United States Patent

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Continuation-in-part of application Ser. No. 341,725, Jan. 31, 1964, now abandoned.

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[54] **PROCESS FOR MELT SPINNING POLYAXYMETHYLENE FILAMENTS HAVING ELASTIC RECOVERY**
4 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** **264/210,** 264/176, 264/231, 264/235, 264/290, 264/346
[51] **Int. Cl.** **D01d 5/12,** D01f 3/10
[50] **Field of Search** 264/176, 210, 168, 231, 235, 290, 346

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ABSTRACT: A process for producing filamentary material of an oxymethylene polymer having an elastic recovery at 70° F. of at least about 70 percent when subjected to a strain of up to 50 percent.

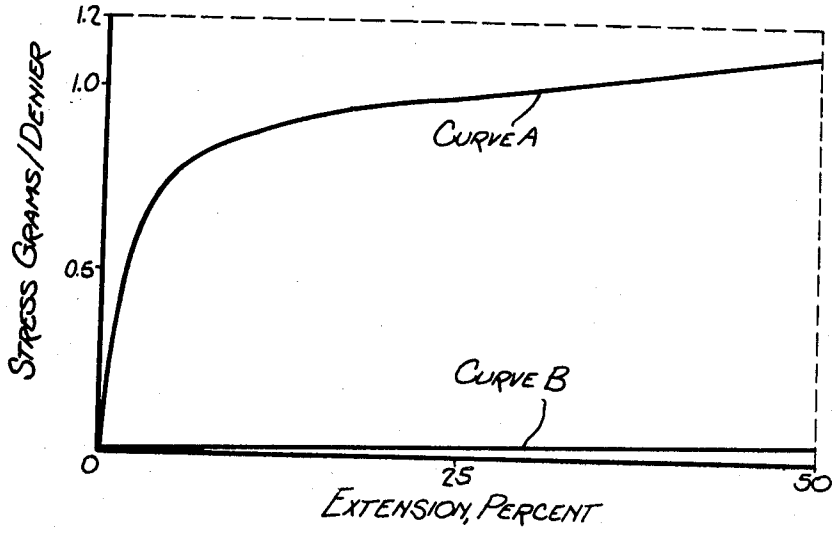


Fig. 1.

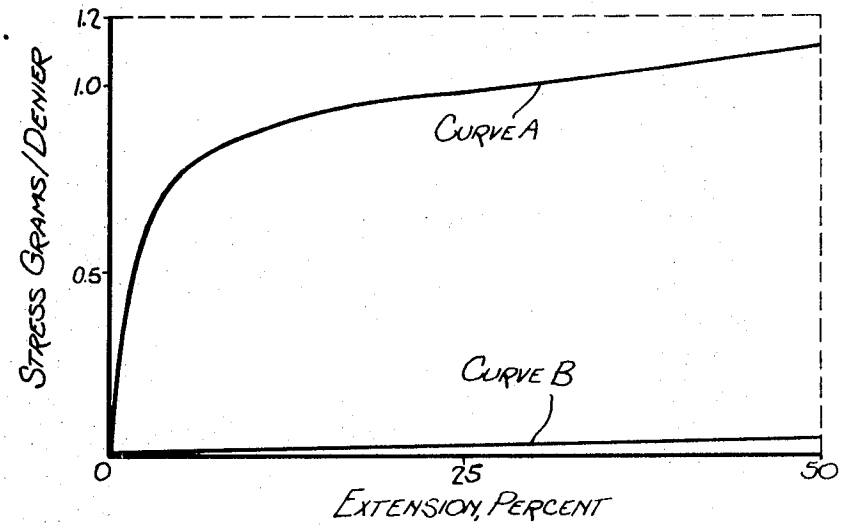


Fig. 2.

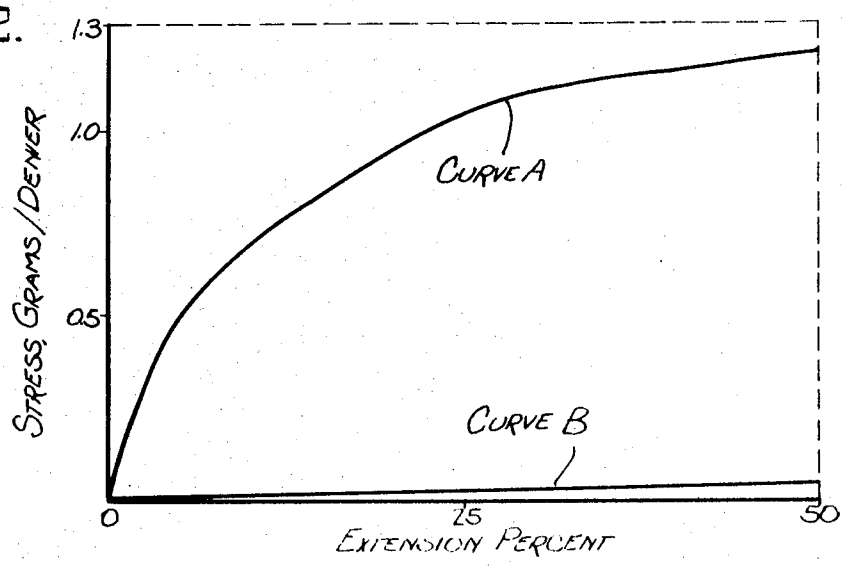
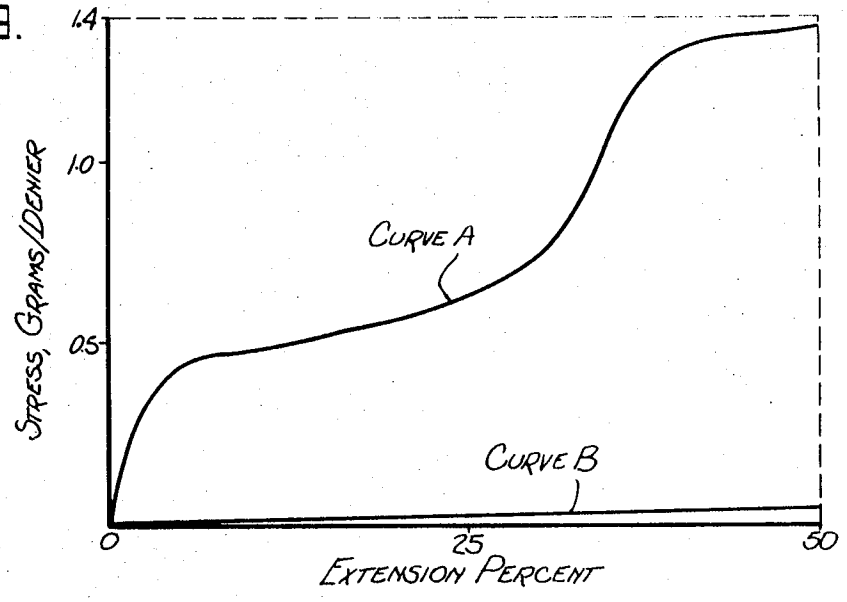


Fig. 3.



PROCESS FOR MELT SPINNING POLYAXYMETHYLENE FILAMENTS HAVING ELASTIC RECOVERY

This is a continuation-in-part of Ser. No. 341,725, filed Jan. 31, 1964, and now abandoned.

This invention relates to the preparation of relatively elastic filaments of an oxymethylene polymer.

It has been proposed to prepare filaments from oxymethylene polymers, e.g., by melt spinning. Such filaments, especially those prepared from oxymethylene copolymers such as the copolymers described in U.S. Pat. No. 3,027,352 issued to Walling et al., have many outstanding properties such as high strength, stiffness and stability. We have now discovered an entirely new type of oxymethylene polymer filamentary material which, unlike the filaments of the prior art, possess a high degree of elasticity after being subjected to a relatively large amount of stretch, e.g., 50 percent or more at 70° F. These new filaments are particularly useful in the preparation of elastic yarns for stretch garments, either alone or in a blend with a nonelastic material. The new filamentary materials have been found to be superior to known elastic fibers, such as spandex fibers, in such properties as breaking tenacity and stiffness as indicated, for example, by initial modulus.

