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3,499,073

MELT SPINNING OF ACRYLONITRILE POLYMERS
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7 Claims

ABSTRACT OF THE DISCLOSURE

Synthetic fibers from acrylonitrile polymers are produced by a melt spinning process. Melt spinning is accomplished without degradation by rapidly extruding a special type of acrylonitrile polymer, having a heat of reaction at the fusion temperature of less than 15 calories per gram, through a heated orifice into the desired shape, stretching and cooling. When compared with wet or dry spinning the melt spinning process permits increasing spinning rate and eliminates solvents handling and recovery without adversely affecting fiber properties.

The invention relates to a process for preparing synthetic fibers made from polyacrylonitrile and copolymers of acrylonitrile in which at least 75 percent by weight of the polymer is acrylonitrile. The invention further relates to the preparation of these fibers by a true melt spinning process wherein spinning is carried out by rapidly extruding an acrylonitrile polymer having a heat of reaction at the fusion temperature of less than 15 calories per gram through a heated orifice into the desired shape, and thereafter stretching, and cooling the melt spun filament.

Polyacrylonitrile and copolymers of acrylonitrile in which at least 75 percent by weight of the polymer is acrylonitrile are well known. Fibers or filaments from these polymers are prepared by well known wet or dry spinning techniques where the polymer is dissolved in a suitable organic solvent such as dimethylacetamide and extruded through a spinneret into a liquid or gaseous coagulating atmosphere. The filament thus formed is washed thoroughly, stretched and cooled. These filaments, noteworthy in view of their wool-like physical and chemical properties, are utilized in the manufacture of carpets and other textile articles. Solutions of acrylonitrile polymers disclosed in U.S. Patents 2,404,714-2,404,727 can be converted into shaped articles by such wet and dry spinning techniques.

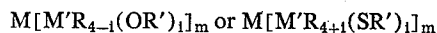
Efforts to melt spin polymers of acrylonitrile have in the past been unsuccessful because fiber-forming polymers of acrylonitrile containing at least 75 percent by weight of acrylonitrile are normally infusible and cannot be melt extruded because of severe heat degradation. A compromise between solution spinning and melt spinning has been described by Rothrock in U.S. Patent 2,706,674 wherein acrylonitrile polymers are heavily plasticized with volatile organic solvents to form polymer gels. These gels are subsequently elevated in temperature to the melting point of the gels whereupon they become flowable to the extent that they can be extruded to form gelled filaments when the temperatures of the melted gels are thereafter lowered below the gel melting points. The gelled filaments so extruded are rich in solvent or plasticizer which must be removed in order to provide filaments having acceptable properties for textile use. It is pointed out that even though the Rothrock process is described as "melt spinning" it is in fact a melt spinning of a polymer gel and not melt spinning of an acrylonitrile polymer.

Formation of shaped articles from acrylonitrile polymers by true melt spinning where little or no diluent is added is highly desirable in order to eliminate solvent

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handling and solvent recovery, and to produce fibers at a higher rate of speed. However, those acrylonitrile polymers which are usually prepared from redox (or other free radical forming catalysts) cannot be utilized in a melt spinning system because they severely and rapidly decompose at their fusion temperatures. This decomposition is characterized by a high positive heat of reaction (greater than 15 calories per gram) at or near temperature of fusion. The heat of reaction is defined as the heat evolved or absorbed during a chemical reaction. Heat degradation of acrylonitrile polymers is an exothermic chemical reaction. The heat liberated upon heating the polymers employed in the process of this invention was accurately measured, in a commercially available calorimeter cell, the Du Pont Calorimeter Cell according to procedures defined in the Calorimeter Section of the Du Pont 900 DTA Instruction Manual.

Acrylonitrile polymers, however, can be prepared which show practically no degradation at or near the melting point. These polymers are characterized by a heat of reaction of less than 15 calories per gram at the fusion temperature within the time of measurement. Polymers exhibiting this property can be prepared by conducting the polymerization of acrylonitrile alone or with other monoethylenically unsaturated monomer interpolymerizable therewith in a non-aqueous liquid medium in the presence of an organometallic coordination complex catalyst at temperatures ranging from about -30° C. to about $+25^{\circ}$ C. The complex catalysts or initiators employed are represented by the formula



wherein M is an alkali metal or an alkaline earth metal, M' is a Group III-A metal, aluminum being preferred, R and R' are the same or different monovalent hydrocarbon radicals having 1 to about 12 carbon atoms, i is an integer of from 1 to 4 and m is an integer of 1 to 2, being equal to the valence of M. These initiator materials and their preparations have been described in U.S. Patent 2,873,290 (Esmay).

