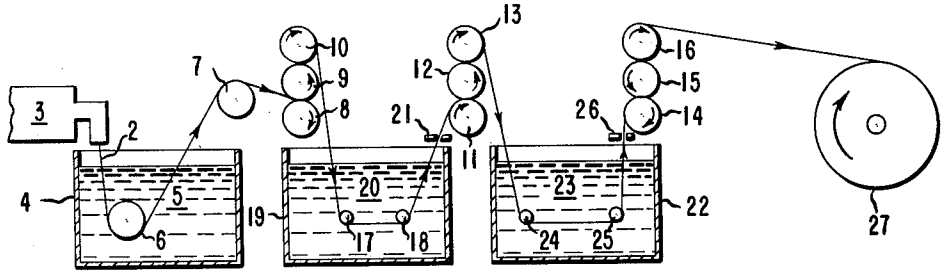
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PROCESS OF PRODUCING POLYCAPROLACTAM MONOFILAMENTS

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PROCESS OF PRODUCING POLYCAPROLACTAM MONOFILAMENTS

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2 Claims. (Cl. 264—178)

This invention relates to novel nylon monofilaments, and more particularly to a polycaprolactam monofilament which possesses a unique balance of properties and is particularly suitable for use as a fish line.

The tensile strength of an extruded filament of a thermoplastic such as polyhexamethyleneadipamide and polycaprolactam may be increased by drawing the filament after extrusion. Drawing operations are frequently classed as "hot" or "cold" drawing, depending upon the relative temperature of the filament during the drawing operation. Any drawing operation at a temperature below the softening point of the filament yields a tenacious, stiff filament because the increase in tensile strength and reduction in elongation necessarily results in increased stiffness of the material. In applications for a filament such as its use in fabrics and for tire cord, high tensile strength and high stiffness are desirable; however, this combination of properties of the monofilaments is undesirable when the material is to be used for fish line and like applications. The requirements for the latter application are high tensile strength, low elongation, and low stiffness and can only be obtained by a unique balancing of the composition and manner of preparation of the filament.

An object of this invention is to provide a unique monofilament of high tensile strength, low elongation, and low stiffness. Another object of this invention is to provide a monofilament which has specific additives that enhance the desirable properties of the filament beyond those of the filament without such additives. Still another object is to provide a process for the preparation of the filament of this invention. These and other objects will appear hereinafter.

The above objects are accomplished by drawing in two stages an unextracted polycaprolactam monofilament containing approximately 10% by weight of a plasticizer. The filament is drawn in water at a draw ratio of 4.3/1 at a temperature of 55° C. in the first stage, and in oil at a draw ratio of approximately 1.2/1 at a temperature of 150°–165° C. in the second stage. The resulting filament has a diameter of 3–30 mils with a desirable tensile strength and beam stiffness. The tensile strength bears a substantially linear relationship to diameter, or caliper, such that at a caliper of 3 mils the filament has a tensile strength of at least 110,000 p.s.i., and at 30 mils has a tensile strength of at least 73,000 with a beam stiffness over the above range of 150,000–230,000 p.s.i. In addition to the drawing operation and the plasticizer in the initial polymer, certain additives such as copper stearate in the amount of 0.01% to 0.1% by weight may be incorporated in the polymer to enhance the knot strength of the filament. A pigment consisting of the oxides of copper, manganese and chromium may also be incorporated into the polymer or placed on the surface of the filament to impart weatherability to the filament, and to camouflage the filament in the water when it is used as a fish line.

Of the numerous drawing processes which are shown in the prior art, practically all result in the production of a somewhat stiff filament which is undesirable for use as a fish line. The filament of this invention is unique in that the filament strength exceeds that of known filaments at

any given caliper, but, at the same time, exhibits a lower stiffness than is associated with filaments which have been drawn by known methods. The elongation of the filament of this invention is less than would be expected from its high tensile strength, thus providing the angler with better control.

