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(54) Title: TENSION-FREE HEAT-TREATMENT OF ARAMID FIBER AND FIBRIDS

(57) Abstract

Fibers of the polyterephthalamide of 4,4′-diaminodiphenic acid are strengthened and heat stabilized by a relaxed heat-treatment.

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TITLE

TENSION-FREE HEAT-TREATMENT OF ARAMID FIBER AND FIBRIDS

RELATED APPLICATIONS

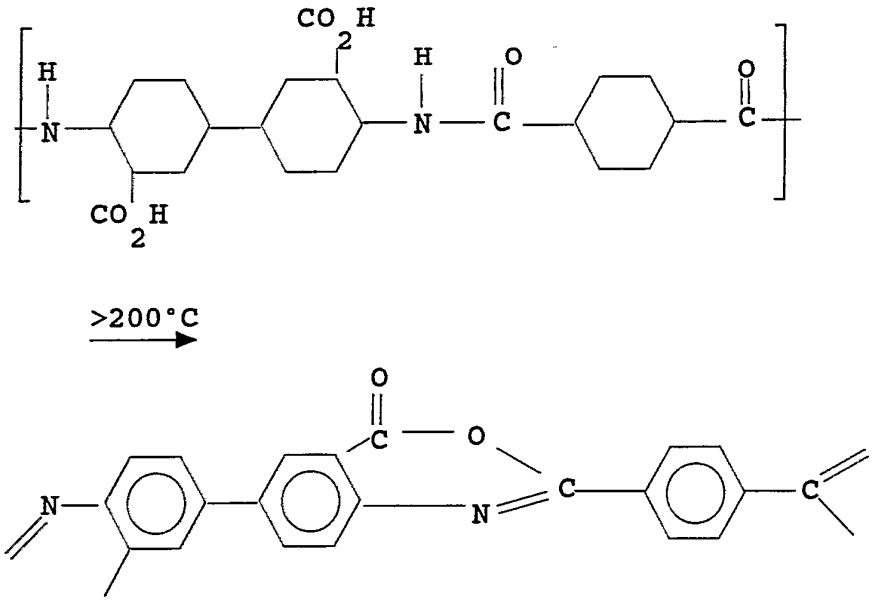
This application is related to my U.S. Application Serial Nos. 07/446,339 and 07/446,338.

BACKGROUND OF THE INVENTION

Oriented para-aramid fibers typified by high strength, high modulus, poly(p-phenylene terephthalamide) fiber show little or no change in tenacity when heated while relaxed or under tension at temperatures of 300-350°C. Relaxed heating at higher temperatures causes a drop in tenacity. Some oriented polyamide fiber such as poly-1,4-benzamide fiber do strengthen when heated under tension by virtue of a crystallization process which improves molecular orientation significantly. Non-para-aramids such as poly(m-phenylene isophthalamide) will show no change or actually decrease in tenacity on heating whether under tension or relaxed, depending on temperature.

In each situation described above, the maximum fiber tenacity is ordinarily attained before the fiber is incorporated into a fabric or other article. Since the present invention deals with tension-free heat-strengthening of aramid fiber and fibrids, it permits the incorporation of fiber into a fabric or fibrids into a paper and subsequent heat treatment to achieve greater strength.

It is believed that the placement of the substituents in the polymer of the as-spun filaments enables the filaments to be heat-strengthened while closely related materials will not survive the heat treatment of the invention. For example,



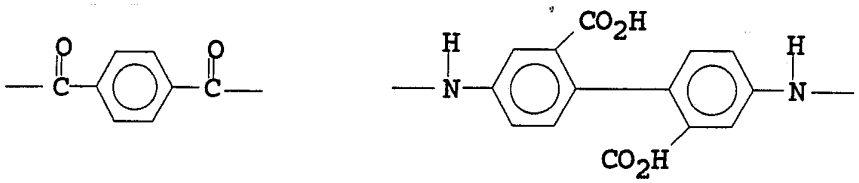
which illustrates thermal cyclization to a class of polymers known as polybenzoxazinones ("Encyclopedia of Polymer Science and Technology" V. 10 pp 682-690, Interscience, N.Y., 1969). In the present invention, this reaction cannot take place, although some dehydration to anhydride may occur upon heat treatment. However, such dehydration does not affect capability of the polymer to form a covalent bond with epoxides and the like.

