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3,584,104

PRODUCTION OF POLYBENZIMIDAZOLE FIBERS

Thomas C. Bohrer, Charlotte, N.C., and Arnold J. Rosenthal, Whippany, N.J., assignors to Celanese Corporation, New York, N.Y.

No Drawing. Continuation-in-part of application Ser. No. 520,646, Jan. 14, 1966. This application Apr. 30, 1969, Ser. No. 820,606

Int. Cl. D01d 5/04; D02j 1/22
U.S. Cl. 264—210

12 Claims

ABSTRACT OF THE DISCLOSURE

The handling difficulties presented by the elongation of a dry spun polybenzimidazole fiber are overcome through the use of the present process. More specifically, the acute problem of a dry spun polybenzimidazole fiber relaxing and falling from a take-up roll or bobbin soon after spinning, and particularly during a washing step, is obviated by dry spinning the fiber and immediately thereafter stretching the fiber at a draw ratio of up to 1.5:1 with the stretching step being conducted while the dry spun fiber is in the presence of steam or water at a temperature of at least 70° C. up to its boiling point. The resulting polybenzimidazole fiber additionally exhibits improved physical properties.

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of our co-pending U.S. Ser. No. 520,646, filed Jan. 14, 1966, and now abandoned.

BACKGROUND OF THE INVENTION

It has been observed in the past that continuous lengths of dry spun polybenzimidazole fiber (e.g. as-spun filament or yarn) have a tendency to spontaneously elongate following dry spinning. For instance, when the as-spun polybenzimidazole fiber is on a take-up roll or bobbin severe fiber handling difficulties commonly arise as the fiber relaxes and falls from the support. This elongation problem is particularly accentuated when bobbins supporting the dry spun polybenzimidazole fiber are subjected to pressure washing to remove residual solvent. The persistent relaxation of the fiber and its failure to adhere to bobbins accordingly renders large scale production extremely tedious.

It is an object of the invention to provide a process for the production of polybenzimidazole fiber which eliminates the handling difficulties heretofore encountered with such dry spun fiber.

It is another object of the invention to provide a process for the production of polybenzimidazole fiber which is capable of being taken up on bobbins after dry spinning and retained thereon without having the fiber relax and fall from the same.

It is another object of the invention to provide a process for producing polybenzimidazole fiber which exhibits improved physical properties.

These and other objects, as well as the scope, nature, and utilization of the invention will be apparent from the following detailed description and appended claims.

SUMMARY OF THE INVENTION

It has been found that an improved process for the production of polybenzimidazole fiber comprises dry spinning polybenzimidazole fiber and immediately thereafter subjecting the fiber to a stretching treatment in the presence of a medium selected from the group consisting of:

- (a) steam and
- (b) water at a temperature of at least 70° C. up to its boiling point,

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and at a draw ratio of up to 1.5:1, and subsequently collecting the resulting stretched polybenzimidazole fiber.

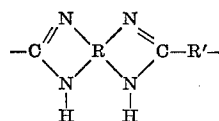
The resulting polybenzimidazole fiber while present on a roller or bobbin may be pressure washed without elongating and falling from its support.

DETAILED DESCRIPTION OF THE INVENTION

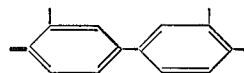
The starting polymer

Polybenzimidazoles are a known class of heterocyclic polymers which may be prepared, for example, as described in U.S. Pat. No. 2,895,948 to Brinker et al., or in U.S. Pat. No. 3,174,947 or Reissue Pat. No. 26,065 to Marvel et al., which are herein incorporated by reference. Polybenzimidazoles consist essentially of recurring units of the following Formulas I and II.

