

1

2

3,509,013

**COMPOSITE POLYPROPYLENE FILAMENT**

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7 Claims

**ABSTRACT OF THE DISCLOSURE**

Composite filaments are prepared of stereoregular polypropylene wherein at least one component is unmodified polypropylene and at least one component is polypropylene modified by addition thereto of a crystallinity modifier.

This invention relates to synthetic fibers which exhibit a high degree of bulk or crimp. In particular, it relates to filaments of stereoregular polypropylene of novel construction which crimp or bulk spontaneously.

In recent years, synthetic fibers have come to assume an increasingly larger position in the textile market. Where wool and cotton were at one time virtually unchallenged as the materials many applications by nylon, polyester and acrylic fibers, and more recently by the olefin fibers, particularly polypropylene. The synthetic fibers possess properties such as ease of care, durability, mechanical strength, and warmth, with light weight, to name a few, which are not found in the older, natural textile materials.

However, wool fabrics have advantages of their own which to date have been extremely difficult and expensive, if at all possible, to reproduce in the synthetics. Principally, the woolen yarns or fibers possess a high degree of natural crimp. This results in their exhibiting a high bulk and excellent covering properties as well as good elastic properties such as stretch ability, compressional resilience and liveliness. In addition, wool has a very pleasing surface feel or handle which consumers have come to prefer.

Many attempts have been made to prepare synthetic fibers or yarns which, when converted into a fabric, would result in a fabric exhibiting the desirable properties of wool in addition to the desirable properties of the synthetic. These attempts all take the form of attempts to impart a crimp to the synthetic yarn. The most successful such attempts have been those which impart a spiral or helical crimp.

It has been proposed to impart a helical crimp by spinning the synthetic polymer in the form of a conjugate filament having two or more different, though usually related polymers joined in side-by-side or sheath and core relationship. When the filament is drawn in the customary manner known to the synthetic fibers art, and thereafter relaxed, the different polymer segments exhibit different relaxation or shrinkage potentials. This differential shrinkage results in formation of helical coiling of the individual filaments. When such filaments are collected into a yarn, the resultant yarn assumes a high bulk due to the difficulty experienced by the filaments in remaining in close proximity to one another.

In British Patent 979,003, it is proposed to prepare a self-bulking filament of polypropylene by spinning a conjugate filament comprised of two different polypropylene components which differ in their reduced specific viscosities (RSV—0.1% solution in Tetralin at 135° C.) by at least 0.1. The differential shrinkage of the two polypropylene components causes the previously referred to helical coiling when the yarn is relaxed after stretching.

It has now been found that polypropylene conjugate fibers capable of a high degree of spontaneous crimping can be prepared by spinning a conjugate filament of at

least two polypropylene components possessing different crystalline structures. The difference in the crystallinity between the several polypropylene components appears to cause differences in shrinkage characteristics of the components, resulting in non-uniform shrinkage of the components upon relaxation following drawing thereof. This non-uniform shrinkage produces the desired helical crimp in the filaments resulting in substantially increased bulk.

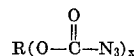
The spontaneous crimping undergone by the filaments of this invention takes place irrespective of any differences in the intrinsic viscosity of the polypropylene components. That is to say, the two or more components can be of the same or different viscosity and the benefits of this invention will still be observed.

The difference in crystalline structure between the polypropylene components can be induced by any convenient method known for accomplishing this end. For example, certain modifications of the polymerization process are known whereby polypropylene can be produced of lesser crystallinity than that normally associated with stereoregular polypropylene. Preferably, however, the difference in crystallinity is brought about by addition of a chemical modifier prior to the spinning of the polymer into filaments.

One effective chemical modification by which the crystallinity of polypropylene can be altered is the addition of a nucleating agent. Materials useful as nucleating agents are usually fine particle crystalline organic or inorganic materials which are otherwise inert to and insoluble in polypropylene. These materials are believed to function by providing nuclei around which crystalline spherulites can form, thus promoting a more rapid and complete transformation of the polymer to the crystalline state. Examples of such materials include, inter alia, silica, talc, titanium dioxide, crystalline aluminum salts, and sodium salts. Some, though by no means all, examples of such nucleating agents are disclosed in U.S. Patents 3,207,737 and 3,207,739, both assigned to Shell Oil Co. A preferred nucleating agent, found highly effective in the process of this invention, is sodium benzoate.

