



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 482 882 B1

(12)

EUROPEAN PATENT SPECIFICATION

(49) Date of publication of patent specification: **27.12.95** (51) Int. Cl.⁶: **D01D 5/11**

(21) Application number: **91309740.8**

(22) Date of filing: **22.10.91**

(54) **A process for flash spinning fiber-forming polymers**

(30) Priority: **23.10.90 US 602344**
19.04.91 US 688017
21.11.90 EP 90312694

(43) Date of publication of application:
29.04.92 Bulletin 92/18

(45) Publication of the grant of the patent:
27.12.95 Bulletin 95/52

(84) Designated Contracting States:
DE FR GB IT LU NL

(56) References cited:
EP-A- 0 431 801
US-A- 3 081 519
US-A- 3 987 139
US-A- 4 007 247
US-A- 5 009 820

(73) Proprietor: **E.I. DU PONT DE NEMOURS AND COMPANY**
1007 Market Street
Wilmington
Delaware 19898 (US)

(72) Inventor: **Coates, Dan Mayo**
912 Mankin Road
Midlothian,
Virginia 23113 (US)
Inventor: **McMillin, Carl Kenneth**
104 Durrington Circle
Richmond,
Virginia 23236 (US)
Inventor: **Chen, John Chu**
21 Kent Drive
Hockessin,
Delaware 19707 (US)

(74) Representative: **Jones, Alan John et al**
CARPMAELS & RANSFORD
43 Bloomsbury Square
London, WC1A 2RA (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 482 882 B1

DescriptionFIELD OF THE INVENTION

5 The invention relates to a process for flash-spinning plexifilamentary film-fibril strands of polymers that are substantially plasticizable in carbon dioxide and/or water, and have a melting point less than 300 °C. More particularly, the invention relates to plexifilamentary film-fibril strands that are flash-spun from mixtures of carbon dioxide, water and the polymer.

10 BACKGROUND OF THE INVENTION

The disclosures of EP-A-0 431 801 falling under the terms of Art 54(3) EPC are a process for flash spinning plexifilamentary film-fibril strands of ethylene vinyl alcohol copolymer, optionally with 0 to 6 weight % of polyolefin, by the steps of forming a spin mixture of water, carbon dioxide and the copolymer at a
15 temperature of at least 130 °C, at a pressure that is greater than the autogenous pressure of the mixture and then flash spinning the mixture into a region of substantially lower temperature and pressure.

Blades and White, United States Patent 3,081,519 describe flash-spinning plexifilamentary film-fibril strands from fiber-forming polymers. A solution of the polymer in a liquid, which is a non-solvent for the polymer at or below its normal boiling point, is extruded at a temperature above the normal boiling point of
20 the liquid and at autogenous or higher pressure into a medium of lower temperature and substantially lower pressure. This flash spinning causes the liquid to vaporize and thereby cool the exudate which forms a plexifilamentary film-fibril strand of the polymer. According to Blades and White, the following liquids are useful in the flash-spinning process: aromatic hydrocarbons such as benzene, toluene, etc.; aliphatic hydrocarbons such as butane, pentane, hexane, heptane, octane, and their isomers and homologs; alicyclic
25 hydrocarbons such as cyclohexane; unsaturated hydrocarbons; halogenated hydrocarbons such as methylene chloride, carbon tetrachloride, chloroform, ethyl chloride, methyl chloride; alcohols; esters; ethers; ketones; nitriles; amides; fluorocarbons; sulfur dioxide; carbon disulfide; nitromethane; water; and mixtures of the above liquids. The patent further states that the flash-spinning solution additionally may contain a dissolved gas, such as nitrogen, carbon dioxide, helium, hydrogen, methane, propane, butane,
30 ethylene, propylene, butene, etc. Preferred for improving plexifilament fibrillation are the less soluble gases, i.e., those that dissolve to a less than 7% concentration in the polymer solution under the spinning conditions.

Blades and White state that polymers which may be flash spun include those synthetic filament-forming polymers or polymer mixtures which are capable of having appreciable crystallinity and a high rate of
35 crystallization. A preferred class of polymers is the crystalline, non-polar group consisting mainly of crystalline polyhydrocarbons, such as polyethylene and polypropylene.

