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3,544,262

FIBERS OF ACRYLONITRILE-HYDROXY ETHYL METHACRYLATE POLYMER CROSS-LINKED BY PHOSPHORIC ACID

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ABSTRACT OF THE DISCLOSURE

An acrylic fiber with good hot-wet properties formed by heat-curing a phosphoric acid cross-linked fiber of a copolymer of at least 70% by weight of acrylonitrile and at least 4.5 mole percent of hydroxy ethyl methacrylate.

This invention relates to improved cross-linked acrylic fibers and, more particularly, to fibers of polyacrylonitrile which are especially adapted by virtue of their improved hot-wet dimensional stability to use in preparing fabrics having good shape retention characteristics. More specifically, it relates to the provision of cross-linked fibers by treating with aqueous phosphoric acid a fiber formed from a copolymer of at least 70 weight percent of acrylonitrile and at least 4.5 mole percent of hydroxyethyl methacrylate on the basis of acrylonitrile and then heat-curing the so-treated fiber.

Synthetic filamentary materials composed of polyacrylonitrile or copolymers of polyacrylonitrile containing at least 70% acrylonitrile have found wide textile usage due to their good abrasion resistance, high light stability, excellent dyeability and, when dry, good dimensional stability. For certain types of textile uses, however, particularly when wash-wear characteristics are required, other types of synthetic fibers such as polyesters or polyamides have been more desirable since they generally have better hot-wet properties. Fabrics and garments formed from fibers possessing good hot-wet properties are able to hold their shape and resist wrinkles when exposed to hot washing or dyeing operations. Conventional acrylic fibers, though possessed of desirable qualities in most respects, have relatively poor hot-wet properties. When exposed to hot-wet conditions, acrylic fibers tend to eventually elongate or stretch when weak forces are applied, such behavior being known as "creep." When exposed to stronger stretching forces under hot-wet conditions, acrylic fibers have relatively poor "elastic recovery" (i.e., the ability to recover their original length when the force is removed). Since good hot-wet characteristics are a prime prerequisite to the acceptance of a fiber for use in wash-wear garments, acrylics have not been widely accepted for such uses.

There have been several attempts to improve the hot-wet properties of acrylic fibers. It is known that homopolymeric acrylic fibers have lower creep than fibers prepared from copolymers and that the higher the comonomer concentration in the polymer, the higher the resultant creep. It has been suggested that fibers prepared from highly branched polymers exhibit slightly lower creep properties. At best, techniques involving branched polymers have resulted in only modest improvements in hot-wet properties at the expense of other properties such as loop elongation and dyeability. For example, copolymers of acrylonitrile and acrylamide may be formed into fibers and cross-linked with formaldehyde, etc., but are not useful in textile products due to their very low loop elongation properties.

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It is an object of the present invention to provide a fiber of polyacrylonitrile with good hot-wet properties. It is another object of this invention to provide an acrylic fiber with high elastic recovery and good resistance to hot-wet creep. It is further an object of the present invention to provide improved acrylic fibers which are useful in making fabrics and garments which may be exposed to hot-wet conditions with improved shape retention. It is a still further object to provide a process for preparing such improved fibers.

In accordance with this invention, these and other objects are accomplished by treating a fiber formed from a copolymer consisting of at least 70 weight percent of acrylonitrile and at least about 4.5 mole percent of hydroxy ethyl methacrylate (HEMA) on the basis of total monomers, with an aqueous solution of phosphoric acid and curing said fiber with heat whereby intermolecular cross-linking is accomplished.

The fibers of the present invention can be obtained from any copolymers of acrylonitrile as prepared by known methods, many being described in U.S. Pat. 2,626,946. It is critical, however, that the copolymer have about 4.5 to 7.5 mole percent of hydroxy ethyl methacrylate comonomer. Polymerization with acrylonitrile is carried out through the vinyl group, thus leaving the hydroxyl group unreacted. The copolymer may also contain other ethylenically unsaturated materials in addition to the HEMA. It has been found that copolymers containing less than 4.5 mole percent HEMA comonomer have insufficient sites for cross-linking, while copolymers containing in excess of 7.5 mole percent are difficult to spin since the high HEMA content results in a water-laden polymer which is too weak to hold its fiber form without breaking.

Fibers are formed from said copolymers by any of the spinning processes known to the art such as the so-called "wet," "dry" or "semi-melt" techniques. A wet-spinning technique is preferred wherein said copolymer is dissolved in an aqueous solvent for the polymer, such as concentrated aqueous sodium thiocyanate. The resultant spinning dope is passed through a spinnerette into a bath which is a non-solvent for the polymer, thus forming a gel which is further washed to remove solvent, and stretched to impart orientation and strength. The stretched fibers may be relaxed; either while wet or in a dried state, to relieve internal stresses. The stretched fiber is treated by applying to it an aqueous solution containing between 1% and 10% phosphoric acid by preferably between 1% and 5% phosphoric acid. Finishing agents, such as anti-static or softening agents, may also be added to the aqueous solution, if desired. Any method may be used to apply such agents such as by passing the fiber through a solution; or by boiling the fiber in the solution or by spraying or padding it with solutions of the desired finishing agents. The fibers so treated are then heated to between 50° C. and 150° C. to cause the cross-linking reaction. The higher the temperature, the shorter the time required. Curing may be accomplished with the fibers in a dry or wet state. Thus, if desired, the fibers may be dried and then cured or cured while wet and then dried. The conditions or treatment may be chosen so that varying degrees of cross-linking will take place.

