(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 154 425**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **85300928.0**

(22) Date of filing: **12.02.85**

(51) Int. Cl.⁴: **D 01 F 6/90**
D 01 F 6/92, D 01 D 5/08
D 01 D 5/28

(30) Priority: **05.03.84 GB 8405694**

(43) Date of publication of application:
11.09.85 Bulletin 85/37

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

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(54) Melt spinning of a blend of a fibre-forming polymer and an immiscible polymer.

(57) A process of melt spinning a fibre-forming polymer having a high viscosity, more particularly polyethylene terephthalate having an intrinsic viscosity greater than 0.70 or nylon 66 having a relative viscosity greater than 45 and more preferably greater than 55, in which before melt spinning, there is added to the fibre-forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre-forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning.

EP 0 154 425 A2

MELT SPINNING OF A BLEND OF A FIBRE-FORMING POLYMER AND AN IMMISCIBLE POLYMER

This invention relates to the manufacture of synthetic fibres by melt spinning and drawing a high molecular weight, high viscosity, fibre-forming polymer, more particularly polyethylene terephthalate or nylon 66, containing another polymer which is immiscible in a melt of the fibre-forming polymer.

Recently there have been a number of disclosures relating to the production of melt-spun synthetic fibres from a fibre-forming polymer in which another polymer is added to the fibre-forming polymer before it is spun. The most relevant known to applicant are now discussed.

Japanese Patent No 56-118912 (Teijin KK) is concerned with the manufacture of a high strength fibre by melt spinning polyethylene terephthalate containing between 1 and 7 parts by weight % of a bisphenol type polycarbonate. The melt spun fibre is wound up at a speed of 1500 m/minute or less. It is stated that the limiting viscosity of the polyethylene terephthalate used must fall between 0.55 and 0.70. If it falls below 0.55, satisfactory strength and modulus cannot be developed in the fibre. On the other hand, when the limiting viscosity is in excess of 0.70, recognisable improvement in strength becomes insignificant or disappears and there is a tendency for the modulus value to decline as well.

In European Patent Application No 82305737.7 we have described a process of melt spinning a fibre-forming thermoplastic polymer at a minimum wind up speed of 1 kilometre per minute in which, before melt spinning, there is added to the fibre-forming polymer, between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre-forming polymer, such other polymer having an average particle size of between 0.5 and 3 microns in the melt with the fibre-forming polymer immediately prior to spinning. The intrinsic viscosity of the polyethylene terephthalate used was 0.63 and the relative viscosity (RV) of the nylon used was 40.

An advantage of the process described in European Patent

Application No 82305737.7 is that it allows significant productivity gains to be achieved. The effect of blending the immiscible polymer with the fibre-forming polymer is that of wind up speed suppression ie the properties of the spun fibre are those that would be obtained from a fibre which had been spun at a lower wind up speed.

Nevertheless it would appear from a reading of European Patent Application No 82305737.7 that the effect of wind up speed suppression cannot be realised at wind up speeds lower than 1 kilometre per minute. However, we have now realised that the effect of wind up speed suppression is really orientation suppression and so, if a sufficiently high molecular weight, ie high viscosity, fibre-forming polymer is spun, wind up speed suppression occurs even at wind up speeds below 1 kilometre per minute.

According to the present invention therefore, we provide a process of melt spinning a fibre-forming polymer having a high viscosity, more particularly high viscosity polyethylene terephthalate or nylon, in which before melt spinning, there is added to the fibre-forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre-forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning.

In preference, in order to achieve good tensile properties, the additive polymer has an average particle size in the melt of substantially less than 3 microns and more preferably of the order of 1 micron.

The term "high viscosity" is used, in relation to polyethylene terephthalate, to mean that it has an intrinsic viscosity greater than 0.70 and, in relation to nylon 66, to mean that it has a relative viscosity greater than 45 and more preferably greater than 55.