U.S. Patent 3,169,899 lists polyester, polyoxymethylene, polyacrylonitrile, polyamide, polyvinyl chloride, etc. as other polymers that may be flash spun. Still other polymers mentioned in the patent are flash spun as mixtures with polyethylene, including ethylene vinyl alcohol, polyvinyl chloride, polyurethane, etc.
40 Example 18 of U.S. 3,169,899 illustrates flash spinning from methylene chloride of a mixture of polyethylene and ethylene vinyl alcohol in which polyethylene is the predominant component of the polymer mixture.

Flash spun polyethylene products have achieved considerable commercial success. "Tyvek®" is a spunbonded polyethylene sheet product sold by E. I. du Pont de Nemours and Company. These sheets are used in the construction and packaging industries. "Tyvek®" is also used in protective apparel since the
45 flash spun product provides a good barrier to particulate penetration. However, the hydrophobic nature of polyethylene results in a garment which tends to be uncomfortable during hot, humid weather. A more hydrophilic flash spun product is clearly desirable for garment and some other end uses. Additionally, flash spinning of any of the polymers would preferably be achieved from an environmentally safe, non-toxic solvent.

Trichlorofluoromethane (Freon-11) has been a very useful solvent for commercial manufacture of plexifilamentary film-fibril strands of polyethylene. However, the escape of such a halocarbon into the atmosphere has been implicated as a serious source of depletion of the earth's ozone. A general discussion of the ozone-depletion problem is presented, for example by P.S. Zurer, "Search Intensifies for Alternatives to Ozone-Depleting Halocarbons", Chemical & Engineering News, pages 17-20 (February 8, 1988). The
55 substitution of environmentally safe solvents for trichlorofluoromethane in a commercial flash spinning process should minimize the ozone depletion problem.

There now has been discovered in accordance with this invention, flash spun polymer products desirable for uses such as garments, construction and packaging, which are flash spun from an envi-

ronmentally acceptable mixture comprising carbon dioxide and water.

SUMMARY OF THE INVENTION

There is provided by this invention a process for flash spinning plexifilamentary film-fibril strands of a fiber-forming polymer that is substantially plasticizable in carbon dioxide or water and has a melting point less than 300 °C, comprising the steps of:

- (a) forming a spin mixture of water, carbon dioxide and the polymer at a temperature of at least 130 °C and a pressure that is greater than the autogenous pressure of the mixture; and
- (b) thereafter flash spinning the mixture into a region of substantially lower temperature and pressure, wherein the carbon dioxide is present in the range of from 30 to 90 percent based on the total weight of the spin mixture, and provided that the polymer constituent of the spin mixture does not consist of ethylene vinyl alcohol copolymer together with from 0 to 6.5% of a polyolefin, the percentage being based on the total weight of the spin mixture.

Preferably, the polymer is a polyolefin selected from the group consisting of polyethylene, polypropylene, ethylene vinyl alcohol copolymers and combinations thereof. An especially desirable combination is polyethylene with ethylene vinyl alcohol to which is grafted about 10% by weight of a high density polyethylene.

As used herein, the terms "substantially plasticizable" mean that the polymers are softened and become less viscous by imbibing the carbon dioxide and/or water.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "plexifilamentary film-fibril strand" or simply "plexifilamentary strand", as used herein, means a strand which is characterized as a three-dimensional integral network of a multitude of thin, ribbon-like, film-fibril elements of random length and of less than about 4 microns average thickness, generally coextensively aligned with the longitudinal axis of the strand. The film-fibril elements intermittently unite and separate at irregular intervals in various places throughout the length, width and thickness of the strand to form the three-dimensional network. Such strands are described in further detail by Blades and White, United States Patent 3,081,519 and by Anderson and Romano, United States Patent 3,227,794.

Polymers particularly useful in the practice of this invention are polyethylene, polypropylene, grafted and ungrafted copolymers of ethylene and vinyl alcohol (hereinafter sometimes referred to as "EVOH"), graft copolymers of acrylic acid, polyurethane, and combinations thereof. The copolymers of ethylene and vinyl alcohol have a copolymerized ethylene content of about at least 20 mole%. The ethylene vinyl alcohol copolymer may include as an optional comonomer other olefins such as propylene, butene-1, pentene-1, or 4-methylpentene-1 in such an amount as to not change the inherent properties of the copolymer, generally in an amount of up to about 5 mole%, based on the total copolymer. The melting points of these ethylene vinyl alcohol polymers are generally between about 160 and 190 °C. Ethylene vinyl alcohol polymers are normally prepared by copolymerization of ethylene with vinyl acetate followed by saponification of the acetate groups to the hydroxyl groups. At least about 90% of the acetate groups should be saponified, this being necessary to achieve sufficient mixing of the polymer. This process is well known in the art.