Insofar as the initiator materials represented by the formulas given above are sensitive to moisture and oxygen, care should be taken to conduct the polymerization under an inert atmosphere such as nitrogen.

It has been discovered that acrylonitrile polymers prepared by the above complex catalyst system at a temperature ranging from about -30 to about $+25^{\circ}$ C. can be spun not only by conventional wet or dry spinning processes, but they are sufficiently stable and fusible at temperatures ranging from 250 – 300° C. as indicated by a heat of reaction of less than 15 calories per gram to be melt spun.

Melt spinning or extrusion according to this invention is accomplished by rapidly extruding these acrylonitrile polymers through heated orifices of a desired shape, and thereafter stretching, and cooling the melt spun filament. The process of the invention avoids rapid and severe degradation of the acrylonitrile polymer by utilizing an acrylonitrile polymer characterized by a heat of reaction of less than 15 calories per gram at or below the fusion temperature. It has been found that small amounts of organic plasticizers or solvents which may be dry blended prior to melting the polymer appear to lubricate or facilitate the spinning technique. Generally, the materials are employed in amounts of less than about 15 percent by weight of the blend. Typically, solid ethylene carbonate is dry blended with the polymer and the blended composition is fed to the extrusion apparatus.

The compositions employed in this invention are those fiber-forming polymers containing at least 75 percent acrylonitrile alone or these polymers blended with up to 15 percent of an organic plasticizer based on the total

weight of the resultant blend. The fiber-forming polymers or blends of polymer and plasticizer are rapidly heated to melt at the spinneret surface to a temperature between about 250° C. and about 325° C. and extruded under pressure into a cooling atmosphere. The acrylonitrile polymer employed in the process of this invention must, as above indicated, be further characterized by having a heat of reaction at the fusion temperature of less than 15 calories per gram.

Melt spinning of the acrylonitrile polymers discussed above may be carried out in conventional melt extrusion equipment if provision is made for rapidly heating the polymer to 250–325° C. and holding the polymer for no longer than about 6 minutes at a temperature within the range. The apparatus used in this method of the invention is similar to that described by W. M. Palmer and N. L. Larue in U.S. Patent 2,955,320. This equipment feeds powdered or granular polymer or polymer blend to a heated spinneret face by a rotating screw. The material is compressed into a thin layer between the screw and spinneret face at which point the polymer is rapidly heated and extruded. The spinneret may be of conventional design having multiple orifices of any desired size and shape. The extruded filament sets up as the temperature is reduced to below the fusion temperature and may be wound up on conventional equipment.

The process of this invention and the advantages thereof can best be understood by reference to the following examples which are illustrative and not to be construed as limitation. Parts and percentages are given by weight unless otherwise indicated.

EXAMPLE I

This example is illustrative of a typical method for preparing acrylonitrile polymers with a redox catalyst and subsequently attempting to melt spin the polymer.

Polyacrylonitrile was prepared by subjecting acrylonitrile to suspension type polymerization conditions using potassium persulfate-sulfur dioxide-iron redox catalyst system. The polymerization was carried out by adding acrylonitrile to an aqueous medium maintained at 50° C. over a two-hour period. The catalyst was likewise added over a two-hour period. The polymer thus formed was recovered by filtration, thoroughly washed, and dried at 50° C. to a constant weight.

The dried polymer was introduced into the melt spinning apparatus, described above, where the polymer was rapidly heated to the fusion temperature and extruded. Although the spinneret temperature was varied from 250–325° C., with the residence time being varied from 1–5 minutes, no filaments were obtained. The extrudate was observed to provide only brown and black drips evidencing severe degradation of the polymer. The heat of the reaction of this polymer as determined by the Calorimeter Cell described earlier, was 22 calories per gram.

EXAMPLE II

A copolymer consisting of 94 percent acrylonitrile and 6 percent vinyl acetate was prepared using the procedure and redox catalyst of Example I. The resulting polymer was dry blended with 10 percent solid ethylene carbonate and introduced into the melt spinning equipment. Although several combinations of spinneret temperature and residence time were tried, no filaments could be obtained. The heat of reaction of this polymer was 19.7 calories per gram.

EXAMPLE III

This example is illustrative of a typical method for preparing acrylonitrile polymers with a complex catalyst and the subsequent step of melt spinning the polymer.

The catalysts are prepared from sodium tetraethylaluminate (NaAlEt_4) activated by alcohols, mercaptans or oxygen. The catalysts are active over a wide range of temperature from -120°C . to 50°C . For the purpose of

this invention the temperature range of -30° to 25°C . is preferred.

