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(54) Process for the preparation of polyethylene terephthalate monofilaments.

(57) A process for the preparation of a polyethylene terephthalate monofilament is provided in which a non-drawn monofilament formed from 100 ppw of polyethylene terephthalate and 5-150 ppw of a modified polyethylene terephthalate is subjected to two drawings, the first at 85-100°C in humid conditions, increasing the size by 2.8 to 4.0 times, the second at 180-250°C in a gas atmosphere, increasing the size by 1.5-2.5 times, and then to heat treatment at 180-250°C and a take-up ratio of 0.9-1.0.

The monofilament prepared has been found to have a substantially identical or higher knot strength against tension and transparency, and an increased knot strength against impact than previously used polyethylene terephthalate monofilaments, and the monofilament also has been found to be superior to conventional nylon monofilaments without loss of linear strength and transparency. Such monofilaments find use as fishing line and racket gut.

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Process for the preparation of polyethylene terephthalate monofilaments

The present invention relates to a process for the preparation of polyethylene terephthalate monofilaments.

Monofilaments derived from polyethylene terephthalate have a high rigidity as compared with nylon monofilaments and have suitable qualities for use as fishing lines, especially leaders, gut for tennis rackets and other uses requiring rigidity. However, conventional polyethylene terephthalate monofilaments have shown the disadvantage that, although the monofilaments have a knot strength against tension almost identical with that of nylon monofilaments of the same fineness, their knot strength against impact is so small as to be in the range of between one-sixth and one-tenth of that of the nylon monofilaments.

A process for the preparation of polyethylene terephthalate monofilaments has been disclosed in Japanese Laid Open Patent Application No. 103308/1980. By that process a polyethylene terephthalate monofilament not subjected to drawing is drawn to 3 to 3.5 times its original size in water having a temperature of in the range of from 85 to 95°C and the monofilament is further drawn to 1.7 to 2.3 times the first drawn size in a gas having a temperature of

in the range of from 150 to 260°C. The monofilament is then subjected to heat treatment in a gas having a temperature in the range of from 200 to 260°C through take-up ratios (or relax ratios) of between 1.0 and 0.95. Although polyethylene terephthalate monofilaments produced by this method have been found to be remarkably improved in knot strength, especially knot strength against impact, the knot strength against impact shown by the monofilaments is still inferior to that of nylon monofilaments.

It is an object of the present invention to provide an improved polyethylene terephthalate monofilament which has a knot strength against both impact and tension substantially identical with or superior to a nylon monofilament, without loss of linear strength.

The present invention provides a process for the preparation of a polyethylene terephthalate monofilament in which a non-drawn monofilament made of a mixture comprising 100 parts by weight of polyethylene terephthalate and in the range of from 5 to 150 parts by weight of modified polyethylene terephthalate having a molar ratio of terephthalic acid to isophthalic acid in the range of from 97/3 to 80/20 is drawn to 2.8 to 4.0 times its original size at a temperature in the range of from 85 C to 100°C under humid heating conditions and is further drawn to 1.5 to 2.5 times its first drawn size in a gas having a temperature in the range of from 180 to 250°C and then, the second drawn monofilament is heat treated in a gas having a temperature of in the range of from 180 to 250°C through a take-up ratio of in the range of from 0.9 to 1.0.

A polyethylene terephthalate monofilament prepared according to a process of the present invention has a knot strength against tension substantially identical to or higher than conventional polyethylene terephthalate monofilaments and also has a far greater knot strength against impact than

such filaments. More importantly, a monofilament prepared by a process of the invention has been found to be stronger than a conventional nylon filament in terms of both tensile strength and knot strength. A monofilament of the invention also does not show any whitening of the filament. Whitening in a filament indicates that although the filament is strong the filament can split easily in the vertical direction in use; this is an important disadvantage with regard to fishing lines.

Where the conditions for the process of the present invention and the amounts of the compounds used in the process are substantially lower or higher than that specified, the monofilaments produced do not exhibit the advantagous properties described. In particular, where conditions or amounts of a higher order are used, whitening occurs.

Polyethylene terephthalate suitable for use in the present invention should have an ultimate viscosity of between 0.4 and 1.5, preferably of between 0.6 and 1.2 (the ultimate viscosity is the viscosity, at a temperature of 30°C, of a solution containing 1g resin per 100 ml of solvent, the solvent being a mixture of tetrachloroethane and phenol in a weight ratio of 1/1).

