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3,097,415

ACRYLONITRILE FIBER AND PROCESS FOR PREPARING SAME

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This invention relates to the preparation of new and useful acrylonitrile fibers. More particularly, this invention relates to the preparation of void-free fibers of acrylonitrile polymers and copolymers possessing a high level of shrinkage.

Acrylonitrile polymer fibers having some shrinkability have been known for some time. However, fibers having a high level of shrinkability, i.e., on the order of about 35% and higher, which possess the desirable properties of conventional acrylonitrile fibers have heretofore been unknown. Attempts to produce such fibers having the softness of hand, high weather resistance, high chemical resistance, and a consolidated structure free from internal voids have not met with success. Maintenance of the consolidated structure has proved to be one of the most difficult problems.

The void-containing fibers heretofore produced have not been found to be completely satisfactory. Due to their porous structure they tend to absorb finishing oils and other treating agents. When these agents leave the surface of the fibers, they are no longer available to impart the desired properties, e.g., antistatic properties and the like, to the fibers. The end result is that problems are encountered in processing the fibers. Moreover, in some types of fabric construction, it is important that the fibers have a non-porous structure. The porosity of a porous fiber and, hence, its opacity may be affected by later treatments such as washing and ironing. As a result, fabrics prepared from such fibers exhibit undesirable color and luster changes during use.

It is, therefore, an object of this invention to produce acrylonitrile fibers possessing high shrinkability. It is another object of this invention to produce fibers of high shrinkability which have a consolidated structure. Still another object of this invention is to provide a process for the production of fibers having the desired high shrinkage and consolidated structure. Other objects will appear hereinafter.

The objects of this invention are accomplished by treating an undrawn, dry, solvent-free acrylonitrile fiber with a hot aqueous medium and thereafter drawing the fiber from about 1.5 to 2.5 times its original length.

By "dry fibers" it is meant those fibers which have a water content of less than 10%. By "solvent-free" it is meant those fibers from which a sufficient quantity of the spinning solvent has been removed that the amount remaining will not interfere with normal usage of the fiber, that is those fibers which possess about 3% or less of the original solvent. By "undrawn fibers" is meant those fibers which have been given no appreciable permanent stretch. If the original fiber from the spinning machine is extracted in the form of its spun package in order to remove spinning solvent, it will have no stretch whatsoever. If, on the other hand, the original spun yarn is unwound

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from its spinning package and is passed continuously through an extraction bath in order to remove solvent, or is passed through an extraction bath immediately after it leaves the spinning machine in order that solvent may be removed, a slight stretching may result. This is due to the fact that sufficient tension must be maintained on the fiber for proper winding. Fibers so prepared are meant to fall within the definition of "undrawn fibers."

Several methods are available to indicate whether a fiber has a consolidated or void-free structure. For example, U.S. Patent 2,451,420 to Watkins utilizes the area ratio or the ratio of measured fiber area to calculated fiber area as a means for showing the type of structure. A low area ratio is indicative of a consolidated structure. Fiber density is also a good indication of the degree of consolidation of the structure provided that only those fibers of the same chemical make-up are compared. For a given polymeric species, the higher density will indicate the more void-free structure. However, a fiber prepared from an acrylonitrile polymer made with a comonomer such as vinylidene chloride will have a higher density than one made from a copolymer of acrylonitrile with a corresponding amount of methyl acrylate. This requires extreme care in the handling of density data.

In defining the products of the present invention it has been found that the property of birefringence of the fibers may be conveniently used to accurately define their consolidated structure. This property has been found to be essentially independent of the composition of the polymers and copolymers within the scope of this invention. Unlike most fibrous materials, consolidated fibers of acrylonitrile polymers which have been given even a small degree of stretch to orient the molecules in the direction of the fiber length exhibit negative birefringence. The negative birefringence is apparently due to the high degree of polarizability of the nitrile groups which are oriented in the direction perpendicular to the fiber axis by the orientation of the polymer chain molecules along the fiber axis. Any degree of negative birefringence is indicative of an acceptable consolidated structure. In contrast, the oriented porous or void-containing acrylonitrile fibers exhibit positive birefringence. Methods for determining birefringence are well known. Descriptions of suitable methods may be found in Preston, "Modern Textile Microscopy," Emmott & Company, Ltd., London (1933), and Heyn, "Textile Research Journal," 22, 513 (1952).

In practicing this invention, the acrylonitrile fibers may be either wet- or dry-spun. The removal of the solvent is preferably accomplished by passing the spun fiber through an aqueous bath which is maintained at a temperature between room temperature and about 100° C. After reducing the solvent level to about 3% or less by weight, the filaments are dried, with temperatures between about 100° C. and about 130° C. being used to reduce the water content to less than about 10% by weight. While the extraction of the solvent may be accomplished using a relatively wide range of temperatures, it is imperative that the fibers remain essentially undrawn during such treatment, and that drying be accomplished within the range of temperatures indicated.