In the past, of all high polymer solids, only elastomers have been established as a class of the materials that exhibits high "elasticity" (i.e., the ability to retract rapidly from a large extension). On the molecular scale, the deformation of elastomers is controlled by a network of cross-linked flexible polymer chains, where the cross-linking results from either primary chemical bonds or secondary bonding between the chains. Thermodynamically, the deformation has its basis in an entropy effect involving the distortion of polymer chains from their most probable configurations in the unstretched state.

Within the class of crystalline or semicrystalline polymers, some with a low degree of crystallinity (e.g., less than perhaps 15 percent) can manifest rubberlike elasticity, where the crystallites act as the cross-links. However, polymers with an intermediate or high degree of crystallinity usually undergo yielding and "necking" at large extensions, and this tendency is more marked in unoriented specimens. Some rearrangements of both crystallites and disordered chains as well as disruption of the crystallites occur at large strains. The resulting macroscopic deformation of the material is largely irreversible due to permanent changes in the structure on extension.

Elastic "hard" (nonelastomeric) polyoxymethylene fibers represent a new class of elastic polymeric solids of high crystallinity which are capable of undergoing large elastic deformations due to a specific morphology present in the material. These materials are prepared in the form of extruded fibers under specific conditions of crystallization from the melt (i.e., crystallization under stress).

The polymers that can be used for formation of such elastic materials are oxymethylene polymers, preferably "random" oxymethylene copolymers as hereinafter defined. After melt spinning, the material is subjected to a hot-wet treatment to improve tenacity and elastic recovery and render the material uniformly opaque. The essential morphological feature of the hot-wet-treated elastic materials as revealed by X-ray and light scattering and electron microscopy is the presence of stacked crystalline lamellae with their normals primarily aligned along the fiber and film extrusion direction. The mechanism of elasticity is based on a splaying-apart of these lamellae, involving their reversible bending and torsional deformation during macroscopic deformation of the material. Thus, in contrast to rubber elasticity, where the kinetic units are flexible chain segments, the kinetic units for the elasticity of an elastic "hard" material are the lamellar crystals. Due to the orientation of the lamellae along the fiber and film extrusion direction, the elasticity is exhibited almost exclusively in that direction.

Although subsequent hot-wet treatment increases the elastic recovery of elastic materials, the conditions of the initial crystallization process are important with the respect to the route by which a high degree of elastic recovery is achieved. Inappropriate spinning conditions may lead to fibers

which exhibit not only a relatively low level of elastic recovery, but also require comparatively more stringent hot-wet conditions to reach a good degree of elastic recovery.

It is accordingly an object of this invention to prepare a new elastic filamentary material.

It is a further object of this invention to provide an elastic, random, oxymethylene copolymer filamentary material having properties superior to those of known elastic materials.

It is a still further object to provide a process for the production of the above-described elastic filamentary material.

Other objects will be apparent from the following detailed description and claims.

FIGS. 1 to 3 show typical stress-strain curves for filamentary materials of this invention as more fully described hereinafter at up to 50 percent strain (curve A) as compared with the stress-strain curve of one of the stiffest commercially available spandex yarns (curve B).

In accordance with one aspect of the invention, there is provided filamentary material of an oxymethylene polymer having an elastic recovery at zero recovery time (hereinafter defined) at 70° F. of at least about 70 percent when subjected to a strain, for example, of up to 50 percent, and preferably an elastic recovery at zero recovery time of at least about 75 percent when subjected to a strain of 35 to 50 percent. More specifically, the material has at 70° F. an elastic recovery at zero recovery time of at least about 70 percent, preferably at least about 75 percent when subjected to a strain (or extension) of 50 percent. In particular, filamentary materials having at 70° F. an elastic recovery at zero recovery time of at least about 80 percent or 90 percent after being subjected to an extension of 50 percent are contemplated under the invention.

In general, the elastic recovery after 2 minutes recovery time of the above-described filamentary material is at least 10 percent greater than the values of elastic recovery at zero recovery time. Thus, filamentary materials are contemplated under the invention which have an elastic recovery at 70° F. after 2 minutes recovery time (as hereinafter defined) of at least about 80 percent when subjected to a strain of up to 50 percent and preferably an elastic recovery at 70° F. after 2 minutes recovery time of at least about 85 percent when subjected to a strain of about 35 to 50 percent. More specifically, material is contemplated which has an elastic recovery at 70° F. after 2 minutes recovery time of at least about 80 or 85 percent, e.g., about 85 to 98 percent, when subjected to a strain of 50 percent. In particular, filamentary material having at 70° F. an elastic recovery after 2 minutes recovery time of about 90 to 100 percent is included within the invention.

The filamentary material of this invention also has comparatively high elastic recoveries when stretched to extensions substantially higher than 50 percent. Thus, material is contemplated having at 70° F. an elastic recovery after 2 minutes recovery time of at least about 70 percent, e.g., about 72 to 95 percent from a 100 percent strain, and at least about 60 percent, e.g., about 60 to 85 percent from a 150 percent strain.

The filamentary material maintains a substantial degree of its elasticity at elevated temperatures. Thus, the filaments may, when subjected to a strain of 50 percent, have elastic recoveries after 2 minutes recovery time of at least about 70 percent, e.g., about 75 to 97 percent, at a temperature of 130° F.; at least about 70 percent, e.g., about 72 to 96 percent at a temperature of 190° F.; and at least about 60 percent, e.g., about 62 to 82 percent at 250° F.

The values for elastic recovery given above are for the first cycle of strain and recovery, using the procedure described hereinafter. It has been found in addition that the elastic recovery of the filamentary material between consecutive cycles changes little, after the material has been subjected to several cycles of strain and recovery. Thus, material is contemplated which, when subjected to seven cycles of 50 percent strain and recovery, has an elastic recovery at 70° F. with zero recovery time which decreases less than 1.5, and generally less than 1.0 percentage units between the start of the sixth and the start of the seventh cycle.

While various values are given above for elastic recovery after zero and 2 minutes recovery time, it should be un-

derstood that the material of the invention is capable of recovering an additional amount, i.e., may have a still higher elastic recovery, when the recovery time is substantially greater than 2 minutes.

In addition to these elastic properties the filaments generally have, e.g., at 70° F., a breaking tenacity of at least about 1.0, preferably at least about 1.3, e.g., about 1.3 to 2.5 grams/denier, a breaking elongation of at least about 55 percent, preferably at least about 75 percent, e.g., about 75 to 200 percent, and an initial modulus of at least about 2 grams/denier, preferably about 5 to 30 grams/denier. Thus the filaments produced under this invention have other good mechanical properties as well as elasticity, e.g., stiffness and strength.

The tensile properties of the preferred polyoxymethylene copolymer fibers essentially remain constant on going from room temperature to −190° C., including the absence of necking behavior. On the other hand, the corresponding nonelastic fibers become brittle at the low temperature, reflecting the glassy state of the polymer. The observed superiority of the elastic fibers over the spandex fibers at the low temperature is unexpected.

Thus the tensile properties, including elastic recovery, of elastic "hard" fibers of a polyoxymethylene random copolymer undergo a small change over the temperature range −190° C. to 23° C., compared with "nonelastic" polyoxymethylene and spandex fibers. The tensile properties of the elastic "hard" materials are relatively free from the embrittling effects of low temperatures, which is commonly observed at temperatures below the glass transition of amorphous and semicrystalline polymers. In particular, a relatively high value of break elongation of the elastic materials at very low temperatures is remarkable. These observations indicate that tensile deformation of the elastic materials is accommodated largely by a reversible deformation of lamellar crystals.

In addition to the above mechanical properties, the filamentary material of the invention generally has a birefringence of at least about 0.03, e.g., from about 0.04 to 0.08, **and most often from about** 0.05 to 0.07.

