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DRY SPINNING PROCESS

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This invention relates to a process for improving the properties of filaments derived from hydrolyzed olefin/vinyl organic ester interpolymers.

Hydrolyzed olefin/vinyl organic ester interpolymers are conveniently converted to filaments by dissolving the hydrolyzed interpolpolymer in a solvent, e. g., a trichloroethylene-ethanol mixture, a primary aliphatic alcohol, a primary or secondary aliphatic amine, and thereafter spinning the resultant solution. While filaments are thus produced readily, said filaments have limited utility on account of the fact that they tend to be brittle and have relatively low tenacities.

This invention has as an object the provision of hydrolyzed ethylene/vinyl organic ester interpolpolymer filaments which have been spun from solution and which have improved properties, particularly high tenacities and decreased brittleness. Additional objects will become apparent from the following description and claims.

These and other objects and advantages are accomplished according to the herein described invention which broadly comprises heating for a period of at least 5 hours at a temperature within the range of from its sticking temperature to 20° C. below said sticking temperature in a taut condition, a filament, previously spun from solution, of a substantially completely hydrolyzed interpolpolymer of ethylene with a vinyl ester of a monocarboxylic acid having the general formula RCOOH , wherein R is of the group consisting of hydrogen atoms and hydrocarbon radicals, said acid being free from unsaturated linkages between acyclic carbon atoms and any carbon atom alpha to the carbon atom in the carboxyl group of said acid being attached to at least one but not more than three carbon atoms, the mol ratio of ethylene to vinyl organic ester prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter drawing the treated filament at least 100% of its original length.

A preferred embodiment of this invention comprises spinning from solution a substantially completely hydrolyzed ethylene/vinyl acetate interpolpolymer, the mol ratio of ethylene to vinyl acetate in said interpolpolymer prior to hydrolysis having been within the range of from 2/1 to 4/1, and immediately thereafter heating said filament for a period within the range of from 5 hours to 8 hours at a temperature within the range of from its sticking temperature to 10° below said sticking temperature, and then within two days

drawing the resultant filament at least 100% of its original length.

The following example, in which proportions are in parts by weight unless otherwise specified, is given for illustrative purposes and is not intended to place any restrictions on the herein described invention:

Example

An interpolpolymer of ethylene and vinyl acetate (of molar ratio of ethylene to vinyl acetate of 2.5/1) was prepared by the controlled addition of ethylene at about 1000 atm. pressure and at about 65° C. to vinyl acetate containing a small amount of benzoyl peroxide catalyst. The ethylene/vinyl acetate interpolpolymer was hydrolyzed in a benzene-methanol solution with excess caustic and the interpolpolymer was washed free of caustic and dried. A solution was prepared by dissolving 250 parts of the hydrolyzed ethylene/vinyl acetate interpolpolymer in a mixture of 1000 parts of trichloroethylene and 275 parts of ethanol. This solution, which had a viscosity of 50 poises at 60° C., was spun through a multi-hole spinneret into a heated tube so that the solvent was removed from the filaments by passage through the tube. This yarn lacked strength and was shown by X-ray diffraction patterns to be unoriented.

A portion of the unoriented yarn was heated at fixed length in air in an oven at a temperature of 105–110° C. for 24 hours. It was then drawn in saturated steam at atmospheric pressure at a draw ratio of 8.33/1 to give an oriented yarn which had a tenacity of 5.4 g./d. at 7% elongation.

When a portion of the yarn was oriented by stretching in saturated steam at atmospheric pressure at the maximum draw ratio which could be employed (7.5/1) but without any preheating, the drawn yarn had a tenacity of only 4.1 g./d. at 8% elongation.

The process of this invention is applicable to any hydrolyzed interpolpolymer of ethylene with a vinyl ester of an organic acid having the general formula RCOOH , wherein R is of the group consisting of hydrogen atoms and hydrocarbon radicals, said acid being free from unsaturated linkages between acyclic carbon atoms and any carbon atom alpha to the carbon atom in the carboxyl group of said acid being attached to at least one but not more than three carbon atoms, provided the mol ratio of ethylene to vinyl organic ester in said interpolpolymer prior to hydrolysis was within the range of from 1/1 to 5/1.

Included among examples of said interpolymers are interpolymers of ethylene with vinyl formate, with vinyl acetate, with vinyl propionate, with vinyl butyrate, with vinyl stearate, with vinyl benzoate, with vinyl cyclohexanoate, with vinyl isobutyrate, with vinyl palmitate, with vinyl myristate, with vinyl toluate, with vinyl naphthoate, and the like. Inasmuch as the acid group of the vinyl ester is removed by hydrolysis, it is usually most economical to use an interpolymers of ethylene with vinyl acetate which is the most readily available vinyl ester. On account of the superior products had therewith, we prefer to employ an interpolymers of ethylene with a vinyl ester of an organic acid having the general formula $C_nH_{2n+1}COOH$, wherein n is a positive integer within the range of from 1 to 3.