Modified polyethylene terephthalate having a molar ratio of terephthalic acid to isophthalic acid ranging from 97/3 to 80/20 (referred to hereinafter as "a modified polyethylene terephthalate") is prepared by mixing terephthalic acid or an ester-forming derivative thereof, such as dimethyl isophthalate, and isophthalic acid or an ester-forming derivative thereof, such as dimethyl isophthalate, in a molar ratio of between 97/3 and 80/20 and then, subjecting the mixture to condensation polymerization with ethylene glycol or ethylene oxide by any suitable production method for a polyester.

The modified polyethylene terephthalate suitably has

an ultimate viscosity of in the range of from 0.4 to 1.5, preferably from 0.6 to 1.2

Preferably, the mixture of polyethylene terephthalate and the modified polyethylene terephthalate used contains from 10 to 100 parts by weight of the modified polyethylene terephthalate.

In the mixture of polyethylene terephthalate and the modified polyethylene terephthalate, the molar ratio of terephthalic acid to isophthalic acid is usually in the range of from 99:1 to 90:10, preferably of from 99:1 to 95:5. The ratio will vary according to the amount of isophthalic acid in the modified polyethylene terephthalate and the mixing ratio of polyethylene terephthalate and the modified polyethylene terephthalate.

Polyethylene terephthalate and the modified polyethylene terephthalate can be mixed by suitable methods in which, for example, pellets of both the components are blended, the blended substance subjected to fusion kneading using an extruder and extruded so as to be formed into a pellet.

A non-drawn monofilament may be produced by subjecting the specified mixture of polyethylene terephthalate and the modified polyethylene terephthalate to fusion spinning in usual manner. The non-drawn monofilament should suitably have a fineness of more than 100 denier, usually more than 200 denier, but less than some ten thousands denier.

According to a process of the present invention, the non-drawn monofilament is drawn twice under specific conditions and then heat treated under specific conditions.

In the conditions specified, the temperature of the surrounding fluid is an average of 3 or more temperatures of the fluid measured adjacent to the monofilament within 1 cm from the monofilament. The drawing magnification is the value given from consideration of the speed ratio of a feed

roller and a take-up roller.

If the temperature at both drawing stages is too low, a monofilament having a high knot strength against impact cannot be obtained. If the temperature is too high, its knot strength is improved but an undesirable whitening phenomenon of the monofilament occurs. If the drawing magnification is too low, its knot strength is not improved. If the drawing magnification is too high, an undesirable whitening phenomenon of the monofilament occurs.

In the first drawing stage, the temperature under wet or humid heating conditions is preferably in the range of from 93 to 97°C. The drawing magnification in that stage is preferably in the range of from 3.0 to 3.5. A residence time of the monofilament in the drawing is usually in the range of from 2 to 10 sec., preferably from 3 to 6 sec.

It is to be noted that drawing under wet or humid heating refers to drawing in, for example, hot water or steam.

The monofilament thus drawn as described above is further drawn in heated gas to 1.5 to 2.5 times the first drawn size in the second drawing stage. As the gas, air or inert gases such as nitrogen may be employed but usually air is used. The temperature of the medium in the second drawing stage is preferably in the range of from 180 to 240°C. The drawing magnification is preferably in the range of from 1.8 to 2.2. The residence time of the monofilament in the drawing is normally in the range of from 1 to 10 sec., preferably from 2 to 4 sec.

As noted above, after the second drawing stage the monofilament is then heat treated. Again if the temperature is too low, a monofilament having a high knot strength against impact cannot be obtained and, if the temperature is too high, an undersirable whitening phenomenon of the monofilament occurs. It is important that drawing should

not be performed in the heat treatment. If drawing is performed in the heat treatment, a monofilament having a high knot strength against impact cannot be obtained.

The temperature in the heat treatment is advantageously higher than that for the above-described drawing and is preferably in the range of between 185 and 245°C. The residence time of the monofilament in the heat treatment is generally in the range of from 1 to 3 sec., preferably from 1 to 2 sec.