Attached hereto and made a part of the present specification is a schematic drawing showing an apparatus which may be employed to practice the process of the present invention. A molten strand 2 of polycaprolactam is forced from a standard type of extruder 3 and directed through a standard 3-roll, 2-stage drawing apparatus using a common set of central draw rolls. The drawing apparatus consists of a first-stage draw which employs a quench tank 4 filled with water as indicated by item 5. The strand begins to solidify upon contact with the surface of the water and is then directed under a roll 6 to an initial positioning roll 7 which roll feeds the filament to the first set of draw rolls 8, 9, and 10. When using this common type of 2-stage draw apparatus, the filament is directed through a second set of draw rolls 11, 12, and 13 thence through a third set 14, 15, and 16 in the same manner as through rolls 8, 9, and 10. As is known in the art, the central roll in each set is a rubber-coated idler roll and the outer rolls which are steel covered are driven at a predetermined speed. The differential speed of the first and second set of draw rolls permits the filament to be drawn in a ratio proportional that differential speed. Also set forth in FIGURE 1 are the conventional type draw pins 17, 18, 24, and 25 which assist in the drawing operation. The liquids indicated as items 20 and 23 in tanks 19 and 22 may be of different characteristics and means 21 and 26 may be provided to remove the respective liquid from the filament before the filament is immersed in the following liquid, or wound on a conventional type of spool. The operation of this process is more fully described hereinbelow.

Unlike improvements made to other types of equipment, the precise balance of properties in the filament of this invention is not readily apparent with simple visual inspection, but may readily be measured by laboratory techniques as set forth below. The measurements, and the formulas using these measurements, for defining beam stiffness, tensile strength, and breakload, are given below. A comparison of the filament of this invention with those of the prior art may be made by comparing these quantities for two lines to determine the filament which possesses the lower apparent stiffness at substantially equivalent filament strengths.

(1) Tensil strength (T.S.) in p.s.i. $= \frac{1.27 \text{ B.L.}}{D^2}$

(2) Bean stiffness (B.S.) in p.s.i. $= \frac{0.00237W}{D^4 d}$

Formula 1 above gives the tensile strength (T.S.) for a filament having a diameter (D) in inches and using the cross-sectional area and the breakload (B.L.) in pounds as measured on an Instron Universal Tensile Tester using a 10-inch gap (filament segment) and drawing at 10 inches per minute in an atmosphere at 23° C. and 50% relative humidity. Formula 2 gives the beam stiffness (B.S.) of a line having a diameter (D) in inches. The beam stiffness is measured by attaching a weight of W grams to the center of a filament suspended between two supports spaced one inch apart, and by measuring the deflection (d) in cms. which the weight has caused the filament to sag from the horizontal. This measurement is made in an atmosphere of air at 23° C. and 50% relative humidity after the weight has been on the filament for 30 seconds.

Two filaments (A) and (B) may be compared by taking two lines of equal breakload and comparing Equation

1 for each filament, which by simple mathematics reduces to:

$$(3) \qquad TS_a D_a^2 = TS_b D_b^2$$

By definition, the effective stiffness of a filament is the reciprocal of the deflection, and the effective stiffness may be expressed in terms of beam stiffness from Equation 2:

$$(4) \qquad \text{Effective stiffness (E.S.)} = \frac{\text{B.S. } D^4}{0.00237W}$$

The ratio of effective stiffnesses of two filaments to be compared may be seen to be a ratio of Equation 4 for each filament:

$$(5) \qquad \text{Comparative stiffness: } \frac{ES_a}{ES_b} = \frac{D_a^4 \text{ B.S.}_a}{D_b^4 \text{ B.S.}_b}$$

If one arbitrarily assigns to the filament of this invention an effective stiffness (E.S.) of 1 then the filaments of the prior art will possess an effective stiffness greater than 1. Measurements and calculated values for comparative stiffnesses are given in the following examples which are intended to illustrate and not to restrict the present invention.

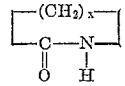
Example I

The polycaprolactam used in this example had an inherent viscosity (I.V.) of 1.3 as measured at 0.5% by weight in a solution of m-cresol at 25° C., calculated according to the formula set forth in column 4 of United States Patent 2,895,948, issued on July 21, 1959, to K. C. Brinker et al., and a monomer content of about 10% by weight of the polymer. This unextracted polymer flake was dried and thereafter extruded in a standard 1" extruder manufactured by the National Rubber Machine Company using a barrel temperature of 260° C. and a die temperature of 250° C. at a rate of ½–¾ pound per hour. The strand was immediately quenched in water at about 7° C. for 1–2 seconds and led to a standard 3-roll, 2-stage, drawing apparatus using a common set of central draw rolls. The first stage draw was effected in water at 55° C. at a draw ratio of 4.3/1 (ratio=final length over original length) and the second draw was effected in silicone oil at 160° C. at a draw ratio of 1.2/1. The drawn filament (approximately 10–12 mils in diameter) was then wiped to remove the oil clinging thereto and wound at moderate tension on a suitable spool. The following properties are averaged properties exhibited by ten samples of this line:

Tensile Strength	Percent Elongation	Overhand Knot, p.s.i.	Beam Stiffness, p.s.i.	Clinch Knot, p.s.i.
105,100	18.9	54,200	208,700	88,000

The knot strength was measured by tying the given knot in the filament, pulling the knot tight, suspending the knot equidistant from the clamps in the Instron Universal Tensile Tester, and following the procedure described hereinabove for determination of the tensile strength. The properties of this filament indicate that it would be outstanding for use as a fish line.

