Nov. 17, 1970 KEIZO UEDA ET AL 3,541,198

PROCESS FOR MANUFACTURING COMPOSITE FILAMENTS

Filed March 19, 1969

FIG. 1

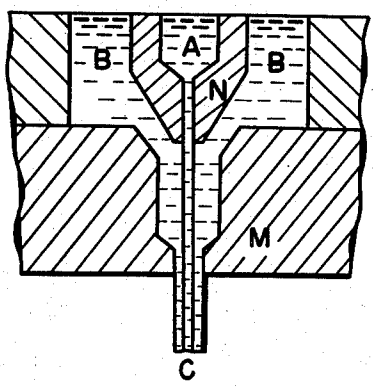


FIG. 2

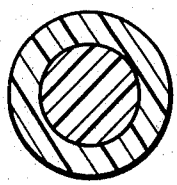


FIG. 3

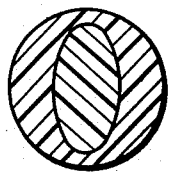


FIG. 4

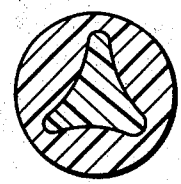


FIG. 5

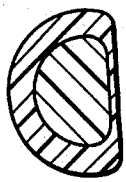
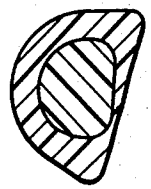


FIG. 6



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PROCESS FOR MANUFACTURING COMPOSITE FILAMENTS

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Claims priority, application Japan, Dec. 7, 1963, 38/66,030

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U.S. Cl. 264—171

4 Claims

ABSTRACT OF THE DISCLOSURE

A novel method for manufacturing heat crimpable filaments. Two different synthetic linear polymers having a ratio of melt viscosity greater than 2 are conjugately spun in such a manner that these polymers have a cross sectional arrangement in which one of said polymers substantially concentrically surrounds the other. Thereafter they are mechanically treated to cause the polymers to become eccentric relative to each other.

This application is a continuation-in-part of application Ser. No. 416,071 filed Dec. 4, 1964, and now abandoned.

The present invention relates to a process for manufacturing composite filament which consists of two components, one of which surrounds the other and when viewed in cross-section is eccentrically disposed with respect to the other. Hitherto a number of attempts have been made to obtain a composite filament by simultaneous spinning of two different polymers, the two components being bonded together in side-by-side relationship or in such a manner that one of them eccentrically surrounded the other along the length of the filament. The reason was that the crimp potential was attained early by the unsymmetrical arrangement of the components in relation to the center of cross-section of the filament.

However, when two components were arranged in such a way at the time of spinning, extreme difficulties sometimes occurred in said spinning depending on the combination of polymers. Particularly where the conjugate spinning of, for example, polyamides, polyesters, polyolefins, was carried out by the melt spinning process, said spinning encountered very serious difficulties if any two of those polymers had different melting points or melt viscosities. Ordinary side-by-side conjugate spinning encounters difficulties when the ratio of melt viscosity, at the melt spinning temperature, of the two polymers subjected to the conjugate spinning is over 2. It is extremely difficult when the ratio is over 3 and is almost impossible when over 4. (The said ratio of melt viscosity is the value obtained by dividing the higher melt viscosity of the melt viscosities of the two polymers by the lower viscosity.) In other words, the bonded or composite filament in which two polymeric components of different viscosity were eccentrically arranged in the cross section of the filament tended to bend immediately after extrusion from the spinning nozzle to that side where the more viscous polymeric component was present in larger amounts. If the bending was large, the extruded polymer stuck to the nozzle surface, thus making spinning impossible.

On the other hand, it is generally agreed that the greater the difference in the properties of two polymeric components, the better the crimp potential which is achieved. Also where the two components have different melting points, more satisfactory crimping is obtained.

It can be generally stated that materials of different melting points have different viscosities at the same temperature. If polymers of different melting points have the same viscosity at a given temperature, it is usually the case that such polymers have widely different molecular weights. It is extremely difficult to produce good yarns from such polymeric filaments by stretching.

