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PROCESS FOR MAKING CRIMPED FILAMENTS OF POLYESTER

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Int. Cl. D02q *1/10*
U.S. Cl. 28—72.13 11 Claims

ABSTRACT OF THE DISCLOSURE

Crimped filaments of terephthalate polyester are prepared by wetting unoriented filaments of terephthalate polyester with a non-solvent for the polyester, drawing the wetted filaments uniformly in the longitudinal direction but non-uniformly in the cross-sectional direction of the filaments, and subjecting the drawn filaments to an elevated temperature under conditions which will allow shrinkage or contraction of the filaments. In the drawing step, a pin is used which has a specified convex surface and is maintained at a specified temperature.

This invention relates to a process for making crimped polyester filaments and fibers.

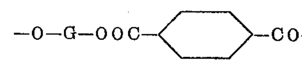
It is known to make polyester filaments having three-dimensional crimps by the process comprising non-uniformly quenching as-melt-spun polyester filaments by, for example, applying a unidirectional, horizontal cooling gaseous current to the filaments, thereby forming filaments having different birefringences in its transverse direction, drawing the same, and heat-treating the same under the conditions as will allow shrinkage thereof. However, the imparted crimp exhibits insufficient stability, and the product shows such shortcomings as low initial modulus and yield point, and excessively great breaking elongation.

The object of the present invention is to overcome the aforesaid drawbacks inherent in the conventional practice. In order to accomplish this object, the invention provides a process for making crimped filaments of terephthalate polyester which comprises wetting terephthalate polyester filaments having a birefringence of 0.001 to 0.012 with a non-solvent for the filaments, drawing the wetted filaments at a draw ratio within the range of 1.5 to 6.0 while contacting them with a pin which has a convex surface portion with a radius of curvature ranging from 1 to 5.5 $(1+0.01V)\sqrt{D}$ mm. and which is heated to a temperature ranging from $(Tg-20)$° C. to $(Tg+25)$° C., along the circumference of said convex portion, and developing crimp in the filaments by treating the drawn filaments at a temperature not lower than 100° C., under the conditions as will allow shrinkage or contraction thereof. In the above drawing step Tg represents the glass transition temperature of the filaments, V represents the drawing velocity expressed by m./min., and D denotes the denier of a single filament.

In the aforedescribed conventional art, potentially crimpable, drawn filaments are prepared by uniform stretching of spun filaments which have been imparted the internal microstructures non-uniform in the direction of radii through their spinning and quenching steps. In contrast, the basic concept of the invention resides in the stretching of uniform spun filaments, which stretching is uniform in the longitudinal direction but non-uniform in the sectional direction of the filaments, thereby providing potentially crimpable, drawn filaments which are uniform in macroscopic or configurational view, but

are not uniform in sectional direction with respect to microscopic structure.

The "terephthalate polyester" mentioned in this specification and claims refers to the polyester of which at least 85%, preferably at least 90%, of recurring structural units is expressed by a general formula,



in which G stands for a divalent organic radical of 2–10 carbons, which is bound to the adjacent oxygen atom through a saturated carbon atom.

The "intrinsic viscosity" of the polymer or filament mentioned in this specification is defined by the formula below:

$$\lim_{C\to 0}\frac{\ln \eta r}{C}$$

in which ηr is normally referred to as relative viscosity, the value being obtained by dividing the viscosity of a dilute solution of the test specimen in a solvent by the viscosity of the solvent employed, measured at the same temperature using the same unit; and C is the concentration of the polymer in gram per 100 cc. of the solution. In the present specification, the viscosities are measured at 35° C., using ortho-chlorophenol as the solvent.

Also the "glass transition temperature (Tg)" mentioned in the specification and claims is determined by the method described in, for example, U.S. Pat. No. 2,556,295. The Tg of polyethylene terephthalate as-spun filaments having an inherent viscosity of 0.65 is approximately 70° C.

The "draw ratio" referred to in the specification and claims means the ratio of wind-up rate of the filaments to their supply rate in the drawing step. The wind-up rate is also referred to as drawing velocity or draw rate.

