

1

3,654,232

SURFACE BROMINATED FIBERS COMPRISED OF POLY(1,4 - CYCLOHEXYLENE-DIMETHYLENE TEREPHTHALATE)

Winston J. Jackson, Jr., and John R. Caldwell, Kingsport, Tenn., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Filed Feb. 5, 1971, Ser. No. 113,029

Int. Cl. C08g 53/20

U.S. Cl. 260—75 T

4 Claims

ABSTRACT OF THE DISCLOSURE

Fibers comprised of poly(1,4-cyclohexylenedimethylene terephthalate) having improved resistance to burning are prepared by contacting the fiber with a brominating agent in the presence of a chlorinating agent, and the sum of bromine and chlorine on the surface of the fiber is at least four percent of the weight of the fiber and the toughness of the fiber is reduced not more than 20 percent, based on the toughness of the fiber before contacting the fiber.

This invention relates to the halogenation of the surface of fibers comprised of poly(1,4-cyclohexylenedimethylene terephthalate) wherein the sum of bromine and chlorine on the surface of the fiber is at least four percent of the weight of the fiber and the toughness of the fiber is reduced not more than 20 percent, based on the toughness of the fiber before contacting the fiber.

Fibers having improved resistance to burning are becoming of increasing importance in numerous applications. The advantages of fire-resistant or self-extinguishing wearing apparel, draperies, rugs, coatings and the like are obvious.

It is well known in the art that halogen can be an effective flame retarder. It is further well known that bromine in many instances is a more effective flame retarder than chlorine. The halogenation of polyester fibers using chlorine and bromine is also known in the art. Specifically, U.S. 2,829,070 to Osborn discloses a process of surface treating, with a mixture of chlorine and bromine, a fiber of a linear polyester, particularly a polyester of terephthalic acid and a glycol selected from the series $\text{HO}(\text{CH}_2)_n\text{OH}$ wherein n is an interger from 2–10 inclusive.

We have now found that when the process of Osborn is practiced using a fiber comprised of poly(1,4-cyclohexylenedimethylene terephthalate), the toughness of the fiber is reduced not more than 20 percent based on the toughness of the fiber before contacting the fiber when the sum of bromine and chlorine on the surface of the fiber is at least four percent of the weight of the fiber. These advantageous results are not obtained when the process of Osborn is practiced using the specifically disclosed polyester of terephthalic acid and a glycol selected from the series $\text{HO}(\text{CH}_2)_n\text{OH}$ wherein n is an integer from 2–10 inclusive.

Accordingly, it is an advantage of this invention to provide a fiber of improved resistance to burning which has less than 20% reduction in toughness.

Other advantages and features of this invention will be readily apparent to those skilled in the art from the following description and appended claims.

2

In broad summary, one embodiment of this invention comprises a process for halogenating the surface of a fiber comprising contacting with a brominating agent in the presence of a chlorinating agent in the temperature range of about 0° C. to about 150° C., a fiber comprised of a highly polymeric linear polyester of

- (A) at least 80 mole percent terephthalic acid, and
- (B) at least 80 mole percent 1,4-cyclohexanedimethanol,

wherein the sum of bromine and chlorine on the surface of the fiber is at least four percent of the weight of the fiber and the toughness of the fiber is reduced not more than 20 percent, based on the toughness of the fiber before contacting the fiber.

In broad summary, another embodiment of this invention comprises a fiber comprising a highly polymeric linear polyester of

- (A) at least 80 mole percent terephthalic acid, and
- (B) at least 80 mole percent 1,4-cyclohexanedimethanol,

wherein the sum of bromine and chlorine on the surface of the fiber is at least four percent of the weight of the fiber and the toughness of the fiber is reduced not more than 20 percent, based on the toughness of a similar fiber with no bromine and chlorine on the surface of the fiber.

The preparation of a highly polymeric linear polyester of poly(1,4-cyclohexylenedimethylene terephthalate), as well as the manufacture of fibers comprised thereof, are accomplished according to methods well known in the art. Therefore, these various methods need not be described in detail herein.