A particularly advantageous EVOH polymer can be prepared by grafting long chains of polyethylene or polypropylene (i.e., blocks), onto the random ethylene vinyl alcohol copolymer. The grafting process is accomplished by properly mixing EVOH and a pendant anhydride containing polyolefins in the molten state under shear through either a batch or continuous mixing device (e.g., haake mixer or extruder). The grafted polymers appear to be more compatible with additional polyolefins used in most of the flash spinning experiments. A polyolefin graft level of 5-50% by weight is most useful.

The process requires forming a spin mixture of the polymer, water and carbon dioxide. The water is present in the range from 5 to 50 percent based on the total weight of the spin mixture. The carbon dioxide is present in the range from 30 to 90 percent based on the total weight of the spin mixture. The polymer is present in the range from 1.5 to 25 percent based on the total weight of the spin mixture.

As noted above, the spin mixture may also comprise ethylene vinyl alcohol copolymer and an additional polymer present in the range from 0 to 25 percent based on the total weight of the spin mixture. Conveniently, polyethylene and polypropylene are the preferred additional polymers.

The spinning mixture may optionally contain a surfactant. The presence of such a surfactant appears to assist in emulsifying the polymer, or in otherwise aiding in forming a mixture. Examples of suitable nonionic surfactants are disclosed in U. S. Patent No. 4,082,887, the contents of which is herein incorporated by

reference. Among the suitable, commercially available, nonionic surfactants are the "Spans", which are mixtures of the esters of the monolaurate, monooleate and monostearate type and the "Tweens", which are the polyoxyethylene derivatives of these esters. The "Spans" and the "Tweens" are products of ICI Americas, Wilmington, DE.

5 The required temperatures for preparing the spin mixture and for flash-spinning the mixture are usually about the same and usually are in the range of 130 to 275 °C. The mixing and the flash-spinning are performed at a pressure that is higher than the autogenous pressure of the mixture. The pressure during the spin mixture preparation is generally in the range from 1,200 to 6,000 psi.

Conventional flash-spinning additives can be incorporated into the spin mixtures by known techniques.
10 These additives can function as ultraviolet-light stabilizers, antioxidants, fillers, dyes, surfactants and the like.

EXAMPLES

15 Equipment

Two autoclaves were used in the following non-limiting examples. One autoclave, designated a "300cc" autoclave (Autoclave Engineers, Inc., Erie, PA) was equipped with a turbine-blade agitator, temperature and pressure measuring devices, heating means, a means of pumping in carbon dioxide under pressure and
20 inlets for loading the ingredients. An exit line from the bottom of the autoclave was connected through a quick-acting valve to a spin orifice 0.079 cm in diameter. The spin orifice had a length to diameter ratio of 1 with a tapered conical entrance at an angle of 120 degrees. The second autoclave, designated a "1 gallon" autoclave (again made by Autoclave Engineers, Inc.), was equipped in an analogous manner to that of the "300cc" autoclave.

25 Test Procedures

The surface area of the plexifilamentary film-fibril strand product is a measure of the degree and fineness of fibrillation of the flash-spun product. Surface area is measured by the BET nitrogen absorption
30 method of S. Brunauer, P.H. Emmett and E. Teller, Journal of American Chemical Society, Vol. 60, pp. 309-319 (1938) and is reported as m²/g.

Tenacity and elongation of the flash-spun strand are determined with an Instron tensile-testing machine. The strands are conditioned and tested at 70 °F (21.1 °C) and 65% relative humidity. The strands are then twisted to 10 turns per inch and mounted in the jaws of the Instron Tester. A 1-inch gauge length and an
35 elongation rate of 60% per minute are used. The tenacity at break is recorded in grams per denier (gpd).

The denier of the strand is determined from the weight of a 15 cm sample length of strand.

In the non-limiting examples which follow, all parts and percentages are by weight unless otherwise indicated. The conditions of all Examples are summarized in Table I.