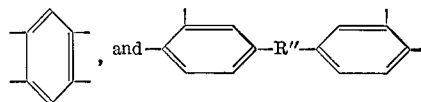
Formula I is:



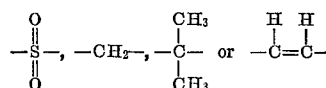
wherein R is a tetravalent aromatic nucleus (preferably symmetrically substituted), with the nitrogen atoms forming the benzimidazole rings being paired upon adjacent carbon atoms, i.e., ortho carbon atoms, of the aromatic nucleus, and R' is a member of the class consisting of an alkylene group (preferably those having from 4 to 8 carbon atoms), a cycloaliphatic ring, an aromatic ring, and a heterocyclic ring such as pyridine, pyrazine, furan, quinoline, thiophene, and pyran. Preferred R groups are 3,3',4,4'-biphenylene,



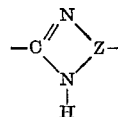
and 1,2,4,5-phenylene,



wherein R'' is —O—, —S—,



Formula II is:



wherein Z is an aromatic nucleus having the nitrogen atoms forming the benzimidazole ring paired upon adjacent carbon atoms of the aromatic nucleus.

Preferably, the fibers produced in accordance with the present process are prepared from aromatic polybenzimidazoles, that is, from polymers consisting essentially of the recurring units of Formula II and of Formula I wherein R' is an aromatic ring or a heterocyclic ring.

As set forth in U.S. Pat. No. 3,174,947 and in Reissue Pat. No. 26,065 to Marvel et al., the aromatic polybenzimidazoles having the recurring units of Formula II may be prepared by self-condensing a trifunctional aromatic compound containing only a single set of ortho disposed diamino substituents and an aromatic, preferably phenyl carboxylate ester substituent. Exemplary of polymers of this type is poly-2,5(6)-benzimidazole prepared by the auto-condensation of phenyl-3,4-diaminobenzoate.

As also set forth in the above-mentioned patents, the aromatic polybenzimidazoles having the recurring units

of Formula I may be prepared by condensing an aromatic tetraamine compound containing a pair of ortho-diamino substituents on the aromatic nucleus with a dicarboxyl compound selected from the class consisting of (a) the diphenyl ester of an aromatic dicarboxylic acid, (b) the diphenyl ester of heterocyclic dicarboxylic acid wherein the carboxyl groups are substituents upon carbon in a ring compound selected from the class consisting of pyridine, pyrazine, furan, quinoline, thiophene and pyran and (c) an anhydride of an aromatic dicarboxylic acid.

Examples of aromatic polybenzimidazoles which have the recurring structure of Formula I and which may be formed into fibers in the present process include:

poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole;
poly-2,2'-(pyridylene-3'',5'')-5,5'-bibenzimidazole;
poly-2,2'-(furylene-2'',5'')-5,5'-bibenzimidazole;
poly-2,2'-(naphthalene-1'',6'')-5,5'-bibenzimidazole;
poly-2,2'-(biphenylene-4'',4'')-5,5'-bibenzimidazole;
poly-2,6-(m-phenylene)-diimidazobenzene;
poly-2,6-(p-phenylene)-diimidazobenzene;
poly-2,2'-(biphenylene-4'',4'')-5,5'-bibenzimidazole;
poly-2,2'-octamethylene-5,5'-bibenzimidazole;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)sulfide;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)sulfone;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)methane;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)propane-2,2; and
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)ethylene-1,2.

where the double bonds of the ethylene groups are intact in the final polymer. The preferred aromatic polybenzimidazole fiber is prepared from poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole.

Examples of non-aromatic polybenzimidazoles which have the recurring structure of Formula I and which may be formed into fibers include:

poly-2,2'-amylen-5,5'-bibenzimidazole;
poly-2,2'-octamethylene-5,5'-bibenzimidazole;
poly-2,2'-cyclohexenyl-5,5'-bibenzimidazole;
poly-2,2'-hexamethylene-5,5'-di(benzimidazole)propane-2,2; and
poly-2,2'-cyclohexenyl-5,5'-bibenzimidazole.

