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CRIMPED AND CRIMPABLE VINYLIC FILAMENTS AND FIBERS

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ABSTRACT OF THE DISCLOSURE

A polyvinyl chloride filament and textile fiber having characteristics approaching those of natural fibers and three-dimensional deformation which is relatively permanent is produced by extruding at least two polyvinyl chloride solutions of vinyl-chloride polymers of different syndiotactic indices, both substantially in excess of 1.6, through a common orifice to produce a continuous filament any cross-section of which consists at least in part of each of said polymers, stretching said filament, and heating said filament to differentially shrink the polymers constituting same and thereby produce said three-dimensional deformation.

Our present invention relates to synthetic-resin filaments and fibers and, more particularly, to fibers consisting of vinylic polymers such as polyvinyl chloride and copolymers thereof.

The use of synthetic-resin fibers for textile purposes has, as is well-known, been sharply limited by the fact that resinous filaments and fibers are generally so straight as to be incapable of forming staple, thread and the like for knitting and weaving. Thus, synthetic-resin filaments as produced have not been practical substitutes for naturally occurring fibers such as those of wool and cotton and have not been capable of sustaining conventional textile treatments such as carding, spinning, weaving etc. because of the lack of waviness of the fiber or filament. It has thus been proposed heretofore to treat synthetic-resin fibers in such manner as to impart to them a succession of crimps, undulations or bends which give the filaments some of the characteristics of natural fibers with respect to subsequent textile treatment. Thus, a synthetic-resin filament emerging from an aperture of a spinneret, is normally smooth, straight and continuous and is, subsequent to emergence, subjected to deformation in any of several ways under such proposals. In general, the object is to permanently deform the filaments but yet permit it to have resilient characteristics so that, upon tensioning, it can be stretched but subsequently returns to its original condition. Crimping has been carried out heretofore by mechanical bending of the filaments, the crimps being substantially coplanar so that a three-dimensional deformation was not obtainable. When, for example, the filaments were provided with planar undulations and set by a heat-treatment, the deformations frequently were nonpermanent in the sense that they disappeared even in subsequent textile processing (e.g. during dyeing at an elevated temperature). Both the planarity and the retentivity of the crimp are disadvantageous for the reasons mentioned above and efforts have been directed toward obtaining three-dimensional crimping or deformation more in keeping with the characteristics of natural fibers, especially wool, and a permanence or retentivity of such nature that the crimping will not be lost merely as a consequence of the subsequent textile treatment or is restorable even if completely or partially lost.

Thus it has been suggested that two distinct synthetic resins having different degrees of shrinkage (i.e. ratio of loss in length to original length) upon heating may be subjected to joint extrusion from the same spinneret orifice to yield a composite filament which, when heated, naturally deforms to produce a spiral or helical configuration which is retained during subsequent treatment. Care must be taken, however, to ensure that the two distinct resins combined in a single filament do not have a tendency to separate.

These techniques, however, cannot be applied to polyvinyl chlorides since the combination of polyvinyl chlorides with other vinyl polymers or even vinyl-chloride copolymers do not yield a stable composite fiber. Combination of polyvinyl chloride with other fiber-forming resins is also unsatisfactory as a consequence of the incompatibility of the resins or differences in their dimensional stability. Investigations have also shown that mere combination of polyvinyl chlorides of different molecular weight in a composite fiber also does not yield the permanent, stable and three-dimensional crimping required.

It is, therefore, the principal object of the present invention to provide a polyvinyl-chloride filament and textile fiber having characteristics approaching those of natural fibers and three-dimensional deformation which is relatively permanent.

Another object of this invention is to provide an improved method of making a filament or fiber of the character described.

A further object of this invention is to provide a crimped fiber and method of making same whereby the crimping, subsequent to its formation, is restorable even after temporary elimination of the deformation.

These objects and others which will become apparent hereinafter, are attained, in accordance with the present invention, through the discovery that it is possible to produce composite filaments of two polyvinyl chlorides having differential thermal shrinkage sufficient to effect three-dimensional crimping when the polyvinyl chlorides both have a high syndiotactic index although their indices of syndiotacticity are different. This invention is an outgrowth of researches into synthetic-resin fibers of polyvinylchloride at high syndiotactic index as described and claimed in the commonly owned application Ser. No. 269,257, filed April 1, 1963, by the present joint applicants.