40 Example 1

The "1 gallon" autoclave was loaded with 600 g ASPUN® 6801 and 700 g water, then the vessel was closed. The exit manifold of the autoclave was fitted with a spin orifice of 0.035" with a tapered conical entrance at an angle of 120 degrees. A vacuum educator was used to pump the vessel to 20 in. mercury
45 pressure for 15 seconds to remove most of the air but not to significantly remove water. The vessel was then pressurized with carbon dioxide until 1500 g of carbon dioxide had been added, the amount measured with a "Micro-motion" mass flow instrument. Agitation was begun and set to 1000 rpm. Heating of the vessel was begun and continued until the goal temperature of 170 °C was reached. Pressure was adjusted by bleeding small amounts of vapor until the pressure stabilized at 4,500 psi. The mixture was held at
50 170 °C for 1 minute, the agitator slowed to about 250 rpm and the exit valve promptly opened to permit the mixture to flow to the spin orifice, which had been heated to 210 °C. The result was the formation of a finely fibrillated continuous yarn.

Example 2

55 The procedure of Example 1 was used except that the autoclave was loaded with 300 g ASPUN® 6801, 125 g Selar® OH 4416 ethylene/vinyl alcohol copolymer of melt index 16 (E.I. du Pont de Nemours and Co., Wilmington, Delaware), 840 g water, and was charged with 1700 g carbon dioxide. Spinning gave a

finely fibrillated continuous yarn very much like that of Example 1 except the yarn is more hydrophilic and has some elastic recovery properties.

Example 3

5

The "300 cc" autoclave was used and operated in the same manner as the "1 gallon" autoclave. Through an addition port, the autoclave was loaded with 30 g Alathon®/7050 high density linear polyethylene, melt index 17:5, (Occidental Chemical Corporation, Houston, Texas) and 56 g water. Most of the air was removed from the autoclave by brief evacuation to 20 in. mercury. The autoclave was then pressurized with 146 g carbon dioxide, the agitator set to 2000 rpm and heating begun up to a goal temperature of 170 °C. When the goal temperature was reached, the pressure was adjusted by venting small amounts of the mixture to give 4,500 psi. The mixture was then agitated an additional 15 minutes. The exit valve was opened and the mixture spun through the spin orifice. The result was a pulp consisting of finely fibrillated fibers of high quality, ranging from 1/16 to 2 inches in length. The fibers are useful for formation of sheet structures made by known paper making processes.

Example 4

The procedure of Example 3 was followed, except the autoclave was charged with 30 g ASPUN® 6801 resin, 15 g Selar® OH 4416 resin, and 56 g water, and was pressurized with carbon dioxide to a pressure of 3700 psi at spinning. The result was a continuous, finely fibrillated continuous plexifilamentary yarn.

Example 5

The procedure of Example 1 was followed, except the autoclave was loaded with 500 g ASPUN® 6801 resin, 100 g SELAR® OH 4416 resin, 700 g water and 1300 g carbon dioxide; then the autoclave was heated at 170 °C to a goal pressure of 5,500 psi. The agitator was changed to a multiple high shear paddle/turbine design. High quality continuous finely fibrillated yarn was produced that gave a twisted break tenacity of 1.45 g/denier at 38% elongation.

30

Example 6

Example 5 was re-run under the same conditions but the spinning temperature was increased to 180 °C. The yarn was essentially equivalent to Example 17 and measured 1.72 g/denier tenacity at 38.7% elongation. Surface area was measured by the nitrogen absorption technique to be 4.44 m²/g.

35

Example 7

The procedure of Example 1 was followed except that the autoclave was loaded with 300 g Alathon® 7050, 100 g of "E64179-124-1" (a ethylene vinyl alcohol copolymer to which has been grafted about 10% by weight high density polyethylene), 1200 g carbon dioxide and 500 g distilled water. A slotted spinning nozzle designed to produce a flat rather than cylindrical web shape was used. The goal temperature was 175 °C. Otherwise, the procedure was the same as Example 1. The result was the formation of a finely fibrillated continuous yarn that had a twisted tenacity of 4 g/denier, an elongation of 46% and a surface area of 13 m²/g as measured by the BET method.

45

"E64179-124-1" is not a commercially available product. It is prepared by taking SELAR® OH 4416 and modifying it through in situ grafting with high density polyethylene resin that has itself been modified. The high density polyethylene resin was modified in a twin screw extruder through the controlled addition of a peroxide initiator and maleic anhydride. The modified resin is referred to as "HDPE-G-MAN" (high density polyethylene grafted by maleic anhydride addition). The SELAR® OH 4416 was modified through in situ grafting with the "HDPE-G-MAN" at about 10% by weight in a twin screw extruder at 220 °C. The anhydride/hydroxyl reaction provides the grafting site to chemically link up the HDPE and the EVOH.