A "take-up" or "relax" ratio is the ratio of the speed of rotation of the take-up roller, or filament winding drum, to that of the feed roller, or filament releasing drum. For example, a take-up roller rotating at 90 m per minute and a feed roller rotating at 100 m per minute would give a take-up ratio of 0.9.

If the take-up ratio is too small, the monofilament will become loose, and give rise to difficulty of process operations. The take-up ratio is preferably in the range of from 0.95 to 0.98.

A total drawing magnification given as a result of all three stages, i.e. the product of values of the drawing magnification for each of the two drawing steps and a value of the take-up ratio in the heat treatment is suitably in the range of from 5.5 to 6.5, preferably from 6 to 6.25.

Knot strength against tension in the dried state is a value measured in accordance with JIS-L1070 while knot strength against impact in the dried state is a value of a force required for cutting a knotted portion of a monofilament by applying an impact to the monofilament in its longitudinal direction with one end of the monofilament being fixed to a jig and the other end being held by the jig, such as by the use of an impact tester.

In accordance with the present invention, a polyethylene terephthalate monofilament having a substantially

identical or higher knot strength against tension and transparency and a far higher knot strength against impact in comparison with polyethylene terephthalate monofilaments produced by previously proposed methods, can be produced. It has been found, in comparison with conventional nylon filaments, that a filament of the present invention is in the range of from 10 to 15% stronger in terms of tensile strength and in the range of from 15 to 20% stronger in terms of knot strength. Such monofilaments are of high industrial value.

The following Examples illustrate the invention.

In the Examples, knot strength against impact was measured using a Universal Impact Tester manufactured by Toyo Seiki Seisakusho Co., Ltd. and the transparency was based on a visual inspection in which a monofilament 2000 m. in length was wound around a bobbin of 10 cm diameter and 20 cm height.

Examples 1 to 5 and Comparative Examples 1 and 2

Polyethylene terephthalate (Novapet 1110B produced by Mitsubishi Kasei Kogyo Co., Ltd.), in pellet form having an ultimate viscosity of 1.10 and modified polyethylene terephthalate, in pellet form, having an ultimate viscosity of 0.73, obtained by condensation polymerization of a mixture, having a molar ratio of 90:10, of dimethyl terephthalate to dimethyl isophthalate, and ethylene glycol were mixed in usual manner at the ratios shown in Table 1 to produce a non-drawn monofilament having a fineness of 2400 denier. The non-drawn monofilament was fed at a rate of 20m/min. and was subjected to first drawing in hot water, second drawing in air, and heat treatment in air under conditions described in Table 1.

The knot strength against tension in the dry state, knot strength against impact in the dry state, and transparency of the monofilament thus obtained are also shown in Table 1. Meanwhile, for comparative purpose, a monofilament of each of the above-described polyethylene terephthalate and modified polyethylene terephthalate was

drawn and heat treated independently under the same conditions as those of Example 1. The results are also shown in Table 1.

Example 6 and Comparative Example 3

One hundred parts by weight of polyethylene terephthalate (Novapet 1075B produced by Mitsubishi Kasei Kogyo Co., Ltd.), in pellet form, having an ultimate viscosity of 0.715, and 25 parts by weight of modified polyethylene terephthalate, the same as that employed Example 1, were mixed to produce a non-drawn monofilament having a fineness of 2400 denier, in usual manner.

After the non-drawn monofilament was fed at a rate of 20m/min., it was drawn to 3.0 times its original size in hot water at a temperature of 96°C and then drawn to 2.14 times the first drawn size in air at a temperature of 200°C and heat treated in air at a temperature of 230°C and a take-up ratio of 0.98.

The monofilament thus obtained had a knot strength against tension, of 5.3 g/d in the dry state, a knot strength against impact, of 85 $kg.cm/mm^2$ in the dry state and was transparent. For comparative purpose, only the above-described polyethylene terephthalate was used and was drawn and heat treated in the same manner as described above. The monofilament thus obtained had a knot strength against tension, of 5.3g/d in the dry state, a knot strength against impact, of 60 $kg.cm/mm^2$ in the dry state and was subject to slight whitening.

Example 7

One hundred parts by weight of polyethylene terephthalate, in pellet form, the same as that employed in Example 1, and 67 parts by weight of modified polyethylene terephthalate, in pellet form, having an ultimate viscosity of 0.745 obtained by condensation polymerization of a mixture, having a molar ratio of 95:5, of dimethyl terephthalate to dimethyl

isophthalate and ethylene glycol were mixed so as to produce a monofilament in the same manner as in Example 6.