It has now been found, surprisingly, that all the disadvantages of composite polyvinyl fibers can be eliminated and the advantages of differential shrinkage between different polymers obtained when the two polymers joined in a single filament are polyvinyl chloride homopolymers or copolymers (consisting at least of 85% by weight vinyl chloride) which are produced in substantially identical manners but at different temperatures within, however, a range insuring that the polymer will have a syndiotactic index greater than 1.6, the polymerization temperatures thus lying between 0° C. and −60° C. The filament or staple of the instant invention is, consequently, a composite fiber of high syndiotactic index whose cross-section shows at least two distinct and mutually adjacent zones of polymers of different syndiotactic index and thermal shrinkage but, neverthless, with each syndiotactic index greater than 1.6. A convenient way of insuring the production of polymers having excellent compatibility is to carry out the polymerization reaction as indicated above, in similar processes except at different temperatures within the indicated range.

The term "syndiotactic index' or "index of syndiotacticity" (IC) is used to define the stereoregularity of a polymer and is determined, as described by Burgleigh in the Journal of the American Chemical Society (volume

82, page 749) as the infrared-absorption ratios at the IR bands D635 and D692 cm.$^{-1}$. The ratio of the intensities at these bands can be evaluated by dissolving the polymers in cyclohexanone at 120° C. to obtain a solution from 0.8 to 1% by weight of the polymer, cooling the solution rapidly, and evaporating it in vacuo at 50° C. (10 mm. Hg) on a flat glass surface to yield a film having a thickness of 20–30 microns. The IR analysis can be carried out by conventional spectrophotometry e.g. via a Perkin-Elmer 21 spectrophotometer having a double radius and a potassium bromide prism. The utility of the syndiotactic index is based upon the discovery that the bands D635 and D692 cm.$^{-1}$ are absorbed by the syndiotactic configuration of the polymer and the isotactic or atactic configuration, respectively, in amounts essentially proportional to the relative ratio of these configurations in the polymer. The index thus constitutes a measure of the stereo-regularity of a polyvinyl chloride.

According to a feature of the present invention, the composite fiber must have at least two distinct and mutually adjacent sections of polymers of different syndiotacticity and thermal shrinkage, the zones being more or less equal in cross-sectional area. The zones can be, therefore, sector-shaped or generally cylindrical with the two polymers being coaxial rather than radially side by side along a diametrical plane. The filament is produced by extruding the two vinyl-chloride polymers through the same orifice of a spinneret or the like and thereafter subjecting the filament to a thermal treatment capable of shrinking the polymers differentially to produce a spiral or helicoidal deformation that is resilient, sable and uniform and which, even upon extension of the filament to reduce the clamp, is retrievable by subsequent treatment. The resulting filament has an excellent workability and is suitable for use with conventional textile machines and thereby yield yarns having considerable bulk, a high covering capacity and a particularly advantageous softness. In general, the differential shrinkage of the filament (with reference to the shrinkage of the two polymers) must be at least 1% and preferably should be greater than 2%. The fiber or filament should be stretched in a conventional manner subsequent to extrusion and prior to or concurrently with thermal treatment with a stretch ratio ranging between substantially 1:4 to 1:10 and preferably from 1:6 to 1:8.

The shrinkage of filaments composed of polymers having different syndiotactic indices is demonstrated in the following table in which we show the polymerization temperature of the polymer and its shrinkage in boiling water. The polymers are produced by the same process with the exception of the polymerization temperature (e.g. by any of the methods described for vinyl-chloride polymerization or copolymerization ni commonly owned application Ser. No. 386,061, filed July 29, 1964, and entitled, "Process and Catalytic Composition for the Solution Polymerization of Vinylically Unsaturated Monomers." For the tests shown in the table, the fibers consisted of homopolymers of vinyl chloride with the filaments being produced by wet spining from a solution of cyclohexanone extruded into a coagulating bath (in the usual manner) consisting of a mixture of cyclohexanone, ethyl alcohol and water. The filaments are stretched in boiling water with a ratio of 1:8 (i.e. length prior to stretching:stretched length).

Table

Polymerization temperature, ° C.:	Shrinkage in boiling water (percent, about)
+50	50
−10	15
−15	12
−30	10
−40	7

The shrinkage is based upon the change in length in percentage for a skein of the filament immersed in boiling water for 5 minutes, the shrinkage being given as

$$\text{Shrinkage}=\frac{Li-Lf}{Li}\times 100$$

where Li=initial length of filament prior to immersion, and Lf=length of filament after immersion in boiling water for 5 minutes.