Applicants have sought to provide a method of manufacturing complete filaments in which said difficulties are reduced.

The invention provides a process for manufacturing a composite filament consisting of two components eccentrically disposed relative to each other so that the components form in the cross section of the single composite filament two distinct zones which extend along the entire length of the filament in an eccentric fashion, which process comprises first melt spinning two different linear synthetic polymers or two varieties of the same linear synthetic polymer, the different polymers or different varieties having a ratio of melt viscosities of at least 2, and preferably greater than 3, through a common spinneret orifice in such a manner as to form a composite filament having a "sheath-core" structure in which the two components are substantially concentrically disposed relative to one another, and at a cross section of the filament anywhere along its length one of the two components entirely surrounds the other such that they are substantially free from eccentricity, and thereafter deforming the filament at an elevated temperature by mechanical means in such a manner that the two components thereof become eccentrically disposed relative to each other.

The deformed filament can be directly used in manufacturing products with distinctive features resulting from the combinations of various types of polymer. Moreover, the products made from the filament deformed by the process of the present invention can be made to develop crimps whenever required, or can be crimped in advance by means of heat or a swelling agent. In addition, the filament of the present invention can, where necessary, be made into staple fibre.

Examples of the process according to the invention will now be described, with reference to the accompanying diagrammatic drawings, in which:

FIG. 1 is an axial sectional view of one construction of apparatus for extruding a composite filament which constitutes an intermediate in the making of a composite filament according to the invention;

FIGS. 2–4 illustrate some examples of the cross sections of composite filaments constituting intermediates in the making of a composite filament according to the present invention; and

FIGS. 5 and 6 are two examples of the cross sections of a composite filament obtained by the present invention.

FIG. 1 shows two polymeric components A and B which are to be bonded together. The polymer A is injected into the polymer B through a first nozzle N and then extruded together with the polymer B through a second nozzle M.

The nozzles M and N are axially aligned with one another. Therefore, the polymers A and B assume relative positions which are substantially free from eccentricity, and retain their identity even when extruded into the air through the nozzle M. This also occurs when the outlets of the first and second nozzle are in the same plane.

FIGS. 2–4 are three examples of the cross sections of filaments in which the components are arranged in a relationship which is substantially free from eccentricity. FIG. 2 shows two concentric circles. The cross section of the filament is not always required to have a geometric form such as a circle or a polygon, but it is necessary

that the geometrical centers of the two cross sections should substantially coincide with one another, and that each should be substantially symmetrical around its geometric center. The term "symmetrical form around its geometrical center," as used herein, means that more than one axis of symmetry passes through the geometric center, or a plane of symmetry passes through the gravitational center. However, since the spun filament in actual practice has an irregular cross section, some deviations from the aforementioned definitions may be allowable, provided that the bending of the filament upon extrusion can be prevented in such a manner that its processability is not impaired.

FIGS. 5 and 6 represent examples of the cross sections of a composite filament in which the arrangement of its components was initially non-eccentric, and the arrangement was later converted into an eccentric arrangement by mechanical deformation. The mechanical method for imparting such a deformation can be, for example, edge crimping the filament over a heated sharp knife edge or the edge of a small heated member, the edge of which has a minute radius of curvature, or compressing the filament by causing it to travel through a pair of loaded rollers, thereby deforming the cross section of the filament continuously, the rollers being heated. It is desirable that the edge or roller used in mechanical deforming be heated to a temperature of 80–170° C., preferably to 100–150° C.

The ratio of melt viscosity is determined as follows:

(1) The amount (e.g. in g./min.) of each of the polymers extruded from an orifice under conditions of fixed temperature and pressure is measured by a method almost the same as the method of measuring the melt index, wherein a sample of material which will fill a cylinder of about 1 cm.^{2} in cross-sectional area is pressed from above by a plunger and is extruded from an orifice directed downwards.

(2) The temperature at which the above measurement is carried out is held substantially equal to the conjugate spinning temperature. The conjugate spinning temperature is the one where both polymers have superior spinnability, that is, 15° C. higher than the melting point of the polymer having the higher melting point. As a specific example thereof, a desirable spinning temperature for nylon 6 is 260° C.–300° C., the one for nylon 66 is 280° C.–300° C., and the one for polyethylene terephthalate is 280° C.–320° C.

