Preparation of UV-resistant PET fibres by direct melt spinning with on-line addition

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In order to solve the uniform dispersion of inorganic particles and dispersion characterization, a batch of UV-resistant fibres has been manufactured by direct melt spinning with on-line addition. By combining image analysis software with OM images, the dispersion of TiO_2 has been quantitatively analyzed. The formula of mass fraction of inorganic particles in fibre is deduced on the basis of crystallinity, and the calculated value is found consistent with theoretical value. Additionally, the comparative study of direct spinning and chip spinning shows that the former presents better dispersion of inorganic particles and superior performance. The tenacity of fibres from melt-direct spinning increases by 13.87%, the CV value decreases by 75.19% and Heywood diameter of TiO_2 particles decreases by 13.97%. According to national standard (GB/T 18830-2009), UPF values of the fabric are found much greater than the standard [UPF>40, T(UVA)<5%].

Keywords: Direct melt spinning, Dispersion, Polyethlene terephthalate fibre, TiO_2 particles, UV-resistant fibre

1 Introduction

Nowadays, the functionalization of poly (ethylene terephthalate) (PET) fibres mainly focuses on *in-situ* polymerization and melt blending method, and the subsequent spinning methods consisting of chip spinning and direct melt spinning. *In-situ* polymerization method requires nanoscale particles dispersion in polymerization process and it is suitable for the addition of a small amount of functional inorganic particles. However, the effect of inorganic particles on polymerization reaction should be a further ~~...~~ functional masterbatch containing inorganic particles needs to be fabricated preliminary, the masterbatch-dilution approach is employed to achieve the required content of inorganic particles in finish fibre.

Direct melt spinning is the primary means of fabricating conventional PET fibres, which eliminates chip transportation and saves energy in re-melting process of the chip. Currently, direct melt spinning accounts for about 70% PET capacity in

China. Thus, direct melt spinning is the inevitable trend of the development of the fibre industry. Both *in-situ* polymerization method and melt blending method are utilized to prepare functional fibres as a manner of direct melt spinning. Differently, in *in-situ* polymerization direct spinning process, there exists a series of problems such as fewer fibre varieties, inflexible changing varieties, more intermediate material and relatively high cost of production. Nevertheless, direct melt spinning with on-line addition refers to direct addition of ~~...~~ mponents based on the original direct spinning pipeline with auxiliary equipment, which can skillfully solve the above problems[1]. If the technology is successfully promoted, the technical level of direct spinning polyester fibres may be significantly improved.

Similar to other methods, the key point of direct melt spinning with on-line addition is to solve uniform dispersion of inorganic particles in polymer matrix. Dispersion is an operation to reduce non-uniformity of mixture, in which the dispersed phase is refined and distributed. A few studies show that the evolution process of dispersed phase morphology

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depends on melt shear viscosity, shear rate and the size of aggregates. The final size of dispersed phase is closely related to dispersion force, whose maximal value (F_m) can be expressed by[2,3] the following equation:

$$F_m = 3\pi\eta\dot{\gamma}r_1r_2 \qquad \qquad \dots (1)$$

where η is the shear viscosity; $\dot{\gamma}$, the shear rate; and r_1, r_2, represent diameter of particles in contact with each other.

In recent years, it has been reported that there appears a large number of patent applications and licensing on preparation of functional and differential fibres[4,5]. The technological process in these patents can be summed up as follows: functional masterbatches are squeezed into melt out of extrusion screw, and delivered to spinning box after mixing by efficient static mixer. However, these techniques involve static mixers, a dynamic mixer for large-scale industrial production has not been reported.

In previous study, we have developed three-dimensional dynamic (3-DD) efficient mixers based on the dispersion mechanism of inorganic particles in polymer melt, which matches with direct melt spinning. On premise of the mixer stable operation, UV-resistance PET micro/nano fibres are manufactured based on the theory of 'viscosity similar, similar compatibility'[6].

2 Materials and Methods

2.1 Materials

Polyethlene terephthalate(η=0.67 dL/g, bright polymer), purchased from Heng Li Chemical Fiber Co., Ltd., Jiangsu, China, was used in melt form. The UV-resistant masterbatch, (primary diameter of TiO_2 particles 23nm) was purchased from Jwell International Co. Ltd., South Korea.

2.2 Preparation of UV-resistant PET Fibres

The industrial implementation of on-line controllable addition system was conducted in Jiangsu Hengli Chemical Fiber Co., Ltd. The processing technology of the fibre is listed in Table 1. The pre-oriented yarn (POY) fibres of 135dtex/72fibres (135dtex/72f) and 83dtex/72f were manufactured by direct melt spinning with on-line addition system (Fig.1).

2.3 Testing and Analysis

The dispersion of TiO_2 particles was conducted in virtue of optical microscopy (OM). A bunch of multifilament's (about 1cm) was placed on a slide, and

then the miltifilaments were separated into a single fibre state with the aid of glycerol. Transmission optical microscopy (LABORLUX 12 POL, Leitz, Germany) with charge-coupled device (CCD) camera (No.WV-BP330/G, Panasonic) was employed to observe the dispersion state of TiO_2 particles in micro/nano fibres.