50

Example 8

55

The procedure of Example 7 was followed except that 380 g Alathon®/7050 and 20 g of "64179-124-1" was used. The result was essentially the same as Example 7 except that the resulting yarn was much less hydrophilic and hand sheets made from the yarn exhibited bonding characteristics more like that expected

of pure polyethylene yarn.

Example 9

5 The procedure of Example 8 was used except that into the autoclave were loaded 300 g of Shell PP WRS5-675 (polypropylene polymer commercially available from Shell Chemical Company, Short Hills, New Jersey), 100 g of "64179-124-5" (a ethylene vinyl alcohol copolymer as described in Example 7 except that to which has been grafted about 20% polypropylene by weight), and 1555 g carbon dioxide. The goal temperature was 200 °C. A finely fibrillated 20 inch wide swath was produced that was slightly more coarse
10 that seen when polyethylene was the polymer.

Example 10

15 The procedure of Example 8 was used except that 300 g of "HTX-6133" (a melt spinnable polyurethane polymer (a butylene/poly (alkylene ether) phthalate)), 120 g Alathon®/7050 high density polyethylene and 1715 g carbon dioxide were loaded into the autoclave. The goal temperature was 180 °C. A very finely fibrillated yarn was produced with a unique "silky" feel and elastomeric properties.

HTX-6133 is a very soft HYTREL® resin comprised of 77 wt.% soft segment and 23 wt.% hard segment. It is specifically described in the Examples (Preparation of Elastomer A) in U.S. Patent 4,731,407
20 (Benim et al.), the entire contents of which are incorporated by reference herein.

Example 11

25 The procedure of Example 3 was used except that the autoclave was loaded with 15.5 g of Selar® 4416 ethylene vinyl alcohol copolymer of melt index 16 (commercially available from E.I. du Pont de Nemours and Company, Wilmington, Delaware), 15.5 g of Polybond® 1011 acrylic acid graft copolymer with polypropylene of melt index 20 (commercially available from British Petroleum Chemicals, Hackettstown, New Jersey), 49 g distilled water and 120 g carbon dioxide. The mixture was stirred at 200 °C and 5000 psi pressure for 15 minutes prior to spinning through a 0.0031 inch spin orifice. A well fibrillated, continuous
30 plexifilamentary yarn was produced.

TABLE 1

Example#	%EVOH	%Additional Polyolefin	%Surfactant	%H2O	%CO2	T °C	Spinning P(psi)
1	0	21.4 LDPE	0	25.0	53.6	170	4500
2	4.2	10.1 LDPE	0	28.3	57.3	170	4500
3	0	12.9 HDPE	0	23.2	62.9	170	4500
4	0	12.9 LDPE	0	23.2	62.9	170	3700
5	3.8	19.2 LDPE	0	26.9	50.0	170	5500
6	3.8	19.2 LDPE	0	26.9	50.0	180	5500
7	4.8	14.3 HDPE	0	23.8	57.1	175	4500
8	1.0	18.1 HDPE	0	23.8	57.1	175	4500
9	4.1	12.2 PP	0	20.4	63.3	200	4500
10	11.4*	4.6 HDPE	0	19.0	65.1	180	4500
11	7.8	7.8 PP/AA	0	24.5	60.0	200	5000
HDPE = high density polyethylene LDPE = low density polyethylene PP = polypropylene AA = acrylic acid * Polymer used was polyurethane and not EVOH							

55 Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

Conversions

- 1 psi = 6.895 kPa
 1 gallon = 3.79 litres
 5 1 denier = 1.11 d tex
 1 inch = 2.54 cm