The starting filaments to which the subject process is conveniently applied possess a birefringence ranging from 0.001 to 0.012. With the birefringence less than 0.001, it is difficult to draw the filaments with configurational uniformity. Whereas, the optimum draw ratios of the filaments having birefringences substantially higher than 0.012 are extremely low, and the filaments' non-uniform drawing in the sectional direction is difficult. It is discovered that satisfactory potential crimpability cannot be imparted to the filaments having such high birefringences.

The starting filaments are preferably substantially amorphous, having a crystallinity not exceeding 10%. The preferred starting filaments composed of polyethylene terephthalate possess a density of 1.35 g./cc. or below. The starting filaments may be the as-spun yarns which have been melt-spun and quenched, i.e., undrawn yarns, or they may be those which have been incompletely drawn.

The starting filaments may possess the total denier of up to approximately 10,000 deniers, and a single filament denier (D) or titer of approximately 1 to 600 deniers. Normally the starting filaments have circular cross-sections, but they may have other modified cross-sectional configurations. From the starting filaments having Y-shaped or trilobal cross-sections, lustrous, soft and silky products having excellent hand can be obtained.

It has been discovered that the wetting of the starting filaments with a non-solvent prior to the drawing is critical to obtain the object of drawing in accordance with the invention, i.e., for performing the drawing which is configurationally uniform but non-uniform in sectional direction from microscopic viewpoint. As will be demonstrated in the later-given working Example 1, drawing of dry filaments fails to impart satisfactory potential crimpability to the filaments. An appropriate wetting agent is any non-solvent for the polyester, which exhibits entirely or substantially no swelling action to the polyester. Suitable non-solvents include water, carbon tetrachloride, methanol, ethanol, ethylene glycol and the like, water being the most advantageous. The temperature of the water or other non-solvent liquids is not critical, but the temperature range of 0–60° C., particularly room temperature minus 40° C., is effective for development of excellent crimp at the final stage. For wetting the starting, laments with water or other non-solvents for the polyester, any suitable means can be optionally employed; for example, the filaments may be passed through a bath of the wetting agent and withdrawn, or the agent may be applied to the filaments with a roller.

The wetted filaments are drawn at a draw ratio within a range of 1.5 to 6.0, while keeping contact with a heated pin. The drawing atmosphere is the air. The temperature of the pin may range from $(Tg-20)$ to $(Tg+25)°$ C., in broadest term, Tg being the glass transition temperature of the filaments expressed by degree in centigrade. In practice it is recommended that the optimum drawing temperature should be selected from the range of $(Tg-10)°$ C. to $(Tg+20)°$ C. When the pin temperature is too low, configurationally uniform drawing cannot be performed, and the products contain considerable undrawn portions. Whereas, if the pin temperature is too high, uniform drawing is given also to the microscopic structure, and an internal fine structure which is non-uniform in the sectional direction cannot be obtained. Normally the optimum pin temperatures are within the range of $(Tg-10)°$ C–$(Tg+8)°$ C., when the drawing velocity is relatively low, for example, 500 m./min. or below. In case the operation is performed at higher drawing velocity, a higher pin temperature than the above upper limit can be employed. The optimum pin temperature is also affected by the storage period of the filaments to be drawn. Filaments which have been stored for a prolonged period are recommendably drawn at relatively higher temperatures.

In order to impart the transversely non-uniform, internal fine structure to the filaments by the drawing, the pin must possess a convex surface portion having a radius of curvature within the range of 1 mm. to $5.5(1+0.01V)\sqrt{D}$ mm., preferably $(1+0.001V\sqrt{D})$ mm. to $5.5(1+0.006V)\sqrt{D}$ mm. The filaments are drawn while keeping contact with the pin along the circumference of said convex portion. "Along circumference of the convex surface portion" signifies that only the certain definite length along the circumference of the convex portion is contacted with the filaments. In that case, the filaments being in contact with the convex surface portion of pin are subject to the passing force toward the direction of radius of curvature of said portion. The pin may be columnar of cylindrical, but so far as it possesses the convex surface portion having a radius of curvature within the specified range, its shape as a whole is not critical. The contact of the filaments with the convex surface portion of the pin may be secured by winding the former around the latter by one or two turns, but the winding is not necessarily required. In some cases it is advantageous to operate in such a manner that only a limited portion of the total length along the circumference of convex surface portion is contacted with the filaments, and the direction of the filaments is varied before and after the contact with that pin. It is discovered that the internal fine structure which is non-uniform in the sectional direction cannot be imparted to the filaments when a pin or plate having excessively large radii of curvature is used, and the products