The dried fibers are then treated in a hot aqueous medium. As will be more fully demonstrated later herein, the dried fibers must be exposed to the hot aqueous

medium for a minimum period of at least about fifteen seconds. In addition, the temperature of the medium must be from about 96° C. to about 110° C. After the hot aqueous treatment, the fibers must be drawn from about 1.5 to 2.5 times their original length. The fibers so prepared have a consolidated or void-free structure and have a shrinkability of at least about 35%. Shrinking of the fibers may be accomplished by exposing the fabric in which they appear to a heated atmosphere as will be more fully described later herein.

The invention will be further illustrated by the following examples in which parts and percentages are by weight unless otherwise specified. The invention is not intended to be limited by the details set forth in the examples.

Example I

A multi-filament tow of acrylonitrile fibers was prepared by dry spinning a solution in dimethylformamide of a terpolymer of 94.0% acrylonitrile, 5.7% methyl acrylate, and 0.3% sodium styrenesulfonate. The size of the tow was 44,400 tex (400,000 denier), and the individual filament size was 0.44 tex (4 denier), both according to measurements on solvent-free samples. The solvent was extracted from the tow by passing it through a series of nine tanks containing aqueous extractant at 98° C. The aqueous extractant consisted of aqueous solutions of dimethylformamide, the tanks containing smaller amounts of dimethylformamide in the order in which they were contacted by the tow. The tow entered the extraction process at 70 yards per minute and was removed from the last tank at 94 yards per minute. It was then dried at 127° C. for eight minutes, after which it was found by analysis to have a water content of less than 1% and a dimethylformamide content of 1.4%.

The dry, solvent-free, essentially undrawn tow was then boiled in water for thirty minutes, after which it was fed into a stretching apparatus consisting of two flat parallel plates in contact with the tow surface, each plate measuring 14 inches in the direction of yarn travel and 10 inches in the direction perpendicular to the yarn travel. The plates were heated to a surface temperature of 118° C. and the tow was fed in at a speed of 23 yards per minute. The tow was collected at a speed of 43 yards per minute so that it was given a 90% stretch in the apparatus, that is it was stretched 1.9 times its original length.

A number of individual filaments from the drawn tow were examined and all were found to possess negative birefringence. According to measurements on five filaments, the average birefringence was -44 millimicrons. Other filaments taken from the tow were found to possess a shrinkage of 41.7% in boiling water and a shrinkage of 37.6% in dry heat at 143° C. They had a density of 1.183 grams/cc. After shrinkage in boiling water, the individual filaments were found to be 0.3 tex (2.7 denier per filament).

The major portion of the tow was crimped at 60° C. in a stuffer box type crimper and was then cut to 1¼ inch lengths on a cutter of the type described in U.S. Patent 2,747,663 to Cook. This staple was blended with varying amounts of 1.5-2.2 tex (14-20 denier) acrylonitrile staple fibers having a shrinkage in boiling water of less than 3%. These blends were converted to knit pile fabrics and the fabrics were then heat treated in the manner described by Bartovics et al. in U.S. Patent 2,815,558. The resulting fabrics were fur-like fabrics having guard hair effects.

Example II

A dry, solvent-free, essentially undrawn tow of acrylonitrile fibers was prepared as in Example I. This tow was boiled in water for five minutes and was then stretched 2.12 times its original length in water at 75° C. This product had 40% shrinkage in boiling water. All filaments examined showed negative birefringence. The fibers were found to have a density of 1.172 grams/cc.

Example III

This example is included to show the importance of the described sequence of operating steps in order to produce a product of the desired properties.

The spun tow of Example I still containing its solvent was stretched to 2.1 times its original length by passing it through a series of nine tanks containing aqueous solutions of dimethylformamide, the amount of dimethylformamide being smaller in each successive tank and being essentially zero in the final tank. The temperature of the liquid in the tanks was 70° C. The warm wet tow was passed immediately to a stuffer box type crimper and after crimping it was cut to 1¼ inch lengths. The cut staple was dried in an oven at 50° C.

The resulting product which contained less than 3% dimethylformamide had a filament size of 0.21 tex (1.9 denier). It showed 38% shrinkage in boiling water and 34.5% shrinkage at 143° C. under dry conditions. However, this product, though of the same chemical composition as that of the previous examples, had a density of only 1.138 grams/cc. and was positively birefringent, showing a birefringence of +31 millimicrons.

