

[54] **CRIMPABLE BICOMPONENT FILAMENT**

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[57] **ABSTRACT**

Improved bicomponent filaments for use in stretch hosiery are composed of a poly(hexamethylenedodecanedioamide) component and an N-alkyl substituted poly(hexamethylenedodecanedioamide) component. The filament are strong and develop a high crimp with high crimp recovery during knitting and subsequent hot finishing treatments.

7 Claims, No Drawings

CRIMPABLE BICOMPONENT FILAMENT

BACKGROUND OF THE INVENTION

This invention relates to composite filaments and particularly to improved composite filaments prepared from synthetic linear polyamides.

Synthetic polyamide filaments and yarns have been predominant in the women's hosiery market for many years. In this market, there is now an increasing demand for the so-called stretch hose. Hose of this type are much smaller than conventional hose but have the ability to stretch much more and thereby provide improved fit as well as reducing the number of sizes of hose required to fit the range of leg sizes normally encountered.

Composite hosiery filaments have been produced as disclosed by Olson in U. S. Pat. No. 3,558,760 which have the ability to crimp under restraint sufficiently to distort the stitches in hosiery fabric, so that the fabric has more stretch than a conventional hosiery fabric. Although those composite filaments have produced good stretch hose, further improvements in crimpability under fabric restraint are desirable, particularly in the production of miniature stretch hose.

While some improvements in crimpability may be achieved with prior art yarns by selection of suitable processing conditions, it has been difficult to accomplish this without loss in stretch and consequently, a reduction in hose wear life. Also it has been very difficult to operate commercially under conditions which produce the maximum crimp.

The use of an elastomeric component in composite filaments has been proposed for improving the crimp, but the tenacity of such filaments has been inadequate for hosiery and the filaments have crimped spontaneously when removed from the package.

It is desirable to have composite filaments which develop very little crimp when removed from the package, so that they may be easily handled in a hosiery knitting operation, but which develop a tendency toward greater crimp as the hose is knit so that the greige hose are relatively small and have a tight fabric structure which reduces picking (accidental snagging) in subsequent hosiery mill operations. The filaments should have a tendency to develop even higher crimp on subsequent treatment at elevated temperatures, such as those used in dyeing or boarding operations.

SUMMARY OF THE INVENTION

The present invention provides composite polyamide filaments having an improved balance of crimp characteristics and strength. The invention also provides composite filaments which develop little or no crimp when removed from the package but which develop a substantial tendency to crimp in a knitting operation and a still greater tendency to crimp on subsequent treatment at elevated temperatures.

The filament of this invention has two or more distinct, continuous, filament components in adherent, eccentric arrangement along the length of the filament. The polyamide of one component consists essentially of poly (hexamethylenedodecanedioamide). The polyamide of a second component consists essentially of N-alkyl substituted poly (hexamethylenedodecanedioamide) wherein the alkyl substituent has two to four carbon atoms and 25 to 50 percent of polyamide nitrogen atoms have alkyl substituents. Preferably this latter

polyamide is a copolymer wherein 75 to 50 percent of the polymer units are hexamethylenedodecanedioamide and 25 to 50 percent of the polymer units are N,N'-dialkyl-hexamethylenedodecanedioamide. Preferred N-alkyl substituents are ethyl and n-butyl.

The polyamide components are readily prepared, melt-spun into composite filaments and drawn to provide filaments having a tenacity of at least 6 grams per denier at break. The components may be arranged in a side-by-side relationship to provide a helical crimp with a crimp elongation of at least 40 percent when the composite filament is subjected to atmospheric steam while it is under 1.2 milligrams per denier load. Similar results can be obtained with sheathcore arrangements of the components.

The filaments of this invention are prepared by extruding the homopolyamide and copolyamide in either a side-by-side or a sheath-core relationship to form a filament (or two or more filaments as a yarn), quenching and drawing the filament in the conventional manner, passing the drawn filament through a heating zone under low tension to develop crimp and thereafter stretching the filament to remove crimp. A temperature in the heating zone of at least 115°C. is preferred for the desired crimp characteristics. The temperature required will, of course, depend on the length of the heating zone and the speed of the filament passing through the zone.