exhibit poor crimpability. On the other hand, macroscopically uniform drawing is difficult to perform with a pin having a radius of curvature less than 1 mm. Generally speaking, when the drawing velocity is relatively low, for example, 500 m./mm. or below, the optimum radius of curvature is within the range of 1 mm. to $5.5\sqrt{D}$ mm., but when the velocity is greater, pins of greater radii of curvature can be used.

The drawing velocity itself is not critical, but in individual practice the optimum pin temperature and radius of curvature of the pin are necessarily selected from the above-specified ranges in accordance with the drawing velocity employed. Normally the greater is the velocity, a greater radius of curvature and/or higher drawing temperature may be employed. The drawing is operable at the velocity as low as 50 m./min. or even below, but such is not only commerically disadvantageous, but also with such low speed the radially non-uniform, internal fine structure is difficult to obtain. For this reason normally a drawing velocity of at least 50 m./min. is advantageous. The upper limit of the velocity depends on the drawing techniques. For example, it is not impossible to operate at a drawing velocity as high as approximately 2,000 m./min., or even higher. Practical velocity ranges approximately 50 to 1,500 m./min., preferably approximately 300 to 800 m./min.

The drawn filaments possess potential crimpability, and can be converted to crimped products by treating the same under the conditions as will allow their shrinkage, at a temperature no lower than 100° C. This crimp-developing treatment may be given to the filaments without further processing, or to the staple fibers obtained by cutting the filaments. Furthermore, the filaments or staple fibers may first be formed into textile goods such as yarn, woven or knitted fabrics, non-woven fabrics, carpet, etc., and thereafter subjected to the heat treatment. "The conditions as will allow shrinkage of the filaments" include not only the tension-free treatment in which the filaments can freely shrink, but also such conditions under which the filaments can shrink by a certain limited amount. When the treating temperature is too low, not only is the number of crimps developed less, but the crimps are unstable. Also the filaments treated at relatively low temperatures are occasionally irregular in size along the longitudinal direction. Thus a relatively higher temperature range is preferred for the crimp-developing treatment, as long as melting of the filaments can be avoided. Normally, a temperature of at least 150° C., particularly those exceeding approximately 200° C., are preferred. A treating temperature ranging approximately from 205–240° C., particularly from approximately 220–240° C. is recommended. Dry heat is preferred and more advantageous in the heat treatment for crimp-developing, although wet heating is usable.

The crimped products obtained by the subject process produces crimps of higher stability than those in the conventional products. The products of the subject process also exhibit medium initial modulus (normally ranging approximately 300–500 kg./mm.$_2$) and not excessively high breaking elongation (normally approximately 80% or less). In those physical properties, the products of the invention form clear contrast to the conventional crimped products based on cooling anisotropy. Again the subject process is simpler in operation and less expensive, compared with the conventional art.

The following examples are given to illustrate the present invention, in which the crimp density (number of crimps per 1 inch) was measured as follows: crimped, single filament is withdrawn from the crimped specimen, and subjected to a load of 5 mg./den. whereupon the number of crimps per 1 inch was counted. The average value for 25 strands of such filaments was calculated.

EXAMPLE 1

Polyethylene terephthalate having an intrinsic viscosity of 0.65 was molten at 295° C., and spun at a rate of 700 m./min. to provide spun filaments at 280 deniers/36 filaments, having a birefringeence of 0.0045. The spun filaments were wetted with 40° C. water, and wound by one turn onto a cylindrical pin of 10 mm. in radius and which was heated to 65° C. The filaments were thus drawn by 4.3 times at a rate of 300 m./min., and subsequently shrunk as exposed to the air of 230° C. under substantially no tension. Uniformly crimped filaments having no irregularity along their longitudinal direction were obtained. The product had 23 crimps per inch, and excellent feeling and hand. The product's initial modulus was 436 kg./mm.^{2}, and breaking elongaton was 62%. The product was dyed very evenly.