Any polybenzimidazole polymerization process known to those skilled in the art may be employed to prepare the polymer which is utilized in the present process.

With respect to aromatic polybenzimidazoles, preferably equimolar quantities of the monomeric tetraamine and dicarboxyl compound are introduced into a first stage melt polymerization reaction zone and heated therein at a temperature above about 200° C., preferably at least 250° C., and more preferably from about 270 to 300° C. The reaction is conducted in a substantially oxygen-free atmosphere, i.e., below about 20 p.p.m. oxygen and preferably below about 8 p.p.m. oxygen, until a foamed prepolymer is formed. Usually, the first stage reaction is continued until a prepolymer is formed having an inherent viscosity, expressed as deciliters per gram, of at least 0.1, and preferably from about 0.13 to 0.3, with the inherent viscosity (I.V.) used in the present specification being determined from a solution of 0.4 gram of the polymer in 100 ml. of 97 percent H₂SO₄ at 25° C.

After the conclusion of the first stage reaction, which normally takes at least 0.5 hour and preferably 1 to 3 hours, the foamed prepolymer is cooled and then powdered or pulverized in any convenient manner. The resulting prepolymer powder is then introduced into a second stage polymerization reaction zone wherein it is heated under substantially oxygen-free conditions, as described above, to yield a polybenzimidazole polymer product, desirably having an I.V., as measured above, of at least 0.6, e.g., 0.80 to 1.1 or more.

The temperature employed in the second stage is at

least 250° C. preferably at least 325° C., and more preferably from about 350 to 425° C. The second stage reaction generally takes at least 0.5 hour, and preferably from about 1 to 4 hours or more.

Dry spinning

The polybenzimidazole fiber may be spun according to polybenzimidazole dry spinning procedures known in the art. Suitable solvents for the polybenzimidazole which may be used to form the spinning solution include dimethylacetamide, dimethylformamide, dimethylsulfoxide, and N-methyl-2-pyrrolidone.

The polymer solutions may be prepared, for example, by dissolving a sufficient quantity of the polybenzimidazole in the solvent to yield a solution suitable for extrusion containing about 10 to 45 percent by weight polymer based upon the total weight of the solution, and preferably about 20 to 30 percent by weight. One suitable means for dissolving the polybenzimidazole in the solvent is by mixing the polymer while in particulate form with the solvent at a temperature above the atmospheric boiling point of the solvent, for example, 25 to 120° C. above such boiling point, and at a pressure of 2 to 15 atmospheres for a period of 1 to 5 hours. This polybenzimidazole solutioning technique is described in detail in U.S. Ser. No. 517,834, filed Dec. 30, 1965, and now abandoned, of Anthony B. Conciatori and Edward C. Chenevey, which is assigned to the same assignee as the instant invention and is herein incorporated by reference. Preferably the polybenzimidazole solution is filtered to remove any residual amount of undissolved polymer prior to dry spinning.

During the spinning operation the polybenzimidazole solution may be extruded through a spinneret into a conventional down-draft spinning column containing a circulating inert gas such as nitrogen, noble gases, combustion gases or superheated steam which serves as the evaporative medium. Conveniently, the spinneret face is at a temperature of from about 130 to 170° C., the top of the column from about 120 to 220° C., the middle of the column from about 140 to 250° C., and the bottom of the column from about 160 to 320° C. The temperature within the column preferably progressively increases from the top to the bottom and the exact temperature range utilized is selected to exceed the boiling point of the specific polybenzimidazole solvent being employed as will be apparent to those skilled in the art. After leaving the spinning column, the as-spun polybenzimidazole fiber is taken up, for example, at a speed in the range of from about 50 to 350 meters per minute. When the drawing step (discussed hereafter) is conducted in heated water, it is recommended that the dry spun fiber be taken up at a speed in the range of 50 to 150-meters per minute. However, when the drawing step is conducted in steam, the dry spun fiber may be taken up at a faster rate, i.e. up to 350 meters per minute or higher.