The crystallinity of the polypropylene can also be modified by subjecting the same to a small amount of bridging. By "bridging" in this specification is meant a very light cross-linking, sufficient to modify the rheological or morphological properties of the polymer to a slight extent, but insufficient to effect any substantial change in the melting point or in the solubility thereof in perchloroethylene at 110° C.

The bridging is preferably accomplished by means of a chemical agent added to the polymer in an amount sufficient to accomplish only the desired light cross-linking. A preferred class of chemical compounds which can be used to accomplish this bridging are the polyfunctional azido compounds exemplified by sulfonazides and azidoformates. The sulfonazides have the general formula  $R(SO_2N_3)_x$  where R is an aliphatic or aromatic hydrocarbon radical inert to reaction with polypropylene and x is an integer from 2 to about 8. Exemplary sulfonazides are 1,5-pentane bis(sulfonazide), 1,10-decane bis(sulfonazide), 1,3-benzene bis(sulfonazide), 1-octyl-2,4,6-benzene tris(sulfonazide), 4,4-diphenyl methane bis(sulfonazide), 4,4'-diphenyl ether bis(sulfonazide), 2,7-naphthalene bis(sulfonazide), etc. The azidoformates have the general structural formula



where R is an organic radical inert to reaction with polypropylene and x is an integer from 2 to about 8. Exemplary azidoformates include alkyl azidoformates such as tetramethylene bis(azidoformate) and pentamethylene

bis(azidoformate); cyclic alkyl azidoformates, aralkyl azidoformates; azidoformate ethers, etc.

A more complete discussion of bridging of polypropylene with polyfunctional azido compounds is contained in my U.S. Patent 3,382,306.

As stated, the amount of the bridging agent employed to effect the desired alteration of the crystalline character of the polypropylene is quite small. Normally, this will be on the order of about 0.1 to about 0.8 mole of azido compound per mole of polypropylene. If greater amounts are employed, the material begins to lose the desirable properties of the polypropylene, tending to become less and less tractable as the amount of cross-linking increases. Lower amounts usually do not provide a sufficient amount of alteration of the crystalline structure.

The novel filaments of this invention can be composed of two or more different polypropylene components. In most cases, two components will be present. This arrangement normally provides sufficient variation between components to cause the desired amount of crimping. Also, as the number of components increases, the degree of sophistication of the extruding equipment, and thus the difficulty and expense of fabricating the same, likewise increases. In only a very few cases will it be necessary or desirable to prepare filaments having more than two, or at the most, three components.

The different polypropylene components of the filaments of this invention can be arranged in either side-by-side or sheath and core configuration. Normally, the side-by-side arrangement is satisfactory and preferred. The sheath and core arrangement is normally employed in cases where there is a significant difference in properties between the polymers in the two components, e.g., where one is less durable, or less stable, or less chemically inert than the other. The sheath and core arrangement allows the inner component to be protected by the outer component. In the instant case, very little, if any, difference in properties other than crystallinity exists between components. Thus, there is usually no need for the protection afforded by the sheath and core. However, if other considerations make it desirable, the sheath and core arrangement can be employed.

Spinning equipment suitable for preparing filaments of either of these configurations is well known in the art and forms no part of this invention. For disclosures of equipment for forming these filaments, reference can be had to U.S. 3,192,562, 3,181,201, 3,176,346, 3,176,345, 3,176,343, 3,176,342, 3,161,914, and many others.

The basic design feature of these spinnerets is the provision of polymer in more than one stream with the streams converging and contacting each other at a point at or near the extrusion orifice. Specific spinneret design determines whether the resulting filament possesses the side-by-side or sheath-core configuration. Contact between the streams is always made while the polymer is in the molten state so that the several components can fuse into a single, well-adhered composite structure upon cooling.

Generally speaking, the spinning of the polymer into filaments is accomplished according to standard methods except for the simultaneously spinning of a multiplicity of polymer streams. That is to say, the polymer is extruded under pressure in the form of a melt through an orifice and subjected to a substantially non-orienting melt draw-down whereby the thickness of the filament is reduced. Thereafter, the shaped filament is subjected to a cold, orienting draw. The crimp is then developed in the drawn yarn by heating the same while in a substantially tension-free state.

In most cases, spinning is effected through a spinneret having a plurality of orifices in the face thereof. The resulting plurality of filaments is usually collected together into a yarn which is then subjected to the remainder of the treatment steps as an entity. When the yarn has undergone the drawing and relaxation steps, it assumes sub-

stantially greater bulk due to the helical coil or crimp imparted to the individual filaments.

The orienting draw is conducted at a temperature below the melting point of the polypropylene in order to develop the optimum tensile properties of the filaments. Preferably, the drawing temperature will be between about 25 and 100° C. The filaments are usually drawn about 150 to 250% in order to develop the optimum in tensile properties and also to develop the necessary differential shrinkage potential. A draw of at least about 100% is required to produce sufficient shrinkage to result in useful crimped filaments or yarn.

Drawing is effected according to techniques well known in the art. A preferred method is drawing between a differentially driven feed roll and draw roll. Heat is applied to the feed roll to promote proper drawing temperature, while the draw roll is normally maintained at about room temperature. In some cases, the draw roll can be heated, if desired.

In some cases, the stretched filaments crimp spontaneously as soon as the stress imposed by the drawing operation is relaxed. In other cases, the filament can be made to crimp by applying a predetermined quantity of heat thereto, while it is in the completely relaxed state, allowing the filament to shrink and bringing the differential shrinkage effect into play. The heat treatment is effected at a temperature close to the temperature of drawing, i.e., at about 100 to 135° C. After the crimp has formed, the yarn is subjected to a heat treatment at about 100 to 135° C. for about 0.5 to 10 minutes in the fully relaxed state to stabilize the crimp.

The filaments of this invention can be prepared having about 30 to 125 crimps per inch of filament length. In general, the crimp frequency can be varied by varying the differential in crystallinity and accordingly the differential in shrinkage of the several filaments. This, in turn, is controlled by the amount of modifying agent added to the modified component. Normally a crimp frequency of about 50 to 75 crimps per inch is satisfactory.

The additives employed to effect the alteration of the crystallinity can be added to the polymer by any method commonly employed in the art for this purpose. Deposition from a solvent, dry milling, masterbatch mixing and hot roll milling are examples of useful methods. Usually, the additive will be incorporated into the polymer prior to melting, although in some cases it can be added to the molten polymer.

The invention having been described in some detail, the following examples are presented in illustration thereof. In each case, the polymer employed is a stereoregular polypropylene prepared by the polymerization of propylene at low temperature and pressure in the presence of a catalyst comprised of a titanium halide and an organo-aluminum compound. In the examples, parts and percentages are by weight unless otherwise indicated.

#### EXAMPLE 1

Stereoregular polypropylene, RSV 1.9 (reduced specific viscosity measured as a 0.1% solution in decahydronaphthalene at 135° C.) was fed in two streams by means of separate feed pumps to a spinneret adapted to extrude side-by-side conjugate filaments. The spinneret contained 35 orifices, 0.016 inch in diameter. The polymer was spun at 287° C., at a linear rate of 71 meters per minute and drawn off from the spinneret at a rate of about 283 meters per minute, resulting in a draw-down of 40 to 1.

The polymer feed to one side of each spinneret orifice was a standard commercially available polypropylene containing 0.15 part of a stabilizer comprised of the reaction product of 1 mole of acetone with 2 moles of nonyl phenol per hundred parts of resin. The feed to the other side of the orifice was the same polymer, but it contained, in addition, 0.1 part sodium benzoate per hundred parts of resin.

5

The composite yarn was drawn between differentially driven steel feed and draw rolls. The feed roll, heated to about 100° C., advanced the yarn at a linear rate of about 37 meters per minute. The draw roll was maintained at room temperature and driven about 130 meters per minute. The yarn was thus drawn about 3.5 to 1.

When the tension imposed by the stretching was relaxed, the composite filament spontaneously formed a helical crimp of about 75 crimps per inch. This crimp was stabilized by heating the yarn for 10 minutes at 110° C. in a fully relaxed state. The resultant high bulk yarn exhibited good covering power and a high degree of elasticity. When stressed, the helical crimps were drawn out, but returned immediately upon relaxation of the stress.

#### EXAMPLE 2

The procedure of Example 1 was repeated except that polymers having different viscosities were employed. One side of each filament was a polypropylene of RSV 1.9, stabilized with 0.15 part of the acetone nonyl phenol reaction product, and containing about 0.1% sodium benzoate. The other side was a polypropylene of RSV 1.3, stabilized with the same stabilizer, but containing no nucleating agent.

After stretching and relaxing, this yarn exhibited a helical crimp of about 90 crimps per inch on the average and had excellent covering power and elasticity.

#### EXAMPLE 3

The procedure of Example 1 was repeated except that the modified polypropylene component of each filament contained 0.03% by weight of decamethylene disulfonazide. Extrusion was accomplished at 287° C.

The resultant filaments had high bulk and elasticity, exhibiting a helical crimp of about 110 crimps per inch.

#### EXAMPLE 4

A composite filament was prepared as in Example 1 where one component of each filament was unmodified, stabilized polypropylene having RSV of 1.3 and the other component was stabilized polypropylene having an RSV of 1.9 and containing 0.03% decamethylene disulfonazide.

This filament had a helical crimp of about 90 crimps per inch.

In the examples, each of the yarns was produced in such a way that the modified and unmodified polypropylene each constituted about 50% of the mass of each individual filament. It is, however, within the scope of this invention to produce such filaments wherein either component can comprise about 15 to 85% of each filament.

The filaments of this invention can be employed by themselves to prepare yarns having high bulk in the manner shown in the examples, or they can be blended and twisted with filaments of unmodified polypropylene. In this latter application, the different filaments are twisted or combined while holding the conjugate filament under tension. When this tension is released, the conjugate filament tends to contract to its preferred helically coiled configuration, and, in doing so, causes the unmodified

6

filament to be similarly contracted. The result is an entanglement of the filaments and a substantial increase in volume of the total yarn.

The high bulk yarns prepared by the technique of this invention resemble wool in their properties and their hand. Accordingly, they are useful in most applications where wool is currently popular. This includes such applications as knitted wear, sweaters, socks, and the like, carpeting, and upholstery fabrics.

What I claim and desire to protect by Letters Patent is:

1. A conjugate filament capable of spontaneous crimping comprised of at least two fiber-forming polymer components, one of said components being unmodified stereoregular polypropylene, and one of said components being stereoregular polypropylene containing an additive to modify the crystallinity thereof.

2. The conjugate filament of claim 1 where the several components are disposed in side-by-side relationship.

3. The conjugate filament of claim 2 where the unmodified stereoregular polypropylene component comprises about 15 to 85% of the mass of the filament.

4. The conjugate filament of claim 2 where the crystallinity modifying additive is sodium benzoate, said sodium benzoate being present in the amount of about 0.03 to 1.0% by weight of the polypropylene.

5. The conjugate filament of claim 2 where the crystallinity modifying additive is an azido compound selected from the class consisting of bis-sulfonazides and bis-azidoformates.

6. The conjugate filament of claim 5 where the crystallinity modifying additive is decamethylene disulfonazide, said decamethylene disulfonazide being employed in the amount of about 0.005 to 0.05% by weight of the polypropylene.

7. A process for forming a spontaneously crimpable polypropylene filament which comprises extruding in conjugate, mutually adherent relationship a fiber-forming polypropylene component comprising unmodified stereoregular polypropylene and at least one component comprising a fiber-forming stereoregular polypropylene containing a crystallinity modifying agent, drawing said filament at least about 150% and relieving the drawing tension on said filament.

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