The preferred technique for reducing tension in the heating zone and then removing crimp is by passage of the precrimped filament over a series of snubbing pins in its advance away from the draw roll, a suitable heating means such as an air jet being interposed between the draw roll and snubbing pins, as shown, for example, in FIGS. 1 and 4 of Olson U. S. Pat. No. 3,558,760. From the snubbing pins, the filament passes around a power-driven roll, rotating at a lower peripheral speed than the draw roll to permit the filament to retract between the rolls. The degree of retraction permissible will depend on the amount of shrinkage, independent of crimping, which occurs between the two rolls. This, in turn, will depend to a considerable extent on the temperature in the heating zone. Generally, a high degree of snubbing is desired to provide very low tension and maximum shrinkage in the heating zone.

The two components are usually present in approximately equal amounts by weight of the filaments; however, the ratio may be varied as required to achieve the desired properties. With sheath-core filaments, it may be desirable to employ a somewhat larger percentage of the N-substituted polyamide component in the core.

In producing sheath-core filaments, the core should be highly eccentric in order to develop the required retractive force on crimping. This means that part of the sheath will be very thin, i.e., the minimum thickness of the sheath will range from 5 percent of the filament diameter to 0.1 percent or less.

Either or both of the components may contain any of the various additives commonly employed in the production of fibers, such as delusterants, pigments, dyes, antioxidants, antistatic agents and surface-modifying agents.

In addition to the exemplified yarns, other deniers and other filament counts may be employed. Although hosiery filaments are usually of round cross section, other shapes may be employed and may be particularly useful in certain end uses such as in tricot knit fabrics

or certain woven fabrics. For such purposes, cross sections of trilobal shape, shield shape, heart shape, cruciform shape and various multilobal configurations may be employed.

The filaments of this invention exhibit a surprisingly good combination of high crimp elongation, high strength and high crimp recovery. They may be processed to give a desirably low shrinkage level in the hose finishing process. Crimp elongation levels in excess of 40 percent, when crimped in 100° C. steam atmosphere under 1.2 mg./den. load, can readily be achieved at tenacity levels of at least 6 grams per denier at break, i.e., based on the filament denier at the breaking elongation. Crimp recovery is normally at least 85 percent and shrinkages of 3 percent or lower are readily attained. In addition, the filaments when removed from the package after normal storage and relatively straight (substantially uncrimped) and thus, easily handled, but when stretched slightly and then allowed to relax the filaments develop a considerable amount of crimp. This latter characteristic results in a reduction in the size of greige hose knit from the filaments since the filaments are stretched to some extent on knitting and tend to develop crimp when the hose is relaxed. The filaments tend to develop additional crimp when subjected to hot aqueous treatment as in a dye bath and require no separate or special treatment to develop the necessary crimping tendency.

Also, these filaments have the ability to generate very small coils and this provides a high compressive force in the hose at a given fabric density. This, in turn, leads to a more comfortable fit over a wide range of leg sizes. The coil diameter of a given filament may be varied considerably by varying the hose finishing temperature. For instance, a filament having a crimp diameter of 0.19 mm. with 100° C. steam treatment has been found to give a crimp diameter of 0.11 mm. at 150° C. This permits the hosiery manufacture to vary the characteristics of the hose substantially by appropriate selection of finishing conditions.

The expression "inherent viscosity" as used herein signifies the natural logarithm of the ratio of flow time in a viscometer of a polymer solution containing approximately 0.5 percent by weight of polymer, relative to the flow time of the solvent by itself, divided by the concentration. Measurements of inherent viscosity are made with 0.25 gram of polyamide in 50 milliliters of meta cresol at 25° C.

Shrinkage and crimp elongation of the filament are determined as follows:

A 750 denier skein of monofil or multifilament yarn is prepared by winding the requisite number of turns on a reel to give a skein of about 55 centimeters length when suspended with a weight attached. The denier of the filament bundle representing the collapsed skein will, of course, be twice that of the original skein, i.e., 1500 denier. The skein is hung on a hook with a 500 gm. weight suspended from its other end. After 1 minute, the length (a) of the skein is measured. The 500 gm. load is removed and a 1.8 gm. load is applied in its place so that the skein is under a tensile load of 1.2 mg./den. (mgd), i.e., a tension slightly in excess of that on the yarn when knitted into a fabric. The skein with the weight attached is subjected to 100° C. steam at atmospheric pressure (hereinafter referred to as "atmospheric steam") for 1 minute, after which the skein is allowed to dry in air for 10 minutes. The skein length

