture content or to moisten the filaments with water since this neutralizes the electrostatic charges on the filaments. Moreover, wet filaments appear to cold-draw with greater facility than dry filaments. The process of cold-drawing differs from the stretch-spinning known to the artificial fiber art in that it may be carried out very rapidly and in that the degree of elongation produced is very great. It is further unique in that it transforms a synthetic product which is essentially crystalline into one showing fiber orientation.

It will be noted that the above process differs from dry spinning in that the filaments set up as a result of the cooling effect of the air and not as a result of the evaporation of solvent. This means that the filaments can be reeled up directly, whereas dry spinning requires an extensive removal of solvent before the filaments become hard enough to be reeled upon a bobbin.

It is surprising that the presence of the melting point depressor in the above filaments does not interfere with their cold-drawing into oriented fibers. Another unusual property of the filaments is that they yield fibers comparable in strength and elastic properties with those obtained without the use of a depressor. This is generally not the case with other fiber-forming materials; for example, fibers spun from a mixture of cellulose acetate and a high boiling agent, which acts as a melting point depressor, are much weaker than those prepared from cellulose acetate alone and removal of the depressor is necessary in order to obtain fibers of good strength.

While the fibers consisting of polyamide and

melting point depressor are quite strong and are useful as such, it is desirable for some purposes to remove the depressor therefrom. This can be done either before or after cold-drawing. A convenient method for removing the depressor consists in passing the fibers through a liquid which dissolves the depressor but not the polymer. Solvents such as alcohols, esters and ketones are very suitable for this purpose. If the depressor is a phenol, e. g., hydroxydiphenyl, it can be removed by washing with dilute alkali solutions. The depressor can be recovered from the alkali solutions by precipitation with acids. If organic solvents are used to remove the depressor, the latter can be recovered by distilling off the solvent. The most suitable solvent to select will of course depend upon the nature of depressor in the fibers. In general the depressor-free fiber has a higher softening point than the fiber containing depressor and is less affected by solvents and chemical agents.

The amount of melting point depressor which is added to the polyamide is generally less than 30% by weight of the polyamide but higher amounts can be used in some cases although this tends to interfere with the cold-drawing operation unless the depressor is first removed. The quantity of depressor added will depend upon its compatibility with the polyamide, the extent to which it is desired to lower the spinning temperature of the polyamide, and if the depressor is to be left in the fiber, on the nature of the fiber which is desired. In most cases the addition of 5 to 20% by weight of the depressor to the polyamide is sufficient to lower the spinning temperature of the latter to the point where thermal decomposition is avoided.

The following examples illustrate the preparation of fibers according to the methods of this invention:

EXAMPLE I

The polyamide used in this example was prepared by heating hexamethylene diammonium adipate (diamine-dibasic acid salt), containing 2.4 molar per cent of hexamethylene diammonium acetate as viscosity stabilizer and 17% by weight of o-hydroxy-diphenyl as the melting point depressor and solvent, for a period of four hours at 288° C. The fiber-forming polyamide thus obtained (polyhexamethylene adipamide) had an intrinsic viscosity of 0.8. Approximately 200 g. of the polymer, containing the o-hydroxy-diphenyl (approximately 17%) used in its preparation, was spun from melt at 255-257° C. under a pressure of 50 pounds applied with nitrogen. The temperature is approximately 30° C. lower than that required to spin the polyamide in the absence of the melting point depressor. The spinneret contained 10 orifices each 0.0078" in diameter placed at the bottom of 0.125" cone-shaped protrusions extending downward from the face of the spinneret. The extruded filaments were collected on a motor-driven drum having a peripheral speed of 400 ft. per minute. The entire charge was spun in this way during the course of 75 minutes without any bubbling whatsoever. A portion of the filaments obtained in this way was soaked in 95% ethyl alcohol for several hours to remove the melting point depressor and then cold-drawn. The remaining portion was first cold-drawn and then washed free of depressor by soaking in alcohol. Table I below shows that undrawn filaments with or without depressor are comparable in tenacity and residual elongation. This is also true of fibers cold-drawn