SUMMARY OF THE INVENTION

The present invention provides a process for strengthening heat stabilizing fibers of the polyterephthalamide of 4,4'-diaminodiphenic acid, consisting essentially of heating the fibers, free from tension, at a temperature in the range of 310°C to 365°C for at least 2 minutes, preferably in an inert atmosphere.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to strengthening and heat-stabilizing fibers of the polyterephthalamide of 4,4'-diaminodiphenic acid (DPA-T). The polytereph-thalamide of 4,4'-diaminodiphenic acid



is described along with its preparation in my U.S. application Serial No. 07/446,338 filed December 5, 1989. The process contemplates heating as-spun fibers of the polymer in a relaxed condition, at a temperature and for a time sufficient to increase the tenacity of the fibers by at least 25% and preferably by at least 50%. The ability to employ a relaxed heat-treatment on the fibers has the advantage of avoiding the need for a more costly hot drawing process step to provide tension. In other cases, as with fibrids, no other way of building up properties may be available since there may be no way to provide tension while heating. By "as-spun" is meant the condition in which the fibers are in prior to relaxed heat treatment. Thus, the fibers may be in the form of a loose batt of staple fibers, a non-woven web, a woven or knitted fabric or some other article form, before being heat-strengthened in said relaxed condition. Also contemplated is the heat-strengthening of coatings, films or fibrids of the polymer and preferably, wet-laid papers containing the fibrids. Presence of the CO_2H groups on the surface of the fiber provides a means for forming strong covalent bonds with resins or binders such as epoxides.

The fiber, film or other extruded articles or fibrids are strengthened and heat-stabilized by heating at temperatures in the range of 310°C to 365°C and preferably at temperatures above 325°C but below decomposition temperatures. The heating is conducted for at least 2 minutes, preferably from 5 to 15 minutes. Increases in tenacity of at least 25% and preferably at least 50% and more are readily attained

as can be easily measured in the case of fibers. The fiber or fibrids are treated while free of tension as they would be in a loose batt, woven or knitted fabric or paper containing the fibrids. Finally, the heat-treatment is conducted under an inert atmosphere such as nitrogen to minimize degradation.

The as-spun fiber or as-prepared fibrids are amorphous in nature and remain amorphous upon heat-treatment. However, as will be seen by the data presented below, significant changes do occur upon heat-treatment. Tenacity, mentioned previously, increases substantially. The heat-strengthened fibers exhibit improved dimensional stability and much lower moisture regain than is the case with as-spun fibers. This is believed to be due to formation of strong interchain hydrogen bonds via the CO_2H groups.

The polymer may be prepared and spun as follows:

(A) Polymer Preparation

In a thoroughly dry resin kettle fitted with a cage-type stirrer, slow flow of dry nitrogen to exclude moist air, thermometer, and external ice bath cooling, a slurry of 4,4'-diaminodiphenic dihydrochloride acid (15.45 g; 0.0448 mole) with anhydrous dimethylacetamide (282 g; 302 ml) was treated at room temperature with diethylaniline (13.34 g; 0.0896 mole) predried by distillation from P_2O_5) to form a clear solution. This was cooled to 10°C and terephthaloyl chloride (9.09 g; 0.0448 mole) added quantitatively. The resulting viscous solution, after stirring for 2 hr at room temperature, was combined with 2.50 g anhydrous calcium oxide to neutralize HCl of polymerization. The resulting 5-6% DPA-T

solution was isotropic at rest but distinctly anisotropic under stress. It had inherent viscosity 7.21, measured at 0.5% solids with dimethylacetamide.

(B) Spinning

The above 5-6% DPA-T dope at 70°C was expressed by an oil-driven piston, via filtration screens, through a 5-hole spinneret (hole diameter = 0.012 cm), through a 1.25-1.86 cm air gap into a coagulating bath of water at 21°C. Fibers were wound up at 41 m/min and a spin-stretch factor of 7.6, under a spray of water to remove solvent traces. After soaking overnight in water, the fiber was allowed to dry out at room temperature. Average (of 5 breaks) tenacity (T), elongation (E), modulus (Mi) and filament denier (dpf) were 2.58 gpd/9.6%/126 gpd/11.6 den. Wide-angle X-ray analysis showed no crystallinity but orientation angle (O.A) was 60.1°. The straw-colored fiber had density of 1.486. Thermomechanical analysis (TMA) indicated a glass transition temperature (Tg) of 302°C and elongation at 400°C = 4.26%.