(3) A pressure used is 50 kg./cm.^{2}.

(4) The orifice has a rounded shape 0.25 mm. across and 0.25 mm. in length.

(5) Where the extruded amount (g./min.) of polymer A is Wa and that of polymer B is Wb ($Wa \leqq Wb$).

The ratio of the melt viscosity of polymer A, ηa, and that of polymer B, ηb is measured as follows:

The melt viscosity:

$$\eta a/\eta b = Wb/Wa$$
$$(Wa \geqq Wb)$$

EXAMPLE 1

Nylon-6 which contained 0.4% of water soluble matter and had an intrinsic viscosity of 1.14 as measured with metacresol solvent at 30° C. and nylon-6 which contained 11.8% of water soluble matter and had an intrinsic viscosity of 0.81 as measured with metacresol solvent at 30° C. could not be subjected to the operation of conjugate spinning by the ordinary side-by-side nozzles conventionally used for said conjugate spinning. The ratio of melt viscosity measured at 275° C. was 3.70. When these two polymers were concentrically extruded (with a cross-sectional area ratio of 1:1) by the non-eccentric conjugate spinning nozzles illustrated in FIG. 1 with the less viscous polymer placed on the outside to form the sheath, and at a temperature of 275° C. spinning was successfully carried out. A filament of 45.0 denier thus obtained was stretched at a stretch ratio of 4.6 at room temperature, but did not develop crimping. Further, when said filament was subjected to no-load treatment in hot water at 100° C. for 10 minutes, followed by drying, no crimping appeared. The filament thus stretched was edge crimped with a sharp knife edge, heated to 120° C., and deformed the components viewed in cross-section had shapes as shown in FIG. 5. This filament could, of course, be directly used. When it was subjected to no-load treatment in hot water at 100° C. for 10 minutes, it produced 7 crimps per cm., the degree of crimping accounting for 49.8%.

In comparison thereto, a drawn filament obtained from only said nylon-6 having the higher viscosity and extruded under the same conditions had a crimp recovery percentage of only 37.1% after being mechanically deformed by an edge, held in boiling water and dried. This is very much inferior to that obtained by the present invention.

EXAMPLE 2

Nylon-6 with a melt viscosity of 880 poises at 280° C. and an intrinsic viscosity of 0.95 in a metacresol solution was designated as polymer P_3. Nylon-6 polymers having ratios of melt viscosity of 1.61, 2.89, 3.90 and 4.54 with respect to polymer P_3 were designated as polymers P_4, P_5, P_6 and P_7, respectively. Polymer P_3 was conjugately spun with each of polymers P_4–P_7, and the conjugate spinning was both the side-by-side type and the concentric sheath and core type, where the sheath was constituted of polymer P_3. The spinning was carried out at a temperature of 280° C. with a cross-sectional area ratio of 1:1. The spinnability for each of the foregoing combinations is shown in Table 1.

TABLE 1

Combination of polymers	Spinnability: Side-by-side type	Spinnability: Sheath-core type
P_4/P_3	Good	Good.
P_5/P_3	Somewhat difficult	Do.
P_6/P_3	Extremely difficult	Do.
P_7/P_3	Incapable of being spun	Do.

When undrawn filaments, which were spun and wound, were drawn to 3.89 times their initial length at room temperature, there was obtained drawn filaments of 15 denier/monofilament. The crimp recovery percentage which was obtained by holding each drawn filament in boiling water is shown in Table 2.

TABLE 2

Combination of polymers	Crimp recovery percentage: Side-by-side type	Crimp recovery percentage: Sheath-core type
P_4/P_3	5.2	3.8
P_5/P_3	12.8	4.1
P_6/P_3	25.4	3.9
P_7/P_3		5.4

In determining the above-mentioned percentage of crimp recovery, the length of filament l_1 was obtained after leaving the filament, which had been held in boiling water of 100° C. under no load for 10 minutes and dried in air, under a load of 0.2 g./denier for 1 minute. A length of filament l was measured after leaving the same filament under a load of 2 mg./denier for 1 minute. The crimp recovery percentage (%) was then determined by means of the following formula:

$$\text{Crimp recovery percentage } (\%) = \left(1-\frac{l_2}{l_1}\right)\times 100$$

After that the crimp recovery percentage of the filament spun by means of the sheath-core type conjugate spinning, which had been mechanically deformed with a heated edge, and then held in boiling water as in Example 1. The result is shown in Table 3.

