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(54) **Heat treatment for increasing compressive strength of PPTA filaments**

(57) The invention pertains to a method for obtaining a PPTA yarn with increased compressive strength by the steps of air gap spinning a PPTA spin dope to PPTA filaments, bundling the filaments to the yarn, washing and optionally neutralizing and drying the yarn, **characterized in that** these steps are followed by applying a heat treatment to the PPTA yarn comprising heating the

yarn at a temperature of 340 to 510 °C for 5 sec to 5 min under exclusion of oxygen. The invention further relates to a PPTA yarn thus obtained having filaments with an average compressive strength σ_c of at least $0.8 + 2.5 \cdot 10^{-3} \cdot (E - 100)$ GPa, wherein E is the modulus in GPa.

EP 2 218 807 A1

Description

[0001] The invention relates to a method for obtaining a PPTA [poly(para-phenylene terephthalamide)] yarn with increased compressive strength and to PPTA yarn thus obtained.

[0002] It is an objective of the present invention to provide PPTA yarns having filaments with improved compressive properties. It was found that this objective could be reached if the yarn receives an after treatment wherein the yarn is subjected to particular heating conditions.

[0003] Heating PPTA yarn is a common process to remove water that adheres to the yarn after neutralizations and washing during the spinning process. Such heating processes typically are performed at about 150 to 250 °C for typically not longer than a few seconds.

[0004] Yarns spun from anisotropic solution of high molecular weight aromatic polyamides are known in literature. The process of making wholly aromatic polyamides is taught by Kwolek et al. in US 3,063,966. The processing for spinning wholly aromatic polyamide yarns from anisotropic solutions is taught in US 3,154,610 and US 3,414,645. The preparation of anisotropic dopes of aromatic polyamides is disclosed in US RE 30,352.

[0005] Several attempts to improve compressive properties of polymeric yarns in general, and PPTA yarns in particular, are known. Sweeny reported the thermal elimination of halogens from the aryl moieties followed by the cross-linking of the halogen-free aryl moieties, in order to create inter-chain covalent bonding between the aryl moieties and increasing the compressive strength (Sweeny, W., Improvements in compressive properties of high modulus yarns by crosslinking. J. Polym. Sci., Part A: Polym. Chem., 1992, 30(6): p. 1111-1122).

[0006] D.J. Sweeney et al. in High Perf. Polym., 14, 133-143 (2002) performed a heat treatment on unmodified PPTA yarn (Kevlar-29 fiber) to improve the compressive strength of the yarn. Yarns were slowly heated to 400, 440, or 470 °C and held at that temperature for 5 to 10 minutes. The yarns were slowly brought to these temperatures by using a heating rate (ramp) of 2.5 to 7.5 °C/min. Thus the minimum period that the yarns were kept between 340 and 400 °C was 13 minutes, and the period between 360 and 400 °C was at least 10 minutes. Thus the yarns were heated for relatively long periods and only moderate improvements were found at compressive strengths which were found to be from 0.31 to 0.63 GPa.

[0007] Common heating conditions have been described in US 3,869,430. The yarns are heated within a zone maintained at a temperature of at least 150 °C under a tension of at least 0.45 cN/dtex. The use of 150 °C for a period of 60 seconds under a tension of 9 cN/dtex has been found satisfactory for a 171 dtex yarn. Higher temperatures can be used, but using very short heating times. Thus the use of a 650 °C zone has only given good results with a 360 dtex yarn for periods of from 0.6 to 1.0 second at 5.5 cN/dtex. Extension of the time at this high temperature leads to higher modulus but also to a serious loss in tensile strength. Thus zone temperatures as high as 800 °C or more could only be used at sufficiently short times and low tensions. The use of high temperatures and long times under these conditions leads to excessive degradation of the yarn resulting in losses of tensile strength and/or inherent viscosity.

[0008] Contrary to most of the prior art attempts wherein modified PPTA was used, the present invention allows standard spin dope preparation and dry jet wet (air gap) spinning techniques that can be used without modifications of the aryl moieties as opposed to earlier described. Yarns were prepared from PPTA having a compressive strength as high as 1.3 GPa or even higher.

[0009] The standard search to compressive strength of PPTA filaments has been published in a paper by M.G. Northolt and D.J. Sikkema in Adv. in Pol. Sci., 98, page 336 (1990). These authors disclose that the compressive strength of polymer filaments increases with increasing modulus, but for PPTA filaments the compressive strength σ_c does not exceed the maximum value of about 0.85 GPa.

[0010] It has now been found that the compressive strength of PPTA yarn can considerably be increased with regard to these commonly known PPTA yarns by applying a heat treatment, without the need to use halogenated or otherwise modified aryl moieties, which treatment is fundamentally different from the usual heat treatments that are performed for drying the yarn.

