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[54] WET-SPINNING SHAPED FIBERS

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[58] **Field of Search**.....264/177 F, 182; 161/177

[56] **References Cited**

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[57] **ABSTRACT**

A process for wet-spinning filaments of diversiform cross-sectional configuration comprising; extruding a fiber-forming polymer solution through orifices of diversiform cross-sectional configuration in a spinnerette of low thermal conductivity into a cold aqueous coagulating liquid while simultaneously and continuously withdrawing the resulting coagulum from said coagulating liquid at a linear velocity at least 0.5 times the average linear velocity of said polymer solution through said orifices.

8 Claims, No Drawings

WET-SPINNING SHAPED FIBERS

This is a continuation of Ser. No. 696,495, filed Jan. 9, 1968 and now abandoned.

This invention relates to a process for wet-spinning filaments of diversiform cross-sectional configuration. More particularly, this invention relates to producing such filaments from solutions of polymers, such as acrylonitrile polymers, by a wet-spinning process wherein the extrudate from the spinnerette is coagulated by leaching solvent therefrom.

Recently, synthetic fiber technology has advanced to the stage wherein it has become recognized that useful properties can be imparted to synthetic fibers by making them of diversiform cross-sectional configuration. Such "diversiform cross-sectional configurations" include multi-lobal fibers (e.g. trilobal or tetra-lobal cross-section), ribbon fibers (rectangular or substantially rectangular cross-section), and dog-bone fibers (something like a figure "8" cross-section). Fibers of such diversiform cross-section configurations may be monocomponent (i.e., uniform composition across the cross-section) or multi-component (i.e., two or more discrete areas of different composition across the cross-section) fibers. Numerous recent references exist disclosing many diversiform cross-sectional configurations and the advantages thereof.

In general, synthetic filaments can be produced from polymeric materials by melt-spinning, dry-spinning, or wet-spinning processes. In the "melt-spinning process" for forming synthetic filaments, polymer liquefied by melting is extruded through spinnerette orifices to form an extrudate which is coagulated by cooling. Typically, polyamide, polyester, and glass fibers are produced by melt-spinning. In the "dry-spinning process" for forming synthetic filaments, polymer liquefied by dissolving in a volatile solvent is extruded through spinnerette orifices to form an extrudate which is coagulated by evaporation of the volatile solvent. Typically, cellulose acetate solutions in acetone, acrylonitrile polymer solutions in dimethylformamide, etc. are spun into fibers by dry-spinning. In the "wet-spinning process" for forming synthetic filaments, polymer liquefied by dissolving in a solvent is extruded through spinnerette orifices to form an extrudate which is coagulated by removal of solvent in a liquid coagulating medium. In wet-spinning fibers of some polymers, such as from solutions of acrylonitrile polymers in aqueous nitric acid, aqueous salt, or organic solvents, the solvent is removed by leaching it out of the extrudate in a cold aqueous coagulant. In wet-spinning fibers of other polymers, such as from viscose (aqueous sodium hydroxide solution of cellulose xanthate), the solvent is removed by chemical reaction with an aqueous sulfuric acid coagulant.

The various synthetic filaments of diversiform cross-sectional configuration found in the recent prior art were made by melt-spinning or dry-spinning processes since, with these processes, it was generally necessary only to replace the spinnerettes having round orifices with other spinnerettes having appropriately shaped orifices. Because of the numerous well-known advantages of wet-spinning processes, it would be highly desirable to be able to spin such fibers by a wet-spinning process. However, when attempts were made to similarly modify wet-spinning processes, particularly ones wherein coagulation was effected by leaching solvent out of the extrudate with a cold aqueous coagulant, fibers of substantially circular cross-sectional configuration were still produced. Perhaps this anomalous result arises because coagulation is a much slower process when solvent has to be leached out of the extrudate as compared to evaporation of solvent or cooling molten polymer.