TABLE 3

Combination of polymers:	Crimp recovery percentage (%)
P_4/P_3	39.5
P_5/P_3	43.0
P_6/P_3	51.8
P_7/P_3	55.2

EXAMPLE 3

85 parts of undecamethylene-diamine terephthalate and 15 parts of ε-caprolactams were mixed and heated to 275° C. in a nitrogen stream. After a 6-hour reaction, a polymer was obtained which had a melting point of 255° C. and an intrinsic viscosity of 0.8 as measured with metacresol at 30° C. The conjugate spinning of this polymer and the nylon-6 which had a melting point of 216° C. and an intrinsic viscosity of 0.09 as measured with metacresol solvent at 30° C. was conducted at 285° C. through the nozzle shown in FIG. 1 so that the cross-sectional areas were in a ratio of 1:1, with the latter polymer on the outside. The ratio of melt viscosities of the two polymers at a temperature of 285° C. was 3.30, the viscosity of the nylon-6 being lower. In this operation the orifice of the first nozzle N and that of the second nozzle M, in FIG. 1, had a Y-shape and a circular shape, respectively. The conjugate filament of 46.8 denier thus obtained had a cross section shown in FIG. 4. When stretched at a stretch ratio of 4:1 at room temperature, this filament did not develop crimping. However, said filament which, after stretching, was treated in hot water at no load for 10 minutes and dried showed a slight crimping, namely, 1.6 crimps per cm. When it was compressed by causing it to travel between the nip of two loaded metal rollers heated to 140° C., the aforementioned stretched filament developed practically no crimping and was found directly available for use. When further hot water treatment was applied to obtain a crimped filament, the crimp thus provided assumed a spiral form. The filament had 8.5 crimps per cm., indicating a degree of crimping of 69%.

Ordinary side-by-side type conjugate spinning of these two polymers at 285° C. could be carried out only with considerable difficulty, while the conjugate spinning was easily carried out when the concentric sheath-core type spinning was used.

EXAMPLE 4

99.2 parts of the adipate of metaxylylene-diamine and 0.8 part of the acetate of the same and 100 parts of water were mixed and maintained at 250° C. for 2 hours in an autoclave which had been purged with nitrogen. When the mass was further polymerized at 270° C. for 6 hours by slowly reducing the pressure to atmospheric, a polymer was obtained which had a melting point of 245° C. and an intrinsic viscosity of 0.88 as measured with metacresol at 30° C. On the other hand, when 90 parts of ε-caprolactam and 10 parts of the nylon-66 salt were mixed and copolymerized in nitrogen streams at 260° C. for 4 hours a copolyamide (nylon 6/nylon 66) was obtained which had a melting point of 198° C. and an intrinsic viscosity of 0.90. The ratio of melt viscosities of the two polymers at a tempertaure of 275° C. was 3.0, the viscosity of copolyamide (nylon 6/nylon 66) being lower. The two polymers were jointly extruded at 275° C. through the nozzle shown in FIG. 1 and a composite filament was obtained with a ratio of the cross-sectional areas of 1:1 and with a 61.8 denier, in which the nylon constituted the outer sheath of annular cross-section concentric with the circular portion of caprolactam. When stretched at a stretch ratio of 4:4 at 50° C. and subjected to the same hot water treatment as practiced in Example 1, the filament developed practically no crimping. However, when its cross-section was deformed, as illustrated in FIG. 6, by edge crimping with steel wire of 0.3 mm. diameter at 140° C., which was provided immediately after the stretch pin at 50° C. and through which an electric current was passed, crimps appeared at the rate of 4.1 per cm. When further hot water treatment was applied, this filament produced 11.7 crimps per cm., the degree of crimping accounting for 79.4%.