(b) is then measured. The 1.8 gm. load is then removed, the 500 gm. load is again applied for 1 minute, and the length (c) of the skein determined. The 500 gm. load is then replaced by the 1.8 gm. load. After the 1.8 gm. load has been applied for 2 minutes, the length (d) of the skein is measured. The crimp elongation, shrinkage, and crimp recovery of the filament are calculated from the following equations:

$$\text{Crimp Elongation, percent} = 100 (c-b/b)$$

$$\text{Shrinkage, percent} = 100 \times (a-c/a)$$

$$\text{Crimp Recovery, percent} = 100 \times (c-d/c-b)$$

The crimp diameter of the filament under a tension of 1.2 mgd is determined by taping 1-inch lengths of the crimped tensioned skein on a microscope slide and projecting the magnified image on a grid covered screen by means of a projection microscope.

The strength of the filaments or yarns is usually expressed in terms of tenacity and may be measured by conventional means. Values given herein were measured on yarn conditioned at 72° F. (22.2° C.) and 65 percent RH using an Instron tester. The tenacity after boil-off is measured on yarn which has been boiled in water for 30 minutes under no load, dried at 72° F. (22.2° C.) and conditioned as above. The tenacity of a conventional yarn is calculated on a basis of the denier of the yarn as measured before testing. However, since the yarn of this invention elongates considerably before breaking, the actual denier at the breaking point is substantially lower than the measured denier. Therefore, tenacity based on the breaking denier is a more useful value for comparing different fibers. Tenacity in grams per denier at break (T_{bd}) may be calculated from the usual tenacity value (T) and the percent elongation at the breaking point (E) as follows:

$$T_{bd} = T(1+E/100).$$

EXAMPLE 1

The salt of hexamethylenediamine and dodecanedioic acid is prepared as follows: 9,080 gm. of dodecanedioic acid are dissolved in 46 liters of anhydrous methanol with stirring and heating until solution is complete. To this solution is added 5,500 gm. of an 84.9 percent aqueous solution of hexamethylenediamine, the diamine solution being added rapidly with rapid mixing. The resulting solution is cooled to 10°–15° C. to precipitate the salt, with continued agitation for 2 hours. The salt is then filtered off, washed with 7.6 liters of cold methanol, dried in a vacuum oven at 70°–80° C. under 75–125 mm. Hg. pressure for 16 hours. A solution of 10 gm. of the resulting salt in 100 milliliters of water is found to have a pH value of 7.7.

The salt of N,N'-diethylhexamethylenediamine and dodecanedioic acid is prepared as follows: 5,000 g. of N,N'-diethylhexamethylenediamine are added to 4.3 liters of isopropyl alcohol. The diamine solution is added with stirring to a 50°–60° C. solution of 6,510 gm. of dodecanedioic acid in 44 liters of isopropyl alcohol, the solution being kept under a nitrogen atmosphere. The warm solution is stirred until a clear solution is obtained. 44 liters of isopropyl alcohol are then added to the mixture which is cooled to 0°–10° C. to precipitate the salt. If the salt fails to precipitate on cooling, 2 gallons of ethylacetate are added to bring about precipitation. The salt is then filtered off and dried at 50° C. for 24 hours.

A copolymer is prepared by combining equal weights of the above salts in an autoclave under a nitrogen atmosphere. Other additives are 1.5 percent by weight of hexamethylenediamine, 0.6 percent formic acid, 0.2 percent boric acid, 0.03 percent potassium phenylphosphinate and 8.6 percent water. The salts and the additives are heated in the closed autoclave with agitation to a temperature of 215° C. over a period of 120 minutes. The pressure in the autoclave is then reduced to atmospheric and the temperature increased to 295° C. over a period of 90 minutes. This temperature is maintained for 30 minutes while the autoclave is flushed with dry nitrogen. While maintaining the temperature, the pressure in the autoclave is reduced to 10 millimeters of mercury or less and held for 60 minutes. The polymer is then cooled to 250° C., extruded and cut to flake in the conventional manner. The flake is then dried in a vacuum oven at 120° C. for 24 hours. The final polymer has an inherent viscosity of 1.75.

A polymer is prepared from the salt of hexamethylenediamine and dodecanedioic acid in the conventional manner, cut into flake and dried. The final polymer has an inherent viscosity of 1.40.

