[54] **PROCESS OF FORMING POLYOLEFIN FIBERS**

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[57] **ABSTRACT**

The process of forming polyolefin fibers comprising forming a solution of a linear, high molecular weight polyolefin in a solvent at a temperature above the melt dissolution temperature of the polyolefin, and dispersing the polyolefin solution in a precipitant under conditions of shear stress sufficient to form polyolefin fibers having a microfibrillar structure.

10 Claims, No Drawings

PROCESS OF FORMING POLYOLEFIN FIBERS

BACKGROUND OF THE INVENTION

The formation of fibers of polyolefins has previously been effected by extruding the polyolefin through spinnnerets to form continuous filaments, and chopping the filaments into short lengths called "staple" fibers.

U.S. Pat. No. 2,988,782 discloses a process for producing "fibrids" by dispersion of a solution of a synthetic polymer in a precipant for the polymer under shear conditions such that the product of the absolute rate of shear in reciprocal seconds and the time in microseconds required for the precipitate to form is at least about 100 and no more than about 1,300,000. The polymeric particles formed by this process are called "fibrids", which have a morphology that is non-granular and has at least one dimension of minor magnitude relative to its largest dimension.

U.S. Pat. No. 3,431,242 discloses that it is difficult, if not impossible, to form fibrids of certain polymers, such as polyethylene and polypropylene.

U.S. Pat. No. 3,119,801 discloses a process for precipitating olefin polymers from solution so as to segregate molecular weight fractions. The higher molecular weight fraction, i.e., up to about 100,000, precipitates as a fibrous material when the solution is cooled slowly with mechanical agitation.

British Pat. No. 1,142,253 discloses a process for forming polyolefin fibers by mechanically agitating a supercooled solution of the polyolefin.

Copending patent application Ser. No. 874,687, filed Nov. 6, 1969, discloses a process for forming polyolefin fibers of high molecular weight by polymerizing an olefin in a suitable solvent at a high reaction rate and under shear stress.

Copending applications Ser. No. 27,053, filed Apr. 9, 1970, and Ser. No. 69,194, filed Sept. 3, 1970, disclose a process of producing high molecular weight polyolefin fibers by forming a fibrous gel and refining the gel to form fibers.

SUMMARY OF THE PRESENT INVENTION

The present process forms polyolefin fibers by forming a solution of a linear, high molecular weight polyolefin in a suitable solevent at a temperature above the metl dissolution temperature of the polyolefin, and dispersing the polyolefin solution in a suitable precipitant under conditions of shear stress sufficient to form polyolefin fibers. The fibers thus produced are fibrillatable, have a high surface area, form nonwoven sheets having good strength and optical properties, and are similar in size and gross morphology to natural cellulosic fibers.

The linear polyolefin solution may be formed by polymerizing an olefin in a suitable solvent in the presence of a coordination catalyst system and in the absence of a chain transfer agent at a temperature above the melt dissolution temperature of the polyolefin in the solvent. Alternatively, a preformed linear polyolefin of high molecular weight may be dissolved in a suitable solvent. The solvent chosen must have a solubility parameter that does not differ too greatly from that of the polyolefin to be formed.

The polyolefin solution is dispersed in a precipitant which is at least partially miscible with the solvent and which has a solubility parameter such that when mixed

the polyolefin solution forms a mixture that has a solubility parameter that does not differ too greatly from that of the polyolefin. Alternatively, the precipitant can be completely immiscible with the solvent, in which case the solubility parameter of the precipitant is immaterial.

DESCRIPTION OF PREFERRED EMBODIMENTS

It is essential for satisfactory fiber formation that the polyolefin employed in the present process has an ultra-high (viscosity average) molecular weight which, in the case of polyethylene and polypropylene is in excess of about 200,000, and preferably in excess of about 500,000. Phrased another way, the melt index of the polyolefin should be less than 0.1 and preferably substantially zero. If the polyolefin does not have a high molecular weight, few or no microfibrils will be formed and the product will consist almost entirely of lamellae. While a solution of polyolefin having a lower molecular weight can sometimes be formed into fibers by the process described herein, the fibers thus formed are exceedingly weak when compared to the fibers made up of microfibrils and macrofibrils, in accordance with the present process.