The monofilament thus obtained had knot strength against tension, of 5.48 g/d in the dry state, a knot strength against impact, of 77 kg.cm/mm^2 in the dry state and was transparent.

TABLE 1

	(3)		(4)	(5)		(6)		(7)		(18)
	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	
(1) 1.	100	100	96	3.0	215	2.04	227	0.98	5.01	102	(19)
2.	100	43	"	"	"	"	"	"	5.87	90	"
3.	100	25	"	"	"	"	"	"	6.00	90	"
4.	100	25	"	"	200	2.13	"	"	6.73	60	"
5.	100	18	"	"	215	1.79	"	"	5.21	71	"
(2) 1.	100	0	"	"	"	"	"	"	4.71	42	(20)
2.	0	100	"	"	"	2.04	"	"	4.91	42	"

1: Embodiment
2: Comparative example
3: Mixing ratio
4: 1st drawing
5: 2nd drawing
6: Heat treatment
7: Knot strength in draw state
8: Polyethylene terephthalate (parts by weight)
9: Modified polyethylene terephthalate (parts by weight)
10: Temp. (^{o}C)
11: Magnification
12: Temp. (^{o}C)
13: Magnification
14: Temp. (^{o}C)
15: Take-up ratio
16: Tension (g/d)
17: Impact (kg.cm/mm^{2})
18: Transparency
19: Transparent
20: Slightly opaque

Claims:

1. A process for the preparation of a polyethylene terephthalate monofilament, comprising the steps of:

forming a non-drawn monofilament from 100 parts by weight of polyethylene terephthalate and in the range of from 5 to 150 parts by weight of modified polyethylene terephthalate, said modified polyethylene terephthalate having a molar ratio of terephthalic acid to isophthalic acid in the range of from 97:3 to 80:20;

drawing said non-drawn monofilament to in the range of from 2.8 to 4.0 times its initial size at an average temperature in the range of from 85 to 100°C under wet heating conditions;

drawing said first drawn monofilament to in the range of from 1.5 to 2.5 times its first drawn size in a gas at an average temperature in the range of from 180 to 250°C; and

heat treating said second drawn monofilament in a gas at an average temperature in the range of from 180 to 255°C at a take-up ratio in the range of from 0.9 to 1.0.

2. A process as claimed in claim 1, wherein the monofilament is formed from 100 parts by weight of polyethylene terephthalate and in the range of from 10 to 100 parts by weight of modified polyethylene terephthalate.

3. A process as claimed in claim 1 or claim 2, wherein the first drawing is carried out at a temperature in the range of from 93 to 97°C.

4. A process as claimed in any one of claims 1 to 3, wherein the monofilament is drawn in the first drawing stage to in the range of from 3.0 to 3.5 times its original size.

5. A process as claimed in any one of claims 1 to 4, wherein the second drawing is carried out at a temperature in the range of from 180 to 240°C.

6. A process as claimed in any one of claims 1 to 6, wherein the monofilament is drawn in the second drawing

stage to in the range of from 1.8 to 2.2 times its first drawn size.

7. A process as claimed in any one of claims 1 to 6, wherein the heat treatment is carried out at a temperature in the range for from 185 to 245°C.

8. A process as claimed in any one of claims 1 to 7, wherein the take-up ratio in the heat treatment stage is in the range of from 0.95 to 0.98.

9. A polyethylene terephthalate monofilament which is formed from a mixture of 100 parts by weight of polyethylene terephthalate and in the range of from 5 to 150 parts by weight of modified polyethylene terephthalate, the modified polyethylene terephthalate having a molar ratio of terephthalic acid to isophthalic acid in the range of from 97:3 to 80:20.

10. A monofilament as claimed in claim 9, in which the molar ratio of terephthalic acid to isophthalic acid is in the range of from 99:1 to 90:10.

11. A monofilament as claimed in claim 10, wherein the molar ratio is in the range of from 99:1 to 95:5.

12. A monofilament as claimed in any one of claims 9 to 11, which is prepared by a process as claimed in any one of claims 1 to 8.

13. Fishing tackle or a racket which incorporates a monofilament as claimed in any one of claims 9 to 12.