The two above prepared polymers are melted and pumped to a spinneret assembly of the type illustrated in FIG. 2 of U. S. Pat. No. 3,558,760 to Olson, with holes arranged to spin three filament yarns. The polymers are extruded in side-by-side relation to produce filaments containing about 50 percent of each of the two polymers. The filaments are quenched in air at 25° C. and then converged into a three-filament yarn. The yarn is given 4 passes around a feed roll rotating at 330 yds. (302 meters/min.) peripheral speed and its associated separator roll and then is given 7 passes around a feed roll having a peripheral speed of 1,300 yds./min. (1,189 meters/min.) and its associated separator roll. The yarn is then passed to another roll operating at 1,300 yds./min. (1,189 meters/min.) and then to a roll operating at 1,250 yds./min. (1,143 meters/min.) and is finally wound into a package in the conventional manner at 1,200 yds./min. (1,097 meters/min). Subsequently, the yarn is withdrawn from the package and given an additional 1.3X draw in order to reduce the elongation to the desired range of 25–30 percent. The yarn is then passed from the draw roll through a tubular air jet device of the type illustrated in U. S. Pat. No. 3,558,760, FIG. 5, where the yarn is subjected to hot air, the temperature being 160° C. at the jet inlet. The yarn is passed through the jet device at 420 yds./min. (384 meters/min.) then around a series of four snubbing pins of 3/16 inch (4.8 mm.) diameter where the yarn is passed in contact with the pins for a total cumulative angle of 1,100°. The yarn is then passed around a power driven roll rotating with a peripheral speed which is 28 percent less than the speed of the draw roll. From the snubbing pins the yarn is passed to a conventional winding device and wound into a package. The denier of the final yarn is 22.

Table 1 below gives properties of the yarn prepared as above, designated yarn A, in comparison with properties obtained on a commercial bicomponent yarn, yarn B, of the same denier-filament count, which is used in the manufacture of stretch hosiery. Yarn A has better tenacity and elongation at break, both before boil-off (BBO) and after boil-off (ABO) and has greatly improved crimp elongation.

TABLE 1

Yarn	A	B
Denier-Filaments	20-3	20-3
Tenacity, T, gpd (BBO)	4.3	4.2
Elongation at break, % (BBO)	53	45
Tenacity, T _{bd} , gpd (BBO)	6.6	6.1
Tenacity, T, gpd (ABO)	3.8	3.6
Elongation at break, % (ABO)	74	50
Tenacity, T _{bd} , gpd (ABO)	6.6	5.4
Crimp Elongation, %	100	20
Crimp diameter, mm.	0.165	0.152
Crimp spacing (pitch), mm.	0.29	0.71
Helix length, mm.	0.56	0.81
Crimp recovery, %	85	81

When the above yarn is knitted into miniature style stretch hose, it is found that greige hose, immediately after knitting, are relatively small in size due to the tendency of the yarn to crimp at this point. Table 1-A shows a comparison of the hose, designated hose A, with hose knit from yarn B above. The relative reduction in hose size after various treatments is shown with the commercial greige hose, hose B, taken as 100. As can be seen, the yarn A of this invention gives a greige hose of greatly reduced size, and treatment of this hose with boiling water is sufficient to reduce the size below that obtained by treatment of the commercial hose, B, with 118° C. steam.

TABLE 1A

Hose	A	B
Greige Hose, relative size	49	100
After Boil-Off	26	52
After 118° C. steam	24	32

EXAMPLE 2

Drawn yarn is prepared as in Example 1 except that the two salts are combined in a ratio of 30.5 percent by weight of N,N'-diethylhexamethylenedodecanedioamide and 69.5 percent by weight of hexamethylenedodecanedioamide.

After drawing the yarn is passed through a tubular jet device as in Example 1 except the inlet temperature is 212° C. and the yarn is passed in contact with the snubbing pins for a cumulative angle of 1,360°. Yarn and hose properties are shown in Tables 2 and 2-A below in comparison with the properties of yarn and hose B of Example 1.