A "random" oxymethylene copolymer, as the term is used above, contains recurring oxymethylene, i.e., $-CH_2O-$, units interspersed with —OR— groups in the main polymer chain where R is a divalent radical containing at least two carbon atoms directly linked to each other and positioned in the chain between the two valences, with very substituents on said R radical being inert, that is, those which do not include interfering functional groups and which will not induce undesirable reactions, and wherein a major amount of the —OR— units exist as single units attached to oxymethylene groups on each side. A random copolymer may thus be distinguished over a block copolymer wherein repeating units of each monomer make up block segments containing little or no units of any other monomer. Thus, in block copolymers containing oxymethylene and other units, substantially all of the other units are attached to like units rather than oxymethylene units on each side. Particularly preferred are random copolymers which contain from 60 to 99.6 mol percent of recurring oxymethylene groups. In a preferred embodiment R may be, for example, an alkylene or substituted alkylene group containing at least two carbon atoms. Examples of preferred polymers include copolymers of trioxane and cyclic ethers containing at least two adjacent carbon atoms such as the copolymers disclosed in U.S. Pat. No. 3,027,352 of Walling et al.

The preferred random oxymethylene copolymers which are treated in accordance with this invention are thermoplastic materials having a melting point of at least 150° C. and are normally millable at a temperature of 200° C. They have a number average molecular weight of at least 10,000. These preferred polymers have a high thermal stability. For example, if the stabilized oxymethylene polymer used in a preferred embodiment of this invention is placed in an open vessel in a circulating-air oven at a temperature of 230° C. and its weight loss is measured without removal of the sample from the oven, it will have a thermal degradation rate of less than 1.0 wt. percent/min. for the first 45 minutes and, in preferred instances, less than 0.1 wt. percent/min. for the same period of time.

The preferred random oxymethylene copolymers which are treated in this invention have an inherent viscosity of at least one (measured at 60° C. in a 0.1 weight percent solution in p-chlorophenol containing 2 weight percent of α-pinene). The preferred copolymers of this invention exhibit remarkable alkaline stability. For example, if the preferred copolymers are refluxed at a temperature of about 142°–145° C. in a 50 percent solution of sodium hydroxide in water for a period of 45 minutes, the weight of the copolymer will be reduced by less than 1 percent.

As used in the specification and claims of this application, the term "copolymer" means polymers having two or more types of monomeric units, including terpolymers and higher polymers. Suitable oxymethylene terpolymers are those having more than two different kinds of monomeric units such as those disclosed in U.S. Pat. application Ser. No. 229,715, filed Oct. 10, 1962 by Walter E. Heinz and Francis B. McAndrew, which application is assigned to the same assignee as the subject application.

In accordance with another aspect of the invention, the filamentary material of this invention is formed by melt spinning a fiber-forming oxymethylene polymer, i.e., extruding the polymer in the form of a melt through the orifices of a spinneret at a shear rate of about 250 to 2,500 reciprocal seconds to form filaments which are taken up at a "drawndown" or "spin draw" ratio of at least about 25, e.g., up to about 350, preferably about 90 to 235 when the quench temperature is 70° F. The product as spun may have elastic properties as described above, and may be formed into a yarn package, or may be subjected to further treatment as described hereinafter before packaging. In any case, the yarn which is packaged for ultimate use will have the elastic properties described above.

The "shear rate" of extrusion is defined by the expression $4q/\pi r^3$, where q is the volume rate of extrusion of the molten polymer through each orifice in cc./sec., and r is the radius of the orifice in centimeters. The shear rate is an indication of the shearing force exerted between the molten polymer of the orifice wall as the polymer is being extruded.

The "spin draw" or "drawndown" ratio is the ratio of the velocity of initial yarn takeup to the linear velocity of extrusion of the molten polymer.

In one embodiment of this process, the polymer is melt spun by extrusion through orifices having a diameter for example in the range of about 5 to 25, preferably about 10 to 20 mils, at a linear speed, for example of up to about 15, preferably about 6 to 12 feet/min. at a shear rate within the range set out above, to form filaments which are taken up initially at a speed, for example, in the range of about 150 to 1,500, preferably about 450 to 1,050 feet per minute, at a drawdown ratio within the ranges set out above. The "quench" temperature, i.e., the temperature of air or other inert gas such as stream, nitrogen or argon, at the outlet side of the spinneret, is suitably up to about 285° F. A stack or column must be employed downstream of the spinneret if the desired quench temperature is substantially above or below the ambient temperature of air, and may also be useful for better control when air at ambient temperature is used as the quench. However, in the latter case, the polymer may also be extruded directly into air.

In accordance with another aspect of the invention, the as-spun filaments are afterdrawn or stretched at a temperature up to about 250° F., e.g., 50° to 250° F., at a draw ratio within the range of about 1.2 to 2.3, preferably about 1.3 to 1.5. The stretching may be carried out by first taking up the yarn on godet rolls from which it is wound on a package and stretching in a separate operation, or in a combined operation, wherein the yarn is initially taken up by one set of godet rolls from which it travels to a second set of godet rolls traveling at a speed faster than the first set so that the cold-drawing step is accomplished between the two sets of rolls.

In another embodiment of the process, the freshly spun filaments are passed around a frictional device in the spinning cabinet, e.g., a snubbing pin or pigtail guide which prevents all the tension exerted on the filaments downstream of the frictional device from being translated back to the face of the

spinneret, and the filaments downstream of the frictional device are cold-drawn, e.g., by taking up the filaments on godet rolls at a speed greater than that at which they pass around the frictional device. The overall draw ratio between spinneret face and takeup rolls may be for example within the ranges given for drawdown ratio.

While the yarn so produced possesses a considerable degree of elasticity, it is preferable to subject such yarn to a second afterdrawing step in amount sufficient to render the fibers uniformly opaque, e.g., at a draw ratio within the ranges given above for the afterdrawing step. As is the case when no frictional device is used, the subsequent afterdrawing step may be carried out in a separate operation wherein the yarn from the freshly spun yarn is taken up on godet rolls from which it is wound on a package and is subsequently drawn by conventional means, or as part of a combined operation wherein the yarn from the first takeup godet rolls travels directly to a second set of rolls rotating at a speed greater than that of the first set, with the afterdrawing taking place between the rolls.

The initial spinning operation is carried out in a unit which melts the solid polymer and pumps it at a constant rate and under fairly high pressure through the small holes of a spinneret. It is generally desirable to melt spin a polymer having incorporated therein one or more thermal stabilizers. Suitable combinations of stabilizers are shown, for example, in French Pat. No. 1,273,219.

Melt spinning temperatures, i.e., of the molten polymer being extruded from the orifices of a spinneret, may range from about 380° to 420° F. for the preferred random oxymethylene copolymers.

The polymer is generally melted by subjecting chips of the polymer to the action of a heated screw extruder. The chips are suitably between about 200 and 2 mesh. The melt is forced through the spinneret orifices by a metering pump. Generally, a filter or sand pack is maintained upstream of the orifices to remove particles or gels which might block them. Preferably, the polymer is maintained as a melt for not more than 20 minutes.

The spinneret may contain, for example, from one to about 500 orifices. Elastic monofilaments, for special uses such as tow rope, may be extruded through orifices up to 100 mils in diameter. The liquid streams emerge from the orifices, generally downwardly, into a gaseous medium, which may be air or an inert gas and solidify.

Filamentary material having the indicated physical properties and also a denier/filament of up to about 20 and even as low as about 1 is contemplated within the invention.

The following examples further illustrate the invention. All properties were measured at 70° F. unless otherwise stated.

EXAMPLE I

A copolymer of trioxane and 2 weight percent based on the polymerizable mixture of ethylene oxide was prepared as described in U.S. Pat. No. 3,027,352 and aftertreated to remove unstable groups as described in application Ser. No. 102,096, filed Apr. 11, 1961. The copolymer was then further stabilized by blending with 0.5 weight percent of 2,2'-methylene bis (4-methyl 6-tertiary butyl phenol) and 0.1 weight percent of cyanoguanidine based on the weight of the polymer.