[0011] To this end the invention relates to a method for obtaining a PPTA yarn with increased compressive strength by the steps of air gap spinning a PPTA spin dope to PPTA filaments, bundling the filaments to the yarn, washing and optionally neutralizing and drying the yarn, characterized in that these steps are followed by applying a heat treatment to the PPTA yarn comprising heating the yarn at a temperature of 340 to 510 °C for 5 sec to 5 min under exclusion of oxygen.

[0012] Thus this method renders PPTA yarns having improved compressive strength by applying a heating process for a relatively long time at relatively low tensions. This heating step is in addition to the commonly used steps of making PPTA yarns, including air gap spinning, which includes coagulating the spun filaments and bundling these to yarn, followed by one or more of well-known process steps as washing, neutralizing, drying, winding and the like.

[0013] The best compressive strength improvement is obtained when the heat treatment of the yarn is performed at a temperature of 360 to 480 °C for 20 sec to 2 min. It was found that the results improved at higher temperature at the lower end of the claimed time period, thus better results are obtained when the heat treatment is performed at a tem-

perature of 410 to 440 °C for 20 sec to 1 min, or even better when performed at a temperature of 425 to 435 °C for 20 sec to 1 min. In general shorter heating times are used at higher heating temperatures.

[0014] The best results are obtained when apart from temperature and heating time also the tension is controlled. Preferably the heat treatment is performed at a tension of 0.02 to 3 cN/dtex, more preferably at a tension of 0.1 to 0.5 cN/dtex, and most preferably at a tension of 0.1 to 0.3 cN/dtex.

[0015] The heating step of this invention is performed under exclusion of oxygen. The presence of oxygen during this treatment has a negative influence on the tenacity of the yarn. Oxygen therefore must be removed as good as possible from the heating device, such as an oven, for instance by flushing with inert gas such as nitrogen, helium, and the like. In any case the amount of oxygen must be brought to less than 1 vol%, preferably less than 0.5 vol%.

[0016] The PPTA yarns were spun from anisotropic solutions of aromatic polyamides in sulfuric acid, but other solvents such as NMP/calcium chloride can also be used. The aromatic polyamides were prepared using conventional polycondensation reaction techniques. The spin dopes could be prepared by mixing the polymer with sulfuric acid ice. The yarns can be spun via the known dry jet wet spinning procedure.

[0017] The present method of the additional heat treatment may render PPTA yarns wherein the filaments have compressive strengths that have never been obtained earlier. Thus at any modulus the compressive strength of the filaments (of PPTA yarns) is higher than in the similar yarns not having undergone the additional heat treatment. The invention therefore has also to its objective PPTA yarns wherein the average compressive strength σ_c of its filaments is at least $0.8 + 2.5 \cdot 10^{-3} \cdot (E-100)$ GPa, wherein E is the modulus in GPa.

The term "average compressive strength" (σ_c) means the average of the measured compressive strength values of 3 filaments that are at randomly taken from the yarn.

[0018] Thus according to M.G. Northolt and D.J. Sikkema common PPTA yarns have filaments with compressive strength 0.5 GPa at a modulus of 50 GPa, whereas this PPTA yarn after the heat treatment of this invention has a compressive strength of at least about 0.68 GPa. PPTA yarns with compressive strength 0.95 GPa or higher are yarns that have never been obtained earlier. PPTA yarns having filaments with compressive strengths of at least 0.95 GPa, more preferably of at least 1 GPa, are therefore novel and also an objective of this invention. These yarns with extreme high compressive strength filaments are obtained by selecting optimum heating conditions with regard to temperature and heating time.

[0019] The invention is further illustrated by the following non-limitative examples.

General procedure for heat treatment

[0020] The treatment was done in an oven of 3.66 m length. The oven was under nitrogen to a residual level of less than 0.3 vol% oxygen.

Measurement of the compression strength

[0021] Yarns were equilibrated at 21 °C and 65% RH. The compressive strength was determined via the elastica loop test (ELT) according to D.J. Sinclair, J. Appl. Phys., 21 (1950) 380. In this test a filament is bent into a single asymmetric loop wherein the diameters are a few millimeters, immersed in paraffin, covered with a glass slide, which is then gradually contracted. Images were acquired during contraction, followed by measuring the c- and α -axes, wherein the c-axis is the largest diameter and the α -axis is the smallest diameter of the loop. The compressive strength σ_c is calculated from c^* , which is determined by taking the intersection of two lines that can be drawn through the graph c/a before and after kink bend formation. The c^* is obtained by semi-automatic drawing both lines. Before kink bend formation the theoretical ratio c/a is 1.34. The compressive strength is calculated according to the equation:

$$\sigma_c = 2.85 \frac{E \cdot r}{c^*}$$

wherein

σ_c : is compressive strength in GPa

E is Youngs modulus in GPa from tensile measurements

r is initial radius of the filament in mm, as determined with optical microscopy

c^* : is value of the c-axis at which the c/a-ratio starts to deviate from 1.34.