According to another feature of the present invention, the two polymers of different syndiotactics are extruded from a common orifice as respective spinning solutions having substantially identical absolute viscosities. The differential shrinkage (see table) should be at least 1% and preferably greater than 2%, which corresponds to a temperature difference of at least 5° C. with respect to the polymerization temperature for polymers having a high syndiotactic index. The polymers having a temperature of polymerization above about 0° C. are not characterized by the high syndiotacticity with which the present invention is concerned. In general, however, it may be stated that one of the polymers of the composite should have a polymerization temperature between substantially −30° C. and −50° C. while the other is polymerized similarly but at a temperature between substantially −10° C. and −20° C. Excellent results are obtained when, in accordance with this feature, one of the polymers of a composite is produced at −40° C. while the other is produced at a temperature of −15° C. While the crimping may disappear during susequent treatment as a result of stretching and tension, it reappears and is fully restored by subsequent heat treatment during, for example, a standard textile treatment (e.g. hot dyeing) or by a simple boiling or heating treatment specially provided (at the original crimping temperature, for example). A permanent and restoring crimping may be achieved by a single heat treatment or by a plurality of alternate stretchings and heatings depending upon the degree of crimping desired and the type of crimp. Because of the perfect compatibility of the two polymers, whose only essential difference is their syndiotacticity and thermal shrinkage, no problem with regard to the dimensional stability of the composite is noted. The two polymer components can be disposed side by side so that every cross-section is a cross-section through continuous layers of both components, the shell-and-core arrangement being also suitable. While reference to polymerization of vinyl chlorides and their copolymers (containing at least 85% by weight vinyl chloride) is intended to encompass all methods involving the low-temperature production of such compounds with high syndiotactic index (above 1.6), specific mention is made of the techniques and system described in the commonly owned copending application Ser. No. 386.061 filed July 29, 1964. Spinning of the polymer can be effected by any conventional technique, e.g. by wet or dry spinning for example as described in application Ser. No. 269,257, filed April 1, 1963, of the present applicants. The composite fibres thus obtained have all of the advantages characteristic of polymers having a high syndiotactic index and possess, for example, a high tenacity (greater than 2.5 gr./den.), a shrinkage in boiling water of less than 2% after crimping, high resistance to organic dry-cleaning solvents (e.g. trichloroethylene and perchloroethylene) and dyeability with disperse dyes at boiling temperatures.

In general, a filament or fiber produced in accordance with the present invention will have continuous layers or sections extending the full length of the filament and constituting at least part of the cross-section at any point along the length so that each component forms at least part of any cross-section of the filament. The filaments, threads or fibers, will, moreover, have a three-dimensional (e.g. helical) crimping and at least three undulations/cm., a tenacity greater than about 2.5 gr./den., a shrinkage in boiling water after crimping less than about 2%, and a

shrinkage in trichloroethylene at 40° C. of less than 1%.

The invention will be more apparent from the following specific examples illustrating the best mode presently known to use for taking advantage of the instant invention. It should be noted that the intrinsic viscosity η as used hereunder is a measure of the molecular weight of a polymer in accordance with the expression

$$\eta=2.4\times10^{-4}(\overline{Mn})^{0.77}$$

where η is the intrinsic viscosity of the polymer (measured at 25° C.) for a polymer solution of 1% in cyclohexanone, $\overline{Mn}$ being the average molecular weight of the polymer.

EXAMPLE 1

100 parts by weight of polyvinylchloride of high syndiotactic index, obtained by polymerizing vinyl chloride at −40° C. in accordance with application Ser. No. 386,061 and having an intrinsic viscosity $\eta=1.3$ gr./dl., are dissolved at 135° C. with stirring over a period of 30 minutes in 450 parts by weight of cyclohexanone.

100 parts by weight of polyvinylchloride of high syndiotactic index obtained by polymerizing the vinylchloride at −15° C. in otherwise identical manner and having an intrinsic viscosity $\eta=1.5$ gr./dl., are dissolved at 135° C. with stirring over a period of 30 minutes, in 400 parts by weight of cyclohexanone.

The two solutions thus obtained have about the same absolute viscosity of 50 poises at 130° C. and are fed to a spinneret having 80 holes with a diameter of 150μ, so that equal quantities of the two polymers are supplied to each orifice.

The extruded filaments are coagulated in a suitable coagulating bath in a conventional manner, the bath consisting of cyclohexanone, ethyl alcohol and water. After coagulation, the skein of filaments thus obtained is washed, stretched with a stretch ratio of 1:7, sized and dried under tension at a temperature between substantially 120° C. and 130° C.

The continuous filament thus obtained shows:

Titer	den	240
Tenacity	gr./den	3.9
Elongation at break	percent	18
Shrinkage in boiling H_2O	do	10

Through treatment in boiling water, with unimpeded shrinkage, the filament curls up and after drying with hot air at 60° C., the crimping characteristics are tested and show:

Number of undulations per cm.=7

$$\text{Degree of crimping}=\frac{L_2-L_1}{L_2}=0.15$$

wherein:

L_2=length of stretched end
L_1=length of crimped end

The mechanical characteristics of the ends after shrinkage in boiling water for 30 minutes, are the following:

Titer	den	260
Tenacity	gr./dl	3.2
Elongation at break	percent	32
Shrinkage in boiling water	do	0
Shrinkage in trichloroethylene at 40° C.	do	0.2
Shrinkage in air at 130° C.	do	4

A cross-section of the filament was examined under the microscope and it was observed that all the ends were conjugated and that each cross-section consisted of about 50% of each type of polymer.