Ordinary side-by-side type conjugate spinning of these two polymers at 275° C. was carried out only with considerable difficulty.

EXAMPLE 5

Conjugate spinning was carried out with polyethylene terephthalate which had a melting point of 264° C. and an intrinsic viscosity of 0.61 as measured with metacresol solvent at 30° C. and another polymer obtained by copolycondensation of 95 parts of polyethylene terephthalate and 5 parts of polyethylene isophahalate which had a melting point of 240° C. and an intrinsic viscosity of 0.58. The ratio of melt viscosities of these two polymers at 290° C. was 2:1, the viscosity of the copolyester being lower. Said conjugate spinning was conducted at 290° C. so that the cross-sectional areas of the components were in a ratio of 1:1 with the latter polymer on the inside to form a core in such a manner that the cross-section of the composite filament thus produced had a concentric form. The 14.8 denier composite filament after being stretched at a stretch ratio of 3:4 at 60° C. was edge crimped with a sharp knife edge heated to 150° C. The composite filament then had a cross-section in which the components were eccentrically arranged. When this filament was further treated in boiling water under no load for 10 minutes and dried, 6.2 crimps appeared per cm.

Ordinary side-by-side type conjugate spinning of these two polymers at 290° C. met with considerable difficulties.

EXAMPLE 6

Polyethylene terephthalate having an intrinsic viscosity of 0.60 in orthochlorophenol solution at 30° C. was designated polymer P_{10}. Copolyesters of polyethylene terephthalate/polyethylene oxybenzoate (weight ratio 10/1) and having ratios of melt viscosities at 290° C. of 1:1, 2:3, and 3:5 with respect to polymer P_{10} were designated polymers P_{11}, P_{12} and P_{13}, respectively. The ordinary side-by-side type conjugate spinning of polymers P_{10} and P_{11} was easily carried out, but when polymer P_{10} was combined with each of polymers P_{12} and P_{13}, there was considerable difficulty in side-by-side conjugate spinning.

Combinations of polymer P_{10} with each of polymers P_{11}, P_{12} and P_{13} in a sheath-core arrangement by concentric type conjugate spinning of each combination at 290° C. and with polymer P_{10} as the sheath was carried out smoothly. In other words, said combinations had superior spinnability. The undrawn filaments thus prepared were drawn 3.6 times on a draw pin heated to 80° C. to obtain 15 denier/monofilament. When the drawn filaments were mechanically deformed with a heated edge, held in boiling water and then dried as in Example 4, the relation between the crimp recovery percentage and the respective combination of polymers was as shown in Table 4.

TABLE 4

Combination of polymers:	Crimp recovery percentage (%)
P_{11}/P_{10}	32.1
P_{12}/P_{10}	45.6
P_{13}/P_{10}	49.0

What is claimed is:

1. A process for manufacturing a heat crimpable composite filament consisting of two components eccentrically disposed relative to each other so that the components in a cross-section of the single composite filament form two distinct zones which extend along the entire length of the filament in an eccentric fashion, which process comprises first melt spinning two different linear synthetic polymers taken from the group consisting of

polyamides, polyesters and polyolefins, and having a ratio of melt viscosities at the spinning temperature of greater than 2 through a common spinneret orifice in such a manner as to form a composite filament having a "sheath-core" structure in which the two components are substantially concentrically disposed relative to one another, and at a cross-section of the filament anywhere along its length one of the two components entirely surrounds the other and is substantially concentric with the other, and thereafter applying a continuous laterally directed force against the thus spun composite filament for changing the relative positions of the components in the cross-section to other than a concentric disposition, while the filament is heated to a temperature at most slightly less than the melting point thereof.

2. A process as claimed in claim 1 in which the mechanical deformation is effected by drawing the filament over a knife edge.

3. A process as claimed in claim 1 in which the mechanical deformation is effected by passing the filament through the nip of a pair of heated and loaded rolls.

4. A process as claimed in claim 1 in which the ratio of melt viscosities of said polymers is over 3.

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U.S. Cl. X.R.

28—72.13; 264—168, 210, 290