As noted earlier, in one embodiment of this invention the fiber is comprised of a polyester of at least 80 mole percent terephthalic acid. In a preferred embodiment the dicarboxylic acid is substantially all terephthalic acid. Dicarboxylic acids that can be used as comonomers with at least 80 mole percent terephthalic acid include aliphatic, alicyclic, and aromatic dicarboxylic acids having up to 40 carbon atoms. Examples of such acids include oxalic, malonic, succinic, adipic, 1,4-cyclohexanedicarboxylic, isophthalic and the like. It will be understood that the corresponding esters of these acids are included in the term "dicarboxylic acid." Copolyesters may be prepared using two or more of the above dicarboxylic acids or esters thereof.

Also in one embodiment of this invention the fiber is comprised of a polyester of at least 80 mole percent 1,4-cyclohexanedimethanol. In a preferred embodiment the organic diol is substantially all 1,4-cyclohexanedimethanol. Organic diols that can be used as comonomers with at least 80 mole percent 1,4-cyclohexanedimethanol include aliphatic, alicyclic, and aromatic diols having up to 40 carbon atoms. Examples of some of these diols include ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol and 1,3-cyclohexanedimethanol. Copolyesters may be prepared using two or more of the above diols.

The polyesters of this invention have an inherent viscosity of at least 0.5 and preferably at least 0.6 or more measured at 25° C. using 0.23 grams of polymer per 100 ml. of a solvent composed of 60 volumes of phenol and 40 volumes of tetrachloroethane.

In one embodiment of this invention the toughness of the fiber is reduced not more than 20 percent, based on the toughness of the fiber before contacting the

fiber. In another embodiment of this invention the toughness of the fiber is reduced not more than 20 percent, based on the toughness of a similar fiber with no bromine and chlorine on the surface of the fiber.

Toughness is a measure of the area under the stress strain curve. Since this curve is approximately a triangle, toughness in this disclosure and claims is defined as $\frac{1}{2}$ of the tenacity (in grams per denier) times the elongation (in percent) divided by 100 and is expressed in grams per denier.

Tenacity in this disclosure and claims is a measure of the strength of the fiber and is expressed in grams per denier, abbreviated g./d., and is calculated by dividing the initial denier of the fiber under study into the tension in grams required to break the fiber. The values of tenacity in this disclosure and claims can be determined by using a 5-inch specimen in an Instron Model TM tester at a rate of extension of 100 percent per minute.

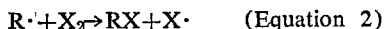
Elongation in this disclosure and claims is a measure of the extent to which a fiber is stretched when it breaks. It is expressed as a percentage and is calculated by dividing the original length of the sample into the increase in length and multiplying by 100. It is measured on an Instron Model TM tester by using a 5-inch specimen at a rate of extension of 100 percent per minute.

Although the exact manner in which the surface of the fiber becomes halogenated is not fully understood, one theory suggests the following explanation.

Bromination of polyesters takes place at an appreciably slower rate than chlorination. Our new, improved process consists of carrying out the bromination reaction in the presence of chlorine which, we have found, greatly increases the rate of bromination and the degree of bromination of the polymer. The reason for this, presumably, is because chlorine radicals are more energetic than bromine radicals and react more readily with the polyester to remove a hydrogen atom in the first step of the halogenation mechanism:



wherein R is the remainder of the polyester chain and $X\cdot$ is a bromine or chlorine free radical. According to T. L. Cottrell, "The Strengths of Chemical Bonds," 2d edition, Butterworths, London, 1958, the energy required to dissociate a hydrocarbon, $R\cdot H$, wherein H is a tertiary hydrogen atom is about 89K cal./mole (94K cal./mole for a secondary hydrogen and 100K cal./mole for a primary hydrogen atom); the energy released when the HBr bond is formed is 87K cal./mole, and 102K cal./mole is released when the HCl bond is formed. Consequently, Equation 1 is endothermic when X is bromine and exothermic when X is chlorine. Therefore, it is assumed that this step of the halogenation takes place considerably more readily when X is chlorine. The second step of the halogenation is quite exothermic for both chlorine and bromine:



The bond dissociation energy for bromine is 46K cal./mole, and that for chlorine is 57K cal./mole; the energy released by formation of RBr is about 65K cal./mole, and that for RCl is about 81K cal./mole. Equation 1, therefore, is the rate-determining step.