As stated previously, the polyolefin may be performed, i.e., pellets purchased from a manufacturer, but preferably the polyolefin is formed by polymerization in a suitable solvent at a temperature above the melt dissolution temperature and fibers formed directly from this solution.

Olefinic monomers which may be polymerized to form the fibers of the present invention are any of those which can be polymerized to a crystalline polyolefin by the employment of a coordination type of catalyst. The preferred monomers are the monoolefins, ethylene and propylene. Other olefins which may be employed are diolefins such as butadiene and isoprene; alpha olefins such as 1-butene, 1-pentene, and 4-methyl pentene-1; cycloalkyl and aryl substituted olefins such as vinyl cyclohexane and styrene. In addition to forming fibrous homopolymers of the foregoing olefins, fibrous copolymers and block copolymers may be formed by the employment of mixtures of the foregoing olefins.

Reference is made to copending application Ser. No. 69,194 for suitable polymerization techniques and conditions.

The temperature employed in forming the solutions of the present invention is maintained between about the melt dissolution temperature of the polymer to be formed and the decomposition temperature of the solvent or polymer. It is preferred to operate between the melt dissolution temperature and that temperature at which the polyolefin microfibrillar structure is destroyed. This temperature, which shall be called the "temperature of molecular randomization", is the temperature at which birefringence of the polymer solution disappears and can be determined by use of conventional techniques. If the temperature of polymerization or temperature of dissolution of a preformed polyolefin is above the temperature of molecular randomization, it has been found that the polyolefin solution must be subjected to a higher degree of shear stress during precipitation in order to form satisfactory fibers. It is generally preferable to operate between about 100° C. and about 165° C. for polyethylene.

The melt dissolution temperature of any particular polyolefin in a solvent is easily determined. Low con-

centrations of the polyolefin (e.g., 0.1 and 1.0 percent by weight) are placed into the solvent in a vial, which is sealed and placed in an oil bath. The temperature of the oil bath is raised slowly (10° C./hr.) until the last trace of polymer disappears. This temperature is the melt dissolution temperature. For ultra-high molecular weight (about 10 million) polyethylene at low concentration (0.1 percent by weight) in xylene, the melt dissolution temperature is 106° C. For a dilute solution of high molecular weight polypropylene in xylene, the melt dissolution temperature is 102° C. At higher concentrations the melt dissolution temperature approaches the melting point of the polyolefin. Lowering of molecular weight lowers the melt dissolution temperature at a given concentration.

The solvent employed in the process of the present invention is important to the formation of fibers. The solvent employed must have a solubility parameter which is not too different from the solubility parameter of the polyolefin.

A detailed discussion of solubility parameter (δ) is set forth in copending application Ser. No. 874,687, and in the book "Polymer Handbook", edited by Brandrup and Immergut, Interscience Publishers, 1966, pps. IV–341068; and in "Encyclopedia of Polymer Science and Technology", Vol. 3, Interscience Publishers, pps. 833–62.

In order to qualify as a suitable reaction medium for forming a solution of polyethylene, the solvent chosen should preferably be between about 6.5 and 9.5 (cal/cc)$^{1/2}$, and probably should not be outside the range of about 6.0–10.0 (cal/cc)$^{1/2}$.

The solubility parameter of polyethylene at 25° C. is about 7.9–8.3 (cal/cc)$^{1/2}$.

Similarly, the solvent chosen for polypropylene fiber formation should desirably have a solubility parameter approaching 7.9–8.2 (cal/cc)$^{1/2}$. The preferred range is between about 6.0 and 10.0 (cal/cc)$^{1/2}$.