Other oils such as "Ucon" 50HB–280X (a polyalkylene glycol oil sold by Union Carbide Corp.) which do not degrade the polymer have been found to be operable in the second stage draw in place of the silicone oil described above. Other plasticizers which are operable in this invention include the cyclic lactams of the general formula



where x is a positive integer of 4, 5, or 6. Additional experiments have indicated that the desired range of plasticizer concentration is 3%–15% by weight of the polymer.

Example II

To the starting polymer of Example I was added sufficient "Ferro Black" F–1335 to reach a concentration of 0.1% by weight of the polymer by tumbling the pigment and a binder with the polymer for about one hour before extruding the filament as described in Example I. "Ferro Black" F–1335 is a pigment containing a mixture of the oxides of chromium, copper, and manganese, and is sold by the Ferro Corporation. Several calipers of filament were extruded and the properties of this filament (shown below as S) were compared with three known commercial filaments, designated as A, B, and C. The formula as set forth hereinabove for comparative stiffness was used for the comparison of the filaments and the averages of the test data are given below.

Brand	Caliper (mils)	Suggested Load (lbs.)	Tensile Strength	Elongation (Percent of Length)	Beam Stiffness	Comparative Stiffness
S	8.8	6	102,000	25	185,000	1.00
A	11.5	6	79,100	31	206,000	1.85
B	11.2	6	72,100	26	265,000	2.90
C	9.6	6	84,400	28	204,000	1.65
S	12.1	10	93,500	25	193,000	1.00
A	15.0	10	71,400	32	164,000	1.52
B	13.9	10	80,700	32	243,000	1.79
C	12.8	10	78,400	26	215,000	1.67
S	20.4	30	86,800	27	172,000	1.00
A	22.0	30	71,800	37	162,000	1.36
B	27.1	30	63,500	31	219,000	2.02
C	22.6	30	76,700	29	204,000	1.52

Brand A was an uncolored resin and Brands B and C were tinted. When the line of this invention was placed in a standard U.V. weatherometer with Brand A, it was discovered that the instant filament possessed better properties after 1000 hours of exposure than Brand A possessed after only 250 hours of exposure. This result and the results from the above comparison indicate that the filament of this invention is vastly superior to those of the prior art. With the exception of weatherability, the unmodified filament of Example I has properties similar to the six pound filament of this example. The slight decrease in tensile strength of the filament of this example as compared to the unmodified filament of Example I may be due to the pigment and binder placed in the polymer of this example. The low elongation of the filament of this invention makes the filament especially suitable for use as a fish line.

A number of determinations of tensile strength indicate the general ranges of tensile strengths of the filament of this invention are from 106,000 p.s.i. to 130,000 p.s.i. at a caliper of 6 mils and 80,000 p.s.i to 104,000 p.s.i at a caliper of 25 mils although some filaments have been produced which fall above this range. The range of beam stiffness for numerous filaments was found to be from 150,000 to 230,000 p.s.i. for filaments in the above caliper range. The properties of beam stiffness of the pigmented filaments of this example are comparable to the unmodified filament of Example I. The amount of pigment may vary from 0.05%–0.25% by weight of the filament. The composition and amount of pigment employed should be such that sufficient weatherability and color (light gray) may be imparted to the filament at pigment concentrations low enough so that the strength of the line is not adversely affected.

Example III

In this example, a particular additive was employed to further improve the remarkable properties of the instant line. To the unmodified polymer of Example I was added 0.05% copper stearate by tumbling the polymer flake with the additive for a few hours followed by extrusion

and work up as set forth in Example I. The filament (10–13 mils in diameter) had the following properties:

Tensile Strength	Percent Elongation	Overhand Knot, p.s.i.	Beam Stiffness, p.s.i.	Clinch Knot, p.s.i.
109,000	20.3	69,500	229,300	106,300

The additive improved the tensile strength approximately 3.5% and the overhand knot strength approximately 25% over the same properties of the line of Example I with no noticeable impairment of the limpness or of the elongation of the filament. Experiments such as the above indicate that the acceptable and preferred range of concentration of the copper stearate is 0.01%–0.1% by weight of the polymer. Other additives are also operable to further improve the properties of the instant line and are discussed hereinbelow. Similar improvements were obtained by adding 0.05% of copper stearate to the pigmented filament of Example II. In this case, the copper stearate was first added to the polymer flake, which was then tumbled for one hour, and then the pigment was added and the tumbling continued for an additional hour, followed by extrusion and workup.

