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3,402,231

PROCESS FOR PREPARING SYNTHETIC FIBERS FOR PAPER PRODUCTS

Filed May 21, 1964

2 Sheets-Sheet 1

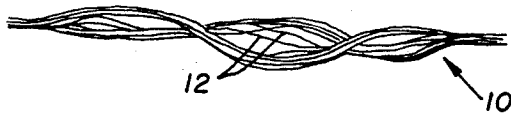


FIG. 1.

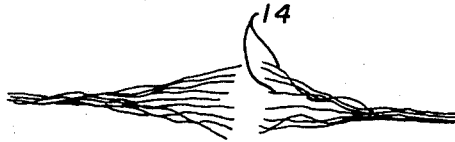


FIG. 2.

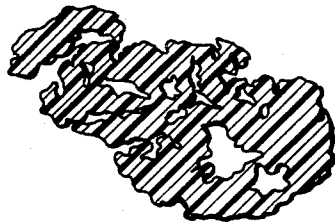


FIG. 3.

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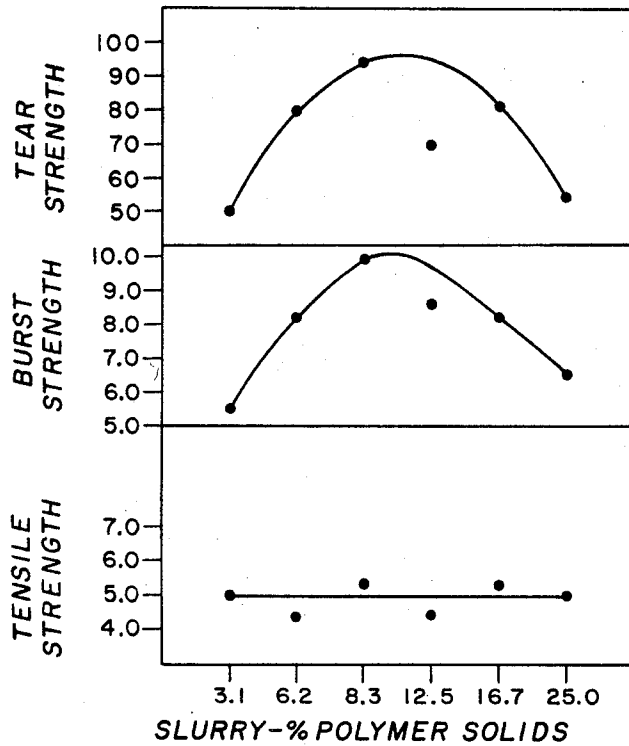


FIG. 4.

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PROCESS FOR PREPARING SYNTHETIC FIBERS FOR PAPER PRODUCTS

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ABSTRACT OF THE DISCLOSURE

Fibrous filamentary materials are produced from polyacrylonitrile polymers dispersed in water containing sodium carboxymethylcellulose. The dispersion is heated in a pressure vessel to form a viscous polymer melt which is extruded into a restricted area wherein a high velocity stream of steam is directed transverse to the travel of the emerging extrudate imparting a stretch thereto. The filamentary materials are comprised of loosely bonded fibrils which can be separated easily by beating or other abrasive forces.

The present invention relates to the production of shaped articles from acrylonitrile polymers. More particularly, the invention relates to a continuous process for preparing novel cross sectional fibers suitable for paper products which are comprised of a multitude of loosely bonded fibrils by the use of a non-solvent impregnant.

Heretofore, the production of synthetic filaments has been directed almost entirely toward the manufacture of textiles. The discovery has now been made that paper and other non-woven materials can be manufactured from acrylonitrile polymers. These products exhibit several beneficial properties which are exceptionally desirable. Some excellent qualities exhibited by synthetic paper made from acrylonitrile polymers are added strength, dimensional stability, weather resistance, color stability, and others. The synthetic fibers which are produced by conventional spinning processes for utilization in the textile industry are non-fibrillating and must be bonded by a suitable resin or by other well known methods. Therefore, non-fibrillating fibers are not economically suitable for making paper or unbonded non wovens.