Solubility parameter values for polyolefins other than polyethylene and polypropylene are to be found in Table 4, pages IV-362-67 of "Polymer Handbook", cited above, or can be calculated as set forth in copending application Ser. No. 874,687. It should be noted that the solubility parameters set forth in "Polymer Handbook" are calculated from the heats of vaporization at 25° C., and that different values will be obtained at the more elevated temperatures employed herein. At such elevated temperatures, the solubility parameter may approach close enough to that of the polyolefin to be formed to be a useful solvent, whereas at lower temperatures it would not be useful.

An alternate approach to the definition of solubility characteristics of solvents useful in the practice of the present invention is difference in solubility parameter (δ_s $-\delta_p$) of the solvent and polyolefin. For polyethylene, it has been determined that ($\delta_s$$-\delta_p$) should desirably be less than about $\pm$ 2.0 (cal/cc).

Alternatively, instead of polymerizing the olefin above the melt dissolution temperature, a previously prepared linear polyolefin of ultra-high molecular weight may be dissolved in a solvent having the solubility parameter characteristics previously described at such temperature and the resulting polymer solution treated in the same manner as for the polymer solutions formed by direct polymerization to form polyolefin fibers. In the case of polyethylene, the preformed polymer should be medium or high density polyethylene.

Low density polyethylene, such as is formed by high pressure processes without a coordination catalyst, does not form fibers by the process of the present invention. Similarly, in the case of polypropylene, atactic polypropylene does not form fibers.

The concentration of polyolefin in the solution should be greater than about 0.2 percent by weight. However, when the concentration exceeds about 20 percent by weight, the solution becomes too viscous to handle. Therefore, the concentration of polyolefin in the solution should not be greater than that amount which, at the temperature involved, causes the viscosity of the solution to exceed about 10,000 poises.

After formation of the polyolefin solution, fibers are formed by dispersing the solution under conditions of shear stress in a precipitant. "Precipitant" as used herein is defined as any material which, in conjunction with shear stress, will effect formation of polyolefin fibers when a polyolefin solution is dispersed therein and which will not dissolve more than about 0.2 percent by weight of the polyolefin at the precipitation temperature. The precipitant may be either miscible (partly or wholly) in the solvent or immiscible.

It has been found that in order to effect satisfactory fiber formation, the absolute sum (Σ) of (δ_p $-\delta_s$) + (δ_p $-\delta_{ppt}$) should be less than about 4.0, i.e., ($\delta_p$$-$ δ_s) + (δ_p $-$ δ_{ppt}) $= \Sigma$ and $\Sigma < 4.0$. By "absolute" sum is meant that plus or minus signs obtained with either (δ_p $- \delta_s$) or ($\delta_p - \delta_{ppt}$) are ignored. The solubility parameter of the precipitant is δ_{ppt}.

It is preferred to employ the same material as both solvent and precipitant. This is possible because polyolefins must be heated to above the melt dissolution temperature to go into solution, and the same material employed as the solvent acts as a nonsolvent or precipitant at temperatures below the melt dissolution temperature. Thus, a hot solution of polyolefin can be dispersed in cold solvent (precipitant) and precipitate as fibers under conditions of shear stress.

As stated previously, materials that are completely immiscible in the solvent may also be used as the precipitant. Examples of suitable immiscible materials include water, aqueous solutions of salts, ethylene glycol, glycerine, methyl alcohol, dimethyl sulfoxide and dimethyl formamide. Generally speaking, immiscible materials are those having a solubility parameter greater than about 14. It is believed that the reason why immiscible materials are operable as precipitants, while "poor" solvents that are miscible do not work, is that an emulsion is formed with the polyolefin solution as the dispersed phase wherein the continuous (precipitant) phase acts to rapidly cool the solvent containing the polyolefin to below the melt dissolution temperature whereby the polyolefin is precipitated as fibers.