Accordingly, it is an object of the present invention to provide a wet-spinning process for preparing filaments of diversiform cross-sectional configuration. It is a further object of this invention to provide a wet-spinning process for forming such fibers of acrylonitrile polymers by suitable and minimal modifications to existing wet-spinning processes involving extruding solutions of acrylonitrile polymers into cold aqueous coagulating liquids.

These objects, and others as will appear or become evident from this specification, are mainly obtained by (a) use of a spinnerette of low thermal conductivity having orifices of diversiform cross-sectional configuration in combination with (b) withdrawing the freshly formed coagulum (into which the extrudate is converted by the cold aqueous coagulating liquid) at a linear rate in excess of 0.5 times the average linear velocity with which the polymer solution passes through said orifices.

While the present invention is not limited to spinning fibers of any particular diversiform cross-sectional configuration, numerous such shapes for fibers and spinnerette orifices are known and illustrated in such U.S. Pats. as Nos. 1,773,969; 1,964,659; 2,000,388; 2,508,799; 2,302,555; 2,746,839; 2,637,893; 2,816,349; 2,825,120; 2,831,748; 2,838,365; 2,939,201, 2,939,202; 3,017,686; 3,077,633; 3,097,416; 3,109,195; 3,117,906; 3,131,428; 3,156,085; and 3,204,290. In the practice of the present invention, the spinnerette orifices may have any of such diversiform cross-sectional configurations as may be appropriate to the cross-sectional configuration of the fibers to be spun therethrough.

It must be recognized, however, that the cross-sectional configurations of the fibers produced in accordance with the present invention are not necessarily identical to the cross-sectional configurations of the orifices through which they are spun, since, depending upon other conditions, there is a variable tendency for the extrudate to assume a cross-sectional configuration during coagulation which is rounder or more compact than the orifices through which extrusion occurred.

For wet-spinning acrylonitrile polymers, numerous solvents are known. Illustrative of commercially utilized solvents are concentrated aqueous salt solutions of zinc chloride or sodium thiocyanate, concentrated nitric acid solution, and dimethylacetamide although numerous others can be found in such U.S. Pats as Nos. 2,140,921; 3,124,629; 2,698,646 through 2,698,649; 2,558,730 through 2,558,735; 2,790,700; and many others. To form fibers, solutions of acrylonitrile polymers in such solvents are normally extruded into aqueous coagulants which may be water, dilute aqueous solutions of the same materials which are solvents for acrylonitrile polymers when more concentrated or substantially anhydrous, or dilute aqueous solutions containing other materials.

When wet-spinning into aqueous coagulants, it has generally been found important to keep the coagulant cold to convert the extrudate into a clear, strong, flexible coagulum which could be dried to form fibers relatively free of porosity. As pointed out in Craig et al. "Characterization of Acrylic Fiber Sturcture" Textile Research Journal, Vol. 32 No. 6, June 1962, pages 435–448, commercial wet-spinnings of acrylonitrile polymers have long utilized cold aqueous coagulants for this reason.

In such spinning systems, the simple substitution of metal spinnerettes with orifices of diversiform cross-sectional configuration for the metal spinnerettes with circular orifices still yielded round fibers. Thus, until the present invention, it was believed that the highly desirable fibers of diversiform cross-sectional configuration could not be produced by wet-spinning into cold aqueous coagulating liquids. Surprisingly, we have found that such fibers can be formed by the process of the present invention.

In the practice of the process of present invention, it is essential that the spinnerette be of low thermal conductivity. Illustrative of materials of low thermal conductivity of which spinnerettes can be made are plastic materials (e.g. epoxy resins, formaldehyde resins, polyesters, polyamides, polytetrafluoroethylene, etc.), ceramics, and glass. We have found that metal spinnerettes, such as are usually used for wet-spinning synthetic fibers of circular cross-section and for dry-spinning or melt-spinning synthetic fibers of circular or diversiform cross-sectional shapes, have too high a thermal conductivity to be useful for the present invention.