The successfully cross-linked fibers of the present invention may be characterized by partial or complete insolubility in conventional hot solvents for acrylic fibers, such as dimethyl formamide. The fibers of this invention and the process for preparing them should not be confused with methods of improving the hot-wet properties of cellulosic fibers disclosed in U.S. Pat. 3,102,773 which generally involves impregnating a cellulosic fabric with a cross-linking agent. When such techniques are used with

acrylic fibers, no improvement in hot-wet properties is obtained. The fibers of the present invention are not only permanently improved in hot-wet properties, but maintain their original properties of a soft hand, good color and dyeability.

As briefly described above, it is desirable to form wash-wear fabrics from fibers having good hot-wet properties so that when the fibers are exposed to hot aqueous conditions and subjected to low stresses such as those due to agitation in a washing machine, the fiber will tend to resist creeping, i.e. resist stretching, elongating, deformation or distortion. If larger forces such as those encountered in dyeing operations, cause stretching or distortion of the fibers or fabric, then internal stresses should be introduced which tend to return the fibers to their original shape, i.e., the fiber should have elastic recovery. The following tests are designed to measure these properties of fibers.

"Creep" is measured by mounting in a clamp, both ends of a 12 to 14 cm. length of fiber whose denier is predetermined to form a loop, from which a weight (calculated in water at 23° C. to be .1 gm./denier), is hung. The length of the loop is determined by means of a cathetometer. The fiber and weight are immersed in hot water with the moment of immersion taken as 0 time. The length of the loop is measured after one minute, hereafter referred to as (E_1), and again after 10 minutes, hereafter referred to as (E_{10}), such measurements characterizing therefore the amount of stretch occurring after one minute and after 10 minutes. Creep is defined as the simple difference between E_{10} and E_1 , e.g. $E_{10}-E_1$ =creep. The creep is further stipulated by the temperature of the water at which it is measured. By this test, acrylic fibers generally have a creep 2 to 6 times greater than that of polyester fiber depending on the temperature of the water.

Hot-wet "elastic recovery" is determined by a test wherein the ends of a single filament are fixed between two clamps located a measured distance apart from each other. The clamped fiber is placed in water at 70° C., for one minute after which it is elongated 15% of its original length over a one-minute period and held at this length for one minute, after which it is relaxed and allowed to recover for a pre-determined length of time. After the recovery period, the fiber is brought to a taut, no tension position, and the length then determined. The predetermined recovery time is varied from one minute to 10 minutes to obtain recovery as a function of time. The elastic recovery is calculated as follows; i.e.,

$$\text{Elastic recovery} = \frac{[(L_o + .15L_o) - L_F] \times 100}{L_o + .15L_o}$$

wherein

L_o =Original length

L_F =Final length

The following examples and descriptions will serve to exemplify some of the embodiments of the present invention but should not be considered to be limiting with respect to the scope of the invention.

EXAMPLE 1

A copolymer of acrylonitrile and 5.7 mole percent hydroxyethyl methacrylate was prepared by slurry polymerization using a chlorate-sulfite redox catalyst in dilute

nitric acid. The copolymer was dissolved in aqueous sodium thiocyanate (1 part NaCNS and 1 part water) and wet-spun in the conventional manner by passing the solution through a spinnerette into a bath containing dilute aqueous NaSCN to form a filament gel, thereafter working the gel with water, stretching linearly 10× the original length, drying the fiber and relaxing the dried fiber at an elevated temperature. The fiber so produced was readily soluble in hot DMF, and, thus, was not cross-linked. Loop properties were measured to be 1.8 g./denier with a breaking elongation of 28%.

The creep of this fiber at 90° C. wet when measured by the previously described test was $E_{10}-E_1=8.5$, indicating poor stability under hot-wet conditions. The hot-wet elastic recovery, determined by the above described test, ranged between 81.5% and 87.3% from 1 to 10 minutes, respectively. Commercially available Orlon 42 acrylic fiber measured under the same conditions, showed a creep of 6.9 and an elastic recovery of 57.5% to 67.0%.

The above-described test sample was further treated with an aqueous solution containing 0.0885 part formaldehyde and sufficient sulfuric acid to adjust the solution to pH=1.8 at 60° C. for 3 minutes, after which the fibers were squeezed to 2× their original dry weight and redried to about 10% moisture at 75° C. to 80° C., then cured in dry heat at 150° C. for 10 minutes. The sample was no longer soluble in hot DMF, thus proving that cross-linking had occurred. The hot-wet properties of the formaldehyde cross-linked polymer were measured. The hot-wet creep was reduced to 2.6 and the elastic recovery was improved to a range of 83.7% to 91.3% over the 1-minute to 10-minute period. However, loop properties of this fiber had been reduced to only 0.87 g./denier and only 3.5% breaking elongation.