Stretching procedure

The as-spun fiber immediately after its formation and prior to washing is placed to a zone where it is subjected to slight stretching in the presence of (1) steam, or (2) water at a temperature of at least 70° C. up to its boiling point. For instance, after the fiber exits from the dry spinning column and passes around a conventional take-up roller (which also serves as a feed roller for drawing) it may be immediately passed through the drawing zone. The pressure in the drawing zone is preferably atmospheric. In the preferred embodiment of the invention steam is the medium present in the drawing zone, and is confined by an elongated drawing tube. The steam may optionally be superheated prior to its introduction; however, completely satisfactory results are obtainable with non-superheated steam wherein condensation occurs. The steam drawing zone may be either vertically or horizontally disposed. When water is utilized in the drawing zone, it

may conveniently be retained in a trough through which the heated water is circulated.

The polybenzimidazole fiber after passage through the drawing zone is taken up on a roller at a speed greater than that of the feed roller so that a slight stretch is imparted. The relatively slight draw ratio should be greater than 1.0 and up to 1.5:1, e.g. 1.1:1 to 1.5:1, preferably up to 1.2:1. At draw ratios higher than 1.5:1 drawing voids and fiber instability may occur. Following drawing the fiber may be collected in a convenient manner, such as by winding on a suitable bobbin.

Washing procedure

Desirably, the polybenzimidazole fiber is next washed to remove residual spinning solvent and other impurities. Preferably the fiber is washed until it contains less than about 1 percent by weight solvent based upon the weight of the fiber, and more preferably until the fiber is essentially free of spinning solvent. Typically, a simple water wash is employed, however, if desired other wash materials such as acetone, methanol, methyl ethyl ketone and similar dimethylacetamide-miscible and volatile organic solvents may be used in place of or in combination with the water. The washing operation may be conducted by collecting the polybenzimidazole fiber on perforated rollers or bobbins, immersing the same in the liquid wash bath and pressure washing the fiber, for example, for about 2 to 48 hours or more. Pressure washing may be accomplished by passing the wash medium through the interior of a hollow roller or bobbin and forcing the medium through perforations in the same so that the solvent is flushed from the polybenzimidazole fiber wound thereon. Throughout the wash procedure the polybenzimidazole fiber formed in accordance with the present invention retains its stability and may be readily retained on rollers or bobbins without experiencing appreciable elongation.

The washed fibers may then be dried in any suitable type of apparatus such as an electric oven to remove at least the major portion of the wash liquid, for example, at least 60% by weight, of the wash liquid, preferably at least 90% by weight and more preferably, essentially all of the wash liquid. If substantially less than about 60% of the wash liquid is removed prior to subjecting the fiber to drawing (described hereafter), the fiber may undergo foaming therein merely due to the excessive wash liquid content. The drying operation is conveniently conducted at a temperature of from about 150 to 300° C. for about 2 to 100 hours or more. Preferably, the drying temperature does not exceed about 250° C. as above this temperature degradation of the fiber may occur, particularly if an extended heating period, i.e., several hours, is employed.

Following washing and drying of the polybenzimidazole fiber, its properties may be further enhanced by drawing. Such drawing of the washed and dried polybenzimidazole fiber is recommended in order to achieve a fiber having optimum physical properties. The drawing may be conducted according to hot drawing procedures known in the art. Draw ratios may generally range from about 1.5:1 up to slightly below the ratio at which the fiber breaks. For instance, draw ratios of about 1.5:1 to 3.5:1, and preferably 2.0:1 to 3.2:1 may be selected. Particularly preferred drawing techniques are disclosed in U.S. Ser. Nos. 769,862, filed Oct. 23, 1968, of George F. Ecker and Thomas C. Bohrer, and in 770,109, filed Oct. 23, 1968, of Thomas C. Bohrer and Arnold J. Rosenthal. Each of the above-identified co-pending applications is assigned to the same assignee as the instant invention and is herein incorporated by reference.