In the practice of the process of the present invention, it is also essential that the extrudate prior to becoming and as a

nascent coagulum, formed upon extruding the fiber-forming polymer solution directly into the cold aqueous coagulating liquid, be withdrawn from the coagulating liquid at a linear velocity at least 0.5 times the average linear velocity of the polymer solution passing through the spinnerette orifices. In other words, it is essential that the "jet stretch" be at least 0.5X. At jet stretches below about 0.5X, even with spinnerettes of low thermal conductivity, there is too great a tendency for the coagulum to assume a circular cross-sectional configuration. We have found that, other things remaining constant, the higher the jet stretch the less the fiber cross-section deviates from the cross-sectional shape of the spinnerette orifice. The upper limit of jet stretch useful herein is a function of factors extrinsic to the present invention. Obviously, one cannot utilize a jet stretch so high that the freshly forming coagulum breaks. We have found that jet stretches above about 2.0X tend to produce undesirable fiber properties in the final product. To achieve good balance of cross-sectional configuration retention and fiber properties, jet stretches between 0.7X and 1.5X are generally preferred for wet-spinning processes utilizing the present invention.

Except for the aforementioned modifications, the present invention makes use of conventional wet-spinning process technology. Known techniques may be utilized for preparation of the solutions of fiber-forming polymers and for forwarding such solutions to the spinnerette orifices. Also, known techniques for treating the freshly formed coagulum may be utilized for converting it into a fiber suitable for its intended uses. For example, the coagulum formed upon extrusion of an acrylonitrile polymer into a cold aqueous coagulant may then be stretched while still in the wet gel form and containing solvent, washed free of solvent, further stretched at elevated temperature, dried in a relaxed free-to-shrink condition, steam relaxed, etc. as is well known in making fibers of circular cross-section. Alternatively, it may be subjected to any other known processing sequence.

For a more detailed understanding of the present invention, reference may be had to the following examples illustrative of a preferred embodiment thereof. In these examples, all compositions are expressed in weight percentages unless otherwise stated.

The "relative viscosity" (Nr) of each acrylonitrile polymer solution used may be determined in accordance with the procedure published in the Journal of Polymer Science, Part A, Vol. 3, pages 1,359–1371 (1965) where

$$Nr = \frac{\text{absolute solution viscosity at 30° C. (in poises)}}{\text{absolute solvent viscosity at 30° C. (in poises)}},$$

Generally, polymer solutions whose relative viscosities are between about 50 and about 20,000 are utilized for wet-spinning processes. The "dope consistency index" (I) of such a solution may be calculated by the following formula

$$I = \log_{10} [C^5 \times M^{3.4}]$$

wherein C = polymer concentration in solution in grams/cc. and M = weight average molecular weight of polymer. When a concentrated aqueous sodium thiocyanate solution is utilized as the solvent for the acrylonitrile polymer, a dope consistency index of between about 10.5 and about 15.0 represents a relative viscosity of between about 50 and about 20,000. The "aspect ratio" of a generally rectangular cross-sectional configuration (whether of a spinnerette orifice or of a fiber) is calculated by dividing the length of the rectangle by its width.

EXAMPLE 1

An acrylonitrile polymer (89.2 percent acrylonitrile, 10.8 percent methyl methacrylate) was dissolved in a 40 percent aqueous sodium thiocyanate solution to form a spin dope containing 11.3 percent polymer and having a dope consistency index of 13.061. This spin dope was heated to 60° C. and extruded through an epoxy resin spinnerette provided with orifices of rectangular cross-section measuring 2.3 mils × 14.6 mils (aspect ratio = 6.35) into a cold aqueous coagulating liquid which was a 10 percent solution of sodium thiocyanate maintained at about −2° C. The thus formed filamentary coagulum was withdrawn from the bath at a linear velocity of 1.2 times the average linear velocity of the spin dope through the spinnerette orifices (jet stretch = 1.2X). Thereafter, this filamentary coagulum was stretched to two times its original length, washed with water until free of sodium thiocyanate, restretched to about 6 times its previous length in water at about 100° C., dried in a relaxed free-to-shrink condition under controlled temperature and humidity conditions (as described in U.S. Pat. No. 2,984,912), and then relaxed about 36 percent in pressurized steam. The thus formed fibers had good textile properties and an average aspect ratio of about 3.0. This example illustrates a preferred embodiment of the present invention.

