EUROPEAN PATENT APPLICATION

(12)

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(54) **High strength polyester yarn.**

(57) A polyester yarn is disclosed comprising primarily polyethylene terephthalate for use in reinforcing rubber goods and having the following properties:
  (a) an intrinsic viscosity of at least 0.91,
  (b) a tenacity of at least 8 g/d,
  (c) $E_{2.25}$ of 4.5 percent or less,
  (d) ΔH_{mf} of at least 11.4 cal/g,
  (e) $(Tmf - TmF)$ of at least 20°C, and
  (f) an amorphous orientation function of 0.75 or less.

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Description

HIGH STRENGTH POLYESTER YARN

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BACKGROUND OF THE INVENTION

This invention is related to polyester yarn which has high strength and excellent durability and is particularly suitable as a rubber-reinforcing material.

10 The fiber made from polyethylene terephthalate, or from a polyester in which it is the main component, has excellent mechanical properties and thermal properties and it is widely used in the manufacture of tire cords, V belts, conveyor belts and hoses. In particular it takes the largest ratio in the application as the rubber-reinforcing material where polyester fibers of high strength and excellent durability with balanced heat shrinkage and modulus are required.

15 As a method of obtaining a polyester fiber of high strength, for example as seen in US Patent No. 3216187, a method of spinning a polymer having a high degree of polymerization under a low stress to suppress the molecular orientation and drawing the resulting undrawn yarn to a maximum possible draw ratio has been previously proposed. However, although fiber of high strength is obtained by this method, the fiber has a large heat shrinkage because the amorphous section is highly oriented and one can obtain only the fiber with inadequate durability.

20 For this reason, a method of spinning a polymer having relatively high degree of polymerization under a high stress and drawing to a low draw ratio to lower the degree of orientation in the amorphous section and reduce the heat shrinkage to obtain the fiber of good durability has also been proposed. (U.S. Patent No. 4195052). With this method, however, it is difficult to obtain fiber of high strength which is adequate for use as a rubber-reinforcing material.

25 Also, when the polyester fiber is used as the rubber-reinforcing material, it is necessary to subject it to a twisting process and a dip process (process of applying adhesive and heat-treating). Thus, even if the original yarn has good performance, the resultant dipped cord frequently cannot satisfy the required performance.

This invention seeks to provide a polyester fiber which has a high strength and excellent durability with balanced heat shrinkage and modulus and which exhibits excellent performance even after being made into a 30 dipped cord.

SUMMARY OF THE INVENTION.

35 The embodiment of this invention is as follows:-

Polyester yarn which is made from polyethylene terephthalate or from a polyester in which polyethylene terephthalate is the main component, the polyester fiber satisfying the following property characteristics (a) - (f) simultaneously.

(a) Intrinsic viscosity of at least 0.91, preferably at least 1.0,

40 (b) Tenacity of at least 8 g/d, preferably at least 8.4 g/d,

(c) $E_{2.25}$ of 4.5% or less, preferably 3.5% or less,

(d) ΔH_{mf} of at least 11.5 cal/g, preferably at least 12.0 cal/g,

(e) (Tmf - TmF) of at least 20°C, preferably at least 22°C, and

(f) Amorphous orientation (fa) of 0.75 or less, wherein $E_{2.25}$ is the elongation under a load of 2.25 g/d,

45 ΔH_{mf} is the amount of heat at the melting peak in differential scanning calorimeter (DSC),

Tmf is the melting point measured by DSC under a tension of 0.05 g/d, and

TmF is the melting point measured by DSC under no tension.

The polyester in this invention is polyethylene terephthalate or a polyester in which polyethylene terephthalate is the main component (at least 90 mol percent) and various types of dicarboxylic acid and glycol 50 component can be copolymerized therewith in an amount of up to about 10 mol percent. In order to improve the heat resistance, it is preferred to reduce the end carboxyl group content of the polyester by reacting with epoxy compound, carbonate compound, carbodiimide compound, iminoether compound.

In the following, the property characteristics of the polyester fiber of this invention are explained.

First, the polyester fiber of this invention must have a high molecular weight having an intrinsic viscosity of at 55 least 0.91 as measured by 20°C by use of an equal weight mixed solvent of phenol and tetrachloroethane. In particular, an intrinsic viscosity of at least 1.0 is preferred. This is the required condition for the fiber to exhibit high strength and for increasing the formation of tie molecules which participate in the improvement of durability.

The strength is the value obtained using the method of JIS L-1017, i.e., the value obtained by dividing the 60 load at breaking in a load-elongation test with the measured denier determined prior to the test. It needs to be at leat 8.0 g/d, preferably at least 8.4 g/d.