TABLE 2

Yarn	C	B
Denier-Filaments	20-3	20-3
Tenacity, T, gpd (BBO)	4.6	4.2
Elongation at break, % (BBO)	58	45
Tenacity, T _{bd} , gpd (BBO)	7.3	6.1
Tenacity, T, gpd (ABO)	4.3	3.6
Elongation at break, % (ABO)	73	50
Tenacity, T _{bd} , gpd (ABO)	7.3	5.4
Crimp Elongation, %	76	20
Crimp diameter, mm.	0.116	0.152
Crimp spacing (pitch), mm.	0.214	0.71
Helix length, mm.	0.42	0.81
Crimp recovery, %	85	81

TABLE 2A

Hose	C	B
Greige hose, relative area	54	100
After boil-off	34	52
After 118° C. steam	30	32

EXAMPLE 3

Polymers are prepared separately from the respective salts, N,N'-diethylhexamethylenedodecanedioamide and hexamethylenedodecanedioamide following the general procedure of Example 1. The polymers have inherent viscosities of 1.3 and 1.4, respectively.

The two polymers are mixed in a 50/50 weight ratio in a homogenizer at 305° C. and then pumped to a spinneret assembly of the type used in Example 1. The total elapsed time from mixing to extrusion of the polymer is about 90 min. Analysis of the polymer indicates about 12 percent of amide interchange between the two polymers. The block copolymer is extruded in side-by-side relationship with poly(hexamethylenedodecanedioamide) of 0.96 inherent viscosity and processed in the yarn as described in Example 1. Properties of the yarn (D) in comparison with yarn (B) of Example 1 and of hose knitted from the yarn are given below.

TABLE III

Yarn	D	B
Denier-Filaments	20-3	20-3
Tenacity, T, gpd (BBO)	4.3	4.2
Elongation at break, % (BBO)	60	45
Tenacity T _{bd} , gpd (BBO)	6.9	6.1
Crimp elongation, %	69	20
Crimp diameter mm.	0.28	0.152
Crimp spacing (pitch) mm.	0.56	0.71
Helix length, mm.	1.0	0.81
Crimp recovery, %	85	81

The greige hose resulting from Yarn D had a relative area of 37 compared to 100 units for hose made from yarn B with 20 percent CE. Additional area contraction occurred after boil-off and treatment with 118° C. steam.

EXAMPLE 4

Example 3 is repeated except that poly(N,N'-di-n-butyl-hexamethylenedodecanedioamide) is substituted for poly (N,N'-diethylhexamethylenedodecanedioamide). Properties of the yarn (d) in comparison with yarn B of Ex. 1 and hose prepared from the yarn are shown below.

TABLE IV

Yarn	E	B
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Denier-Filaments	21-3	20-3
Tenacity, T, gpd (BBO)	4.3	4.2
Elongation at break, % (BBO)	48	45
Tenacity T _{bd} , gpd (BBO)	6.4	6.1
Crimp elongation, %	67	20
Crimp diameter, mm.	0.14	0.152
Crimp spacing (pitch) mm.	0.28	0.71
Helix length, mm.	0.51	0.81
Crimp recovery %	85	81

The greige hose resulting from yarn E had a relative area of 42 compared to 100 units for hose made from yarn B. Additional area contraction occurred after boil-off and treatment with 118° C. steam.

I claim:

- 1. A composite polyamide filament having a tenacity of at least 6 grams per denier at break, comprising distinct, continuous, filament components in adherent, eccentric arrangement along the length of the filament to provide a helical crimp with a crimp elongation of at least 40 percent when the filament is subjected to atmospheric steam while the filament is under 1.2 milligrams per denier load, the polyamide of one component consisting essentially of poly(hexamethylenedodecanedioamide) and the polyamide of a second component is a copolymer consisting of 75 to 50 percent hexamethylenedodecanedioamide polymer units and 25 to 50 percent N,N'-dialkyl-hexamethylene-dodecanedioamide polymer units.
- 2. A composite nylon filament as defined in claim 1, wherein said alkyl group is an ethyl group.
- 3. A composite nylon filament as defined in claim 1, wherein said alkyl group is an n-butyl group.
- 4. The composite nylon filament defined in claim 1, having said components in side-by-side relationship.
- 5. The composite nylon filament defined in claim 1, having a crimp characterized by a crimp recovery of at least 85 percent.
- 6. Composite nylon filaments as defined in claim 1, wherein the filaments are in substantially uncrimped form.
- 7. A fabric knitted from a plurality of the filaments defined in claim 8 and then heated to develop crimp.

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