TMA was performed using a Du Pont Model 2940 Thermomechanical Analyzer. A fiber speciman in which a length of about 7 mm was marked off, was suspended in a heating chamber. The temperature was raised to beyond 400°C at a fixed heating rate. Increases in the length of the marked off portion on heating were recorded electronically on a chart. The glass transition temperature is indicated by a

distinct change in the rate of dimensional change with temperature.

EXAMPLE 1

Loose bundles of fibers prepared as described above (B) were placed in a nitrogen-filled oven and heated at various temperatures for various times.

The properties shown in Table I were measured on specimens stored in a dessicator at relative humidity of 4%. None of the heat-treated specimens had developed crystallinity.

Only very minor change in length on heating to 400°C is noted. This is most unusual for a poorly oriented polymer, heated above its glass transition temperature. Pyrolytic decomposition becomes rapid at ~560°C.

TABLE I
PROPERTIES OF DPA-T FIBERS, HEAT-TREATED UNDER ZERO TENSION

Heat Treatment	dpf	T**	E(%)	Mi**	Tough-ness	O.A.	Moisture* Content (Dried)	TMA Tg	TMA Elong. at 400°C
As-spun	11.0	2.58	9.6	126	0.20	60.1	17.1%	302°C	4.26%
100°C/3 hr	9.4	2.32	5.7	121	0.10	60.4	11.0%	290°C	3.27%
200°C/30 min	11.6	2.32	10.9	120	0.21	57.8	12.0%	263°C	4.00%
300°C/15 min	8.2	2.31	11.3	130	0.21	55.6	7.1%	275°C	2.25%
325°C/6 min	13.0	3.49	8.8	138	0.23	58.9	6.3%	280°C	1.70%
	13.0	2.87	7.5	123	0.16				
350°C/10 min	9.5	4.28	6.8	142	0.19	53.2	2.7%	267°C	0.71%
350°C/25 min	17.3	1.69	2.0	118	0.02	54.5	5.0%	288°C	0.84%

* By heating at 110°C until constant weight is reached.
** In grams per denier (gpd)

Claims:

1. A process for strengthening and heat stabilizing fibers, films or extruded articles of the polyterephthalamide of 4,4'-diaminodiphenic acid, consisting essentially of heating the fibers, free from tension, at a temperature in the range of from 310°C to 365°C for at least 2 minutes.

2. A process according to claim 1 wherein the fibers to be treated are in a fabric.

3. A process according to Claim 1 wherein heating is continued for from 5 to 15 minutes.

4. A process according to Claim 1 wherein heating takes place in an inert atmosphere.

5. A process for strengthening and heat stabilizing fibrids of the polyterephthalamide of 4,4'-diaminophenic acid, consisting essentially of heating the fibrids, free from tension, at a temperature in the range of from 310°C to 365°C for at least 2 minutes.

6. A process according to claim 5 wherein the fibrids to be treated are in a paper.

7. A process according to Claim 5 wherein heating is continued for from 5 to 15 minutes.

8. A process according to Claim 5 wherein heating takes place in an inert atmosphere.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/03113

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D06M10/00; D21H13/26; D21H25/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	D06M ; D21H ; D01F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	US,A,3 888 965 (STEPHANIE LOUISE KWOLEK) 10 June 1975 see the whole document	1-8
A	US,A,4 162 346 (RUFUS S. JONES, JR. ET AL) 24 July 1979 see column 6, line 48 - column 7, line 26	1-8
A	US,A,3 817 941 (THOMAS I. BAIR ET AL) 18 June 1974 see column 13, line 22 - line 38 see column 13, line 50 - column 14, line 8	1-8
A	WO,A,9 006 229 (THE DOW CHEMICAL COMPANY) 14 June 1990 see the whole document	1-8

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
15 SEPTEMBER 1992	21. 09. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BLAS V.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 303 173 (SUMITOMO CHEMICAL COMPANY) 15 February 1989 see page 4, line 34 - line 56	1,6
P,A	US,A,5 039 785 (ROBERT S. IRWIN) 13 August 1991 cited in the application see example 6	1-8

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9203113 SA 60515

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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US-A-4162346	24-07-79	None		
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