EXAMPLE 2

The process of Example 1 was repeated using the same plastic spinnerette except that the jet stretch was reduced to 0.5X. The fibers so produced had good textile properties with an average aspect ratio of about 1.7. This example (when compound with Example 1) illustrates the functional relationship between jet stretch and degree of fiber cross-sectional modification. This is about the minimum aspect ratio useful for modifying yarn and fabric esthetics.

EXAMPLE 3

The process of Example 2 was repeated using a jet stretch of 0.5X except for the substitution of a platinum-rhodium spinnerette provided with orifices of rectangular cross-section measuring 2.4 mils × 15.6 mils (aspect ratio = 6.5). The fibers so produced were essentially round in cross-section. This example (when compared with Example 2) illustrates the criticality of using spinnerettes of low thermal conductivity in obtaining fibers of diversiform cross-sectional configuration at jet stretches near the low end of the range useful for the present invention.

EXAMPLE 4

The process of Example 3 was repeated using the same metal spinnerette except that the jet stretch was raised back up to 1.2X. No fibers could be obtained due to breakage of all filaments at the face of the spinnerette. This example (when compared with Example 1) also illustrates the criticality of using spinnerettes of low thermal conductivity in obtaining fibers with higher jet stretches. Under the spinning conditions of Example 1, when using metal spinnerettes, the maximum jet stretches obtainable were found to be about 0.5X whereas, with plastic spinnerettes, jet stretches exceeding 2.5X were possible. However, with plastic spinnerettes, some losses in textile properties were observed when jet stretches above about 2.0X were used.

EXAMPLE 5

The process of Example 1 was repeated using the same plastic spinnerette (orifice aspect ratio = 6.35) but with variations in (a) jet stretch and (b) coagulating liquid concentration. Four runs were made, viz., Run A using a jet stretch of 0.8X through a cold aqueous coagulating liquid of 6 percent sodium thiocyanate solution to yield fibers having an average aspect ratio of about 2.5; Run B using a jet stretch of 1.6X through the same 6 percent solution to yield fibers having an average aspect ratio of about 4.0; Run C using a jet stretch of 0.8X through a cold aqueous coagulating liquid of 18 percent sodium thiocyanate solution to yield fibers having an average aspect ratio of about 2.2; and Run D using a jet stretch of 1.6X through the same 18 percent coagulating solution to yield fibers having an average aspect ratio of about 3.4. All these fibers had good textile properties. This example (especially when taken with Examples 1 and 2) illustrates the effects of

variations in jet stretch and coagulant concentrations to be expected in practicing this invention and illustrates the wide range over which some variables can vary.

EXAMPLE 6

Separate spin dopes were prepared by dissolving acrylonitrile polymers (89.2 percent acrylontrile, 10.8 percent methyl methacrylate) in 40 percent aqueous sodium thiocyanate solutions to form (a) an 8.4 percent polymer solution having a dope consistency index of 12.3,410 and (b) a 14.0 percent polymer solution having a dope consistency index of 13.5,905. Each spin dope was heated to 80° C. and extruded, in separate runs, through epoxy resin spinnerettes provided with orifices of rectangular cross-section measuring either (a) 3.0 mils × 15 mils (aspect ratio = 5.00) or (b) 2.4 mils × 19.9 mils (aspect ratio = 8.3) into a 12percent aqueous sodium thiocyanate coagulating both maintained at about −4° C. In each run, the thus formed filamentary coagulum was subjected to a jet stretch of 1.2X and thereafter treated as in Example 1 to produce four separate fiber products. The four runs made were Run E spinning the 8.4 percent polymer solution through orifices of 5.00 aspect ratio to yield fibers having an average aspect ratio of about 1.8; Run F spinning the 14.0 percent polymer solution through orifices of 5.00 aspect ratio to yield fibers having an average aspect ratio of about 2.2; Run G spinning the 8.4 percent polymer solution through orifices of 8.3 aspect ratio to yield fibers having an average aspect ratio of about 3.4; and Run H spinning the 14.0 percent polymer solution through orifices of 8.3 aspect ratio to yield fibers having an average aspect ratio of about 4.4. All these fibers had good textile properties. This example illustrates the effects of variations in orifice configuration and spinning solution consistency index to be expected in practicing this invention.