The above-described polymeric composition was melt spun at 400° F. by means of a gear pump, downward through a 22-hole spinneret having hole diameters of 15 mils and 15 mils in length at a shear rate of about 1,140 reciprocal seconds. The resulting 22 filament yarn was taken up by godet rolls at a speed of 1,000 feet per minute after passing directly through a pigtail guide located in a column 10 feet long containing air at about 80°–90° F. A total of 8.17 cc./minute of polymer was extruded through the spinneret, corresponding to a linear speed of 10.68 feet per minute. The drawdown ratio was thus 1,000 divided by 10.68 or 93.6.

The yarn obtained by this process was uniformly lustrous but turned opaque on stretching to yield.

The as-spun yarn was lubricated with 50 percent aqueous polyalkylene glycol-based "Ucon H–6N" textile finish and was afterstretched in air at room temperature 70° F., using a draw ratio of 2.3 to 1.

The properties of yarn obtained, as spun and afterstretched at room temperature, are shown in table 1.

TABLE I

	As Spun	Afterstretched
Denier	293	188
Initial modulus, grams/denier	18.7	5.1
Tenacity, grams/denier	1.17	1.46
Breaking Elongation, %	200	114
Elastic Recovery from 50% Extension at Zero Recovery Time, %	81.2	77.6
Birefringence, Δn	0.0581	0.0380

EXAMPLE II

The procedure of example I was carried out except that the extrusion temperature was 415° F., the spinneret contained 34 holes each, 12 mils in diameter and 18 mils in length, the gear pump was operated so as to obtain an extrusion rate of 4.90 cc./min. corresponding to a linear extrusion speed of 6.48 feet/min., at a shear rate of about 860, the yarn passed over a kiss-roll where it was lubricated with 25 percent aqueous fatty ester-based "Nopocostat 2152–P" textile finish, and was then passed through a pigtail guide with one wrap taken around the guide stem. The yarn was then taken up by godet rolls at a speed of 500 feet/min. with an overall drawdown ratio of 77.

The resulting yarn had alternating patches of opaque and lustrous zones with the opaque zones exhibiting a relatively high degree of recoverable stretch.

The patchy yarn was drawn at room temperature (70° F.) at a draw ratio of 2 to 1. The resulting yarn was completely opaque, had a total denier of 250, a breaking tenacity of 1.2 grams/denier, a breaking elongation of 160 percent, and an elastic recovery from 50 percent extension at zero recovery time of about 80 percent.

The elastic properties of the as-spun or after-stretched filamentary material of this invention may be improved by a heat treatment. Preferably the treatment is a hot-wet treatment, e.g., contact with hot water or wet steam at a temperature of at least 190° F., e.g. up to about 285° F. for a period of at least 1 minute.

The following examples illustrate the effect of a hot-wet treatment of the product.

EXAMPLE III–VI

The procedure of example II was carried out except that no textile finish was applied, the yarn was passed directly through the pigtail guide rather than being wrapped around the guide stem and yarn was taken up at different speeds, 250, 500, 750 and 1,000 feet/minute (examples III to VI respectively) corresponding to drawdown ratios of 38.6, 77.2, 115.8 and 154.3 respectively. The yarn was not subsequently drawn. Various mechanical properties, other than elastic recovery, of three of the yarns obtained, all of which are lustrous, are given in table 2.

TABLE 2

	Ex.V	Ex.III 250 ft./min.	750 ft./min.	Ex.VI 1000 ft./min.
Denier		726	219	157
Initial modulus,grams/denier		20.9	17.5	23.2
Tenacity, grams/denier		0.8	1.39	1.74
Breaking Elongation, %		372	195	146
Birefringence, Δn		0.0532	0.0617	0.0626

Some values of elastic recovery after 2 minutes recovery time of the four samples of yarn as spun and after a hot-wet treatment or "boiloff" i.e., immersion in water under about 15 p.s.i.g. pressure at a temperature of about 250° F. for 30 minutes, were determined after extensions of 50 percent, 100 percent, 150 percent, 200 percent and 250 percent at temperatures of 70° F., 130° F., 190° F. and 250° F. The results are given in table 3.

TABLE 3.—ELASTIC RECOVERY

Yarn and extension	Temperature of yarn, at— 70° F. As spun	70° F. Boiled off	130° F. As spun	130° F. Boiled off	190° F. As spun	190° F. Boiled off	250° F. As spun	250° F. Boiled off
Ex. III (250 ft./min.) percent:								
50	85.6	97.3	73.0	96.0	73.6	86.9	44.4	62.6
100	73.2	92.5	66.5	87.8	34.1	69.1	34.5	41.5
150								
200	57.7	67.7	47.2	61.2	33.0	35.8	22.3	30.2
250	50.2	56.4	[1] 39.8	60.8	[1] 25.4	[1] 28.4		
300			33.3					
Ex. IV (500 ft./min.) percent:								
50	90.8	97.6	89.2	95.6	74.6	95.2	69.4	71.2
100	76.8	89.3	71.6	88.5	50.7	89.0	44.7	54.3
150	62.5	73.1	51.7		45.8	67.7		
200			49.3	60.7	35.3	56.1	40.0	29.5
250					30.4	38.5		
Ex. V (750 ft./min.) percent:								
50	90.4	96.4	89.0	94.4	80.0	92.2	68.8	80.0
100	74.6	89.6	72.2	87.2	53.6	70.4	45.6	57.2
150	60.8	70.1		75.3		62.0	25.8	
200						[2] 52.5		32.9
Ex. VI (1,000 ft./min.) percent:								
50	91.2	95.6	88.4	93.2	78.6	90.2	65.6	70.2
100	73.2	80.9	64.4	81.8	57.0	78.8	39.6	54.3
150			[3] 57.8	68.9	46.3	58.4		
200							27.5	31.2

[1] At 280%.
[2] At 185% extension.
[3] At 125% extension.

The data in tables 2 and 3 show that filaments may be obtained in accordance with this invention which have very desirable elastic properties, even at elevated temperatures while at the same time having adequate mechanical properties such as breaking tenacity, breaking elongation and initial modulus, and that the elastic properties of the yarn as spun, using a relatively high drawdown ratio, are significantly improved by heat treating the yarn, e.g., by contacting it for a short period with hot water.

EXAMPLE VII

The procedure of example I was followed except that the amount of molten polymer extruded through the spinneret was 4.73 cc./min. at a shear rate of about 660 reciprocal seconds, and the resulting yarn was taken up a speed of 1,250 feet/min. resulting in a drawdown ratio of 201. Samples of the yarn were afterstretched at 70° F. in air at draw ratios of 1.2, 1.3, 1.4 and 1.5, and at 170° F. while in contact with a water-wet cloth covering a hot metal plate, at draw ratios of 1.2 and 1.4. The physical properties of the yarns obtained are shown in table 4.

FIGS. 1, 2 and 3 show stress-strain curves (curve A) obtained up to 50 percent extension, for the yarns of this example as spun (FIG. 1), afterstretched at 70° F. using a draw ratio of 1.5 (FIG. 2), and afterstretched wet at 170° F. using a draw ratio of 1.4 (FIG. 3). In each case, curve B represents a similar stress-strain curve obtained for the stiffest commercial spandex. It can be seen that the yarn included within the invention is in each case considerably stiffer than the spandex, regardless of the aftertreatment. However, the aftertreatment, e.g., afterstretching whether dry or wet and using any of various draw ratios, results in yarns having different stress-strain characteristics which may be utilized in various applications. Thus, the slope of the stress-strain curve of the as spun yarn tapers off rather sharply after a certain stress has been applied (see FIG. 1), whereas this effect is considerably modified by a dry after-stretching treatment (see FIG. 2). Moreover, a hot-wet after-stretching treatment results in a considerable change in the shape of the stress-strain curve, which, after this type of treatment has two points of inflection (see FIG. 3).

The heat treatment, e.g., hot wet treatment described above may be used to improve properties such as elastic recovery of dry afterstretched as well as the as spun yarn. Thus, when the yarn of this example which was dry afterstretched at 70° F. using a draw ratio of 1.5, was subsequently immersed in hot water at 250° F. and 15 p.s.i.g. for a period of 30 minutes, it had the following properties: denier—126; initial modulus—29 grams/denier; tenacity—1.7 grams/denier; breaking elongation—94 percent; elastic recovery at zero recovery time after 50 percent extension—92 percent. It can be seen therefore that a hot-wet treatment of after-stretched yarn resulted in a substantial increase in initial modulus and elastic recovery.