Measurement of the modulus, tenacity, EAB, and toughness

[0022] Modulus, tenacity, EAB (elongation at break), and toughness of the yarns were measured according to ASTM D885.

Preparation of Spine Dope

[0023] In a mixing vessel solid sulfuric acid having a concentration of 99.8% and high molecular weight PPTA were initially mixed at temperatures below 10 °C. Subsequently, the temperature of the polyamide sulfuric acid mixture was allowed to rise to room temperature resulting in a dry sandy mass, for use in making the spin dope. Alternatively, the PPTA and concentrated sulfuric acid can be mixed in a twinscrew extruder above room temperature to directly obtain the spin dope.

Preparation of yarns

[0024] PPTA spin dope was spun to filament yarn of different linear densities and finally washed and dried in the conventional manner. The yarn was heat treated in a tube oven at the temperatures and times as indicated in Table 1 in an inert environment (max. 0.25 vol.% O₂). The properties of these yarns are listed in Table 1. PPTA is poly(paraphenyleneterephthalamide); Comp. = compression

Table 1 Mechanical properties of PPTA yarns after heat treatment

Tension cN/dtex	Heating time sec	Temp °C	Linear density dtex	Tenacity mN/tex	EAB %	Modulus GPa	Toughness J/g	Comp. Strength Gpa
-*	-	-	89	2195	3.2	91	35.7	0.56
0.36	28	380	86	2019	2.5	115	24.9	0.94
-*	-	-	71	2242	3.05	103	34.6	0.63
0.22	28	360	66	1978	2.3	123	22.7	0.98
0.75	28	360	66	1988	2.3	128	22.3	0.98
2.27	28	360	65	2103	2.2	135	22.8	0.86
0.22	28	400	65	2144	2.4	124	24.7	1.05
0.75	28	400	65	2085	2.3	130	22.8	1.01
2.27	28	400	65	2111	2.1	138	22.1	1.05
0.22	28	430	65	2052	2.2	128	22.4	1.25
0.75	28	430	65	2079	2.1	137	22	1.11
2.27	28	430	65	2032	2	145	19.9	0.99
2.27	56	400	65	2124	2.2	140	21.8	0.95
0.22	56	430	64	1903	2	134	18.8	1.22
-*	-		1684	2030	3.09	91.3	30.8	0.5 [#]
1.8	28	410	1649	1700	1.99	122.4	16.6	0.87
1.7	28	430	1642	1670	1.95	123	16.0	0.96
* comparative example: No heat treatment # estimated								

Claims

1. A method for obtaining a PPTA yarn with increased compressive strength by the steps of air gap spinning a PPTA

spin dope to PPTA filaments, bundling the filaments to the yarn, washing and optionally neutralizing and drying the yarn, **characterized in that** these steps are followed by applying a heat treatment to the PPTA yarn comprising heating the yarn at a temperature of 340 to 510 °C for 5 sec to 5 min under exclusion of oxygen.

- 5 **2.** The method according to claim 1 wherein the heat treatment is performed at a temperature of 360 to 480 °C for 20 sec to 2 min.
- 3.** The method according to claim 1 wherein the heat treatment is performed at a temperature of 410 to 440 °C for 20 sec to 1 min.
- 10 **4.** The method according to claim 1 wherein the heat treatment is performed at a temperature of 425 to 435 °C for 20 sec to 1 min.
- 5.** The method according to any one of claims 1-4 wherein the heat treatment is performed at a tension of 0.02 to 3 cN/dtex.
- 15 **6.** The method according to any one of claims 1-4 wherein the heat treatment is performed at a tension of 0.1 to 0.5 cN/dtex.
- 7.** The method according to any one of claims 1-4 wherein the heat treatment is performed at a tension of 0.1 to 0.3 cN/dtex.
- 20 **8.** A PPTA yarn having filaments with an average compressive strength σ_c of at least $0.8 + 2.5 \cdot 10^{-3} \cdot (E-100)$ GPa, wherein E is the modulus in GPa.
- 25 **9.** The PPTA yarn of claim 8 having filaments with an average compressive strength σ_c of at least $0.85 + 2.5 \cdot 10^{-3} \cdot (E-100)$ GPa, wherein E is the modulus in GPa.
- 10.** The PPTA yarn of claim 8 having filaments with an average compressive strength of at least 0.95 GPa.
- 30 **11.** The PPTA yarn of claim 8 having filaments with an average compressive strength of at least 1.0 GPa.



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Application Number
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