Also, $E_{2.25}$ indicates the elongation at a load of 2.25 g/d in the load-elongation curve at the strength measurement. The value is obtained by computer treatment. It needs to be 4.5 percent or less, preferably 3.5

percent or less. A low value of this property means a high intermediate modulus, and it is a necessary condition for reducing the dip elongation phenomenon in the dip treatment process and for achieving high strength and high Young's modulus.

ΔH_{mf} is measured by use of Perkin Elmers DSC-2C differential scanning calorimeter with 3 mg of sample (original yarn) at a rate of temperature increase of 20°C/minute in a nitrogen atmosphere. It needs to be at least 11.5 cal/g, preferably at least 12.0 cal/g. This value depends on the degree of crystallization of the fibers and it indicates the degree of perfection of the microstructure of fibers mainly in the crystalline section. A large value of this indicates that the fiber has high strength, high modulus and high durability.

The melting points of fiber (Tmf and TmF) are measured as follows: 3 mg of the monofilament of original yarn is wound over a copper plate of length 10mm, width 3 mm and thickness of 0.5 mm, under a load of 0.05 g/d or under no load, to a width of 5mm; the front end of the sample is tied and the excess copper plate is cut off; then, the measurement is made under the same conditions as in the measurement of ΔH_{mf}. In the reference side cell of DSC, a copper plate of the same shape is inserted.

TmF is the ordinary melting point and Tmf indicates the super-heating property caused by the tie molecules. With the fibers of this invention, the value of Tmf-TmF (= ΔT) is at least 20°C, preferably at least 22°C characteristically. The value of ΔT is an important indicator of the amount of tie molecules formed. The fiber having a high ΔT has a strong connection of the crystalline section and amorphous section by the tie molecules, and this contributes effectively to the prevention of breading phenomenon which occurs at the boundary between crystalline and amorphous sections; as the result, high strength and high durability are exhibited.

The amorphous degree of orientation (fa) is obtained by the following equation from the birefringence Δn, degree of crustallization X, the intrinsic birefringence of crystal Δnc (= 0.220), the intrinsic birefringence of amorphous section Δna (0.275), and the crystalline orientation function fc:-

$$fa = \frac{\Delta n - Xfc \Delta nc}{(1 - X) \Delta na}$$

Here, Δn is determined by the Berek compensator method using an ordinary polarized microscope. f_c is obtained from the following equation with the average orientation angle θ measured by wide angle X ray diffraction, i.e. the average orientation angle θ obtained by the analysis of average angle width of the diffraction pattern:-

$fc = 1/2 (3 \cos^2 \theta - 1)$

X is determined from the following equation from the sample density ρ measured at 25°C by a density gradient method using ligroin and carbon tetrachloride, the crystal density ρc (= 1.455 g/cm³) and amorphous density ρa (= 1.335 g/cm³):-

$$X = \frac{\rho c (\rho - \rho a)}{\rho (\rho c - \rho a)}$$

fa is related to the durability against the repeated elongation-compression fatigue when the polyester fiber is used as the rubber-reinforcing material. With the polyester fiber of this invention, f_a must be 0.75 or less.

As to the f_c of the polyester fiber of this invention, there is no particular restriction but it generally exhibits a value of about 0.94. The value of X is generally about 0.40 to 0.45.

The polyester fiber of this invention which satisfies the above-mentioned characteristics simultaneously has high strength and excellent durability and also has a balanced heat shrinkage and modulus. Even after being made into the dipped cord, it exhibits excellent performance.

In the following, the method of making the polyester fiber of this invention is described.

First, molten polyester of high intrinsic viscosity (at least 0.91) from a polycondensation apparatus is directly fed to a spinning machine or is first made into chips which are melted in an extruder and then is fed to a spinning machine. Spinning is effected in a manner known per se at a take-up rate of about 700 to 5000 m/minute. In anticipation of the drop in the viscosity which usually occurs in spinning, there is used a polyester of somewhat higher viscosity than the desired intrinsic viscosity of the polyester in the fiber to be obtained.

In the spinning, to achieve uniform cooling and enhance the uniformity of yarn strands, it is necessary to have optimal combinations of the following conditions in connection with the intrinsic viscosity of polyester and spinning speed: number of filaments in the yarn, denier of filament, diameter and arrangement of the discharge hole of spinning die, spinning temperature, length of the heated hood, length of the cooling zone, temperature, speed and mode of blowing (circumferential blowing or side blowing) of the cooling air.

In order to obtain the polyester fiber of this invention, it is necessary to use the high stress spinning method and it is desirable that the stress on the spun yarn is 0.05 to 1.0 g/d. As for the method of increasing the stress of spun yarn, one can use a method involving increasing the spinning speed (take-up speed) or a method involving increasing the rate of cooling of the spun yarn. In this way, the birefringence of the resultant undrawn yarn is made to over 15×10^{-3}, preferably 25×10^{-3} to 70×10^{-3}.