TABLE 4

Property	Draw ratio, at— 70° F. As spun	70° F. 1.2	70° F. 1.3	70° F. 1.4	70° F. 1.5	170° F. 1.2	170° F. 1.4
Denier	126	125	122	135	128	130	110
Initial modulus, grams/denier	26.9	25.6	25.4	15.3	12.5	20	11
Tenacity, grams/denier	1.45	1.35	1.53	1.45	1.59	1.71	1.98
Breaking elongation, percent	105	110	109	104	104	106	91
Elastic recovery from 50% extension at zero recovery time, percent	78	76.8	76.0	77.6	81.6	81.0	75
Birefringence, Δ_n	0.0622	0.0669	0.0617	0.0613	0.0585		0.0569

When the hot-wet-treated yarn described in the previous paragraph was subjected to seven cycles of 50 percent extension at 70° F., the elastic recovery of the yarn at the end of the sixth cycle was 82 percent.

EXAMPLE VIII

The procedure of example I was followed except that the amount of polymer extruded was 3.26 cc./min. at a shear rate of about 450 reciprocal seconds, the temperature of polymer being extruded was 405° F. and the yarn was taken up at a speed of 1,000 meters/min. and a drawdown ratio of 234. Samples of the yarn were afterstretched in air at 70° F. using various draw ratios. Properties of the resulting yarn samples are given in table 5. In determining the elastic recovery of the yarn, each sample was subjected to seven cycles of 50 percent extension at 70° F. and the elastic recovery at zero recovery time was measured at the end of the first cycle and the end of the sixth cycle.

TABLE 5

Property	Draw ratio				
	As spun	1.2	1.3	1.4	1.5
Denier	114	107	94	93	101
Initial modulus, grams/denier	24.5	18.7	15.3	10.8	8.9
Tenacity, grams/denier	1.49	1.47	1.59	1.72	1.73
Breaking elongation, percent	129	98	98	89	88
Elastic recovery—1st cycle, percent	76.4	78.8	78.8	81.6	75.2
Elastic recovery—6th cycle, percent	64	67	70	67	62
Birefringence, Δ_n	0.0656	0.0673	0.0603	0.0649	0.0580

The yarn sample of this example which was afterstretched at a draw ratio of 1.5 as described above, was subsequently subjected to a hot-wet treatment by immersing it in water at 250° F. and 15 p.s.i.g. for 30 minutes. The resulting yarn had a denier of 96, an initial modulus of 20 grams/denier, a tenacity of 1.6 grams/denier, a breaking elongation of 53 percent, an elastic recovery after the first cycle as described above, of 91 percent and an elastic recovery after the sixth cycle of 50 percent extension as described above, of 82 percent.

EXAMPLES IX and X

The procedure of example VIII was followed except that the spinneret contained 13 holes, each of which was 12 mils in diameter by 18 mils in length resulting in a shear rate of 1,600 reciprocal seconds, and the resulting yarn was taken up at a speed of 1,000 feet/minute with a drawdown ratio of about 90 (example IX) or at a speed of 1,250 feet/min. with a drawdown ratio of 110. Properties of the resulting as spun yarns are shown in table 6.

TABLE 6

Property	Example IX	Example X
Denier	93	75
Initial Modulus, grams/denier	19.4	26.7
Tenacity, grams/denier	1.06	1.36
Breaking Elongation, %	105	110
Elastic Recovery from 50% Extension at Zero Recovery Time, %	78	75.2
Birefringence, Δn	0.0617	0.0701

The following examples illustrate the use of quench temperatures, i.e. temperatures of circulating air in the spinning column downstream of the spinneret, of other than room temperature.

EXAMPLES XI and XII

The procedure of example VIII was followed except that different conditions of quench temperature, takeup speed and drawdown ratio were used. These variations in the conditions of the process as well as the properties of the resulting as spun yarns are shown in table 7.

TABLE 7

Condition or Property	Example XI	Example XII
Quench Temperature, °F	221	280
Takeup Speed, feet/min.	750	1500
Drawndown Ratio	172	343
Denier	209	76
Initial Modulus, grams/denier	22.8	17.5
Tenacity, grams/denier	1.12	1.03
Breaking Elongation, %	203	174
Elastic Recovery from 50% Extension at Two Minutes Recovery Time, %	91.2	88.4
Birefringence, Δh	0.0644	0.0588

The data in the above table illustrates that as spun yarn having relatively high elastic recovery may be produced using an elevated quench temperature.

The values of tenacity, breaking elongation, modulus, stress and strain given above were determined in a conventional manner with the use of an Instron Tensile Tester operating at a strain rate of 100 percent/minute. The "initial" modulus as the term is used above was determined by measuring the slope of the stress-strain curve at the point indicated by 1 percent strain.

The values of elastic recovery given above were also determined with the Instron at a strain rate of 100 percent/minute. After the yarn was extended to the desired strain value, the jaws of the Instron were reversed at the same speed until the distance between them was the same as at the start of the test, i.e. the original gauge length. The jaws were again reversed, i.e., immediately for values of elastic recovery at zero recovery time, or after 2 minutes for values obtained at 2 minutes recovery time, and were stopped as soon as the stress began to increase from the zero point. The elastic recovery is then calculated as follows:

$$\text{Elastic recovery} = \frac{\text{Total length when extended} - \text{Final distance between jaws}}{\text{Length added when extended}} \times 100$$

Measurements with the Instron at room temperature were carried out in air at 65 percent relative humidity. Determinations at elevated temperatures were determined in air at 70° F. and 65 percent relative humidity which was heated to the desired temperature.

Values of birefringence were determined with a polarizing microscope equipped with a Berek compensation, in accordance with procedures well known in the fiber arts. The value of birefringence is a measure of the degree of molecular anisotropy of the filament which in turn is indicative of the degree of molecular orientation produced as a result of spinning and drawing procedures.

Although the product and process of this invention have their most desirable embodiments in conjunction with random oxymethylene copolymers as pointed out above, oxymethylene homopolymers are also contemplated, e.g. as prepared by the polymerization of anhydrous formaldehyde or by the polymerization of trioxane which is a cyclic trimer of formaldehyde. High molecular weight oxymethylene homopolymers as well as random copolymers may be

prepared in high yields and at rapid reaction rates by the use of acidic boron fluoride-catalysts such as boron fluoride itself, and boron fluoride coordinate complexes with organic compounds, as described in U.S. Pats. Nos. 2,989,585; 2,989,506; 2,989,507; and 2.989,509 of Hudgin and Berardinelli, 2,989,510 of Bruni; and 2,989,511 of Schnizer, as well as in the above-cited U.S. Pat. No. 3.027,352 of Walling et al.

In addition to the methods disclosed in the above-cited patents, other methods may be used to prepare oxymethylene copolymers and homopolymers contemplated under this invention, including those taught by Kern et al. in Angewandt Chemie 73 (6), pages 177 to 186 (Mar. 21, 1961), e.g. homopolymers in which the end groups have been reacted with an alkanoic acid such as acetic acid or an ether such as dimethyl ether. These reactants cause stable ester or ether end groups, e.g., acetyl or methoxy groups, to form at the ends of the polymer molecules.

The elastic filamentary materials of this invention are useful in a wide variety of applications. Because of the importance of these applications, they will be described in some detail below, under separate headings.

REPLACEMENT FOR WRAPPED-CORE ELASTIC YARNS

In many applications, rubber or so-called spandex fibers are employed as the core in a wrapped-core yarn construction, the wrapping being comprised generally of staple or filament yarns made of conventional high modulus low-stretch fibers such as cotton, rayon, nylon, etc. The process of wrapping is costly and frequently difficult to control. The properties of the wrapped yarn are somewhat unpredictable and often represent only a compromise between what is desired and what can be achieved by the combination of two or more yarns assembled and held together under radically different levels of strain.