Claims

- 10 1. A process for flash spinning plexifilamentary film-fibril strands of a polymer that is substantially plasticizable in carbon dioxide or water and has a melting point less than 300 °C, comprising the steps of:
- 15 (a) forming a spin mixture of water, carbon dioxide and the polymer at a temperature of at least 130 °C and a pressure that is greater than the autogenous pressure of the mixture; and
 (b) thereafter flash spinning the mixture into a region of substantially lower temperature and pressure,
 wherein the carbon dioxide is present in the range of from 30 to 90 percent based on the total weight of the spin mixture, and
 provided that the polymer constituent of the spin mixture does not consist of ethylene vinyl
 20 alcohol copolymer together with from 0 to 6.5% of a polyolefin, the percentage being based on the total weight of the spin mixture.
2. A process according to claim 1 wherein the water is present in the range from 5 to 50 percent based on the total weight of the spin mixture.
- 25 3. A process according to claim 1 or 2 wherein the polymer is present in the range from 1.5 to 25 percent based on the total weight of the spin mixture.
4. A process according to claim 1, 2 or 3 wherein the polymer is selected from polyolefins, polyurethanes, graft copolymers of acrylic acid or a combination thereof.
- 30 5. A process according to claim 4 wherein the polyolefin is selected from polypropylene; polyethylene; or ethylene vinyl alcohol copolymers together with from more than 6.5% to 25% of polypropylene or polyethylene, the percentage being based on the total weight of the spin mixture.
- 35 6. A process according to claim 5 wherein the ethylene vinyl alcohol copolymer has been grafted to between 5-50% by weight high density polyethylene.
7. A process according to claim 6 wherein the ethylene vinyl alcohol copolymer has been grafted to about
 40 10% by weight high density polyethylene.
8. A process according to any preceding claim wherein the spin mixture is formed at a temperature in the range of 130 to 275 °C and a pressure in the range from 8 to 40 MPa (1,200 to 6,000 psi).
- 45 9. A process according to claim 5 wherein the spin mixture comprises ethylene vinyl alcohol copolymer and additional polyolefin present in the range from more than 6.5 to 25 percent based on the total weight of the spin mixture.
10. A process according to claim 9 wherein the additional polyolefin comprises polyethylene or polypropylene.
- 50 11. A process according to any preceding claim wherein the spin mixture further comprises a surfactant present in the range from 0 to 2 percent based on the total weight of the spin mixture.
- 55 12. A process according to claim 9 wherein the ethylene vinyl alcohol copolymer comprises at least 20 mole % of ethylene units.

Patentansprüche

1. Verfahren zum Flash-Erspinnen plexifilamentärer Film-fibrillenstränge aus einem Polymer, das im wesentlichen in Kohlendioxid oder Wasser plastifizierbar ist und einen Schmelzpunkt von weniger als 300 °C aufweist, umfassend die Stufen:
 - (a) Bilden eines Spinnngemisches aus Wasser, Kohlendioxid und dem Polymer bei einer Temperatur von wenigstens 130 °C und einem Druck, der größer ist als der autogene Druck des Gemisches, und
 - (b) anschließend Flash-Verspinnen des Gemisches in eine Region von im wesentlichen niedrigerer Temperatur und niedrigerem Druck, bei dem das Kohlendioxid, bezogen auf das Gesamtgewicht des Spinnngemisches, im Bereich von 30 bis 90 % vorhanden ist, und mit der Maßgabe, daß der Polymer-Bestandteil des Spinnngemisches in Verbindung mit 0 bis 6,5 % eines Polyolefins nicht aus Ethylenvinylalkohol-Copolymer besteht, wobei der Prozentsatz auf das Gesamtgewicht des Spinnngemisches bezogen ist.
2. Verfahren nach Anspruch 1, bei dem das Wasser, bezogen auf das Gesamtgewicht des Spinnngemisches, im Bereich von 5 bis 50 % vorhanden ist.
3. Verfahren nach Anspruch 1 oder 2, bei dem das Polymer, bezogen auf das Gesamtgewicht des Spinnngemisches, im Bereich von 1,5 bis 25 % vorhanden ist.
4. Verfahren nach Anspruch 1, 2 oder 3, bei dem das Polymer ausgewählt wird aus Polyolefinen, Polyurethanen, Propf-Copolymeren von Acrylsäure oder einer Kombination davon.
5. Verfahren nach Anspruch 4, bei dem das Polyolefin ausgewählt wird aus Polypropylen, Polyethylen oder Ethylenvinylalkohol-Copolymeren, in Verbindung mit mehr als 6,5 % bis 25 % Polypropylen oder Polyethylen, wobei der Prozentsatz auf das Gesamtgewicht des Spinnngemisches bezogen ist.
6. Verfahren nach Anspruch 5, bei dem das Ethylenvinylalkohol-Copolymer mit Polyethylen von hoher Dichte zwischen 5-50 Gew.-% gefropft worden ist.
7. Verfahren nach Anspruch 6, bei dem das Ethylenvinylalkohol-Copolymer zu etwa 10 Gew.-% mit Polyethylen von hoher Dichte gefropft worden ist.
8. Verfahren nach einem vorhergehenden Anspruch, bei dem das Spinnngemisch bei einer Temperatur im Bereich von 130 bis 275 °C und einem Druck im Bereich von 8 bis 40 MPa (1200 bis 6000 psi) gebildet worden ist.
9. Verfahren nach Anspruch 5, bei dem das Spinnngemisch Ethylenvinylalkohol-Copolymer und zusätzliches Polyolefin, das, bezogen auf das Gesamtgewicht des Spinnngemisches, im Bereich von mehr als 6,5 bis 25 % vorhanden ist, umfaßt.
10. Verfahren nach Anspruch 9, bei dem das zusätzliche Polyolefin Polyethylen oder Polypropylen umfaßt.
11. Verfahren nach einem vorhergehenden Anspruch, bei dem das Spinnngemisch, bezogen auf das Gesamtgewicht des Spinnngemisches, außerdem ein oberflächenaktives Mittel im Bereich von 0 bis 2 % umfaßt.
12. Verfahren nach Anspruch 9, bei dem das Ethylenvinylalkohol-Copolymer wenigstens 20 Mol-% Ethyleneinheiten umfaßt.