Example IV

A dry, solvent-free, essentially undrawn tow was prepared by continuously extracting a tow spun from the polymer of Example I. The extraction took place at 90° C. with an output speed of 125 yards per minute and with 34% stretch taking place within the process in order to maintain the proper amount of tension on the tow for ease in handling. The size tow obtained after extraction was 58,000 tex (520,000 denier). The individual filaments were 0.33 tex (2.9 denier). The extracted tow was dried at 127° C. for four minutes, after which time it contained less than 1% moisture and 1.4% dimethylformamide.

The dried tow was then passed through an aqueous dye bath held at 96° C., this aqueous bath containing 50 grams per liter of ethylene carbonate, 40 grams per liter of the dye, Brilliant Green Crystals (Color Index 662) and sufficient glacial acetic acid to give it a pH of 5. Immediately upon leaving the dye bath the tow passed through a tube containing atmospheric steam, the length of this tube being sufficient to give the tow an exposure of three minutes to the steam. The tow was then stretched to 1.9 times its original length between metal plates heated to 116° C. The dark green product obtained had a shrinkage of 38.8% in boiling water and showed negative birefringence. After crimping and cutting, the green staple was mixed with low shrinkage staple to produce pile fabrics which showed unusual surface effects after boiling because of the difference in shrinkage between the two fibrous ingredients.

Example V

The extracted dry tow of the previous example was drawn between heated plates in the manner of the previous example without having previously been passed through the dye bath and steaming tube. The drawing operation was difficult to perform due to broken filaments, and the resulting product showed less than 34% shrinkage.

In a series of other experiments, it was determined that the minimum contact time with hot aqueous fluid that was required in order to yield a product which, after stretching, had a shrinkage in excess of 35%, was fifteen seconds, and that the minimum temperature of this aqueous fluid was 96° C. Temperatures as high as 110° C. were not detrimental and times of exposure as high as three hours were found to be satisfactory. Hot water, hot aqueous solutions of common textile treating agents, and steam were all found to be satisfactory media for treatment of the undrawn fibers prior to stretching them.

Example VI

A 30-tex (270-denier) 30-filament acrylonitrile yarn was collected on a perforated spinning bobbin and was extracted on that bobbin with water at 95° C. until the solvent content was below 2%. This undrawn yarn was

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wound onto skeins which were dried in an oven at 100° C. for one hour. The skeins were then boiled for thirty minutes each with an aqueous solution containing an excess of the blue dispersed dyestuff Prototype 62. The yarns from the different skeins were permitted to dry at room temperature and were then stretched between heated plates with different draw ratios and different draw temperatures being used. It was found that plate temperatures between about 118° C. and about 138° C. were satisfactory. The drawing process was unsatisfactory outside of these limits due to excessive breakage. The samples drawn to 150% and 250% of their original length showed shrinkage values in boiling water between 35% and 36%. Samples drawn to less than 150% or to more than 250% of the original length had shrinkage values below 35%. The samples drawn to more than 150% showed increased shrinkage up to the sample which was drawn to 190% of its original length which had a shrinkage of 42%. Shrinkage then dropped off with increasing amount of stretch.

All of these samples were found to possess negative birefringence and densities greater than 1.180 grams/cc.

Although the practice of this invention has been illustrated in terms of dry-spun acrylonitrile fibers, it is equally applicable to those acrylonitrile fibers which have been wet spun. Like the dry-spun material, the wet-spun fiber must be solvent-free, dry, and essentially undrawn before it is given the treatment in the hot aqueous medium which is, in turn, followed by a low degree of stretch. A wide variety of acrylonitrile polymers may be used provided, of course, that they can be formed into filamentous articles capable of being stretched. Polyacrylonitrile may be used as well as copolymers containing at least about 70% acrylonitrile and up to about 30% of any neutral monoethylenically unsaturated monomer copolymerizable with acrylonitrile such as vinyl acetate, methyl vinyl ketone, methyl acrylate, methyl methacrylate, vinyl chloride, vinylidene chloride, as well as other such monomers of the type described in Jacobson U.S. 2,436,926. Small amounts, i.e., up to about 10%, of cationic and anionic monomers, such as sodium styrene sulfonate or 2-vinyl pyridine, may be present to give improved dye receptivity. For best strength, insolubility, and sunlight resistance, polymers of 85% or more acrylonitrile are usually employed.

The solvent used in spinning the fibers may be selected from any of those commonly used in spinning acrylonitrile polymers, e.g., dimethylformamide, dimethylacetamide, and dimethylsulfoxide.