with and without depressor. However, the fibers containing depressor melt at 238° C. as compared with 248° C. for fibers washed free of depressor. Fibers obtained by the above process, freed of depressor either before or after cold-drawing, have properties similar to those of fibers spun from melt in the absence of a depressor. Thus the fibers produced in accordance with this example were comparable in strength with those spun directly from depressor free polyhexamethylene adipamide but were somewhat more uniform and were entirely free of defects of the type produced by bubbles.

TABLE I

Fibers spun from polyamide containing 17% depressor

Melting point depressor	Extent of cold-drawing, percent	Denier		Tenacity, g./b. d.*	Residual elongation, percent
		Original	Break		
Present	None	18.7	4.7	2.7	301
Absent	None	15.5	3.8	2.8	305
Present	164	4.6	1.7	3.5	174
Absent ¹	164	6.1	1.6	4.4	283
Present	400	4.1	3.3	5.3	22
Absent ¹	400	3.3	2.7	5.8	22
Absent ²	400	3.5	3.0	4.9	16
Present	824	2.1	1.6	5.4	29
Absent ¹	824	2.0	1.5	5.3	33
Absent ²	824	2.1	1.4	5.6	45

¹ Drawn before removal of depressor.

² Drawn after removal of depressor.

*Based on denier at the breaking point.

EXAMPLE II

Polydecamethylene adipamide, having a melting point of 225° C. and an intrinsic viscosity of 0.76, was mixed with 5% by weight of p-toluene sulfonethylamide (depressor) and spun from melt through a slot in a platinum spinneret. The slot measured 0.01 x 15 mm. The spinning temperature was approximately 230° C. and the pressure 50 lb./sq. in. The extruded ribbon of polyamide-depressor mixture was cold-drawn and subsequently washed free of depressor. The ribbon was very pliable and strong; it was similar to that obtained without the use of a depressor.

The examples illustrate the preparation of fibers and ribbons from molten polyamide-depressor mixtures. It will be apparent that other forms of useful objects such as films, sheets, rods, and the like can also be prepared from the molten masses. It is not necessary that the polyamide composition be extruded through a spinneret; the molten mass may, for example, be passed through hot rolls and in this way formed into sheets and films. The melting point depressor may be retained or removed from the resultant product depending upon the type of product that is desired. Dyes and other modifying agents may be incorporated in the molten mass prior to conversion into the finished product.

This invention is applicable to the formation of fibers and the like from polyamides of both the amino acid and diamine-dibasic acid types (particularly described in the above mentioned applications) as well as to mixtures of polyamides and to interpolymers derived from the mutual reaction of several polyamide-forming reactants, as for example, from the reaction of two diamines with two dibasic acids. The foregoing examples illustrate the use of polyhexamethylene adipamide and polydecamethylene adipamide in the process of this invention. As examples of other polyamides which may be used are mentioned 6-aminocaproic acid polymer,

9-aminononanoic acid polymer, polytetramethylene adipamide, polypentamethylene adipamide, polyoctamethylene adipamide, polyhexamethylene suberamide, polyhexamethylene sebacamide, poly-p-xylylene sebacamide, and polydecamethylene p-phenylene acetamide.

A valuable class of polyamides for use in this invention comprises those derived from diamines of the formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and dicarboxylic acids (or their amide-forming derivatives) of the formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$ in which R and R' are divalent hydrocarbon radicals free from olefinic or acetylenic unsaturation (non-benzenoid unsaturation), and in which R has a chain length of at least two carbon atoms. Of this class of polyamides those in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$ where x is at least 4 and y at least 3 are an especially valuable sub-class. Products of these classes are capable of yielding excellent fibers, but many have such high melting points that spinning is best carried out in the presence of a melting point depressor.