The intrinsic viscosity of polyethylene terephthalate is measured in ortho-chloro-phenol.

The relative viscosity of nylon 66 is measured on a 8.4% w/w solution in 90% formic acid compared with the viscosity of 90% formic acid itself.

By an "immiscible polymer" we mean that at the spinning temperature such a polymer forms a two phase melt with the fibre-forming thermoplastic polymer. Microscopic examination and optical photographs of such a melt show a two phase system in which the immiscible polymer is in the form of circles (indicating spherical particles) dispersed in the continuous, fibre-forming, polymer matrix.

However we wish the term "an immiscible polymer" to exclude a liquid crystal polymer, ie the additive polymers used in the invention do not form an anisotropic melt in the temperature range at which the thermoplastic polymer may be melt spun. This anisotropic condition may form when a liquid crystal polymer is heated or by the application of shear to the polymer, although in the latter case it must persist for a few seconds.

According to one aspect of the invention we provide a process of melt spinning a fibre-forming polymer, more particularly either polyethylene terephthalate having an intrinsic viscosity greater than 0.70 or nylon having a relative viscosity greater than 45 and more preferably greater than 55, in which before melt spinning, there is added to the fibre-forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre-forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning and taking up the spun fibre at a wind up speed less than 1 kilometre/minute.

According to another aspect of the invention we provide a process of melt spinning a fibre-forming polymer, more particularly either polyethylene terephthalate having an intrinsic viscosity greater than 0.70 or nylon having a relative viscosity greater than 45 and more preferably greater than 55, in which before melt spinning, there is added to the fibre-forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre-forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning and taking up the spun fibre at a minimum wind up speed of 1 kilometre/minute.

In the case of nylon 66 any suitable immiscible polymers

for example polyolefines, such as polyethylene and polypropylene, polyesters, such as polyethylene terephthalate, and polyethylene glycol, may be used.

In the case of polyethylene terephthalate, any suitable immiscible polymers may be used for example polyolefines, such as polyethylene and polypropylene, and polyethylene glycol. A preferred immiscible polymer, however, is nylon 66. The extensional viscosity of nylon 66 is such that the molten spheres of the polymer immediately prior to spinning, deform into microfibrils along the spinning threadline.

We also provide, therefore, melt spun fibres of polyethylene terephthalate made from polymer having an intrinsic viscosity greater than 0.70 containing between 0.1% and 10% by weight of nylon 66 which is present in the melt spun fibres as microfibrils. These microfibrils have an aspect ratio ie length/diameter ratio which is very high eg typically greater than 50 and such microfibrils will have diameters of about 0.5 micron. It is believed that it is the conversion of the spheres of nylon 66 into microfibrils and the extent of this deformation that produces the change of rheology which is responsible for the orientation suppression and in turn wind up speed suppression which is referred to below.

A major advantage of the process of the invention is that it allows significant productivity gains to be achieved. The effect of blending the immiscible polymer with the fibre-forming polymer is that of orientation suppression which manifests itself as wind up speed suppression ie the properties of the spun fibre are those that would be obtained from fibre which has been spun at a lower wind up speed. As the wind up speed increases in normal spinning, in the absence of an immiscible polymer, the properties of the drawn yarn decrease. Accordingly by lowering the effective wind up speed by the addition of an immiscible polymer (while keeping the actual wind up speed the same) it is possible to achieve improved properties such as a higher modulus which is quite surprising in view of the teaching of Japanese Patent No 56-118912.

This is particularly advantageous for industrial fibres

because the drawn properties for a specific final extension fall with wind up speed (see H Brody, J Macro Sci, Phys, B22, 19 (1983)).

A particularly useful property of a sewing thread is its modulus, since it has been found that a higher modulus allows faster sewing speeds and gives less puckering of sewn seams. A higher modulus can, of course, be obtained in the normal drawing process by using a higher draw ratio but this is not very desirable since it can lead to a high break level. The present invention achieves this object in a much more convenient and efficient manner.