It is clear from the foregoing that although vast improvements in hot-wet properties can be made by cross-linking the preferred copolymer with conventional cross-linking agents, the resulting loop properties are degraded to a point which makes the fiber useless for textile purposes.

EXAMPLE 2

To show properties of the improved product of the present invention, a copolymer of acrylonitrile and 7.4 mole percent hydroxy ethyl methacrylate was made and spun into fiber as in Example 1 with the single exception that the stretched, undried gel was relaxed in boiling water for 5 minutes prior to drying at 127° C. In a series of separate experiments, dried fibers were treated by soaking them for 3 minutes in aqueous solutions of phosphoric acid at 60° C., after which they were squeezed to 1.6× their original dry weight, dried at 80° C. to approximately 10% moisture, and then cured in dry heat at 130° C. to 150° C. for 10 minutes. The concentration of phosphoric acid in the aqueous solution was varied from 1% to 5%. In all cases, cross-linking was obtained as indicated by insolubility of the treated fibers in hot DMF. The specific treatment conditions and resulting fiber properties are illustrated in Table I.

TABLE I

Run No.:	Conc. H ₃ PO ₄ (percent)	Cured for 10 min. at, ° C.	Loop ten. g./den.	Percent elong.	Creep 90° C.	Elastic recovery at—			
						1 min.	3 min.	5 min.	10 min
1-----	0.0	130	2.73	44.0	(1)	(1)	(1)	(1)	(1)
2-----	1.0	130	1.96	31.5	4.1	85.9	83.5	88.9	83.6
3-----	1.0	150	1.62	21.5	4.5	-----	-----	-----	-----
4-----	2.5	130	1.84	26.0	3.8	-----	-----	-----	-----
5-----	2.5	150	1.23	18.5	2.9	-----	-----	-----	-----
6-----	5.0	130	1.31	21.5	3.4	-----	-----	-----	-----
7-----	5.0	150	1.34	22.5	3.4	-----	-----	-----	-----

¹ Not measured—should be similar or higher than untreated fiber of Example 1, i.e. greater than 8.5.

Surprisingly, the fiber of Example 1, when cross-linked with phosphoric acid instead of formaldehyde, retains the advantages of reduced creep and high recovery, but, in addition, also retains a good proportion of the original loop properties and is thus useful for textile

purposes. The basic and disperse dyeability of the cross-linked fiber was essentially identical to that of the un-cross-linked control.

EXAMPLE 3

A fiber containing 5.8 mole percent hydroxy propyl methacrylate was prepared and cross-linked as in Example 1 with formaldehyde. Successful cross-linking was obtained as indicated by insolubility in hot DMF. It had the following properties:

TABLE II

Sample	Loop properties		Elastic recovery (70° C.)	Creep (90° C.)
	Ten. (g./d.)	Percent elong.		
Untreated.....	1.97	26.0	81.2-88.5	7.4
Treated.....	0.45	2.0	82.4-86.8	1.6

This shows that the formaldehyde-treated fiber gained hot-wet properties, but was nevertheless useless as a textile fiber due to poor loop properties.

EXAMPLE 4

When a fiber containing 4.7 mole percent hydroxy propyl methacrylate was made and treated in accordance with Example 2 at 1.0% and 2.5% aqueous phosphoric acid, the fiber was found to have the following properties:

TABLE III

Sample	Loop properties		Creep at 90° C.
	Ten. (g./den.)	Percent elong.	
Untreated.....	1.72	24.5	5.4
1% H ₃ PO ₄ *.....	1.90	30.5	5.6
2.5% H ₃ PO ₄ *.....	1.49	22.5	5.5

* Cured at 130° C. for 10 minutes.

It can be seen from the above data that, surprisingly, no improvement in hot-wet creep was obtained, in spite of the fact that the treated samples were cross-linked and insoluble in hot DMF.

We claim:

1. A fiber of a copolymer of at least 70% by weight of acrylonitrile and at least 4.5 mole percent of hydroxy ethyl methacrylate cross-linked by phosphoric acid, said fiber being insoluble in hot dimethyl formamide and having good hot-wet properties.

2. A fiber as defined in claim 1 wherein said copolymer comprises at least 70% by weight of acrylonitrile and between 4.5 and 7.5 mole percent of hydroxy ethyl methacrylate.

3. A process for preparing acrylic fibers useful for making textile products having good hot-wet properties comprising:

(a) spinning a copolymer of at least 70% by weight of acrylonitrile and between 4.5 and 7.5 mole percent of hydroxy ethyl methacrylate to form fibers;

(b) applying to said fibers an aqueous solution of phosphoric acid; and thereafter

(c) heating the thus treated fibers to a temperature and for a time sufficient to effect cross-linking of the polymer molecules in said fibers.

4. A process as defined in claim 3 wherein said aqueous solution of phosphoric acid has a concentration of 1.0% to 10.0%.

5. A process as defined in claim 3 wherein said thus treated fibers are heated to between 50° C. and 150° C.

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