EXAMPLE 7

An epoxy resin spinnerette provided with +-shaped orifices of about 115,000μ^2 cross-sectional area was used to spin a spin dope substantially the same as was spun in Example 1 under substantially the same spinning conditions as in Example 1 except that the jet stretch was 1.17X, the restretching was about 6.25X, and the final relaxation step was omitted. The thus formed fibers had a generally squarish cross-sectional shape with wavy sides. This example illustrates the spinning of a fibers of a different diversiform cross-sectional configuration than the preceding examples.

EXAMPLE 8

An epoxy resin spinnerette provided with Y-shaped orifices of about 90,000μ^2 cross-sectional area was used to spin a spin dope substantially the same as was spun in Example 1 in three separate runs under substantially the same spinning conditions as in Example 1 except that the jet stretches were 1.33X, 1.0X, and 0.75X in the three runs, the restretching was about 6.25X and the final relaxation was in water at about 100° C. The thus formed fibers ranged in cross-sectional configuration from substantially the same shape as the orifices through "arrow head" cross-sections and substantially triangular cross-sections with wavy sides to gibbous triangular cross-sections with decrease in jet stretch. This example illustrates production of fibers of yet another diversiform cross-sectional configuration and the variation of shape produced as a function of jet stretch with the higher jet stretches yielding fibers whose cross-sectional configuration more closely resembled the cross-sectional configuration of the orifices through which they had been spun.

It will be appreciated by those skilled in the art to which the present invention pertains that many modifications of this invention can be made without departing from the spirit thereof. It is intended that all modifications as are included in the foregoing description or are made obvious thereby are to be considered as encompassed within the scope of the subjoined claims.

We claim:

1. A process for wet-spinning filaments of diversiform cross-sectional configuration comprising; extruding a hot fiber-forming acrylonitrile polymer solution in aqueous solution of a solvent-forming salt or organic solvent through orifices of diversiform cross-sectional configuration in a spinnerette of low thermal conductivity directly into a cold aqueous coagulating liquid within which said orifices are disposed to coagulate said acrylonitrile polymer by leaching solvent out of the extrudate so produced while simultaneously and continuously withdrawing the resulting coagulum from said coagulating liquid at a linear velocity at least 0.5 times the average linear velocity of said polymer solution through said orifices but below that at which the freshly forming coagulum breaks.

2. A process as defined in claim 1 wherein said polymer solution comprises an acrylonitrile polymer dissolved in a concentrated aqueous solution of a solvent-forming salt at about 60° C. to about 80° C. and said coagulating liquid comprises a dilute aqueous solution of the same salt maintained at a temperature below about +10° C.

3. A process as defined in claim 2 wherein said salt is zinc chloride or a water-soluble thiocyanate.

4. A process as defined in claim 1 wherein said coagulum is withdrawn from said coagulating liquid at a linear velocity of between 0.5 and 2.0 times the average linear velocity of said polymer solution through said orifices.

5. A process as defined in claim 1 wherein said coagulum is withdrawn from said coagulating liquid at a linear velocity of between 0.7 and 1.5 times the average linear velocity of said polymer solution through said orifices.

6. A process as defined in claim 1 wherein said spinnerette comprises a plastic material which is inert to said polymer solution and said coagulating liquid.

7. A process as defined in claim 6 wherein said plastic material is an epoxy resin.

8. A process as defined in claim 3 wherein said polymer solution has a dope consistency index of between 10.5 and 15.0.

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