As has already been indicated, the compounds used as melting point depressors in the process of this invention are miscible with the molten polyamide, do not react therewith, are stable at the spinning temperature to be used, and have boiling points above the spinning temperature. It is not necessary that the depressor be compatible with the polyamide in all proportions. The necessary lowering in the spinning temperature of the polyamide to avoid decomposition can often be attained by adding only a few per cent of the depressor. As examples of suitable melting point depressors might be mentioned thymol, xlenol, carvacrol, pentamethyl phenol, p-chloro-m-xlenol, alpha-naphthol, beta-naphthol, dinaphthol, diphenylolpropane, dihydroxydiphenyl, diphenylolcyclohexane, p-toluene sulfonbutylamide, p-toluene sulfon-di-butylamide, and the like. Thus the addition of 10% of diphenylolpropane to a polyamide lowers its melting point by some 15 to 20° C. A mixture of compounds may also be used as melting point depressor.

This invention provides a simple and economical method for spinning polyamides. The method is superior to the conventional methods of dry and wet spinning in that the quantity of melting point depressor used is relatively small as compared with the amount of solvent used in the other methods. Moreover, it is not essential that the depressor be removed from the fibers as is the case in the other methods; in some cases the depressor imparts improved properties to the fiber. An advantage which the process of the present invention has over melt spinning in the absence of a depressor is that it lowers the spinning temperature and prevents thermal decomposition of the polyamide. While the process is most useful in the preparation of fibers, it is also applicable to the preparation of related products such as bristles, rods, tubes, films, sheets, ribbons, and foils.

As many apparently widely 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. In a method for decreasing thermal decomposition during the manufacture of shaped articles from molten synthetic fiber-forming polyamide, the steps which comprise forming a

homogeneous mixture comprising the molten polyamide and a melting point depressor chemically inert toward the polyamide and having a boiling point above the temperature of the molten mixture, and forming said articles from the molten mixture at a temperature substantially below that required in the absence of said melting point depressor, said melting point depressor having a boiling point above 225° C. and being one of the class of monomeric, oxygenated, organic compounds consisting of phenols, ketones, and amides.

2. In a method for decreasing thermal decomposition during the manufacture of shaped articles from molten synthetic linear condensation polyamide, the steps which comprise forming a homogeneous mixture comprising the molten polyamide and a melting point depressor chemically inert toward the polyamide and having a boiling point above the temperature of the molten mixture, forming said articles from the molten mixture at a temperature substantially below that required in the absence of said melting point depressor, and removing the melting point depressor from the articles, said melting point depressor having a boiling point above 225° C. and being one of the class of monomeric, oxygenated, organic compounds consisting of phenols, ketones, and amides.

3. In a method for decreasing thermal decomposition during the spinning of filaments from molten synthetic fiber-forming polyamide, the steps which comprise forming a homogeneous mixture comprising the molten poly-

amide and a melting point depressor chemically inert toward the polyamide and having a boiling point above the temperature of the molten mixture, and extruding the molten mixture into filaments at a temperature substantially below that required in the absence of said melting point depressor, said melting point depressor having a boiling point above 225° C. and being one of the class of monomeric, oxygenated, organic compounds consisting of phenols, ketones, and amides.

4. In a method for decreasing thermal decomposition during the spinning of filaments from molten synthetic linear condensation polyamide, the steps which comprise forming a homogeneous mixture comprising the molten polyamide and a melting point depressor chemically inert toward the polyamide and having a boiling point above the temperature of the molten mixture, extruding the molten mixture into filaments at a temperature substantially below that required in the absence of said melting point depressor, and removing the melting point depressor from the filaments, said melting point depressor having a boiling point above 225° C. and being one of the class of monomeric, oxygenated, organic compounds consisting of phenols, ketones, and amides.

5. The method set forth in claim 1 in which said melting point depressor is a phenol.

6. The method set forth in claim 3 in which said melting point depressor is a phenol.

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