For comparison, the foregoing procedures were repeated except that the wetting with water prior to the drawing was omitted. The product had only 4 crimps per inch.

EXAMPLE 2

Polyethylene terephthalate having an intrinsic viscosity of 0.65 was molten at 295° C., and spun at a rate of 900 m./min. to provide the spun filaments of 150 deniers/20 filaments in size, having a birefringence of 0.0055. The filaments were wetted with 30° C. water, and wound by one turn onto a pin of equilateral triangular cross-section, having a circular portion of 1.5 mm. in radius. One side of the triangle was 12 mm. in length, and the pin was heated in advance to 68° C. Thus the filaments were drawn by 4.1 times at a rate of 250 m./min., and subsequently heat-treated in 220° C. air, under no tension. Thus the filaments with very fine crimps were obtained, which gave evenly dyed woven or knitted goods of pleasant hand.

EXAMPLE 3

Polyethylene terephthalate having an intrinsic viscosity of 0.65 was molten at 295° C., and spun through a spinneret having Y-shaped orifices at a rate of 1,000 m./min., to provide spun filaments of 150 de./36 fil. in size, each having Y-shaped cross-section. Their birefringence was 0.0057. The filaments were wetted with water of ambient temperature, and wound around a cylindrical pin by one turn. The radius of curature of the pin was 30 mm., and the pin was heated in advance to 80° C. Thus the filaments were drawn by 3.8 times the original length, at a draw rate of 600 m./min., and subsequently heat-treated in 230° C. air under substantially no tension. The products developed 19 crimps per inch, and wherein each single filament was appropriately twisted. The products furthermore had silky luster and soft hand, were uniform in size along longitudinal direction, and could be dyed very evenly.

By way of a control, the above procedures were repeated, except that the cylindrical pin having a radius of curvature of 30 mm. was replaced by a similar pin having a radius of curvature of 80 mm. The products had 8 crimps per inch, and were far inferior in luster and hand.

EXAMPLE 4

Non-oriented filaments composed of substantially amorphous polyethylene terephthalate having an intrinsic viscosity of 0.65 were wetted with 30° C. water, and wound around a cylindrical pin of 8 mm. in radius by one turn. The pin temperature was varied in each run as indicated in the table below. The filaments were thus drawn at various draw rates as indicated in the same table. The optimum draw ratios for each combination of the drawing conditions are also shown. In each run the filaments were drawn by the indicated, optimum draw ratio. The drawn filaments were shrunk as exposed to 230° C. air under substantially no tension.

The crimp density (number of crimps/inch) and frequency with which the undrawn portion appeared (number/800 mm.) of each product are also given in Table 1 below.

TABLE I

Denier, UD filament	Drawing velocity, m./min.		Temperature, ° C. 40	45	55	70	75	80	90	100
220 de./36 fil., Δn=0.0045, Tg=70° C.	200	Optimum draw ratio	3.4	3.6	4.1	4.3	4.3	4.3	4.4	4.4
		Crimp density	20	18	17	18	16	11	9	6
		Undrawn portions	>100	>100	6	0	0	0	0	0
	400	Optimum draw ratio	3.0	3.1	3.2	3.6	3.8	4.0	4.2	4.3
		Crimp density	25	23	22	22	20	13	10	6
		Undrawn portions	>100	>100	6	0	0	0	0	0
	600	Optimum draw ratio	2.8	3.0	3.1	3.5	3.7	3.9	4.1	4.1
		Crimp density	22	23	23	23	23	22	16	4
		Undrawn portions	>100	>100	8	0	0	0	0	0
340 de./34 fil., Δn=0.0050, Tg=70° C.	200	Optimum draw ratio	3.5	3.6	3.8	4.4	4.5	4.6	4.6	4.7
		Crimp density	20	18	16	18	15	11	9	5
		Undrawn portions	50	45	8	0	0	0	0	0
	600	Optimum draw ratio	3.0	3.1	3.3	3.7	3.7	3.8	3.9	4.4
		Crimp density	21	20	21	20	20	18	15	4
		Undrawn portions	>100	>100	6	0	0	0	0	0