For example, a typical double-wrapped spandex core, cotton wrapped yarn may be produced with the core prestretched 300–400 percent when the wrapping is twisted around it. In the "at rest" state, the core retracts to some strain lower than that at which it was wrapped, thereby causing the wrapper yarns to be compressed into a jammed helix configuration.

Subsequent stretching of such a yarn, then, represents the combined effect of reextending the core from some already partially stretched state and the opening of the jammed helix configuration of the wrapper. The stretch modulus of such a complex combination of material properties and geometric structure is easily disturbed by a number of transient variables in original manufacture and subsequent processing as well as during use of such yarns and fabrics made therefrom. Moreover, the ultimate stretch of such yarns cannot be varied independently of the stretch modulus.

The core wrapper structure attempts to combine the virtues of high elastic recovery from high strain of the core with the relative rigidity of the wrapper. The principal object of such a combination is to achieve relatively high "power" of recovery from fairly high extensions.

The elastic yarns of this invention are very suitable for the replacement of such wrapped-core yarns for many applications. With a relatively high modulus obtained with the yarn of this invention, e.g., in the range of 2–15 grams/den., compared to spandex yarns with a modulus in the order of 0.2–0.5 grams/den., the yarn of the invention need not be prestrained and wrapped in order to exhibit high stretch "power." Used alone (i.e. without a wrapper) the yarn of the invention can provide substantial reduction in weight and bulk at the same level of stretch "power," extensibility, and recovery. Thus, many fabrics may be markedly reduced in weight and bulk, made more sheer, by their use. On the other hand, at the same weight of yarn, density of weave, etc., fabrics produced from the yarn of the invention exhibit substantially more "power" than wrapped-core fabrics.

Used as a single-component yarn, therefore, the yarn of this invention may be substituted directly for wrapped-core yarns at considerable saving in cost and improvement in performance. A typical useful construction is a 3-ply yarn having a total denier of 750 comprised of 75 filaments. Each single yarn is twisted up to 15 t.p.i. and the ply construction back twisted to yield a balanced yarn. One familiar with the art will recognize many variations of yarn denier, twist, ply construction, and denier per filament suitable for individual applications.

REPLACEMENT FOR BARE SPANDEX OR FINE-DENIER STRETCH YARNS

Fine-denier continuous filament yarns (30 up to 100 denier, for example) comprised of a thermosettable polymer (especially nylon) have found considerable application in lingerie and "intimate" garments. While those yarns have customarily been knitted (generally tricot) or woven for such fabrics as standard yarns, increasing interest is displayed in the use of stretch yarns made therefrom.

Stretch yarns of such thermosettable materials are produced by a number of techniques such as stuffer-box crimping, twist-set-untwist, edge-crimping, etc. The stretch characteristic is imparted by building geometric distortability into the individual filaments of said yarns.

An alternative approach to the use of stretch nylon yarns has been dependent on the application of bare or lightly wrapped spandex yarns. Here the stretch and conformability, of course, depends upon the material extensibility of the fiber. Knitted or woven fabrics from such yarns, however, are generally rather limp and suffer from the relatively low degree of thermal stability of the typical spandex materials and their sensitivity to discoloration and fading in storage and use.

The desirable virtues of either the geometrically stretchy nylon stretch yarns, or the bare or lightly wrapped spandex yarns for lingerie where stretch and conformability are desired, may be achieved by the use of light-denier yarns of this invention. A typical application of such yarns is 70- or 100-denier stretch tricot fabric for ladies' slips.

VARIABLE POROSITY PARACHUTE CANOPY FABRIC

Multifilament yarns of this invention which exhibit high elastic recovery from loads approaching 90 percent of ultimate rupture are eminently suitable for the fabrication of variable porosity fabrics. A fabric of this type possessing approximately the following properties may be made from the yarn of this invention:

- Weight 1–2 ounces per square yard
- Permeability of 50–90 cubic feet per minute per square foot at 0.5 inches of water pressure differential
- Ultimate tensile strength of 20 pounds per inch of fabric width in both warp and filling directions
- An exceptionally large permeability at a pressure differential that imposes a fabric tensile load of 15 pounds per inch of fabric width.

A typical fabric construction having these properties is as follows:

Fabric Specifications	
Weight	2 ounces per square yd.
Ends per inch	130
End denier	60
Picks per inch	130
Pick Denier	60
No. of fils per yarn	21
% Crimp filling	6
Strip tensile warp	20 lbs./inch of width
Strip tensile filling	20 lbs./inch of width
Ultimate Elongation Warp	75%
Ultimate Elongation Filling	75%

Yarn Properties	
Yarn Denier	130
No. of filaments	21
T.P.I.	0.5
Ultimate Stress	1.5–2.0
Ultimate Elongation	75%
Stress at 20%	1.0 g.p.d.
Elastic Recovery at 20% Strain	99%
Elastic Recovery at 50% Strain	85–90%
Fabric Performance	
Porosity at low strains:	50–90 cubic feet per minute per square foot at 0.5 inches of water pressure differential
Porosity at a stress of 5 pounds per inch of fabric width:	1,000 cubic feet per minute per square foot at 4.0 inches of water

WOVEN FOUNDATION GARMENTS, ELASTIC BANDAGES, AND LIKE PRODUCTS

Candidate fabrics for woven foundation garments, elastic bandages and similar products comprise anywhere from 5 to 90 percent elastic fiber content in fabric weights from 2 to 15 ounces per square yard. Highly recoverable stretch with presently available materials is possible from strain levels of 20 to 40 percent.

By employing the filamentary material of this invention, it is possible to obtain durable elastic recovery from higher strain levels than presently available with spandex and rubber materials and greater range of available power at given strain levels.

A typical woven batiste foundation fabric is as follows:

Fabric Weight	4 ounces per sq. yd.
Warp—Acetate	140 denier
Ends per inch	65
Filling—yarn of this invention	200 denier
Picks per inch	60
Elastic recovery at 60% strain	95%
Stretch level	50%
Rupture tenacity warp	45 lbs. per inch of width
Rupture tenacity filling	40 lbs. per inch of width
Modulus in pounds at 40% strain	10 lbs. per inch of width

Other stretch fabrics also rely upon the incorporation of bulked/stretch yarns or spandex-type yarns in combination with other less extensible yarns. The elastically recoverable yarns in some of these fabrics comprises, for example, from 5 to 65 percent of the fabric which performs elastically up to strain levels of 100 percent in the elastic direction.

A typical ski pant fabric utilizing the material of this invention contains 150 ends per inch of 70-denier, 21-filament yarn of this invention and 42 picks per inch of 700-denier, 2-fold worsted yarn, and has a plain weave stretched. This abrupt large change in modulus is often undesirable, and can be avoided by using the filamentary material of this invention as the covering yarn. By varying the angle of wrap of such yarn, modulus values, extending over a range of extension of significantly more than 100 percent, can be varied from those typical of spandex up to those typical of the yarns of this invention and the magnitude of any changes in modulus with extension can be reduced greatly from those resulting from the use of conventional fibers in the wrapping yarn.

BLENDS WITH OTHER FIBERS

Spun stretch yarns composed predominantly of conventional fibers such as cotton, wool, nylon, polyester, or other commonly used materials, can be produced by blending such fibers with 5 to 45 percent of staple fiber of this invention. Such blending is carried out in a card, pill box, pin drafter, Pacific Converter, or other normally used blending procedure prior to spinning the yarn. The relatively high modulus of the fiber of this invention makes these blending operations much easier to control than when other elastic fibers having a much lower modulus are used, and drafting and spinning are accomplished with only minor adjustments of normal machine settings. The final product can be used to produce fabrics having usable stretches in the range of 10 to 30 percent, and the high recoverability and high recovery energy provided by the filamentary material of this invention ensures excellent elastic characteristics in the stretch fabric, and minimizes or eliminates the problem of pilling encountered with low-modulus fibers.