Next, this undrawn yarn is drawn in one stage or multiple stages while heating by heating roller, heating plate, steam jet. Drawing can be done by a spin draw method which is conducted as a continuation of the spinning or by a two-process method in which the undrawn yarn is first taken up and then drawn subsequently. As for the draw ratio, an optimal condition is selected by combining the spinning stress at spinning and the drawing temperature and time.

In the following example, the invention is described in further detail.

EXAMPLE

To the chips of polyethylene terephthalate having an intrinsic viscosity shown in Table 1, N-glycidyl phthalimide was added in an amount indicated in Table 1. This was fed to an extruder type melt spinning machine and was spun at a spinning temperature of 300 to 310°C (set to the optimal temperature in this range) using a spinning die having 252 holes of diameter 0.6 mm. Spun yarn was passed through a heated hood of 100 mm length at an atmosphere temperature of 300°C. Then, cooling air at 18°C was blown from the circumferential direction at 40 m/minute velocity over a length of 300 mm. Spinning oil agent was applied by use of an oiling roller. Then the yarn was taken up at a speed of 2000 m/minute to a take-up roller which was heated to 85°C. Thus, undrawn yarn having a birefringence as shown in Table 1 was obtained. (At this time, spinning stress was in the range of 0.08 to 0.20 g/d).

Birefringence of the undrawn yarn was measured by unheating the take-up roller and winding the undrawn yarn on this and taking a sample from this.

Also, without winding up the undrawn yarn, the yarn was given a first stage drawing to a draw ratio of 1.45 between the above-mentioned heated take-up roller and an unheated No. 1 Nelson roller. Next, between the No. 1 Nelson roller and a No. 2 Nelson roller which was heated to 240°C, the yarn was passed through 400°C steam jet apparatus to effect a second stage drawing. Then, between the No. 2 Nelson roller and a conditioning roller which was heated to 100°C, the yarn was subjected to a relation at a ratio as shown in Table 1. The yard is then wound up. The draw ratio in second stage drawing was adjusted to give a total draw ratio as indicated in Table 1 taking the relaxation ratio into consideration.

The physical properties of the drawn yarn (original yarn) of 1000 d/252 f are shown in Table 1.

The denier change produced by changing the relaxation ratio of drawn yarn was adjusted by adjusting the extrusion rate. The end carboxyl group content in the drawn yarn obtained was in the range of 9.5 to 10.8 g/eq/10^6 polymer in all cases. To this original yarn, downward twisting of 49 twists/10 cm was applied in the Z direction by use of a ring twisting machine. Next, two yarn strands were combined and upward twisting of 49/10 cm in S direction was applied to make a greige cord. This was dip-treated by use of a single dipping machine made by the Litzler Company to obtain a dipped cord.

The conditions of the dipping treatment and the method of evaluation of the performance of dipped cord were as follows:-

Conditions of the Dipping Treatment.

(1) Dip Solution:-

A mixed solution consisting of 83 weight parts of resorcinol-formalin-Gentac latex solution (1 weight part of the reaction product of resorcinol and fomaldehyde in a mol ratio of 1:1.2, mixed with 4.3 weight parts, in solid content, of latex to prepare a solution having 20 weight percent concentration; pH adjusted to 9.5 with NaOH) and 17 weight parts of Vulcabond E.

Gentac latex is a trade name of General Tire Company; it is a butadiene-styrene-vinyl pyridine latex. Vulcabond E is a trade name of Vulnax Company; it is an ammonia-water solution of 2,6-bis(2',4'-dihydroxyl phenyl-4-chlorophenol having a solid content of 20 weight percent,

(2) Conditions of drying and heat treatment in the dip treatment:- Drying zone   80°C x 30 sec
Curing zone   240°C x 80 sec x 2 times
Dip tension   0.5 kg/cord

Performance of the Dipped Cord

(1) Tensile Properties

Measurement was done by the JIS L 1017 method. However, heat shrinkage was measured under the condition of 180°C x 30 minutes.

(2) Fatigue Properties

Measurement was made by the JIS L 1017, Goodyear's Mallory Tube Method with tube test angles of 60° and 90° at 850 rpm and the rotation was reversed at 30 minutes. When the angle was 60°, the cord was taken out carefully from rubber at 3 hours of fatigue and the tensile strength was measured to determine the strength retention ratio.

Also, when the angle was 90°, the time (minutes) to the rupture of tube by fatigue was measured.

The performance of the dipped cords is shown in Table 1.