The invention will now be described with reference to the following Examples. In all of these Examples the particle size of the additive, ie immiscible, polymer was of the order of 1 micron.

EXAMPLE 1

Polyethylene terephthalate having an intrinsic viscosity (IV) (measured in ortho-chloro-phenol) of 0.73 was dried at 165°C for 4 hours and blended with 3% by weight of Imperial Chemical Industries PLC. SGS grade nylon 66 on a GKN single screw extruder with an L/D ratio of 26:1. The barrel temperature was 290°C and the screw was rotated at 50 rpm. A lace of 0.1 inch diameter was extruded into a water bath and then passed to a lace cutter. The average output rate was 100 grams per minute. As a control, polyethylene terephthalate alone was extruded in a similar manner.

The chips from the lace cutter were then dried at 165°C for 4 hours and made into candles at 240°C for 8 mins. The candles were then spun on a rod spinner. The spinning temperature was 293°C and the throughput per hole was 96 gm/hr/hole into ambient air with no deliberate quenching apparatus, using 35 thou spinneret holes. After cooling, the filaments so formed were wound up at a wind up speed (WUS) of 200 mpm to 1000 mpm without adjustment of spinning rate so that higher speeds yielded finer filaments. The intrinsic viscosity of the control fibre after spinning was 0.70.

Considerable wind-up suppression was obtained with the blend as demonstrated by higher extensions and lower birefringences. These lower birefringences are an example of orientation suppression, the degree of which depends on the combination of the melt viscosity of

the polymer and the WUS.

The wind up speed suppression produced a potential increase in productivity that can be calculated from the extensibility of the spun filaments as determined on an Instron. The gauge length used was 10 cms and the strain rate was 200% per minute.

If a spun filament has a percent extension-to-break of E, then the maximum draw ratio to which it can subsequently be subjected is roughly (1 + E/100). If a second spun filament has a larger extension-to-break E' then it can be subjected to a larger draw ratio, roughly (1 + E'/100). To make drawn filaments of equal decitex d at these maximum draw ratios the spun filaments must therefore have decitexes of d(1 + E/100) and d(1 + E'/100) respectively. If both filaments are spun at the same speed their production rates are proportional to these decitexes and the percentage increase in productivity of the second filament is

$$\frac{(1 + E'/100) - (1 + E/100)}{(1 + E/100)} \times 100\%$$

This is the function listed in Table 1 as the potential increase in productivity.

TABLE 1

WUS (mpm)	% nylon	Birefringence ($\times 10^3$)	Extension (%)	Potential Increase in Productivity (%)
200	Nil	1.8	350	-
	3	1.2	485	30
400	Nil	4.4	310	-
	3	3.1	390	20
600	Nil	5.1	235	-
	3	3.7	350	34
800	Nil	10.4	220	-
	3	5.0	315	30
1000	Nil	16.4	175	-
	3	5.5	320	53
2000	Nil	69.2	90	-
	3	5.3	260	90

It is evident from the table that the degree of wind-up speed or orientation suppression increases considerably with increasing spinning speed.

At 1000 mpm, the addition of 3% nylon, affords as much as 53% increase in productivity and at 2000 mpm as much as 90% increase in productivity.

EXAMPLE 2

This example gives results for other concentrations of nylon and demonstrates that even very small amounts of nylon are very effective in producing orientation suppression. The same blending and spinning conditions were used as in Example 1 except that the spinneret hole used was 15 thou.