One of the principal factors contributing to the successful formation of polyolefin fibers is the shear stress to which the reaction mass is subjected during dispersion of the polymer solution in the precipitant. Shear stress is essential to successful fiber formation. The mechanism of fiber formation relative to shear stress is not understood. However, it is hypothesized that by subjecting the mixture to a sufficient shear stress, the polyolefin microfibrils are not permitted to fold back upon themselves to thereby form globules of polymer. Instead, due to the shear stress, the microfibrils are stretched out into long chains of fibrils which aggregate themselves into fibers.

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The minimum shear stress required for the formation of fibers is dependent somewhat upon the polyolefin and upon the type of solvent and precipitant employed. The minimum shear stress required for fiber formation is readily determinable by employing the procedures and apparatus described herein for any particular polyolefin solvent, precipitant and temperature at increasing agitator blade velocities, until fiber formation is noted. The agitator blades employed for determining minimum shear stress with the apparatus described should be as close as possible to flat plates in shape and at zero angle of incidence to the flow of fluid past them whereby the minimum shear stress for fiber formation can then be calculated by employing the following equation:

$$T = C_f \cdot dv^2/2 \cdot 1/g$$

where

T = mean shear stress at the flat blade agitator surface

v = mean velocity of main bulk of fluid

d = fluid density

C_f = mean drag coefficient for total dimensions f the blade in the direction of flow

g = gravitational constant

Since the minimum shear stress for fiber formation is dependent upon several factors, an absolute figure for the minimum shear stress cannot be given.

As the shear stress increases above the minimum shear stress required for fiber formation, the fibers tend to become longer. Although no upper limit of shear stress has been discovered beyond which no fiber formation occurs, there are obviously upper limits imposed by practical considerations such as equipment limitations and size of fiber desired. Also, at extremely high rates of shear, fibers may be torn apart, which may not be desirable.

The rate of introduction of the polyolefin solution into the precipitant is not critical. However, it is desirable to effect a uniform dispersion of the polyolefin solution in the precipitant in order to provide more uniform heat transfer and/or shear stress upon individual units of the solution mass.

Therefore, the rate of introduction preferably should not be so great that substantially nonuniform dispersion is obtained.

The temperature difference between the polyolefin solution and the precipitant is not a factor in fiber formation, and, in fact, the precipitation can be carried out isothermally, i.e., where the solvent and precipitant are miscible, the temperatures can be the same. The precipitant may be higher in temperature than the polyolefin solution as long as the solvent and precipitant are miscible and the temperature of the precipitant is less than the melt dissolution temperature of the polyolefin therein. Where the precipitant is immiscible with the solvent, it must be at a temperature such that, for the volumes involved, the polymer solution is lowered to a temperature below the melt dissolution temperature.

The pressures employed in both the preparation of the polyolefin solution and in dispersing the solution in the precipitant are not a factor in fiber formation. Whereever possible, atmospheric pressures are employed. Positive pressure may be applied to the polymer solution to force it from its container into the precipitant. Positive pressure may also be required in preparation of the polyolefin solution where the solvent employed

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has a boiling point lower than the melt dissolution temperature of the polyolefin at atmospheric pressure.

The dispersion of polyolefin solution in precipitant must be carried out by introducing the solution to the precipitant. If the reverse order is employed, i.e., the precipitant is added to the solution, good fibers are not obtained.

The particular apparatus employed in preparing polyolefin fibers by the process of the present invention is not critical. The polyolefin solution may be simply poured from its container into a body of precipitant under conditions of agitation. One satisfactory method of accomplishing this is to pour the polyolefin solution into a Waring Blendor containing the precipitant under mechanical agitation. Other suitable devices include the apparatus illustrated in FIGS. IV and X of U.S. Pat. No. 2,988,782.

Various additives such as antioxidants, pigments, dyes, adhesion promoters, etc., may be mixed with the polyolefin solution or the precipitant prior to or during precipitation.

The viscosity-average molecular weight (M_v) of the polyolefins usable in the present process ranges up to about 20 million and above, preferably between about one-half million to about 20 million in view of the improved strength properties over fibers of lower molecular weight polyolefin. However, if the molecular weight (M_v) falls below a certain minimum value, which for polyethylene and polypropylene is about 200,000, satisfactory fibers will not be obtained.

The molecular weight distributions of the linear polyolefins such as polyethylene usable in the present process (as measured by the ratio of the weight-average molecular weight (M_v) to number-average molecular weight (M_n)) is not critical.

The fibers of the present invention are not completely uniform in cross-section along the length thereof. This is an advantage over staple fibers, which have uniform cross-section, because such nonuniformity contributes to the web forming properties of the fibers. A majority of the fibers of the present invention are oval or circular in cross-section, rather than ribbon-shaped.

When the fibers of the present invention are classified according to TAPPI standard test No. T–233 SU–64 using the Bauer-McNett classifier (having screens of 20, 35, 65, 150 and 270 mesh arranged in sequence), more than 50 percent by weight are retained on the 150 mesh or coarser screens. Polyolefin pulps are made wherein the number average diameter of a majority of the fibers exceeds about 10 microns; such pulps are particularly useful for making synthetic papers. The average length of a majority of the fibers (by number) is greater than about 0.5 mm. Fibers having a diameter up to 200 microns or higher and lengths up to 5 mm or more have been observed.

The fibers of the present invention are made up of fibrils, and can therefore be refined or beaten to produce fibrillation in a manner similar to natural cellulosic fibers. These fibrils are generally larger than about 1.0 micron in diameter. The fibrils are in turn made up of "microfibrils" which are generally on the order of 300 to 10,000 angstrom units in diameter and can usually be seen only by the employment of a scanning electron microscope.

One of the most distinguishing features of polyolefin fibers formed by the process of the present invention is

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the high surface area provided, due at least in part to the microfibrillar and macrofibrillar structure of the fibers. Staple polyolefin fibers typically have surface areas (as measured by the conventional BET gas adsorption technique) of much less than about 1.0 square meter/gram. For example 3 denier melt spun polyethylene staple has a surface area of about 0.16 m²/gram. Cellulose fibers (Whatman No. 1 filter paper) have a surface area of about 1.0 square meter/gram. The polyolefin fibers of the present invention generally have a surface area greater than 1.0 square meter/gram, gen-

In the tables below, the following abbreviations for solvent names have been used: c-hex, cyclohexane; xyl, xylene; pyr, pyridine; o-DB, o-dichlorobenzene; B-alc, benzyl alcohol; and n-C₈, n-octane.

EXAMPLE 1

Varying Molecular Weight

This example illustrates the importance of molecular weight in forming polyolefin fibers. The conditions for the various runs are set forth in Table 1A below. High

TABLE 1A.—PROCESS CONDITIONS

Run number	1	2	3	4	5	6	7	8
Solution parameters:								
$M_v \times 10^{-3}$	56	58	68	130	195	760	810	2,000
Solvent	xyl	xyl	xyl	xyl	xyl	xyl	xyl	xyl
Concentration(g./100 ml.)	1	1	1	2	1	1	1	1
T, °C	110	110	110	110	120	120	120	120
Volume (ml.)	100	110	100	100	100	100	75	100
Precipitation parameters:								
Precipitant	c-hex	c-hex	c-hex	xyl	c-hex	pyr	pyr	c-hex
Volume (ml.)	300	300	300	300	250	200	200	250
T, °C. (precipitant)	25	25	25	25	25	25	25	25
T, °C. (final)	35	40	35	41	40	40	40	40
Mixer, r.p.m.	6,500	6,500	6,500	6,500	6,500	6,500	6,500	6,500
Addition time (seconds)	5	5	5	5	2	2	2	15

erally higher than about 10 m²/gram, and as high as 100 m²/gram or higher.

SPECIFIC EXAMPLES

The same general procedure was followed in all of the examples described below. The specific conditions, such as temperatures, concentrations, etc., we specified in the examples.

In general, a weighed sample of polyolefin is placed into a volume of solvent in a flask and the flask placed into a heated oil bath. The contents of the flask is then raised to a temperature above the melt dissolution temperature of the polyolefin and a solution formed. The polyolefin solution is then placed into a vertical tube heated by an external steam coil and having a spinneret disc located at the bottom end thereof. A one-quart Waring Blendor containing a volume of precipitant is placed directly below the tube. The agitator of the Waring Blendor is activated and the polyolefin solution forced from the heated tube through the spinneret into the precipitant in the Blendor by means of positive nitrogen pressure introduced into the top of the tube.

The tube employed in the examples is a brass tube 14 inches in length with an inside diameter of 1 ¼ inches. The tube is wrapped with a steam coil and covered with glass wool insulation. A brass ball valve is located adjacent the bottom of the tube with a spinneret disc located at the bottom of the tube, below the ball valve. The spinneret disc is 9/16 inch in diameter and contains eight holes 1/32 inch in diameter located in a circle having a ¼ inch radius. For some runs, the disc had four 1/16 inch holes.

density polyethylenes having the viscosity average molecular weight specified were used on all runs. The products obtained are described in Table 1B below. It can be seen by reference to Table 1B below that unless the molecular weight exceeds a value greater than Run 5, suitable fibers are not obtained.

TABLE 1B: PRODUCT DESCRIPTION

Run No.	Description of Product
1	No fiber, only flocs.
2	No fiber, only flocs.
3	No fiber, only flocs.
4	No fiber, only flocs.
5	Very fibrous; fibers were fine, looked soft.
6	Very long and slender fibers; length was 1–5 mm and diameter was up to 0.2 mm; fibers were fibrillated.
7	Very long fibers (1–5 mm); diameter was 0.1–0.3 mm.
8	Very long, fibrillated fibers.

EXAMPLE 2

Miscible Solvents and Precipitants; Comparison of Solubility Parameters

This example illustrates the importance of having a $\Sigma < 4.0$ where the solvent and precipitant are miscible. Table 2A sets forth the conditions employed in the various runs, and Table 2B sets forth solubility parameter information. The solubility parameters specified for the high density polyethylenes employed in all runs, the solvents and the precipitants are for 25° C and not corrected for temperature. It can be seen by reference to Table 2B below that when $\rho >$ about 4.0, the product obtained is not fibrous.

TABLE 2A.—PROCESS CONDITIONS

Run number	1	2	3	4	5	6	7	8	9
Solution parameters:									
$M_v \times 10^{-3}$	2,000	2,000	195	800	760	195	195	760	195
Solvent	xyl	xyl	o-DB	xyl	n-C₈	o-DB	o-DB	n-C₈	o-DB
Concentration (g./100 ml.)	1	1	1.33	1	1	1.33	1	1	1.33
T, °C	120	120	120	120	120	120	120	120	120
Volume (ml.)	100	100	100	75	100	75	85	50	75
Precipitation parameters:									
Precipitant	c-hex	xyl	c-hex	pyr	pyr	o-DB	pyr	B-Alc	(*)
Volume (ml.)	250	250	300	200	200	225	300	165	225
T, °C. (precipitant)	25	25	25	25	25	25	25	25	25
T, °C. (final)	40	40	40	40	40	40	40	40	40
Mixer, r.p.m.	6,500	6,500	6,500	6,500	6,500	6,500	6,500	6,500	6,500
Addition time, sec.	15	15	4	4	4	4	4	4	4

*1,2-propylene glycol cyclic carbonate.

TABLE 2B: SOLUBILITY PARAMETER AND PRODUCT DESCRIPTION

Run No.	$|(\delta_p - \delta_s)|$	$|(\delta_p - \delta_{ppt})|$	Σ	Description
1	0.5	0.1	0.6	Very long, fibrilliated fibers.
2	0.5	0.5	1.0	Very long, fibrillated fibers.
3	1.7	0.1	1.8	Long (up to 5 mm), slender (0.1–0.2 mm) fibers.
4	0.5	2.3	2.8	Long fibers (1–5 mm); 0.1–0.3 mm diameter.
5	0.7	2.3	3.0	Very long (up to 5 mm); slender (up to 0.2 mm) fibrillated fibers.
6	1.7	1.7	3.4	Elongated, borderline fibers.
7	1.7	2.3	4.0	Elongated, borderline fibers.
8	0.7	3.8	4.5	Swollen ribbons and tubes.
9	1.7	5.0	6.7	Gels, sheets, tubes and ribbons.

NOTE: $\delta_p = 8.3$

EXAMPLE 3

Comparison of Polyethylene Fibrids with the Fibers of This Invention

Polyethylene "fibrids" were prepared substantially in accordance with Example 1 of U.S. Pat. No. 3,431,242.

In 800 ml of xylene was dissolved 6.5 g of Doxomean 281 (a high molecular weight polyglycolamine surfactant manufactured by the Wyandotte Chemicals Corporation); there was then added 16 g of a linear polyethylene (melt index of about 0.2, viscosity mol. wt. 130,000 manufactured by Phillips) and 0.8 g of N-phenyl-2-naphthylamine (as an antioxidant). Under a nitrogen atmosphere the mixture was stirred in a 125° C oil bath until solution was complete. This solution was forced through a perforated plate containing four 1-mm diameter holes into a 1-gal Waring Blendor running at high speed and containing 2,500 ml of water at room temperature. This seemed to give better results than pouring the solution as described in the patent. This took about 10 seconds and the Blendor was turned off after 15 seconds more. The product was a gelatinous mass floating on the water. The product was skimmed off, filtered and exchanged to water as follows:

The mass was well suspended in 2,000 isopropyl alcohol in a Waring Blendor at high speed for 5 seconds, filtered and the process repeated once more with isopropyl alcohol, once with 50/50 isopropyl alcohol/water and finally with water. The surface area of the poorly shaped fibers (irregular and nonuniform) and irregular pieces obtained was 4.5 m²/gram.

In comparison with the above fibrids, polyethylene fibers were made by forming a solution (2 grams/100 ml) of high density polyethylene ($M_v = 195,000$) in xylene at 120° C and containing 0.1 percent of the same antioxidant as above. This solution (800 ml) was dispersed in 2500 ml of xylene at a temperature of 25° C with the Waring Blendor operating at 10,000 rpm. The time of addition was 10 seconds and the final temperature of the mixture was about 40° C. The product obtained was very slender, fibrillated fibers having a surface area of 9.3 m²/gram.

EXAMPLE 4

Use of Immiscible Precipitant

This example illustrates the use of an immiscible pre-

cipitant to form fibers in accordance with the present invention. A high density polyethylene having a viscosity average molecular weight of 195,000 was dissolved in xylene (2 grams/100 ml) at 120° C. The polyethylene solution was dispersed in 300 ml of water from the tube previously described fitted with a spinneret having four 1/16-inch holes. The initial water temperatre was 25° C and the final temperature was about 40° C. The Waring Blendor agitator was operated at 6500 rpm. The time for addition of the polyethylene solution was 4 seconds. Fibers were obtained having a length of 0.1–1.0 mm, a diameter less than about 0.1 mm, and a surface area of 11.8 m²/gram.

EXAMPLE 5

Use of Non-mechanical Shear Stress

This example illustrates the use of non-mechanical shear stress, i.e, shear stress effected by fluid frictional forces. A high density polyethylene having a viscosity average molecular weight of 195,000 was dissolved in 300 ml of xylene under a nitrogen atmosphere at 125° C along with 0.3 gram of N-phenyl-2-naphthylamine antioxidant. The solution was placed into a 500-ml stainless steel bomb fitted with a ball valve at the outlet and a spinneret disc with four 1/16-inch holes located beyond the valve. The bomb was then pressurized to 200 psig and the nozzle containing the spinneret immersed about one-half inch under the surface of 1 liter of cyclohexane in a 2-liter beaker. The valve was opened to discharge most of the contents of the bomb into the precipitant as jets from the spinneret. A mass of white fibers was collected and determined to consist of rather long, slender fibers 0.5–3.0 mm long and having a diameter of 0.05–0.2 mm.

We claim:

1. A process of forming polyolefin fibers having a microfibrillar structure comprising forming a solution of a linear, crystalline polyolefin in a solvent having a solubility parameter between about 6 and 10 (cal/cc) at a temperature above the melt dissolution temperature of the polyolefin, the concentration of the polyolefin in the solution being between about 0.2 and 20 percent by weight, the linear polyolefin having a viscosity average molecular weight above about 200,000 and a melt index of substantially zero, and dispersing the polyolefin solution in a precipitant for the polyolefin in a system subjected to a shear stress effective to form polyolefin fibers having a microfibrillar structure.

2. The process of claim 1 wherein the solvent and precipitant are miscible and are selected so that the quantity $|(\delta_p - \delta_s)| + |(\delta_p - \delta_{ppt})|$ is less than about 4.0, where δ_p = the solubility parameter of the polyolefin, δ_s = the solubility parameter of the solvent δ_{ppt} = the solubility parameter of the precipitant.

3. The process of claim 2 wherein the polyolefin is selected from the group consisting of polyethylene having a density greater than about 0.926 and polypropylene having less than about 5.0 percent by weight atactic content.

4. The process of claim 3 wherein the polyolefin has a viscosity average molecular weight from about 500,000 to about 20 million.

5. The process of claim 1 wherein the solvent and precipitant are immiscible.

6. The process of claim 1 wherein the polyolefin solution is formed by polymerizing an olefin in the solvent in the presence of a coordination catalyst at a temperature above the melt dissolution temperature of the

polyolefin to be formed, the polymerization being carried out in the absence of any chain transfer agent.

7. The process of forming polyethylene fibers having a microfibrillar structure comprising forming a solution of a polyethylene having a viscosity average molecular weight greater than about 200,000, a melt index of substantially zero and a density greater than about 0.926 in a solvent having a solubility parameter between 6.0 and 0. (cal/cc)$^{1/2}$ at a temperature between about 110° and 165°C and above the melt dissolution temperature, the concentration of the polyethylene in the solution being between about 0.2 and 20 percent by weight, and introducing the polyethylene solution into a precipitant in a system subjected to a shear stress effective to form polyethylene fibers the majority of which have a length greater than about 0.5 mm and a diameter greater than 10 microns, the precipitant being at least partially miscible with the solvent, the solvent and precipitant being selected to have solubility parameters that are such that the quantity $(\delta_p - \delta_s) - (\delta_p - \delta_{ppt})$ is less than about 4.0, where δ_p = the solubility parameter of polyethylene, δ_s = the solubility parameter of the solvent and δ_{ppt} = the solubility parameter of the precipitant.

8. The process of claim 7 wherein the solvent and precipitant are the same material, the precipitant being at a temperature such that the temperature of the mixture of solution and precipitant is less than the melt dissolution temperature of the polyethylene therein.

9. The process of forming polyolefin fibers comprising forming a solution of a crystalline polyolefin selected from the group consisting of polyethylene and polypropylene in a solvent having a solubility parameter between about 6 and 10 (cal/cc)$^{1/2}$, said polyolefin having an essentially zero melt index, the concentration of the polyolefin being between about 0.2 and 20 percent by weight of the solution, and introducing the polyolefin solution into a precipitant in a system subjected to a shear stress effective to form polyolefin fibers having a length greater than about 0.5 mm and a diameter or width greater than about 10 microns.

10. The process of claim 9 wherein solvent and precipitant are miscible and the solubility parameter of the polyolefin, solvent and precipitant are selected so that the quantity $(\delta_p - \delta_s) + (\delta_p - \delta_{ppt})$ is less than about 4.0, where δ_p = the solubility parameter of polyethylene, δ_s = the solubility parameter of the solvent and δ_{ppt} = the solubility parameter of the precipitant.

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