As demonstrated by the date of Table 1, when the drawing temperature is as low as 45° C. or below, macroscopically uniform drawing is impossible, and the frequency of occurrence of undrawn portions in the products is non-acceptably high. Whereas, at such high drawing temperature as 100° C., drawn product having satisfactory potential crimpability cannot be obtained. The subsequently shrunk product has unsatisfactorily low crimp density. From the standpoint of macroscopically uniform drawing, the drawing temperature is preferably no lower than approximately 60° C. On the other hand, with respect to crimpability, the drawing temperature is preferably not higher than approximately 80° C. when the draw rate is low, such as 200 m./min. or 400 m./min. Whereas, when the draw rate is relatively high, such as 600 m./min., satisfactory results can be obtained with relatively high drawing temperature, such as 80° C. or 90° C.

EXAMPLE 5

Polyethylene terephthalate having an intrinsic viscosity of 0.65 was molten at 295° C. and spun at a rate of 1,000 m./min. to provide spun filaments of 220 de./36 fil. in size. The birefringence of the filaments was 0.0058. The filaments were wetted with 30° C. water, and wound onto a cylindrical pin of 10 mm. in radius by one turn, the temperature of the pin being 70° C., to be drawn by 4.1 times at a draw rate of 300 m./min. and heated at various temperatures as specified in Table II, with substantially no tension. A tricot knitted good was prepared from the above filaments. The knitted good was dyed blue with "Eastman Polyester Blue BLF," under the conditions as follows: dyestuff, 4% OWF; non-ionic activating agent, 0.5 g./liter; bath ratio, 1:100; and temperature, 100° C.

The samples which were shrunk at relatively low temperatures were unevenly dyed. The uneveness was caused presumably by the fact that the shrinkage in the longitudinal direction was not fully performed. The dyed samples were rated by comparison with a separately prepared standard set. The standard set consists of seven grades of 0, 1, 2, 3, 4, 4.5 and 5, the greater index denoting more favorable dyed effect. Thus, index 4 stands for "good," and indices 4.5 and 5 stand for "excellent." The results are given also in Table II.

TABLE II

	Heat treating temperature, ° C.								
	Dry heat 100	Dry heat 130	Dry heat 160	Dry heat 180	Dry heat 200	Dry heat 220	Dry heat 230	Dry heat 260	Wet heat 180
Dyeing unevenness, grade	2	2	3	4	4.5	4.5	5	3.5	4

The dye exhaustion in the above dyeing of the sample treated at 230° C. was approximately 90%, whereas that of the sample treated at 130° C. was about 65%.

Thus heat treating temperatures exceeding approximately 200° C., particularly those ranging from approximately 220 to 240° C. are prepared.

EXAMPLE 6

Polyethylene terephthalate having an intrinsic viscosity of 0.65 was molten at 295° C., and spun to provide the filaments of 280 de./36 fil. in size, having a birefrigence of 0.0045. The filaments were wetted with methanol of ambient temperature, and thereafter drawn by 3.9 times at a draw rate of 200 m./min., as wound onto a 70° C. cylindrical pin of 10 mm. in radius. The drawn filaments were heat treated in substantially tension-free state in a 220° C. cylindrical hot blast store of 50 cm. in length, and wound-up at a rate of 100 m./min. The resultant products had 20 crimps per inch, and both excellent feel and hand.

The above procedures were repeated except that the methanol was replaced by carbon tetrachloride and water containing 2% of polyester fiber finishing agent (emulsified mineral oil), in each run. The products had respectively 12 crimps and 18 crimps per inch.

EXAMPLE 7

Unoriented filaments of 200 de./34 fil. in size, composed of a polyethylene terephthalate-adipate copolymer (containing 2.5 mol percent of polyethylene adipate) having an intrinsic viscosity of 0.60, were wetted with 30° C. water. Thereafter the filaments were drawn by 4.0 times at a rate of 400 m./min., as wound onto a 65° C. cylindrical drawing pin of 6 mm. in radius of curvature, by one turn. The unoriented filaments had a birefringence of 0.0035, density of 1.338, and a glass transition temperature of 64° C.