TABLE 2

% nylon	WUS (mpm)	Birefringence ($\times 10^{-3}$)	Extension (%)
0.5	800	4.8	300
1.0	400	1.7	500
	800	3.1	420
	1500	6.0	320
	2000	9.0	270
6.0	400	3.2	460
	800	4.4	420
	1500	5.8	370
	2000	7.1	320

EXAMPLE 3

This example demonstrates that better tensile properties are obtained at the same WUS by the use of a nylon blend. The improvement shown is in the initial modulus after drawing. The polymers were blended and spun as in Example 1 at 96g/hr/hole and 800 mpm. They were then drawn to a range of final extensions, using a hot pin at 85°C, a hot plate at 170°C and a draw speed of 20 mpm. A special technique was used on the Instron to measure the initial modulus very precisely. The gauge length was 50 cm, the cross head

speed was 5 cm per minute and the chart speed was 100 cm per minute. This gave a load-strain curve which was linear up to 2% strain and from which the initial modulus could be very accurately measured. For a given final extension there was a small scatter of a few percent, and all the results obtained are given in Table 3.

TABLE 3

% nylon	Extension After Drawing (%)	Initial Modulus (cN/tex)
Nil	8.1	811
	8.5	773
	8.6	732
	9.0	671
	10.4	690
	10.7	680
	11.1	711
	11.9	726
	15.5	714
	17.4	688
1.0	6.4	1020
	6.5	991
	6.6	970
	6.8	950
	7.0	934
	7.1	913
	8.5	897
	10.2	866
	10.3	879
	13.8	870
	14.3	813
	15.2	823
	16.5	869
	16.7	796
3.0	7.0	860
	7.3	956

TABLE 3 (cont)

% nylon	Extension After Drawing (%)	Initial Modulus (cN/tex)
	7.4	867
	7.5	861
	8.8	842
	9.3	852
	9.4	886
	11.2	851
	12.6	873
	13.9	850
	14.6	814
	15.1	782
	15.8	802

When smooth curves are drawn through these results, the modulus of the 1% and 3% nylon blends is about 20% higher then the control at 10% drawn extension. The draw ratio of the control for 10% extension was 3.9, while that of the 1% blend was 4.9, giving a productivity increase of 26%.

RH/NDW

CLAIMS

1. A process of melt spinning a fibre-forming polymer having a high viscosity, more particularly high viscosity polyethylene terephthalate or nylon, in which before melt spinning, there is added to the fibre- forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre-forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning.

2. A process of melt spinning a fibre-forming polymer, more particularly either polyethylene terephthalate having an intrinsic viscosity greater than 0.70 or nylon having a relative viscosity greater than 45 and more preferably greater than 55, in which before melt spinning, there is added to the fibre-forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre- forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning and taking up the spun fibre at a wind up speed less than 1 kilometre/minute.

3. A process of melt spinning a fibre-forming polymer, more particularly either polyethylene terephthalate having an intrinsic viscosity greater than 0.70 or nylon having a relative viscosity greater than 45 and more preferably greater than 55, in which before melt spinning, there is added to the fibre-forming polymer between 0.1% and 10% by weight of another polymer which is immiscible in a melt of the fibre- forming polymer and which has an average particle size less than 3 microns in the melt immediately prior to spinning and taking up the spun fibre at a minimum wind up speed of 1 kilometre/minute.

4. A process of melt spinning a fibre-forming polymer as claimed in any one of Claims 1 to 3 in which the additive polymer has an average particle size in the melt of substantially less than 3 microns and more particularly of the order of 1 micron.

5. A process of melt spinning nylon as claimed in any one of the preceding Claims in which the immiscible polymer is a polyolefine, a polyester or polyethylene glycol.

6. A process of melt spinning polyethylene terephthalate as claimed in any one of the preceding Claims in which the immiscible polymer is a polyolefine, polyethylene glycol or nylon 66.

7. Melt spun fibres of polyethylene terephthalate made from polymer having an intrinsic viscosity greater than 0.70 containing between 0.1% and 10% by weight of nylon 66 which is present in the melt spun fibres as microfibrils.

8. Melt spun fibres of nylon made from a polymer having a relative viscosity greater than 45 and more preferably greater than 55 containing between 0.1% and 10% of a polyolefine, a polyester or polyethylene glycol.