Since chlorination takes place more readily than bromination, it is necessary to use an excess of bromine, relative to that of chlorine, if bromination is to be the dominant reaction. When a free radical on the polyester chain is produced by chlorine (Equation 1), an excess of bromine over chlorine is present for this radical to react with (Equation 2). Of course some chlorination will also take place, but the amount of such chlorination can be controlled through regulating the bromine to chlorine ratio. That is, if the bromine to chlorine ratio is high, then the rate of bromination that

will occur on the polyester chain will be higher than the chlorination that will occur. Thus, the average molar concentration of bromine to chlorine should be greater than 1:1. Normally, the average molar concentration of bromine should be at least 2 times and preferably at least 3 times that of the chlorine. Formation of the chlorine free radicals to initiate the reaction may be accomplished with visible or ultraviolet radiation, heat, a free radical catalyst, or a combination of these.

The polyester fibers may be brominated simply by contacting them with gaseous bromine and chlorine in the presence of visible radiation, ultraviolet radiation, and/or heat for a sufficient time for the desired degree of halogenation to be attained. One process consists of immersing the fibers in bromine water and passing in chlorine while the mixture is heated and/or irradiated with visible or ultraviolet radiation. Instead of water, an organic solvent may be used which will not substantially affect the physical properties of the fibers other than to cause slight swelling. The type of solvent which may be used depends upon the polymer structure. In general, suitable organic solvents include carbon tetrachloride, benzene, and chlorobenzene.

The bromination reactions may be carried out at or below room temperature, preferably with the reaction mixtures irradiated with visible or ultraviolet radiation. A more rapid reaction occurs if the mixture is also heated. Temperatures of 0° to 150° C. may be used, depending upon the stability of the polymer, but temperatures of 70° to 120° C. are preferred in aqueous or gaseous systems. The reaction mixture may be heated without illumination with visible or ultraviolet radiation, but a longer reaction time is required.

When the bromination is carried out in a liquid medium, the reaction rate may be enhanced by the use of a free radical catalyst or halogenation promoter instead of, or in addition to, heat or illumination. Since the catalyst initiates the free radical reaction by first dissociating into free radicals itself, the catalyst which is used depends upon the reaction temperature, which must be sufficiently high to cause dissociation at a reasonable rate. Examples of suitable free radical catalysts include acetyl peroxide, benzoyl peroxide, lauroyl peroxide, azobisisobutyronitrile, t-butylperoxypivalate, diisopropylperoxydicarbonate, hydrogen peroxide, the alkali metal persulfates and t-butylperoxide.

At the conclusion of the bromination, the polyester fibers may be rinsed with water or an organic solvent and dried, or they may be only heated in order to remove liquid and gaseous components from the halogenation reaction. Acetone is a preferred solvent for use in rinsing the polyester fibers.

Bromine is the preferred brominating agent, but others may be used under the above reaction conditions in either an aqueous medium or in organic solvents. Examples of other brominating agents include sulfuryl bromide, phosphorus pentabromide, t-butyl hypobromite, sodium hypobromite, potassium hypobromite, and hypobromous acid. Preferably, chlorine gas is used in the process. However, examples of other effective chlorinating agents include sulfuryl chloride, phosphorus pentachloride, t-butyl hypochlorite, sodium hypochlorite, potassium hypochlorite, and hypochlorous acid.

The amount of bromine and chlorine which must be substituted on the surface of the fiber in order to make it self-extinguishing depends primarily upon the size of the fiber as the higher denier fibers require more bromine and chlorine to make them self-extinguishing than the lower denier fibers. In general, three denier polyester fibers become self-extinguishing when they contain about four percent bromine, attached substantially on the surface, and they have improved resistance to burning when they contain at least about one percent bromine. In one embodiment of this invention the sum of the chlorine and bromine on the surface of the fiber is at least four per-

cent of the weight of the fiber while in another embodiment the sum of the chlorine and bromine on the surface of the fiber is at least six weight percent of the fiber. In both these embodiments the toughness of the fiber is reduced not more than 20%, based on the toughness of the fiber before contact or based on the toughness of a similar fiber not containing chlorine and bromine on the surface of the fiber.