Twenty parts of acrylonitrile was added to 100 parts of dimethylformamide which had been carefully vacuum distilled and dried. The solution was cooled to 0°C . and 0.0784 part of catalyst ($\text{NaAlEt}_3\text{OCHMe}_2$) dissolved in 5 parts of dimethylformamide was introduced via a hypodermic syringe. Polymerization under nitrogen was allowed to proceed for 5 hours. The polymer was recovered by precipitation with methanol, filtered, washed, and dried.

The dried polymer was introduced into the previously described melt spinning apparatus and fiber was extruded under pressure through a spinneret at 250°C . into room temperature air. The white fiber was collected and hand drawn $2\times$ over a hot surface. The heat of reaction for this polymer at the fusion temperature was 11.5 calories per gram.

EXAMPLE IV

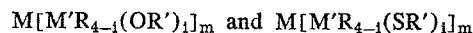
A copolymer consisting of 98 percent acrylonitrile and 2 percent vinyl phenyl sulfone was prepared using the procedure and catalyst of Example III. The polymer was dry blended with 10 percent ethylene carbonate and introduced into the melt spinning apparatus. The spinneret was maintained at 295°C . and white fiber was extruded at 100 feet per minute. The filament was drawn $2-3\times$ over a ceramic pin heated at 110°C . The 7.7 denier fiber had a tenacity of 1.2 grams per denier, an elongation of 12 percent and an initial modulus of 50 grams per denier. The heat of reaction for this polymer was 8.3 calories per gram.

EXAMPLE V

A copolymer consisting of 80 percent acrylonitrile and 20 percent ethyl acrylate was prepared using the procedure of Example III and the complex catalyst sodium triethylisopropylthioaluminate ($\text{NaAlEt}_3\text{SCHMe}_2$). The copolymer was introduced into the melt spinning apparatus with no added diluent. Fibers with properties similar to that of the fiber in Example IV were spun through a spinneret at 295°C . The heat of reaction for this polymer was 12.6 calories per gram.

We claim:

1. The method for formation of filamentary articles of polymers of acrylonitrile having interpolymerized therewith up to 25 percent by weight of a monoethylenically unsaturated monomer inter-polymerized therewith, said polymer being further characterized by having been polymerized in a non-aqueous medium in the presence of an organo-metallic coordination complex catalyst selected from the group consisting of the formulas



wherein M is an alkali metal or an alkaline earth metal, M' is a Group III–A metal, R and R' are the same or different monovalent hydrocarbon radicals having 1 to about 12 carbon atoms, i is an integer of from 1 to 4 and m is an integer of 1 to 2, being equal to the valence of M, which comprises rapidly elevating the temperature of the polymer to the melting point and extruding the heated polymer under pressure through a shaped orifice.

2. The method of claim 1 wherein less than about 15% of a divalent based on the weight of the diluent-polymer mixture is blended with the polymer.

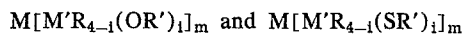
3. The method of claim 2 wherein the diluent is ethylene carbonate.

4. The method of claim 1 wherein the polymer is continuously heated and extruded such that the polymer is held at temperatures above 200°C . for less than 5 minutes.

5. The method for forming filaments from a composition comprising from 80 to 100 percent by weight of an acrylonitrile polymer and up to 15% by weight of ethylene carbonate, said polymer being further characterized by having been polymerized in a non-aqueous medium in the presence of an organo-metallic coordina-

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tion complex catalyst selected from the group consisting of the formulas



wherein M is an alkali metal or an alkaline earth metal, M' is a Group III-A metal, R and R' are the same or different monovalent hydrocarbon radicals having 1 to about 12 carbon atoms, i is an integer of from 1 to 4 and m is an integer of 1 to 2, being equal to the valence of M, and being composed of at least about 75 percent by weight of acrylonitrile and up to about 25 percent by weight of monoethylenically unsaturated monomer interpolymizable therewith, which comprises rapidly heating said composition to between about 250° C. and about 300° C. and immediately thereafter extruding said heated composition under pressure through a shaped orifice to thereby form a synthetic filament.

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6. The method of claim 5 wherein said acrylonitrile polymer is a homopolymer.

7. The method of claim 5 wherein said acrylonitrile polymer is an interpolym.

References Cited

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JULIUS FROME, Primary Examiner

J. H. WOO, Assistant Examiner

U.S. Cl. X.R.

264—206

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Shih-ming Sun and Robert Chiang

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 62, "divalent" should read ---diluent---.

SIGNED AND
SEALED
MAR 9 1971

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents