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MELT SPINNING ELASTIC POLYPROPYLENE MONOFILAMENTS

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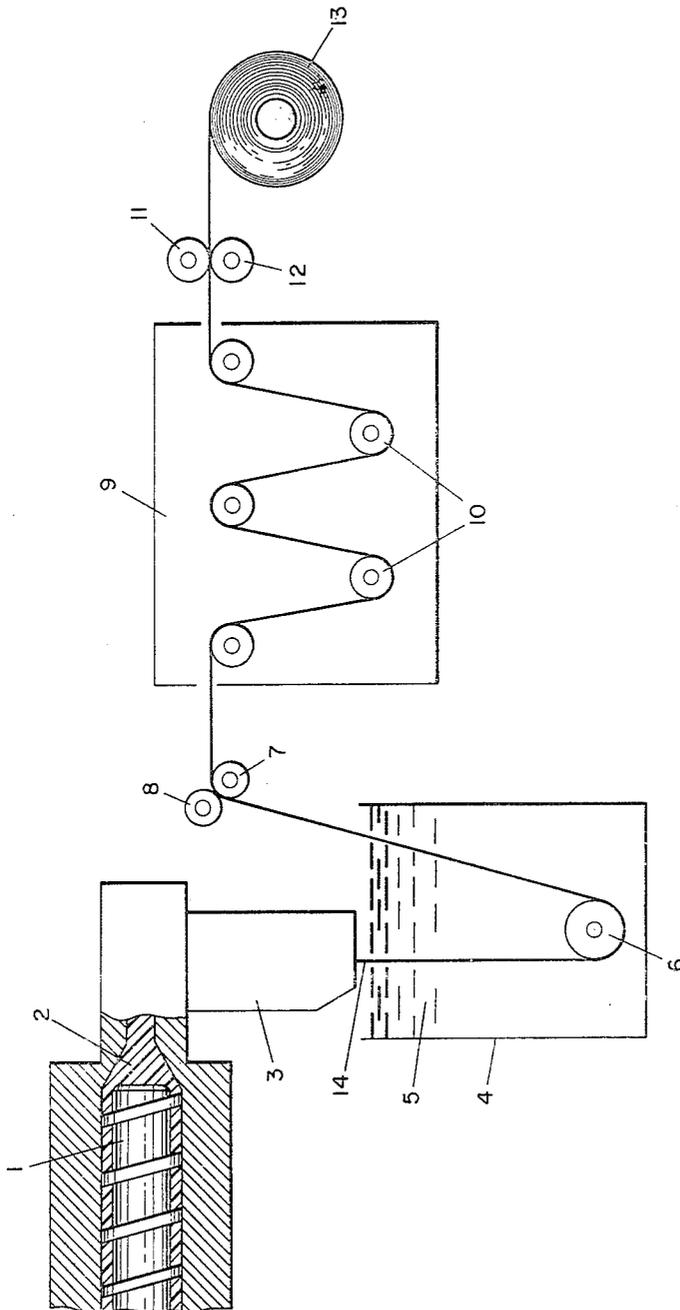


FIG. 1

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MELT SPINNING ELASTIC POLYPROPYLENE MONOFILAMENTS

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4 Claims 10

ABSTRACT OF THE DISCLOSURE

Elastic monofilament of bridged polypropylene can be prepared by extruding molten polypropylene containing a small amount of azido bridging agent into a monofilament, subjecting the said monofilament to a melt draw down of from about 3:1 to about 9.5:1, quenching the monofilament in an inert liquid less than 1/2 inch from the die and then heat treating the monofilament at a temperature between about 130° C. and about 155° C. The said elastic monofilament has a recovery of at least 85% after elongation up to 75%.

The present invention relates to elastic monofilament of bridged stereoregular polypropylene and to a process for the production of such monofilament.

It is known to produce so called stretch yarns of synthetic polymers where stretchability is a result of the physical structure of the yarn rather than inherent elasticity of the synthetic polymers, examples being crimped and highly twisted yarns. Truly elastic monofilaments of synthetic polymers, that is, monofilaments possessing the ability to be stretched repeatedly and regain substantially the original length due to the inherent elasticity of the material from which they are made, are much more rare.

Monofilaments of stereoregular polypropylene are well known. While some of these filaments have been described as "highly elastic," useful elastic monofilaments of stereoregular polypropylene, particularly in the higher denier range, have not been forthcoming and the problem of producing useful elastic monofilaments of such material have been fraught with difficulty.

Now, in accordance with this invention, it has been found that elastic monofilaments of stereoregular polypropylene can be prepared if certain critical process steps are followed. Specifically the process in accordance with this invention comprises extruding molten stereoregular polypropylene containing from about 0.02% to about 0.08% by weight of an azido bridging agent at a temperature between about 200° C. and about 290° C. in the form of a monofilament, subjecting the extruded filament to a melt draw down of from about 3:1 to about 9.5:1, quenching the filament in an inert liquid at a temperature of from about 30° C. to about 110° C. less than 1/2 inch, preferably within about 1/8 to about 1/4 inch from the die, and heat treating the solidified monofilament at a temperature between about 130° C. and about 155° C. The elastic monofilaments prepared in accordance with this invention are useful for many purposes, as for example, in the manufacture of outdoor furniture webbing, automobile seat covers, etc.

The criterion for measuring the elastic properties of

the monofilament is its ability to return to its original length when it is relaxed after being subjected to an elongating stress. This property is referred to herein as "tensile recovery" or more simply as "recovery." It is expressed as a percentage of the imposed elongation which is lost upon removal of the elongating force. Percent recovery (r) is calculated as

$$\text{Percent } R = \frac{L_e - L_r}{L_e} \times 100$$

where L_e represents the distance the sample was elongated, and L_r represents the portion of that elongation which is retained upon release of the elongating stress. The parameter L_r may also be referred to as "permanent set." The percentage of permanent set is equal to 100 minus percent recovery. It should be obvious that higher values of recovery, or conversely, lower values of permanent set indicate greater elastic properties.

The process of the invention is illustrated in the attached drawing in which 1 designates an extruder adapted to extrude molten polymer 2 through a die 3. The numeral 4 represents a vessel containing a quenching liquid 5, e.g., water, in which is submerged an idler roll 6. Numerals 7 and 8 designate nip rolls which convey the monofilament through the quenching liquid, 9 designates a heat treatment oven containing a series of idler rolls 10, 11 and 12 designate an additional set of nip rolls and 13 designates a wind up station.

In operating according to the drawing, the molten polymer 2 is extruded in the form of a monofilament 14 into the inert liquid 5 in the quench tank 4. The monofilament is drawn through the quenching tank by the nip rolls 7 and 8 which are positively driven at a rate 3 to 9.5 times the linear rate of extrusion of the filament through the die. This increase in the linear speed of the monofilament causes stretching of the filament in its weakest section, i.e., the molten portion between the die and the inert liquid. The inert liquid in the quench tank through which the monofilament is drawn is maintained at a temperature sufficient to solidify the filament. A satisfactory temperature is from about 30° C. to about 110° C. The quenched monofilament is drawn from the tank and fed into the heat treatment oven 9 and around the idler rolls 10. In passing through this oven the monofilament is maintained at a temperature below its softening point. The finished monofilament is fed onto wind up station 13 through nip rolls 11 and 12.

The extruded monofilament is subjected to a melt draw of at least 200% or stated otherwise a melt draw down of at least 3:1. By melt draw down is meant the reduction in thickness of the extruded monofilament while it is still in the liquid or molten state prior to quenching. Melt draw down ratio expresses the relationship between the cross-sectional area of the die opening to that of the monofilament. Melt draw down is commonly employed in the production of films and fibers from thermoplastic polymers for several reasons. For example, the melt draw down permits the use of a larger size die than can be used otherwise. This permits greater precision in die manufacture and results in correspondingly greater denier uniformity in the extruded monofilaments. Most preferably the die opening used in the process of this invention will be from about 15 mils to about 50 mils resulting in monofilaments of from about 200 denier to about 1,200 denier.

In the process of this invention the use of melt draw

down is found to be vital to the formation of elastic filaments and as indicated above, the monofilament must be subjected to a draw down of at least about 3:1 in the molten state as it leaves the die. When melt drawing the filament it is necessary to confine the drawing to a relatively small distance. If the draw down takes place over any sizeable distance, the resultant filament exhibits an unacceptable amount of denier variation. To assure that the drawing is thus confined, it is necessary to quench the filament to the solid state within a relatively short distance of the die. Since the filament will draw preferentially in the molten areas rapid quenching tends to isolate the draw area. To obtain the optimum in denier uniformity the monofilament must be quenched within ½ inch of the die.

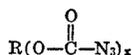
The quenching of the monofilament is effected by immersing the filament in a bath of cooling liquid, e.g., water, maintained at a temperature of from about 30° C. to about 110° C.

The monofilament which is formed by the extrusion, melt draw down and quenching operations discussed above has very little elasticity as it is taken from the quench bath. The elasticity is fully developed by heat treatment at a temperature in the range of from about 130° C. to about 155° C. for a minimum time of about 30 seconds. This can be accomplished very effectively on a continuous basis, as, for example, by the use of a heat treatment oven containing idler rolls through which the monofilament passes after leaving the quench bath. Obviously the more idler rolls the longer the period of time in the heat treatment oven. The heat treatment can also be accomplished by simply forming a roll of monofilament and then placing the roll in a heated oven for the desired length of time. After the heat treatment the monofilaments of bridged polypropylene are capable of at least 85% recovery after elongation up to about 75%.

The azido bridging agents used in the process of this invention are exemplified by the sulfonazides and the azidoformates.

The sulfonazides have the general formula $R(SO_2N_3)_x$ where R is an organic radical inert to reaction with polypropylene and x is an integer greater than 1. 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'-diphenylmethane bis(sulfonazide), 4,4'-diphenyl ether bis(sulfonazide), 4,4'-bis-octadecyl biphenyl-3,5,3',5'-tetra(sulfonazide) 1,4-cyclohexane dimethyl bis(sulfonazide), 4,4'-diphenyl disulfide bis(sulfonazide), 1,6-bis(4'-sulfonazidophenyl) hexane, 2,7-naphthalene bis(sulfonazide), etc. Other sulfonazides may be used, for instance those having functional groups on the organic hydrocarbon such as halogen, carboxyl groups, carbonyl groups, etc., so long as such groups are inert to reaction with polypropylene.

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 of the azidoformates used are the alkylene azidoformates such as tetramethylene-bis-(azidoformate), pentamethylene-bis-(azidoformate); the cyclic alkylene azidoformates such as 1,4-cyclohexanedimethyl-bis-(azidoformate); the aralkylene azidoformates such as α,α' -p-xylene-bis-(azidoformate); the aromatic azidoformates such as 2,2-isopropylidene-bis(p,p'-phenyl azidoformate); the azidoformate ethers such as 2,2'-oxydiethyl-bis-(azidoformate), 2,2'-oxydipropyl-bis-(azidoformate), 2,2'-ethylenedioxydiethyl-bis-(azidoformate), the tetraazidoformate of pentaerythritol-propylene oxide adduct having the general formula:



the azidoformate thioethers such as 2,2'-thiodiethyl-bis (azidoformate), 4,4'-thiodibutyl-bis (azidoformate); etc. It will, of course, be obvious to those skilled in the art that still other azidoformates containing functional groups, which are inert to reaction with polypropylene, such as halogen, carboxyl groups, carbonyl groups, etc., are included in the above definition.

It is known to bridge polypropylene by the use of azido compounds such as the aforesaid sulfonazides. The bridged polymers are completely soluble in the usual solvents for polypropylene, extrude smoothly with reduced sag and have greater hardness, strength, and stiffness and higher density.

In order to improve the elastic properties of the monofilaments of this invention it is necessary that a critical amount of bridging agent be present, i.e., the amount must be sufficient to increase the melt viscosity of the polymer but insufficient to alter its solubility in perchloroethylene at 110° C. This amount of bridging agent is provided by the addition of from about 0.02% to about 0.08% by weight of azido compound. When the amount of azido compound materially exceeds this range the polymer is insolubilized, cannot be extruded and does not exhibit the desired elastic properties. When the amount is below the range, little or no benefit is realized.

The bridging reaction is initiated by heat. The temperature required depends somewhat on the particular azido compound employed but, in general, will be from about 100° C. to about 250° C. This is readily provided by control of the extruder temperature. In other words, the polymer containing the critical amount of azido compound is extruded at a temperature higher than the temperature required to initiate the reaction so that the reaction occurs during the extrusion.

The azido bridging agent can be incorporated into the polypropylene by any of the commonly used methods of admixing additives with a polymer. Exemplary methods are deposition on the polymer flake from a solvent, admixing on a heated mill such as a Banbury mixer, dry blending, dissolving both the polymer and agent in a mutual solvent and then evaporating the solvent, etc.

The general nature of the invention having been set forth the following examples serve to illustrate the invention. It is to be understood that the invention is in no way limited to the examples since it can be carried out by the use of various modifications and changes within the scope of the invention as herein set forth and described. Permanent Set was determined in the examples by extending the monofilament to the specified elongation, holding it in the extended state for 10 minutes, releasing it, and allowing it to relax for 5 minutes. Permanent Set is calculated is the percentage of the imposed elongation which is retained after relaxation for 5 minutes. All parts in the following examples are by weight unless otherwise specified.

EXAMPLES 1-3

Particles of stereoregular polypropylene having a reduced specific viscosity of 2.45 (determined in a 0.1% solution in decahydronaphthalene at 135° C.) and stabilized against light and heat were wetted with a solution in acetone of 1,10-decane bis(sulfonazide). The solution was sufficiently concentrated to deposit 0.03% of disulfonazide on the surface of the polymer flake when the solvent was evaporated. The thus treated flake was melted in a compounding extruder and extruded at a temperature of 250° C. at various rates of speed which were adjusted to give different deniers through a 4 hole 30 mil diameter spinneret die. The monofilaments were drawn away from the die at a rate of 272 feet per minute, resulting in different draw down ratios and different deniers as shown in the table below. The monofilaments were quenched in a water bath at 50° C. located ½ inch from the extrusion die, wound on a bobbin and then placed in a forced draft oven at 150° C. for 15 minutes.

A second batch of the stereoregular polypropylene flake was treated as above and extruded into monofilaments under the same conditions as above except no bis(sulfonazide) was added.

The percentage permanent set of each sample is shown in Table I.

TABLE I

Example No.	Bis(sulfonazide) added	Draw down	Denier	Permanent set, elongation	
				20%	75%
1	Yes	9.5	391	3	8
	No	9.5	391	9	23
2	Yes	5.5	675	3	9
	No	5.5	675	11	25
3	Yes	3.5	1,060	8	12
	No	3.5	1,060	16	29

EXAMPLES 4-6

Particles of stereoregular polypropylene as described in Examples 1-3 were slurried in acetone. To the slurry was added a sufficient amount of tetramethylene bis(azidoformate) dissolved in chloroform to deposit 0.05% of azidoformate on the surface of the polymer flake when the solvents were evaporated. The thus treated flake was melted, extruded, drawn, quenched and heat treated exactly as described in Examples 1-3.

The percentage permanent set of each sample is shown in Table II.

TABLE II

Example No.	Draw down	Denier	Permanent set, elongation	
			20%	75%
4	9.5	391	4	8
5	5.5	675	4	10
6	3.5	1,060	8	13

I claim:

1. A process of forming an elastic monofilament of bridged polypropylene of at least about 200 denier comprising extruding stereoregular polypropylene containing

from about 0.02% to about 0.08% by weight of an azido bridging agent into a monofilament at a temperature of from about 200° C. to about 290° C., subjecting the molten monofilament to a melt draw down of from about 3:1 to about 9.5:1, quenching the monofilament in an inert liquid less than 1/2 inch from the die and heat treating the monofilament at a temperature between about 130° C. and about 155° C.

2. The process of claim 1 wherein the azido bridging agent is a bis(sulfonazide).

3. The process of claim 1 wherein the azido bridging agent is a bis(azidoformate).

4. The process of claim 1 wherein the monofilament is quenched at a temperature of from about 30° C. to about 110° C.

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