The filament thus obtained was purposely stretched in a cold state with a stretch ratio of 1:1.15 in order to take out the crimping. It was found that, through a subsequent treatment in boiling water, the original crimping can practically be restored.

EXAMPLE II

100 parts by weight of polyvinylchloride of high syndiotactic index, obtained by polymerizing vinyl chloride at −30° C. (as previously described) and having an intrinsic viscosity $\eta=1.5$ gr./dl., are disssolved at 135° C. with stirring for 30 minutes, in 450 parts by weight of cyclohexanone.

100 parts by weight of polyvinylchloride of high syndiotactic index, obtained by polymerizing vinyl chloride in a similar manner at −10° C. and having an intrinsic viscosity $\eta=1.7$ gr./dl., are dissolved at 135° C. with stirring for 30 minutes, in 400 parts of cyclohexanone.

The two solutions were drawn in equal quantities through a spinneret with 20 orifices of 250 μ diameter. The extruded filaments were stretched with a stretch ratio of 1:6.

The filament thus obtained showed:

Titer	den	55
Tenacity	gr./den	3.8
Elongation at break	percent	20
Shrinkage in boiling H_2O	do	12

During treatment in boiling water, with unimpeded shrinkage, the filament curls up and, after drying with hot air at 60° C., shows the same characteristics of the filament obtained according to Example I.

We claim:

1. A process for producing polyvinyl-chloride filaments for textile purposes, comprising the steps of extruding at least two polyvinyl-chloride solutions of vinyl-chloride polymers of different syndiotactic indices through a common orifice to produce a continuous filament any cross-section of which consists at least in part of each of said polymers, both of said polymers having a syndiotactic index in excess of substantially 1.6; stretching said filament, and heating said filament to differentially shrink the polymers constituting same and producing a three-dimensional deformation of said filament.

2. The process defined in claim 1 wherein said polymers are produced in substantially similar polymerization steps at temperatures between substantially 0° C. and −60° C., one of said polymer being produced by polymerization at a temperature different from the other of said polymers whereby different syndiotactic indices are imparted to said polymers.

3. The process defined in claim 2 wherein said different temperatures are so selected that said polymers have a differential thermal shrinkage greater than about 1% upon subjection to heat to deform said filament.

4. The process defined in claim 3 wherein one of said different temperatures ranges between substantially −10° C. and −20° C. inclusive while the other of said different temperatures ranges between substantially −30° C. and −50° C. inclusive.

5. The process defined in claim 4 wherein said differential shrinkage is at least 2%.

6. The process defined in claim 5 wherein said filament is stretched, prior to deformation by heating, with a stretch ratio ranging between substantially 1:4 and 1:10.

7. The process defined in claim 6 wherein said ratio is between 1:6 and 1:8.

8. The process defined in claim 7 wherein said solutions have substantially identical absolute viscosities and are passed through said orifice in substantially identical quantities.

9. The process defined in claim 8 wherein the intrinsic viscosity of one of said polymers differs from the intrinsic viscosity of the other of said polymers by approximately 0.2 gr./dl. while the intrinsic viscosity of each of said polymers ranges between substantially $\eta=1.3$ and $\eta=1.7$ gr./dl.

10. The process defined in claim 8 wherein said solutions of said polymers of different syndiotactic indices

are spun by dry-spinning techniques to form a composite filament in which the polymers are disposed side by side.

11. The process defined in claim **8** wherein said solutions of said polymers of different syndiotactic indices are spun by wet-spinning techniques to form a composite filament in which the polymers are disposed side by side.

12. A composite filament consisting of at least two continuous sections of different vinyl-chloride polymers whose syndiotactic indices are above substantially 1.6 but are different from one another, each cross-section of said filament being composed at least in part by one of said polymers, said filament being three-dimensionally deformed and having at least three undulations per cm. of length, a tenacity greater than about 2.5 gr./den., a shrinkage in boiling water of less than about 2% and a shrinkage in a trichloroethylene at 40° C. of less than 1%.

13. A filament as defined in claim **12** wherein each of said vinyl-chloride polymers consists of at least 85% by weight of vinyl chloride, said polymers having a differential shrinkage of at least 1% upon heating to a temperature sufficient to cause permanent three-dimensional deformation of said filament.

14. A filament as defined in claim **13** wherein said vinyl-chloride polymers are produced by similar polymerizations at different temperatures between substantially 0° C. and −60° C.

15. A filament as defined in claim **14** wherein one of said different temperatures ranges between substantially −10° C. and −20° C. and the other of said different temperatures ranges between substantially −30° C. and −50° C.

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