As can be seen from the results of Table 1, polyester fibers which simultaneously satisfy the properties defined in this invention have excellent total balance of the strength, heat shrinkage, modulus and fatigue resistance in the dip cord performance which expresses the performance as rubber-reinforcing material directly. Thus, they are good as rubber-reinforcing materials; No. 5 - 8 have particularly good performance.

TABLE 1

No.	1	2	3	4	5	6	7	8	9	10	11	12
A	1.05	1.10	1.10	1.10	1.20	1.20	1.25	1.25	1.05	1.10	1.10	—
B	0.30	0.32	0.32	0.32	0.34	0.34	0.35	0.35	0.30	0.32	0.32	—
C	26	31	30	33	34	32	36	38	27	29	31	—
D	1.3	1.3	1.0	0.8	0.7	1.3	0.0	0.9	1.2	2.7	4.8	—
E	2.43	2.47	2.48	2.48	2.48	2.45	2.47	2.44	2.44	2.42	2.40	—
F	0.91	0.94	0.93	0.97	1.05	1.03	1.06	1.08	0.89	0.92	0.92	0.97
G	8.1	8.4	8.5	8.6	8.6	8.4	8.8	8.6	7.7	8.1	8.0	9.5
H	4.2	3.7	3.5	3.3	3.0	3.5	3.1	3.4	4.1	4.5	4.8	4.0
I	11.8	12.5	12.6	12.5	13.2	12.7	12.6	12.3	11.7	11.5	11.6	10.8
J	20.9	22.8	22.5	22.7	23.2	23.0	23.5	23.9	20.2	18.9	20.7	21.8
K	0.69	0.66	0.67	0.65	0.62	0.62	0.61	0.61	0.71	0.66	0.67	0.78
L	6.53	6.62	6.67	6.72	7.05	7.07	7.10	7.15	5.91	6.32	6.29	6.35
M	14.8	14.9	15.1	14.8	14.8	14.6	15.0	15.2	14.0	13.9	14.2	15.5
N	4.2	4.5	4.5	4.6	4.5	4.5	4.3	4.2	4.5	4.7	4.4	6.8
O	63	66	67	67	68	67	67	68	65	65	63	59
P	96.4	97.3	97.9	98.7	98.9	98.7	98.8	99.1	91.7	93.4	94.2	—*
Q	560	600	630	650	710	690	710	720	400	430	410	280

A. IV of chips; B. Amount of N-glycidyl phthalimide added; C. Birefringence of undrawn yarn x 10^3; D. Relaxation ratio (%); E. Total draw ratio; F-K. Original yarn properties; F. IV; G. Tenacity (g/d); H. $E_{2.25}$ (%); I. ΔH_{mf} (Cal/g); J. Tmf-TmF(°C); K. Amorphous orientation fa; L-Q. Dip cord performance; L. Tenacity (g/d); M. Elongation (%); N. Heat shrinkage (%); O. Modulus (g/d); P-Q. Fatigue properties; P. angle 60° (%); Q. Angle 90° (%).

*It was impossible to take the cord out.

Note:

(1) Unit of the amount of addition of N-glycidyl phthalimide is wt%.

(2) No. 1-8 are examples of application; No. 9-11 are comparative examples; No. 12 is a reference example showing the example of commercial high strength type polyester fiber.

This invention provides polyester fiber which has high strength and excellent durability and balanced heat shrinkage and modulus and is suitable as rubber-reinforcing material exhibiting excellent performance even after being made into dipped cord.

Claims

1. A polyester yarn comprising primarily polyethylene terephthalate for use in reinforcing rubber goods and having the following properties:

(a) an intrinsic viscosity of at least 0.91,

(b) a tenacity of at least 8 g/d,

(c) $E_{2.25}$ of 4.5 percent or less,

(d) ΔH_{mf} of at least 11.5 cal/g,

(e) (Tmf - TmF) of at least 20°C, and

(f) an amorphous orientation function of 0.75 or less, wherein $E_{2.25}$ is the elongation under a load of 2.25 g/d,

ΔH_{mf} is the amount of heat at the melting peak in differential scanning calorimeter (DSC),

Tmf is the melting point measured by DSC under a tension of 0.05 g/d, and

TmF is the melting point measured by DSC under no tension.

2. A yarn as claimed in claim 1, wherein (Tmf - TmF) is at least 22°C.

3. A yarn as claimed in claim 1 or 2, wherein ΔH_{mf} is at least 12.0 cal/g.

4. A yarn as claimed in any preceding claim wherein $E_{2.25}$ is 3.5 percent or less.

5. A yarn as claimed in any preceding claim, wherein the tenacity is at least 8.4 g/d

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