The fibers which are brominated according to this invention may contain various additives, such as pigments,

similarly soaked in acetone. After drying, the inherent viscosity, the amount of chlorine and bromine on the surface of the fiber, based on the weight of the fiber, and the tenacity and elongation are determined for each of the five fiber samples. The toughness, calculated as $\frac{1}{2}$ the tenacity times the elongation divided by 100, is then calculated and the percent reduction in toughness of the fiber, based on the toughness of the unhalogenated fiber, is calculated. Results of these determinations and calculations are given in Table 1 below.

TABLE 1

Sample Number	Composition	Contacting time, min.	Inherent viscosity	Cl, wt. percent	Br, wt. percent	Sum of Cl and Br, wt. percent	Tenacity, g./d.	Elongation, percent	Toughness, g./d.	Reduction in toughness, percent
1	Poly(ethylene terephthalate)	None	0.59	None	None	None	4.4	34	0.75	
		120	0.21	2.9	2.5	5.4	1.3	8	0.05	93
2	Poly(tetramethylene terephthalate)	None	0.95	None	None	None	4.4	28	0.62	
		30	0.54	1.3	3.3	4.6	1.6	21	0.17	72
		120	0.42	4.3	5.3	9.6	0.3	2	0.003	99
3	Poly(1,4-cyclohexylenedimethylene terephthalate)	None	0.78	None	None	None	3.0	18	0.27	
		15	0.58	0.9	6.8	7.7	2.8	20	0.28	(¹)
4	Poly(1,4-cyclohexylenedimethylene 80/20 terephthalate/isophthalate)	None	0.80	None	None	None	2.8	20	0.28	
		20	0.55	1.1	9.2	10.3	2.5	18	0.23	18
5	Poly(1,4-cyclohexylenedimethylene 90/10 terephthalate/hexahydro-terephthalate)	None	0.74	None	None	None	3.0	20	0.30	
		10	0.62	0.8	5.2	6.0	2.9	19	0.28	7

¹ No reduction.

antioxidants, fire-retardants, and stabilizers. Examples of effective stabilizers include organo-tin sulfur, organo-tin, epoxy, aziridiny, urea phosphite, unsaturated aliphatic compounds, powdered calcium carbonate, and fatty acid salts of metals, such as cadmium, zinc, and tin.

EXPERIMENTAL

Experimental work is conducted to demonstrate that when the invention is practiced using fiber comprised of a polyester of terephthalic acid and 1,4-cyclohexanedimethanol the toughness of the fiber is reduced not more than 20 percent when the sum of the chlorine and bromine on the surface of the fiber is at least four percent of the weight of the fiber, but when the invention is practiced using fibers comprised of a polyester of terephthalic acid and ethylene glycol or terephthalic acid and tetramethylene glycol the same result does not obtain.

In this experimental work a 3-liter, 3-necked flask is equipped with thermometer, gas addition tube, a reflux condenser, and an aluminum foil reflector which is taped to the back side of the flask. Into the flask is then placed 25 ml. of bromine which forms a pool on the bottom of the flask. A 375-watt floodlamp (visible illumination), placed approximately 12 cm. from the flask, is then turned on the flask and the slow addition of chlorine gas is started. After 1 hr., the lamp has increased the temperature in the flask to 105° C.

A first sample of drawn, unheat-set poly(ethylene terephthalate) fiber, a second sample of drawn, unheat-set poly(tetramethylene terephthalate) fiber, a third sample of drawn, unheat-set poly(1,4-cyclohexylenedimethylene terephthalate), a fourth sample of a drawn, unheat-set fiber of 80 mole percent terephthalic acid, 20 mole percent isophthalic acid and 1,4-cyclohexanedimethanol and a fifth sample of a drawn, unheat-set fiber of 90 mole percent terephthalic acid, 10 mole percent hexahydroterephthalic acid and 1,4-cyclohexanedimethanol are prepared.