The above examples indicate that the filament of this invention is superior to those of the prior art and possesses the majority of properties which are desirable for its application as a fishing line. The filament of this invention should find other uses which require similar properties. Although the caliper of the filaments shown in the examples varies from about 8.7 mils to 20.4 mils, the useful range of filament calipers in this invention is from 3 mils to about 30 mils.

The weatherability of this filament is markedly increased by the addition of the pigment specified above as evidenced by the fact that the line of this invention after 1000 hours' exposure in a weatherometer possessed qualities comparable to a known material (Brand A of Example II) after only 250 hours. Pigments of like characteristics are also within the purview of this invention.

The exact nature of the action of the copper stearate on properties of the filament is not known. It is believed that the copper stearate acts both as a lubricant and a stabilizer for the filament. Other lubricants which are operable include zinc stearate, waxes, salts of organic fatty acids, and low molecular weight amides of organic fatty acids. Other stabilizers which are operable include other copper compounds, such as cupric chloride; aromatic amines; and phenolic antioxidants. Generally the copper stearate increases the strength of the filament as evidenced by the increase in overhand knot strength of 25% with a somewhat smaller increase in tensile strength (3.5%).

The preferred drawing process is a two-stage process as set forth in Example I. A single-stage draw may be employed, but with somewhat inferior results with respect to the tensile strength of the filament. The single-stage draw yields a filament with increased transverse stability as shown by an increase of 18% in the overhand knot strength, but is not preferred since the more important property of tensile strength decreases about 5%.

The polycaprolactam is extruded as a filament at a temperature of 240°–260° C., desirably at 250° C., and is solidified by quenching. After quenching the extruded filament in a quench bath at about 5°–25° C., the first stage of drawing is conveniently accomplished in water at a temperature of about 30°–55° C. and at a draw ratio of about 4.2–4.5. It is not critical that water be used as a drawing medium since other inert liquids such as trichloroethylene may be used. The second stage of drawing is accomplished in an oil, e.g., silicone oil, at a temperature of 150°–165° C. and a draw ratio of about 1.15–1.25. This provides a range of overall draw ratio of about 4.8–5.6. It is preferred that the first stage draw the filament about 4.3 times and the second stage about 1.2 times for an overall draw ratio of about 5.2.

Additional process steps may be employed in the drawing operation without adversely affecting the filament properties. Such operations may include two-stage addition of materials to the base polymer before extrusion and mild steam treatment of the filament upon the final windup spool by passing the spool through a steam chamber to reduce the strain in the filament.

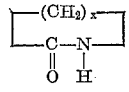
By virtue of the greatly enhanced properties of the monofilament of this invention, its principal use is as a fishing line for bait casting, fly casting, trolling, surf fishing, and in other methods of fishing with a line.

This application is a division of my copending application, Serial Number 821,108, filed June 18, 1959, now Patent No. 3,057,040.

I claim:

1. A process for producing a monofilament fish line, 3–30 mils in diameter, of polycaprolactam comprising extruding a dried, flaked, polycaprolactam containing 3–15% by weight of a plasticizer at a temperature of about 250° C.; quenching the extrudate in water at a temperature of about 5°–25° C.; drawing said extrudate at a ratio of 5.2/1.0 at a temperature of 150°–165° C. in an oil which is substantially unreactive towards said polycaprolactam.

2. A process for producing a fish line of polycaprolactam comprising adding 0.05–0.25% of an inorganic pigment containing the oxides of copper, manganese, and chromium to a dried polycaprolactam polymer flake containing 3–15% by weight of the polymer of a cyclic lactam plasticizer having the general formula



where x is a positive integer from 4 to 6; extruding the polymer thus treated at about 240°–260° C.; quenching the extrudate in water at 5°–25° C., drawing said extrudate in two stages; the first stage drawing being being conducted at 30°–55° C. and at a draw ratio of 4.2/1 to 4.5/1; the second stage drawing being conducted in oil which is substantially unreactive towards said polycaprolactam at a temperature of 150°–165° C. and at a draw ratio of about 1.15/1 to 1.25/1.

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