Revendications

1. Un procédé d'obtention par filature flash de mèches de films-fibrilles plexifilamentaires d'un polymère qui est sensiblement plastifiable dans le dioxyde de carbone ou dans l'eau et dont le point de fusion est inférieur à 300 °C, comprenant les étapes suivantes:
 - (a) formation d'un mélange à filer d'eau, de dioxyde de carbone et du polymère à une température d'au moins 130 °C et sous une pression qui est supérieure à la pression autogène du mélange, et

(b) ensuite, filature flash du mélange vers une zone de température et de pression sensiblement plus faibles,

dans lequel le dioxyde de carbone est présent en une quantité de 30 à 90 pour cent par rapport au poids total du mélange à filer, et

pourvu que le constituant polymère du mélange à filer ne soit pas constitué de copolymère éthylène-alcool vinylique en même temps que de 0 à 6,5% d'une polyoléfine, le pourcentage étant exprimé par rapport au poids total du mélange à filer.

2. Un procédé selon la revendication 1, dans lequel l'eau est présente en une quantité de 5 à 50 pour cent par rapport au poids total du mélange à filer.

3. Un procédé selon la revendication 1 ou 2, dans lequel le polymère est présent en une quantité de 1,5 à 25 pour cent par rapport au poids total du mélange à filer.

4. Un procédé selon la revendication 1, 2 ou 3, dans lequel le polymère est choisi parmi les polyoléfines, polyuréthannes, copolymères greffés d'acide acrylique ou leurs combinaisons.

5. Un procédé selon la revendication 4, dans lequel le polymère est choisi parmi: polypropylène, polyéthylène; ou des copolymères éthylène-alcool vinylique en même temps que plus de 6,5 à 25% de polypropylène ou de polyéthylène, le pourcentage étant exprimé par rapport au poids total du mélange à filer.

6. Un procédé selon la revendication 5, dans lequel le copolymère éthylène-alcool vinylique a été greffé de 5 à 50% en poids de polyéthylène haute densité.

7. Un procédé selon la revendication 6, dans lequel le copolymère éthylène-alcool vinylique a été greffé d'environ 10% en poids de polyéthylène haute densité.

8. Un procédé selon l'une quelconque des revendications précédentes dans lequel le mélange à filer est formé à une température de 130 à 175 °C et sous une pression de 8 à 40 MPa (1200 à 6000 psi).

9. Un procédé selon la revendication 5, dans lequel le mélange à filer comprend un copolymère éthylène-alcool vinylique et une autre polyoléfine présente en quantité supérieure à 6,6 à 25 pour cent par rapport au poids total du mélange à filer.

10. Un procédé selon la revendication 9, dans lequel l'autre polyoléfine comprend du polyéthylène ou du polypropylène.

11. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange à filer comprend en outre un agent tensioactif présent en une quantité de 0 à 2 pour cent par rapport au poids total du mélange à filer.

12. Un procédé selon la revendication 9, dans lequel le copolymère éthylène-alcool vinylique comprend au moins 20% en moles de motifs éthylène.