Appreciable effects are had when the mol ratio of ethylene to vinyl organic ester in the interpolymers prior to hydrolysis is as low as 1/1, and also when it is as high as 5/1. However, the filaments obtained according to the process of this invention have markedly superior strength characteristics when the mol ratio of ethylene to vinyl organic ester in said interpolymers prior to hydrolysis is within the range of from 2/1 to 4/1.

As shown in the example, the interpolation of the vinyl ester with ethylene can be carried out under superatmospheric pressure in the presence of a peroxide-type polymerization catalyst. The resulting interpolymers is hydrolyzed by treatment in solution with an alkali dissolved in a lower alcohol or in aqueous solution. For preparing filaments, the resulting hydrolyzed interpolymers should be at least 80% hydrolyzed and preferably substantially completely hydrolyzed.

For the production of the improved hydrolyzed ethylene/vinyl ester filaments by this invention it is necessary that the filaments be prepared by spinning from solution in solvents, such as trichloroethylene-ethanol, primary aliphatic alcohols, primary or secondary aliphatic amines, and that they be heat-treated such as under conditions previously described before being subjected to a substantial amount of orientation. It has been found that the process described actually produces a loss of strength when applied to filaments obtained by spinning the molten polymer (melt-spinning). It has been shown unlikely that the improvement obtained from the solution-spun (dry-spun) yarn is due to retention of solvent since the solvent is substantially completely removed before the heating has progressed for more than a limited period.

For best results, the filaments should be treated by the described process before they have been permitted to age appreciably. If the filaments have been allowed to remain at room temperature for long periods, e. g., for periods of greater than 4 days, the amount of improvement is not as great. It is preferred that the filament be subjected to the heat treatment less than two days after its preparation and for maximum results the filament employed should be used as soon as possible after it has been formed. Similarly, the heat-treated filament should be drawn within a short time after the heat treatment. This orientation or drawing should usually take place within a time of less than two days after the heat treatment to obtain the maximum strength of the resulting fibers. It has been found that soaking the filament in water after the heat treatment and prior to drawing gives an oriented filament having maximum strength.

The temperature of the heat treating operation is critical for the preparation of strong filaments. The operable temperatures for the heat treatment of the hydrolyzed ethylene/vinyl ester interpolymers filaments are those within the range of from 20° C. below the sticking temperature of the filaments and said sticking temperature. In general, the temperature at which filaments of the yarn will stick together (which temperature is approximately that of the sintering temperature and slightly less than the softening temperature or the zero tensile strength temperature of the filaments) for hydrolyzed interpolymers of ethylene and vinyl acetate of molar ratio of ethylene to vinyl acetate of between 2/1 and 3.5/1 is usually between 108°-112° C. The maximum strengths of the resulting filaments may be obtained by heat treating within the range of from 10° C. below the sticking or sintering temperature and the sintering temperature. For example, for a hydrolyzed ethylene/vinyl acetate interpolymers of molar ratio of ethylene/vinyl acetate of 2.5/1, the sticking temperature is about 108-110° C. and the strength of the resulting filament after heat treatment at 105-107° C. was found to be higher than when the heat treatment was carried out at a temperature of 101°-103° C. Heat treatment at temperatures which are 25° C. or more below the sticking point of the filament has little effect on improving the properties of the resulting filaments. When temperatures of within 2 or 3° C. of the sticking temperature of the filament are employed, care must be taken to prevent local overheating with resulting softening or melting of the filament.

The heat treatment ordinarily requires a time of at least 5 hours. It is preferred that the time be about 8 hours, while periods of time longer than 8 hours have not been found to effect further improvement in properties.

The heat treatment can be carried out in any desired manner. For example, steam, air, oil or other types of baths may be employed. In general, the heating is most advantageously carried out by the use of an air-oven regulated at the desired temperature.

The orientation of the filament may be readily carried out by stretching or tensioning the filament under a tension insufficient to break the orientable polymeric filament. For example, the drawing may be readily effected by maintaining a speed differential between the drawing and feeding rolls when the filament is rewound from a roll. A higher ratio of the drawing to the feeding roll results in an increase in the tenacity of the filament above that which may otherwise be attained. Thus, the heat treatment by the method described in the example resulted in an increase in draw ratio to as high as 8.3/1 while draw ratios of only 7.5/1 could be used without the heat treatment. The tenacity increases in general are 0.5/1.5 g./d. In any case, the draw ratio used in the orientation is at least 2/1, or on a percent basis, at least 100%.

Heat treatment after the tensioning or orienting operation of hydrolyzed ethylene/vinyl ester filaments such as those employed in the treatment of cellulose acetate filaments does not bring about substantial improvement in the properties of these hydrolyzed interpolymers filaments.