In the manufacture of textile products the conventionally produced synthetic fibers are competitive with the natural fibers both in cost and quality. Past experience has shown that synthetic fibers are not similarly competitive in the paper industry. Although certain types of specialty paper having excellent properties can be made from the non-fibrillating acrylonitrile fibers, the known methods employ expensive solvents in the preparation of such fibers whereupon the cost is increased to the extent that the resulting paper is not competitive with paper produced from derivatives of the natural polymers such as cellulose.

Filamentary materials are conventionally produced from acrylonitrile polymer by processes generally referred to by the art as wet spinning and dry spinning. In each of the above processes the basic method is the same. The dry polymer is dissolved in a suitable organic solvent to form a viscous spinning solution suitable for extrusion through an orifice. Thereafter, the extruded polymer solution is converted to solid filaments by removing the solvent. In the wet spinning process this is accomplished by extruding into a liquid bath in which the solvent dissolves but in which the polymer is insoluble. According to the dry spinning process a solid is achieved upon volatilization of the solvent. In both of these processes the loss of the solvent or the process employed to obtain re-

covery thereof is expensive. If a process were employed whereby an inexpensive non-solvent such as water can be substituted for the organic solvent to reduce the cost substantially in the preparation of fibers from acrylonitrile for utilization by the paper industry, it is foreseeable that specialty products prepared from such fibers would be competitive with products prepared from cellulose and the like.

Various methods have been employed in an attempt to prepare shaped articles from infusible acrylonitrile polymer by the use of non-solvent impregnants. These methods have been limited, however, to batch-type processes such as is disclosed in U.S. Patent 2,585,444. Filamentary materials produced by the batch-type method are expensive because of limited production, and duplication of properties from batch to batch is not always achieved. Furthermore, the filamentary materials produced from acrylonitrile polymer dispersed in a non-solvent impregnant by the known processes are generally cellular in nature and will not fibrillate. These cellular filaments do not possess enough strength when beaten and converted to a slurry to support itself in a wet water-leaf form. Thus, the filaments must be highly fibrous and actively interlock when beaten to be suitable for the manufacture of synthetic paper products and the like. From the discussion above it is evident that a process to economically prepare fibrous materials from acrylonitrile polymer for the paper industry which exhibit exceptional fibrillating properties, whereby the cost of converting the fibers to a finished product is reduced, would be highly desirable.

It is therefore an object of the present invention to produce a filament having a novel cross section from an acrylonitrile polymer by using water as an impregnant.

Another object of the present invention is to provide a continuous process for producing shaped articles from a slurry of acrylonitrile polymer mixed with water and a suspension agent.

Still another object of the present invention is to provide a novel filament comprised of a multitude of loosely bonded fibrils coextensively aligned with the longitudinal axis of the fiber.

A further object of this invention is to produce economically acrylonitrile polymer filaments having outstanding properties for use in making paper and other non-woven products.

Other objects of the present invention will become apparent to those skilled in the art from the following more detailed description.

The objects of this invention have been realized by preparing a slurry of acrylonitrile polymers with water which preferably contains a small amount of a water soluble cellulose derivative such as sodium carboxymethyl cellulose (SCMS) which serves as a suspension agent and also improves the fibrillating characteristics of the product, continuously pumping the slurry through a heat exchanger while under pressure to convert the slurry to a viscous melt in a heated pressure vessel and extruding the melt through a jet into a stream of steam in a restricted stretch zone wherein a fibrous material is developed from the extruded melt and simultaneously stretched. The steam in the stretch zone provides the temperature, humidity, and pressure necessary to form a fibrous material having novel properties. By "viscous melt" is meant dispersed polymer particles suspended in the non-solvent solution when the slurry is subjected to suitable heat and pressure. The system pressure is determined by the temperature, flow rate, slurry solids content, and the size and number of holes in the jet.

The polymer employed in this invention may be polyacrylonitrile, copolymers of acrylonitrile, including binary and ternary polymers containing at least 80 percent

by weight of acrylonitrile in the polymer molecule, or a blend comprising polyacrylonitrile or copolymers comprising acrylonitrile with from 2 to 50 percent of another polymeric material, the blend having an overall polymerized acrylonitrile content of at least 80 percent by weight. While the preferred polymers employed in the instant invention are those containing at least 80 percent of acrylonitrile, generally recognized as the fiber-forming acrylonitrile polymers, it will be understood that the invention is likewise applicable to polymers containing less than 80 percent acrylonitrile.

For example, the preferred polymer may be a copolymer of from 80 to 98 percent acrylonitrile and from 2 to 20 percent of another monomer containing the $>C=C<$ linkage and copolymerizable with acrylonitrile. Suitable mono-olefinic monomers, include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates, such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromo-ethylene; methacrylonitrile; acrylamide and methacrylamide; alpha-chloroacrylamide; or monoalkyl substitution products thereof; methylvinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate, and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic esters; N-vinylcarbazole; vinyl furane; alkyl vinyl esters; vinyl sulfonic acid; ethylene alpha, beta-dicarboxylic acids or their anhydrides or derivatives, such as diethylcitrate, diethylmesaconate, styrene, vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine etc.; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5 methyl-1-vinylimidazole, and other $>C=C<$ containing polymerizable materials.

The polymer may be a ternary or higher interpolymer, for example products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile, enumerated above. More specifically, and preferably the ternary polymer comprises acrylonitrile, vinyl acetate, and styrene. For example, the ternary polymer which contains from 80 to 98 percent of acrylonitrile, from 1 to 10 percent of styrene, and from 1 to 18 percent of another monomer such as vinyl acetate.

The polymer may also be a blend of a polyacrylonitrile or of a binary interpolymer of from 80 to 99 percent acrylonitrile and from 1 to 20 percent of at least one other $>C=C<$ containing substance with from 2 to 50 percent of the weight of the blend being a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of at least one other $>C=C<$ containing polymerizable monomer.

In accordance with the present invention, the polymer-water-SCMC slurry may contain from about 2 to 30 percent polymer solids, and preferably contains from 6 to 18 percent polymer. Lower concentrations of polymer may be used with acceptable results, but it is not economically desirable since greater quantities of slurry must be pumped and heated to produce the same quantity of paper. Polymer concentrations in excess of 30 percent are undesirable since the mixture assumes the properties of a wet polymer cake rather than a flowing slurry, and can not be pumped, but must be moved with screw conveyors and the like. Furthermore, the quality of the fiber product is generally poorer when the slurry solids are less than 6 percent or in excess of 18 percent. The slurry may also contain from 0 to 20 percent sodium carboxymethyl cellulose (SCMC) based on the weight of polymer, and preferably contains from 1.0 to 5.0 percent. Concentrations of SCMC at the preferred level promotes longi-

tudinal splitting or separation of the fibrils. When using SCMC concentrations of less than about 1.0 percent the fibrous product of the invention does not possess the high fibrillating characteristics which are desired. At SCMC concentrations greater than 5.0 percent, the fibrous product is slubby or includes small hard nodules which are undesirable for use in paper making.

The polymer slurry is moved with a positive displacement pump through a first heat exchanger wherein the temperature of the slurry is increased to about 140° C., which is less than the temperature required to form the polymer melt. The hot slurry is then passed through a second exchanger wherein it has a short dwell time and is heated to about 190° to 205° C., but preferably 201° to 203° C. to form the polymer melt which is then extruded. It is desirable for optimum results that the slurry be heated in excess of 200° C., but that the exposure time at this temperature be limited to a few seconds (usually less than one minute) to prevent decomposition of the acrylonitrile polymers. As the temperature of the slurry is increased to above about 150° C., a two phase system consisting of a lower polymer melt layer and an upper water layer is formed. The polymer melt phase is comprised of a viscous mass of polymer and water, while the water phase contains very little polymer. Both phases are extruded simultaneously through the vertically positioned jet orifices.

The novel filaments produced in accordance with the present invention are comprised of a multitude of very fine fibrils coextensively aligned with the axis thereof and are characterized by highly porous cross-sections. On an average the pores account for approximately 60 percent of the cross-sectional area. The fibrils are intermittently connected to each other to form a loosely constructed strand. This condition is imparted to the strands by the process employed in accordance with the invention as described hereafter. By extruding the melt into a low pressure area and simultaneously directing a high velocity stream of steam thereon, strands having unusual cross-sectional constructions characterized by large holes and fissures are developed. The larger holes are caused by the escapement of the water content of the melt flashing to steam upon entering the low pressure area. Immediately upon discharge of the melt from the heated pressure vessel through the jet orifices, the strands are formed and stretched by the force imposed on the strands from the stream of steam which is directed transversely against the extruded strands. This is accomplished by extruding into a restricted area and drafting the newly formed strands from the orifices in a stretch zone directed radially outwardly from said orifices. Thus, the cavities or fissures are further elongated in the stretch zone produced by the high velocity steam passing through the restricted passage-way.

The loosely bonded condition of the strands is believed to be caused by the combination of the escaping steam and the application of steam on the emerging strands in the restricted area at the face of the jet. This position is substantiated by the fact that a melt extruded in the absence of the stream of steam is comprised of a filmy cellular substance. Such a material has very little tendency to fibrillate and, accordingly, is not suitable for making paper products. Since fibrillous materials can be more readily processed for utilization in the paper making industry, the unusual tendency of the strands discussed herein to fibrillate enhances substantially the use thereof for making synthetic paper products.

The longitudinal orientation of the fibrils and the longitudinally extending void areas occurring between the fibrils establish a loosely bonded condition in the highly fibrillated strands. A better understanding of this condition may be obtained by reference to the drawing in which:

FIGURE 1 is a microscopic view at about two power

magnification of the strand in which a portion thereof has been scraped to separate the fibrils;

FIGURE 2 is a microscopic view at about two power magnification of a broken strand illustrating the separating propensity of the fibrils;

FIGURE 3 is a microscopic view at about ten power magnification of a cross-section illustrating the fibrillated structure of the strand; and

FIGURE 4 is a graphic illustration of the physical properties shown plotted as ordinates versus percent polymer solids plotted as abscissas of each slurry beaten in a conventional beater for 60 minutes and formed into handsheets.

The strands or filaments of this invention are essentially continuous in nature except for occasional disruptions in their continuity which may be caused by the escape of the non-solvent impregnant from the heated pressure vessel. However, the tow bundle comprising the several strands can be produced in endless lengths. The impregnant is flashed off at intermittent intervals randomly from the several orifices to interrupt extrusion of the filament-forming polymeric material. Because of the disrupted ends, which become entangled in the tow bundle, the tow is preferably collected in a container, but may be collected on a bobbin if desired. Thereafter, the tow can be converted into staple fiber for subsequent processing.

In an attempt to better illustrate the fibrous construction of the filamentary materials, a filament in which a segment thereof has been subjected to a longitudinal scraping action is shown in FIGURE 1. The bond between the fibrils 10 of strand 12 can be broken to separate the individual fibrils by scraping the thumbnail along the strand several times. Another method of demonstrating the looseness of the bonds between the fibrils can be performed by breaking a filament and observing the spreading propensity of the several fibrils 14 as illustrated in FIGURE 2.

The filamentary materials of this invention are manufactured predominantly for utilization in the production of paper and non-woven materials. When converted into pulp on commercial paper-pulping machinery, these filaments produce slurries which will form waterleaves having a greater tenacity than is required to permit the necessary processing thereof. Generally the filaments are not suitable for making a wide variety of textile products because of the rough and porous condition exhibited by these filaments. FIGURE 3 is illustrative of the number of cracks and fissures running lengthwise the filaments.

The material extruded from a single hole or orifice forms a filament which may be characterized by a wide denier and strength variations. The denier may be from 40 to 80 but is preferably about 44. Average physical properties of the 44 denier filaments has been discovered to be as follows: tenacity 2.25 grams per denier; elongation 10 percent; and modulus 53.5.

The filaments may be cut into staple, suspended in water and beaten in a standard paper beater whereby a high degree of fibrillation will be developed. The beaten fiber may then be laid on a screen and a desirable sheet will result therefrom. Quality of the fibrous material may be tested by preparing paper sample sheets in the manner described hereinafter. A collection of tow from the extruding nozzle is cut into approximately one half inch staple lengths. About 150 grams of the staple and 20 liters of water are placed in a container and slurried to form a water slurry containing 0.75 percent fiber solids. The slurry is transferred to a 1½ lb. Valley beater and beaten for 40 to 90 minutes with a 12 pound weight. The degree of fibrillation can be estimated from time to time by a visual examination of a removed sample. When a satisfactory amount of fibrillation has been achieved the sample is transferred to a Nobel and Wood Sheeting Machine for forming 2.5 gram hand sheets 8 x 8 inches and

dried. After the sheet has been pressed and dried completely, it is subjected to a series of physical tests to determine the strength of the finished product. These tests include the Mullins burst test and the Elmendorf tear test. A 1 x 6 inch strip is broken on the Scott Model DH tensile tester to determine the tensile strength of the sample. Results obtained from these tests are the equivalent of 37 pound basis weight paper.

Also, the cut staple may be processed dry to form a soft batt. The individual fibers are subjected to a longitudinal scraping action either by carding or processing in the Rando Webber to develop a fibrillous batt which can be matted to form a soft batt. Such a batt may be utilized as a padding for upholstery applications, filter media, and the like. Utilization thereof is enhanced because of the hydrophobic properties possessed by batting produced from the filaments of this invention and their ability to resist the action of certain chemicals.

In the following examples, which are given for illustrative purposes only and are not limitative, the parts are by weight unless otherwise stated.

Example I

25 parts of a copolymer comprised of 93% acrylonitrile and 7% vinyl acetate and having an average molecular weight of 110,000 was slurried in 300 parts of a water solution containing 0.50 parts of sodium carboxymethylcellulose to produce a slurry of 6.2% polymer solids. The slurry was pumped under pressure through a first heat exchanger wherein the temperature was elevated to 140° C., and thereafter through a second heat exchanger wherein the temperature was further increased to 202° C. to form a two phase polymer melt-water system.

The two phase system was then extruded horizontally through a vertical spinnerette containing 27 holes 0.015 inches in diameter into a high velocity stream of steam directed vertically downward at approximately 100 p.s.i.g. where the filaments were solidified and stretched. The fibrous product was produced at a rate of 2000 feet per minute and collected in a drum as a continuous tow.

The fibrous tow was cut to ½ inch staple and processed into sample sheets of paper as described above. The physical properties of paper sheets obtained at 10 minute intervals over beating times of 40 to 90 minutes are shown in Table I.

All values are normalized to 2.5 gram handsheets which are the equivalent of 37 pound basis weight paper.

TABLE I

Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
40	107	6.5	3.2
50	106	7.4	4.0
60	79	8.2	4.4
70	68	7.4	4.8
80	64	8.0	4.6
90	48	7.7	5.6

Example II

A slurry of the composition described in Example I was extruded at a temperature of 195° C. The physical properties of the handsheets made from these fibers after a beating time of 60 minutes are listed in Table II below and compared with values obtained for Example I.

TABLE II

Extrusion Temp., ° C	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lb./in.)
195	67	7.7	4.9
202	79	8.2	4.4
(202-195)	+12	+0.5	-0.5

Example III

The process as described in Example I was repeated with five different polymer slurry concentrations as shown in Table III. Handsheets of paper made from each of the conditions were evaluated according to the procedure

described above, and had physical properties as shown in Table III.

TABLE III

	Slurry Composition				Paper Physical Prop. ¹		
	Polymer (parts)	SCMC (parts)	H ₂ O (parts)	Solids (percent)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lb./in.)
A-----	12.5	0.25	300	3.1	50	5.5	5.0
B-----	33.6	0.65	300	8.3	94	10.0	5.4
C-----	50.0	1.0	300	12.5	70	8.7	4.5
D-----	66.6	1.3	300	16.7	81	8.1	5.2
E-----	100	2.0	300	25.0	55	6.6	5.0

¹ Paper obtained after 60 minute beating time.

The foregoing data clearly illustrates that the paper tear strength and burst strength are affected by the percent solids concentration of the slurry while tensile strength is not affected substantially. As illustrated by the graphical representation of these data in FIGURE 4 of the accompanying drawing, the tear strength and burst strength are maximum at about 8.3 percent solids slurry concentration.

It should be understood that although the above examples describe in detail some of the more specific features of the invention, they are given primarily for the purpose of illustration and the invention is not to be limited to such examples. For example, although the invention has been described as a new process for producing novel filaments and has been illustrated in the specific examples in connection with the production of hand formed sheets from these novel filaments, it is applicable to continuous production of paper sheets and other non-woven materials of indefinite lengths. Thus, the fibers may be beaten in a continuous manner and the resulting beaten fiber sheeted out on a Fourdrinier machine. In such case, the sheet could be dried by passing same over drying cans and taken up in roll form.

Therefore, it is apparent that an important aspect of the invention is based on the discovery of producing continuous filaments more economically by utilizing a two phase system consisting of a polymer melt phase comprised of a lower polymer melt layer and an upper water layer. The novel filamentary materials formed from the disclosed blends of polymers dispersed in a non-solvent may be fibrillated more easily and to a greater extent than filaments produced theretofore to thereby reduce the cost thereof.

The products made from the filamentary materials of this invention have a high resistance to bursting and tearing both in the wet and dry state. Another important feature of the products is their inherent ability to resist the action of certain chemicals. While the products may be made solely from fibers of the polymer blends illustrated herein, it will be appreciated that other fibrillatable fibers including synthetic, artificial and natural fibers may be combined therewith to manufacture satisfactory sheet-like materials. For example, the fibers of the present invention are compatible with natural cellulosic fibers over a wide range of proportions to obtain paper having improved physical properties.

Since it is apparent that many changes and modifications can be made in the above-described detailed specification without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited except as set forth in the claims.

We claim:

1. A process for producing continuous synthetic filaments each comprised of randomly interconnected fiber elements suitable for utilization in the manufacture of paper products comprising:

(a) dispersing a water soluble anionic cellulose derivative and a copolymer being comprised of at least

80% acrylonitrile, 0% to 10% vinyl acetate and 0% to 10% of at least one other unsaturated monomeric

compound copolymerizable therewith in water to form a slurry,
 (b) elevating the temperature of the slurry to between 130° C. and 150° C. in a first heating zone,
 (c) continuously advancing the heated slurry through a second heated zone in which the temperature of said slurry is increased to 190° C. to 205° C. to form a viscous melt,
 (d) forming continuous filaments having randomly distributed cavities and fissures by extruding said melt through a plurality of orifices, and
 (e) fibrillating and stretching said filaments by contacting said filaments upon extrusion with a perpendicularly directed high velocity stream of inert fluid to elongate the cavities and fissures in the direction of the longitudinal axis of the filaments which promotes longitudinal splitting of the filaments to form said networks of randomly interconnected fiber elements.

2. A process in accordance with claim 1 wherein the polymers are comprised of 93% acrylonitrile and 7% vinyl acetate.

3. A process in accordance with claim 1 wherein the other monomeric compound is styrene.

4. A process in accordance with claim 1 wherein the cellulose derivative is sodium carboxymethyl cellulose.

5. A process in accordance with claim 4 wherein the slurry consists of from 2% to 30% polymer solids.

6. A process in accordance with claim 5 wherein the sodium carboxymethyl cellulose comprises from 6% to 18% of the polymer solids.

7. A process in accordance with claim 6 wherein the viscous melt is characterized by a two phase water-melt system being extruded simultaneously.

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