BULK STRETCH YARNS

Bulked yarns as presently being produced are characterized by being lofty, but not having unusual stretch characteristics. Stretch yarns, on the other hand, may be bulky, but they achieve their stretchiness at the expense of reducing this bulk; that is, by removal of the crimp which causes it. A true bulk stretch yarn would be one in which the bulk is retained when the yarn is stretched. This could be accomplished if the fibers from which the yarn was made had a low enough modulus to ensure that the yarn could stretch by virtue of the fibers themselves stretching, and not primarily or exclusively by a crimp removal mechanism.

Yarns made from the fibers of this invention can be made bulky by drawing them under slight tension over a sharp, unheated edge, followed by stretching and relaxing. This causes the filaments to kink extensively, and results in a very bulky yarn having 50 to 100 percent of highly recoverable stretch. Such bulky stretch yarns are useful for producing light, lofty fabrics, in the range of 3 to 10 ounces per square yard, having excellent cover and the ability to recover their original dimensions after being stretched 50 percent or more. Moreover, much of this bulk is retained over wide ranges of stretch, and thus the fabric cover is not seriously reduced by stretching, making it ideal for applications like bathing suits, formfitting blouses, leotards or other formfitting garments, etc.

Fabrics for these applications can be made somewhat more open from the yarns of this invention than from other types of stretch yarns, thus providing the possibility of constructing lighter, more porous and, therefore, more comfortable fabrics.

STRETCH SEWING THREADS

One of the current problems in the production of garments made from stretch fabrics is to retain that stretch in the seam of these garments. This can easily be accomplished by using a sewing thread which is capable of stretching with the fabric. The sewing thread, on the other hand, must be capable of withstanding the normal stresses imposed by the sewing operation without undue stretch, or seam puckers will result. Sewing threads having the desired characteristic of good sewability and capable of providing the stretch needed in the seams of garments made from stretch fabrics can be made from fiber of this invention in a number of ways. One such thread can be produced in normal sewing thread constructions using the filaments of this invention in place of those made from other fibers. A gradation of stretchability can be provided by producing yarns from blends of staple fiber made from the filaments of this invention in varying amounts with cotton, nylon, or other textile fiber, and using such yarns in conventional sewing thread constructions. Still another suitable yarn for the production of stretchable sewing threads is one in which normal textile fibers are either spun or wrapped around a yarn of this invention as core, in any one of a number of normal core-yarn-manufacturing techniques.

BULK FILLING MATERIAL

Pillows and cushions are generally filled with synthetic or natural fibers to produce a resilient end product. Certain fibrous materials, due to poor elastic recovery from bending

and a tendency to cluster or clump, demonstrate poor durability as pillow or cushion fillers. A cut staple fiber such as that made from the filamentary material of this invention, crimped and/or bulked, has very desirable properties as a filling material. A typical blend for filling pillows made completely from filamentary material of this invention, is as follows:

50% low modulus	6 denier material
50% medium modulus	3 denier material
Staple length	3 inches
Crimps per inch of fiber length	10

STRETCH NONWOVENS

Nonwoven fabrics are relatively stiff materials which do not drape or conform to bodily contours as do normally woven fabrics. A method of improving the quality of a nonwoven fabric in terms of drapeability and recoverability from imposed strains is to construct the nonwoven in part or entirely from fibers of this invention. The highly elastic nature of relatively low modulus fibers of this invention in low deniers can make them desirable materials for stretch nonwovens.

A typical nonwoven is composed of 1½ inch cut staple, low modulus fibers made from 3-denier filaments of this invention and having a web weight of 2.0 ounces per square yard and a 30 percent by weight low modulus high-strength adhesive binder.

TUFTED CARPETS

A typical application, taking advantage of the recovery properties of the material of this invention is in a rug backing (either in total or as a component) for tufted carpets. A tightly woven fabric of suitable construction and weight passes through the tufting machines under fillingwise extension and tension (approximately 25 percent extension). The base fabric is tufted in this form after which the filling tension is allowed to relax. The fabric then contracts, which causes the pile to condense producing a heavier and denser pile than can currently be obtained by the present rug-backing fabrics (jute, cotton, polypropylene). This procedure produces carpets with a denser pile, and therefore with a more enhanced and more luxurious-looking pile than can currently be produced by prior art methods. Besides the advantage of appearance, the more compact pile has better resistance to crushing, better abrasion properties, and longer wear, etc.

A typical construction of such a rug-backing fabric is a plain woven fabric weighing about 9 ounces per square yard constructed from 3,100-denier yarns having a yarn count of 12.5 ends per inch of 13 picks per inch. These yarns can be either continuous filament or spun staple yarns.

WOVEN CARPETS

The filamentary material of this invention has applications in the woven carpet industry as binding yarns in carpets. The high recovery forces of the yarn and fiber imparts higher—and therefore more desirable—binding forces to the pile than can be obtained from current binding yarns. The higher binding forces also prevent pile "pullout" and produce a more stable pile and carpet.

The additional ease of extension of the yarn, with high recovery, also aids in the formfitting and stability of rugs on stairs, over angles, and around objects. In this application it applies to both the binding yarns and to the rug pads used underneath rugs.

The fiber is used in both spun staple yarns or continuous filament yarns in yarn number and construction currently used by the rug industry.

FORM-FIT FABRICS: BEDSHEETS, SHIRT COLLARS AND LIKE PRODUCTS

A typical application of the filamentary material of this invention which takes advantage of the high recovery force of the fiber is in the area of form-fit fabrics such as bedsheets and shirt collars. The advantage of such material in form-fit bedsheets over conventional form-fit sheets is that the higher retractive forces cause the form-fit sheets to adhere more closely to the mattress producing a neater appearance and a more stable sheet than currently available form-fit sheets.

A typical woven sheeting construction utilizing the material of this invention in either continuous filament or staple spun yarns has a fabric width of 40 inches, a fabric weight of 4 yards/lb. (3.3 oz./sq. yd.) and a yarn count of 48 warp ends per inch and 48 filling ends per inch.

The same advantages hold true for other form-fit applications such as shirt collars. These applications utilize either woven or nonwoven fabrics containing the material.

GLOVE FABRICS

Another typical application for the material of this invention, taking advantage of its high recovery and bulking ability properties, is in glove wear fabrics— including woven, knitted, and nonwoven. The advantages of using such material are better bulking characteristics and better extensibility and recovery performance, and the resulting fabrics produce better warmth, better comfort, and more efficient use. The ease of extensibility with high recovery results in more efficient and comfortable gloves than currently in use.

The material may be used in the production of a wide range of glove products, from work gloves to women's fashion gloves.

UMBRELLA FABRIC

A more compact folded umbrella may be made using fabric made from the yarn of this invention, having the ability to stretch 25 percent or more when the umbrella is opened, without serious loss of cover. This can be accomplished by using a high bulk yarn, so that even after the fabric is stretched, the yarn still retains sufficient bulk to fill the fabric interstices and retain the required water repellency. The amount of bulk required varies with the amount of stretch desired, and the construction is adjusted to provide the prime requirement of high cover to provide good water repellency when the umbrella is open (i.e., when the fabric is stretched).

NOVELTY PUCKERED FABRIC

The material of this invention is suitable for a seersucker-type fabric in which bands of puckers run lengthwise in the fabric, and are of a size and frequency controlled by the fabric construction. These are produced by setting up a warp containing alternating bands of yarns made of any normal textile fiber and of the elastic yarns of the invention.

The latter yarns are wound onto the warp beam under tension sufficient to stretch them 5 or more percent, and this stretch is maintained in the loom by adequate warp tensioning. After weaving, the fabric is permitted to relax, and the high energy of recovery provided by the yarns of the invention causes the whole fabric to contract, and in turn causes the surface to pucker in those bands which contain normal warp yarns. The advantage of yarns of the invention in such applications results from its high recovery energy. This permits both very light and very heavy fabrics to be produced more successfully than is possible by currently used procedures.

CAMP COT FABRIC

The filamentary material of the invention is suitable for use in "camp cot" fabric for both military and civilian applications. The purpose of such material is to provide a small amount of recoverable stretch and thereby provide more com-

fort in use than is currently obtained from present camp cots. The material is suitable for use in all current camp cot fabrics, in plain weave, twills and other constructions.