In addition to the beneficial results on filaments obtained by heat treatment as described above, heat treatment of unoriented films and

molded objects of hydrolyzed ethylene/vinyl organic ester interpolymers also leads to remarkable improvement. Heat treated films have higher tensile strength, higher elongation, much greater tear strength, and greater toughness at low temperatures than films not subjected to the heat treatment. The properties of extruded tubing and injection or compression molded objects can also be improved by this method. In the case of films and molded objects, somewhat higher temperatures can often be used than for filaments, since slight softening of such objects is not necessarily objectionable. Temperatures as high as 120° C. may be desirable in some instances. The beneficial effects of high temperatures on the properties of hydrolyzed ethylene/vinyl organic interpolymers can also be obtained by the expedient of casting the films at temperatures near the softening point of the polymer. For this purpose the solvent used in casting should preferably boil at a temperature higher than the casting temperature. Suitable combinations of aromatic hydrocarbons and alcohols, for example, a solvent mixture containing 40% xylene and 60% isoamyl alcohol, boiling at 126° C., have been found to be particularly useful. Films cast at 110–120° C. from such a solvent have much better properties than films cast, for example, at 60–70° C. The properties of films cast at temperatures near the softening point can be further improved by additional heat treatment.

The improved filaments of this invention find use in the production of fabrics, cords, staple fibers, etc. Because of the increased tenacity of the filaments in conjunction with the other properties of the hydrolyzed ethylene/vinyl organic ester interpolymers, the fibers are especially useful in the manufacture of hosiery, ropes, woven belting, fishing lines, etc.

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 we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

Having described the present invention, the following is claimed as new and useful:

1. The process for obtaining an improved dry-spun hydrolyzed ethylene/vinyl organic ester interpolymers filament, which comprises heating for a period of at least five hours at a temperature within the range of from its sticking temperature to 20° C. below said sticking temperature in a taut condition, a filament, previously spun from solution, of a hydrolyzed interpolymers of ethylene with a vinyl ester of a monocarboxylic acid having the general formula RCOOH , wherein R is of the group consisting of hydrogen atoms and hydrocarbon radicals, said acid being free from unsaturated linkages between acyclic carbon atoms and any carbon atom alpha to the carbon atom in the carboxyl group of said acid being attached to at least one but not more than three carbon atoms, the mol ratio of ethylene to vinyl organic ester in said interpolymers prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter drawing the

treated filament at least 110% of its original length.

2. The process for obtaining an improved dry-spun hydrolyzed ethylene/vinyl organic ester interpolymers filament, which comprises heating for a period of at least five hours at a temperature within the range of from its sticking temperature to 20° C. below said sticking temperature in a taut condition, a filament, previously spun from solution, of a hydrolyzed interpolymers of ethylene with a vinyl ester of a monocarboxylic acid having the general formula $\text{C}_n\text{H}_{2n+1}\text{COOH}$, wherein n is a positive integer within the range of from 1 to 3, the mol ratio of ethylene to vinyl organic ester in said interpolymers prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter drawing the treated filament at least 100% of its original length.

3. The process for obtaining an improved dry-spun hydrolyzed ethylene/vinyl acetate interpolymers filament, which comprises spinning a solution of a substantially completely hydrolyzed interpolymers of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate in said interpolymers prior to hydrolysis having been within the range of from 1/1 to 5/1, within four days thereof heating the resultant filament in a taut condition for a period of at least five hours at a temperature within the range of from its sticking temperature to 20° C. below said sticking temperature, and thereafter, within two days of said heating operation, drawing the treated filament at least 100% of its original length.

4. The process for obtaining an improved dry-spun hydrolyzed ethylene/vinyl acetate interpolymers filament, which comprises spinning a solution of a substantially completely hydrolyzed interpolymers of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate in said interpolymers prior to hydrolysis having been within the range of from 1/1 to 5/1, within two days thereof heating the resultant filament in a taut condition for a period within the range of from 5 to 8 hours at a temperature within the range of from its sticking temperature to 20° C. below said sticking temperature, and thereafter, within two days of said heating operation, drawing the treated filament at least 100% of its original length.

5. The process for obtaining an improved dry-spun hydrolyzed ethylene-vinyl acetate interpolymers filament, which comprises spinning a solution of a substantially completely hydrolyzed interpolymers of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate in said interpolymers prior to hydrolysis having been within the range of from 2/1 to 4/1, and immediately thereafter heating the resultant filament in a taut condition for a period within the range of from 5 to 8 hours at a temperature within the range of from its sticking temperature to 10° C. below said sticking temperature, and thereafter, within two days of said heating operation, drawing the treated filament at least 100% of its original length.

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