All five of these samples are tied to the blade of a glass stirrer, preheated to 90° C., and placed in the flask through the center neck. The hanks are not allowed to contact the pool of bromine on the bottom of the flask. The stirrer is slowly turned so that all sides of the polyester fiber hanks are equally exposed to the light.

Portions of each of the fiber samples are contacted with bromine in the presence of chlorine for varying lengths of time. When the halogenated fibers are removed from the flask, they are orange in color due to absorbed bromine. To remove this bromine the hanks are soaked in acetone overnight. The unhalogenated controls are

These data illustrate that when the invention is practiced using fiber comprised of a polyester of 1,4-cyclohexanedimethanol the toughness of the fiber is reduced not more than 20 percent when the sum of the chlorine and bromine on the surface of the fiber is at least four percent of the weight of the fiber, but when the invention is practiced using fibers comprised of a polyester of ethylene glycol or tetramethylene glycol, the same result does not obtain. Specifically, note that for the fibers of this invention in samples 3, 4 and 5 the toughness of the fiber is in one case not reduced when the sum of the bromine and chlorine is 7.7 weight percent while in the other two cases the reduction is less than 20%. Note also that for the poly(ethylene terephthalate) fiber the toughness is reduced 93% with 5.4 weight percent bromine and chlorine and for the poly(tetramethylene terephthalate) fiber the toughness is reduced 72% with 4.6 weight percent bromine and chlorine and 99% with 9.6 weight percent bromine and chlorine.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A fiber produced by a process comprising contacting with bromine, in the presence of chlorine, in the temperature range of about 0° C. to about 150° C., a fiber comprised of a highly polymeric linear polyester of at least 80 mole percent terephthalic acid and at least 80 mole percent 1,4-cyclohexanedimethanol, wherein the sum of bromine and chlorine on the surface of the fiber is at least four percent of the weight of the fiber and the toughness of the fiber is reduced not more than 20 percent, based on the toughness of the fiber before contacting the fiber.

2. The fiber of claim 1 wherein a halogenation promoter is added to the process, the halogenation promoter being selected from the group consisting of acetyl peroxide, benzoyl peroxide, lauroyl peroxide, azobisisobutyronitrile, t-butylperoxy pivalate, di-isopropylperoxydicarbonate, hydrogen peroxide, the alkali metal persulfates, and t-butylperoxide.

3. A fiber produced by a process comprising contacting a fiber comprised of terephthalic acid and 1,4-cyclohexanedimethanol with bromine in the presence of chlorine in the temperature range of 70° C. to 120° C., wherein the sum of bromine and chlorine on the surface of the fiber is at least six percent of the weight of the fiber and the toughness of the fiber is reduced not more than 20 percent, based on the toughness of the fiber before contact.

7

4. The fiber of claim 3 wherein a halogenation promoter is added to the process, the halogenation promoter being selected from the group consisting of acetyl peroxide, benzoyl peroxide, lauroyl peroxide, azobisisobutyronitrile, t-butylperoxy pivalate, di-isopropylperoxydicarbonate, hydrogen peroxide, the alkali metal persulfates, and t-butylperoxide.

8

2,702,283	2/1955	Wilson et al.	260—6
2,754,217	7/1956	Allen et al.	106—15
2,755,260	7/1956	Stilbert et al.	260—17.4
2,829,070	4/1958	Osborn	117—93
3,274,163	9/1966	Elfers et al.	260—78.4
3,285,995	11/1966	Nametz et al.	260—865
3,356,631	12/1967	Jackson et al.	260—31.2
3,454,672	7/1969	Jackson et al.	260—860

References Cited

UNITED STATES PATENTS

2,607,802	8/1952	Britton et al.	260—544
2,658,086	11/1953	Ruh et al.	260—653

10 MELVIN GOLDSTEIN, Primary Examiner

U.S. Cl. X.R.

260—75 H