Following drawing the drawn fiber may be optionally relaxed under conditions wherein a slight decrease in length is imparted to the same in order to enhance its elongation properties. Suitable relaxation temperatures range from about 400° C. to 600° C.

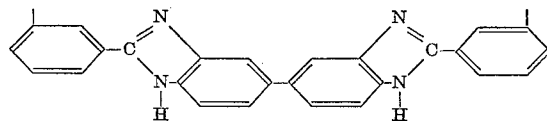
The following examples are given as specific illustrations of the invention. It should be understood, however, that

the invention is not limited to the specific details set forth in the examples.

EXAMPLE 1

This example indicates the advantages of the embodiment of the invention in which an as-spun polybenzimidazole fiber immediately after dry spinning is subjected to a stretching treatment in the presence of steam.

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole was selected as the exemplary polybenzimidazole for use in carrying out the process of the invention in the examples and consists of recurring units of the formula:



A preparation of this polybenzimidazole is described in Example II of U.S. Pat. No. 3,174,947 to Marvel et al.

The polymer (I.V.=0.72 dl./g.) was dissolved in a dimethylacetamide (solids concentration of 23 percent by weight) in accordance with the teachings of U.S. Ser. No. 517,834, filed Dec. 30, 1965, which is herein incorporated by reference. Prior to spinning the dope it was filtered to remove residual undissolved polymer.

The dope was extruded at a temperature of 150° C. through a jet containing 50 holes (each 76 microns in diameter) into an enclosed 23-foot downdraft spinning column in which circulating nitrogen served as the evaporative medium. The top of the column was maintained at 180° C., the middle of the column at 215° C., and the bottom of the column at 240° C. The polybenzimidazole yarn was withdrawn from the spinning column at a speed of 155 meters per minute.

The as-spun polybenzimidazole yarn was next continuously passed through a steam stretch zone consisting of a horizontal tube containing steam at atmospheric pressure. The draw ratio within the steam stretch zone was 1.07:1.

The resulting yarn while present on a perforated bobbin was next pressure washed with water, and dried in air at 150° C. for 160 minutes. The yarn was stable on the bobbin and did not elongate or otherwise fall from the bobbin during the wash treatment.

The dried yarn was next drawn in air at 520° C. at a draw ratio of 2:1. The physical properties of samples of the yarn are reported in the "Drawn Properties" section of the following Table 1.

In the "Relaxed Properties" section of Table 1 the properties of samples of the yarn are reported following relaxation accomplished by passing the yarn over a hot shoe at 425° C. at a draw ratio of about 0.95:1. The significance of the tensile factor "TE 1/2" is more fully discussed in an article by Dr. Arnold J. Rosenthal, "TE 1/2, an Index for Relating Fiber Tenacity and Elongation," Proceedings of the Symposium on Polypropylene Fibers, Sept. 17 and 18, 1964, published by the Southern Research Institute, Birmingham, Ala.

TABLE 1.—WITH TANDEM DRY SPIN-STEAM STRETCH

Drawn properties			Relaxed properties		
Tenacity (grams/ denier)	Elongation (percent)	Tensile factor (TE 1/2)	Tenacity (grams/ denier)	Elongation (percent)	Tensile factor (TE 1/2)
4.5	10.4	14.6	4.0	20.7	18.4
5.2	7.3	14.0	4.7	15.0	18.2
4.6	5.5	10.9	4.0	18.5	17.1
4.9	7.5	11.5	4.4	17.2	18.1
4.9	4.6	10.5	4.4	14.2	16.7

For comparison purposes the above example was repeated with the exception that the dry spun fiber was washed immediately after spinning without the benefit of a tandem dry spin-steam stretch step treatment of the present invention. During the wash step the yarn elongated to the extent it fell from the bobbin and handling