With regard to the removal of solvent from the spun fiber, known extraction methods utilizing liquids are most desirable because they can be carried out without exposing the fiber to excessive heat. Although organic liquids may be used as extractants, water is by far the cheapest and most satisfactory material for this purpose. The extraction may be carried out by forcing water through packages of spun yarn or by placing packages, including skeins, of such yarns in aqueous baths. Extraction may readily be carried out by passing the continuous fibers continuously through aqueous baths. The speed of travel, the bath dimensions, and the number of baths may be varied as desired to bring the solvent content of the fiber to the desired level. Temperatures between room temperature and 100° C. may be used, and temperatures between 70° C. and 100° C. are preferred. The take-up speed in the extraction process may be greater than the input speed by amounts sufficient to maintain tension on the fibers. Normally, the take-up speed will be less than 1½ times the input speed.

As previously indicated, the drying process for the extracted undrawn fiber is critical. Temperatures in excess of 130° C. are to be avoided because they tend to cause discoloration of the fibers. Short times at temperatures near this level are not undesirable, however. Longer drying at temperatures as low as 100° C. may be used.

As stated previously, it is critical that the undrawn, sol-

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vent-free, dry fibers be exposed to an aqueous fluid at temperatures near the boiling point before the fibers are stretched. This fluid may be water, steam, or aqueous solutions of typical textile-treating agents such as dyes, detergents, softening agents, etc. The fluid must be between about 96° C. and about 110° C. Temperatures between about 96° C. and about 102° C. are preferred. The time of treatment may be from about fifteen seconds to about two hours, or more.

Following the treatment with hot aqueous fluid, the fibers must be stretched by about 50% to about 150%, that is, they should be stretched from about 1.5 to about 2.5 times their original length. If desired, the fibers may be dried between the boiling and stretching operations. For ease of operation, it is generally preferable to do so if the stretching operation is carried out in a non-aqueous medium.

As indicated above, the amount of stretch imparted to the fiber should be between about 50% and about 150%. The temperature to which the fiber is raised during the stretching operation should be the minimum temperature commensurate with satisfactory operation. When the stretching takes place in aqueous medium, a temperature of about 70° to 80° C. is sufficient. This temperature range is preferred, though operation within the wider range of 60° to 90° C. will generally be satisfactory. When the stretching takes place in hot air, as between heated plates, the air will be at a higher temperature than that used in the case of wet drawing. Plate temperatures of about 118° C. to about 138° C. have proven satisfactory. The temperature utilized will depend on the length of the heating zone and the speed of travel of the fiber through that zone. As indicated above, the minimum temperature which allows satisfactory operation of the drawing process is the temperature to be preferred.

If the high shrinkage fiber is to be utilized in filament form, it may be wound onto a package following the stretching operation. Application of some textile finishing oil will generally be desired prior to winding on the package. If the high shrinkage fiber is desired in staple form, it will generally be necessary to impart crimp to the fiber and then to cut it. Because of the inherent shrinkage of the fiber, the crimping operation should be carried out at the lowest convenient temperatures.

The fibers of this invention are useful in the form of knit fabrics, woven fabrics, and pile fabrics. In all cases, they can be utilized to produce desirable effects not obtainable by other means. When the high shrinkage fibers are blended with low shrinkage fibers, and the blends are converted into yarns, these yarns may be used to produce loosely constructed knit and woven flat fabrics which will shrink under the influence of boiling water or dry heat to produce fabrics having an unusual degree of bulk and cover due to the loops formed by the low shrinkage fibers when the high shrinkage fibers have shrunk.

As indicated earlier, the high shrinkage fibers are of particular value in the preparation of pile fabrics, particularly those of the artificial fur type. Many natural furs contain hairs of two different lengths. The under fur is composed of short-length hairs and longer, coarser guard hairs are also present. When the fibers of the present invention are blended with low shrinkage fibers, particularly low shrinkage fibers of a slightly heavier denier, the yarn from the blend can be converted to a pile fabric which is trimmed to constant pile height and is then exposed to conditions which bring about the shrinkage of the high shrinkage fibers. These then shrink to take on the appearance of the under fur of a natural fur while the coarser, low shrinkage fibers remain long and simulate the guard hairs.

It will be apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

I claim:

1. An improved textile fiber having a high resistance to penetration by liquid processing agents and a shrinkability in boiling water of at least 35%, said fiber formed of a solid organic synthetic polymeric composition comprising at least 75% polyacrylonitrile and up to 25% of ethylenically unsaturated monomers copolymerizable therewith, said solid composition having a void-free, highly consolidated, high density internal structure with a density of greater than 1.170 grams per cubic centimeter, a molecular orientation in the longitudinal direction corresponding to a drawn condition of from about 1.5 to about 2.5 times its original length, said composition exhibiting a detectable degree of negative birefringence, said fiber containing less than about 1.4% solvent.

2. The improved fiber of claim 1 in which said composition comprises at least 85% polyacrylonitrile and up to 15% of ethylenically unsaturated monomers copolymerizable therewith and which fiber possesses a shrinkability in

boiling water of at least 40%, and a water content of less than 10%.

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