A typical construction for this fabric contains 96 ends per inch by 64 picks per inch in a 40-inch width producing a fabric weighing about 2.5 **yards per pound** (5.8 ounces per square yard).

UPHOLSTERY FABRICS: OUTDOOR AND INDOOR

The filamentary material of the invention is suitable for use in both outdoor and indoor upholstery fabrics. Such material imparts better drape, elastic, and formability properties to these fabrics than they currently exhibit. The ease of extensibility with high recoverability enables easier, more efficient fabrication of the fabric to the furniture as well as producing a neater appearance after fabrication caused by the high recovery giving a tight or snug fit on the padding and structure of the upholstery.

Current upholstery fabrics come in a wide range of types, weights, and construction. The material of the invention may be used, without restrictions, in all types of such fabric either as part of a blend or alone. The material may be in either staple form or in continuous filament form depending upon the desired end characteristics.

SHOE APPLICATIONS: FABRIC AND LININGS

The filamentary material of the invention finds many applications in the shoe industry in both outer shoe and sneaker fabrics as well as inner shoe linings. In use, many shoe fabrics fail in the area of fabrication to the leather. Because of the relative ease of extensibility of the material of the invention, associated with high recoverability, the shoe fabric containing such material can be fabricated to the shoe with less internal stress. Also, during walking—applicable to both shoes and sneakers—the fabric extends easier and recovers more completely thereby producing a more comfortable and longer lasting shoe or sneaker. The lower stresses on the elastic material where the fabric covers the toes results in more comfortable and longer lasting sneakers.

The ease with which fabrics comprising the filamentary material of the invention can be formed and coated or impregnated make it very desirable for shoe linings. Such fabrics adhere to the shape of the shoe easily, without wrinkles, and lend themselves easily to stitching and fabrication of the shoe.

The material is utilized in all presently used shoe fabric and shoe lining fabric constructions. It can be used in the form of spun staple yarns or continuous filament yarns and may comprise 100 percent of the fabric or a component part of the fabric.

COATED FABRICS

The material of this invention is useful in the manufacture of highly elastic coated structures. As is well known to coaters, soft, drapey, elastic-coated fabrics can be made utilizing cotton knit goods as contrasted with typical woven cotton sheetings and twills due to the stretchability of knit fabrics. This stretchability is translated to the coated structure and is useful in formable furniture and automatic upholstery, headlining or for leatherette, as it is known, which is also used for luggage, etc.

In coating knitted fabrics with vinyl compositions or other plastic films by coating or lamination, it is generally noted that knit fabrics require more coating materials to fill the interstices and to obtain level, smooth coatings as compared to those same coatings on flat woven structures.

Woven fabrics containing the material of the invention exhibit stretch characteristics of the knit fabrics while enjoying the benefits of coating virtues of flat woven structures. Better overall reinforcement of plastic films also results from compatible characteristics of stretch of both the yarn and the plastic film to make better performing products.

Fabrics containing the elastic material of the invention can be constructed of either filament or spun yarns as desired and made in roughly comparable weight and strength with typical constructions of other fibers now used, as for example the woven sheeting of cotton such as the 80×80 print cloth of 4 sq. yds. per pound or heavier sheeting of coarse yarns as a typical 48×48 construction of 2.6 sq. yds. per pound. Weights and weaves like typical canvas or special weaves as twills and drills are likewise of use.

To gain extreme extensibility for special uses the material may be knit into fabrics of structure similar in weight and strength to cotton knit goods. The stretch of the yarns of the invention added to that already available from the knit structure yields coated structures of unusual softness, pliability, and elasticity. This enables the coater to produce structures that can be made to conform to odd shapes and around corners without producing unsightly folds or damage to the base fabric.

Coated fabrics using heavy fabrics comprising the elastic material of the invention are highly desirable in coated inflatable or air-supported fabrics. The easy extensibility and high recoverability of this fiber make it easy to fabricate and give a neater appearance at the seams while under air pressure. The fabric adjusts itself easier to changes in air pressure under use because of the extensibility and recovery properties.

NETS

Nets are extremely open structures formed by knotting together the component yarns at the intersections. They are extremely deformable structures because of the relative infrequency of the points of restriction created by the knots. They have little if any tendency to recover from any deformation. A significant amount of recovery could be provided by making the nets out of yarns of this invention, which, because of their ability to stretch and high energy of recovery, make it possible to produce nets with a characteristic not provided by normal net constructions. Thus, formfitting hairnets, useful over a wide range of head sizes, are contemplated from yarns of the invention of 100 denier or less. Expandable containers (e.g. laundry bags) and carrying bags are easily produced from heavier yarns, in the range of 100 to 1,000 denier or more. Also, gill nets are contemplated which are designed to catch a wider range of fish size than do those made from from conventional fibers, in which the larger fish are lost because they cannot get their heads through the mesh. These contain cords or more than 1,000 denier.

SUPPORT HOSIERY

Whereas the majority of support hose utilize relatively coarse yarn constructions to create the necessary amount of support stress at a worn strain (anywhere from 0 to 2 pounds per inch of fabric width depending upon leg size, position on the leg and amount of support required) it is possible to utilize yarns of this invention to produce, in combination with other materials, a much shearer support hose.

One technique whereby elastic filaments are utilized is by laying in continuous filament elastic yarn within the knit loops of the stocking. Using the filament yarn of the invention, a typical construction for a support stocking is as follows:

Wales per inch	30 to 60
Courses per inch	30 to 65
Knit structure	30 denier nylon monofilament with 33 denier filament of the invention laid into the knitted mesh

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process comprising the steps of melt spinning a random oxymethylene copolymer comprising a copolymer of trioxane

with from about 0.5 to 25 mole percent of a cyclic ether having adjacent carbon atoms at a temperature of from about 380° F. to 420° F. at a sheer rate of from about 250 to 2,500 reciprocal seconds, taking up the resulting filamentary material at a drawdown ratio of from about 25:1 to 350:1, subjecting said random oxymethylene polymer filamentary material to an after-stretching operation at a temperature of from about 50° F. to 250° F. and a draw ratio of from about 1.2:1 to 2.3:1, enhancing the elastic recovery and tenacity and rendering said filamentary material uniformly opaque by subjecting said filamentary material to a second after-stretching operation which comprises contacting said filamentary material with hot H_2O at a temperature of from about 190° F. to 250° F. for at least 1 minute at a draw ratio of from about 1.2:1 to 2.3:1 and forming said filamentary material, which has an elastic recovery at 70° F. of at least about 70 percent from an extension up to 50 percent, into a yarn package.

2. The process of claim 1 comprising subjecting the random oxymethylene copolymer filamentary material to a quench temperature up to about 285° F., a first after-stretching operation at a draw ratio of from about 1.3 to 1.5 and a second after-stretching operation at a draw ratio of from about 1.3 to 1.5.

3. The process of claim 1 comprising initially taking up the random oxymethylene copolymer filamentary material at a drawdown ratio of from about 25 to 350, continuously advancing said material at a point beyond the point of initial takeup at a rate greater than that of said takeup such that said fully solidified material is drawn at a temperature of from about 50° F. to 250° F. and a draw ratio of from about 1.2 to 2.3

4. The process of claim 1 comprising taking up the filamentary material just subsequent to extrusion at an overall drawdown ratio of from about 25 to 350, subjecting said material to frictional contact with a solid surface at a point intermediate the points of extrusion and takeup such that the tension exerted on said material at the takeup point is not translated back to the point of extrusion, subjecting said taken-up material to an after-stretching operation at a temperature of from about 50° F. to 250° F. and a draw ratio of from about 1.2:1 to 2.3:1, enhancing the elastic recovery and tenacity and rendering said filamentary material uniformly opaque by subjecting said filamentary material to a second after-stretching operation which comprises contacting said filamentary material with hot H_2O at a temperature of from about 190° F. to 250° F. for at least 1 minute at a draw ratio of from about 1.2:1 to 2.3:1 and forming said filamentary material, which has an elastic recovery at 70° F. of at least about 75 percent from an extension of 50 percent, into a yarn package.