The drawn filaments were passed through a 500 mm.-long cylinder through which hot air of 220° C. was circulated, in substantially tension-free state, and were wound up at a rate of 100 m./min. Uniform crimped filaments which were uniform in size along the longitudinal direction and could be dyed very evenly were obtained. The products had 25 crimps per inch, and excellent feel as well as pleasant hand.

We claim:

1. A process for making crimped filaments of terephthalate polyester which comprises wetting terephthalate polyester filaments having a birefringence of 0.001 to 0.012 with a non-solvent for said filaments, drawing the wetted filaments at a draw ratio within the range of 1.5 to 6.0 while contacting them with a pin which has a convex surface portion with a radius of curvature ranging from 1 to 5.5 $(1+0.001V)\sqrt{D}$ mm. and which is heated to $(Tg-20)$° C. to $(Tg+25)$° C., along the circumference of said convex portion, and developing crimp in the drawn filaments by treating the filaments at a temperature not lower than 100° C., under the conditions as will allow shrinkage thereof, wherein Tg represents the glass transition temperature of the filaments, V represents the drawing velocity expressed by m./min., and D represents the denier of a single filament.

2. The process of claim **1**, in which the starting filaments possess a crystallinity not exceeding approximately 10%.

3. The process of claim **2**, in which the starting filaments are composed of substantially amorphous terephthalate polyester.

4. The process of claim **1**, in which the pin has a convex surface portion having a radius of curvature within a range of $(1+0.001V\sqrt{D})$ mm. to 5.5 $(1+0.006V)\sqrt{D}$ mm.

5. The process of claim **1**, in which the pin is heated to a temperature within the range of $(Tg-10)$° C. to $(Tg+20)$° C.

6. The process of claim **1**, in which the drawn filaments are shrunk at a temperature within the range of approximately 150° C. to 250° C.

7. A process for making crimped filaments of terephthalate polyester, which comprises wetting filaments of terephthalate polyester having a birefringence ranging 0.001 to 0.012 and a crystallinity not exceeding approximately 10%, with a liquid having no dissolving action to the filaments, drawing the wetted filaments at a draw ratio within a range of 1.5 to 6.0 by means of a pin which has a convex surface portion having a radius of curvature ranging from $(1+0.001\ V\sqrt{D})$ mm. to 5.5 $(1+0.006V)\sqrt{D}$ mm. and which is heated to a temperature ranging $(Tg-10)$° C. to $(Tg+20)$° C., while contacting the filaments with the pin along the circumference of said convex portion, and developing crimp in the filaments by treating the drawn filaments at a temperature within a range of approximately 150° C. to 250° C., under such conditions as will allow shrinkage thereof, wherein Tg represents the glass transition temperature of the filaments, V represents the drawing velocity expressed in m./min., and D represents the denier of a single filament.

8. The process of claim **7**, in which the drawn filaments are shrunk at a temperature within a range of approximately 205° C. to 240° C.

9. A process for making crimped filaments of polyethylene terephthalate which comprises wetting polyethylene terephthalate filaments having a birefringence of 0.001 to 0.012 with a non-solvent for said filaments, drawing the wetted filaments at a draw ratio within the range of 1.5 to 6.0 while contacting them with a pin which has a convex surface portion having a radius of curvature ranging from 1 to 5.5 $\sqrt{D}$ mm. and which is heated to a temperature ranging 60° C. to 78° C., along the circumference of said convex portion, at a drawing velocity ranging approximately 50 to 500 m./mm., and developing crimp in the filaments by treating the drawn filaments at a temperature within the range of 150° C. to 250° C. under the conditions as will allow the shrinkage thereof, where D represents the denier of a single filament.

10. The process of claim **9**, wherein the starting filaments possess a density not exceeding 1.35 g./cc.

11. The process of claim **9**, wherein the drawn filaments are shrunk at a temperature within the range of 205° to 240° C.

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