Tensile testing was performed on an Instron machine model 2343 according to GB/T 14344-2008 (Standard of the Peoples' Republic of China). Prior to tensile testing, the linear density of fibres was determined in accordance with GB/T14343-2008 (Standard of the Peoples'

Table 1 — Processing technology of UV-resisitance fibre

| Parameters	Values
Melt conveying	
Temperature of heat medium	285-288°C
Crystallizing & drying	
Moisture contain of masterbatch	≤0.03 g/L
Dehumidifier dew point	≤-60°C
Pre-crystallization temperature	80~100°C
Crystallization time	20~25min
Drying air temperature	120~140°C
Drying time	8~10h
Screw extruder & mixer	
Masterbatch dosage	5~8%
Temperature of screw extruder	260~280°C
Rotation speed of mixer	40~70 r/min
Temperature of mixer	280~288°C
Pressure after melt filter	≥7 MPa
Spinning winding	
Spinning pack pressure	11 MPa
Winding speed	2950 m/min
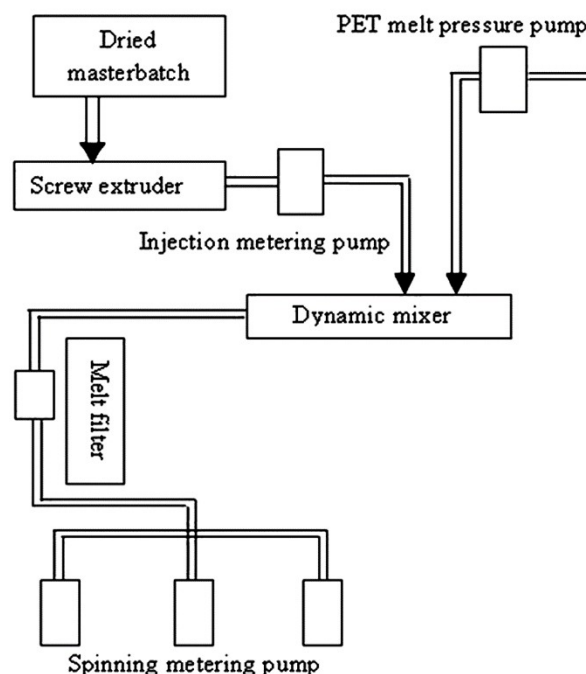
Fig.1 — Flowchart of online-addition controllable adding system

Republic of China). Multifilaments were tested using a gauge length of 200mm and a constant crosshead speed of 200mm/min. All the experiments have been conducted ten times and the average values were accorded.

Density of fibre was measured on small loops of filaments with a density gradient column at 23 ± 0.1℃(ref.7), which contains aqueous solution of NaBr[8]. Before that, the standard curves were plotted with glass beads of known density as a reference. The values of fibre density were obtained after the stable time of 6h. For an average value, three parallel samples were immersed into the density gradient column in each test.

The fibres were knitted or woven into fabrics, and UV-resistance properties of the fibre were evaluated by testing UV protection factor of the above fabrics. The rating system for fabrics specifies an UV protection factor (UPF) value, which can be thought of as a time factor for the protection of skin covered by the UV protective fabric compared to exposure without any protection. The UPF value can be determined using the following eauation[9,10]:

$$UPF = \frac{\int_{250nm}^{400nm} E(\lambda)S(\lambda)\Delta\lambda}{\int_{250nm}^{400nm} E(\lambda)S(\lambda)T(\lambda)\Delta\lambda} \qquad \dots (2)$$

where $E(\lambda)$ refers to erythema effect induced by UV radiation; $S(\lambda)$, the radiation intensity of UV region; $T(\lambda)$, the transmittance of ultraviolet radiation; and $\Delta\lambda$, the wavelength interval.

3 Results and Discussion

3.1 Dispersion of TiO₂ Particles

Figure 2 shows OM images of POY fibres with different masterbatch contents and rotating speeds of the mixer. It clearly illustrates that with the increase in masterbatch content the number of TiO₂ particles increases significantly. When the rotating speed of the mixer is adjusted to 20r/min, there appears micron-sized aggregates in fibres. With the increase in rotating speed, the above-mentioned aggregates disappear. Besides, in the case of 50r/min and 70r/min, the dispersion of the particles shows no significant difference.

Combining image analysis software with OM images, quantitative investigation of TiO₂ dispersion for POY fibres with 0wt%、6wt%、7wt% masterbatch content have been analyzed. The results are listed in Table 2. With the increase in masterbatch content, the number of particles, the average size and area fraction of particles tend to increase. Heywood equivalent diameter of the particles is much smaller than 1μm, which indicates that TiO₂ particles in UV-resistant fibres prapared by direct melt spinning with on-line addition are finely dispersed and evenly distributed.

Chemical fibre filament has a regular shape, so it becomes convenient to determine the density using density gradient column. There exists great differences
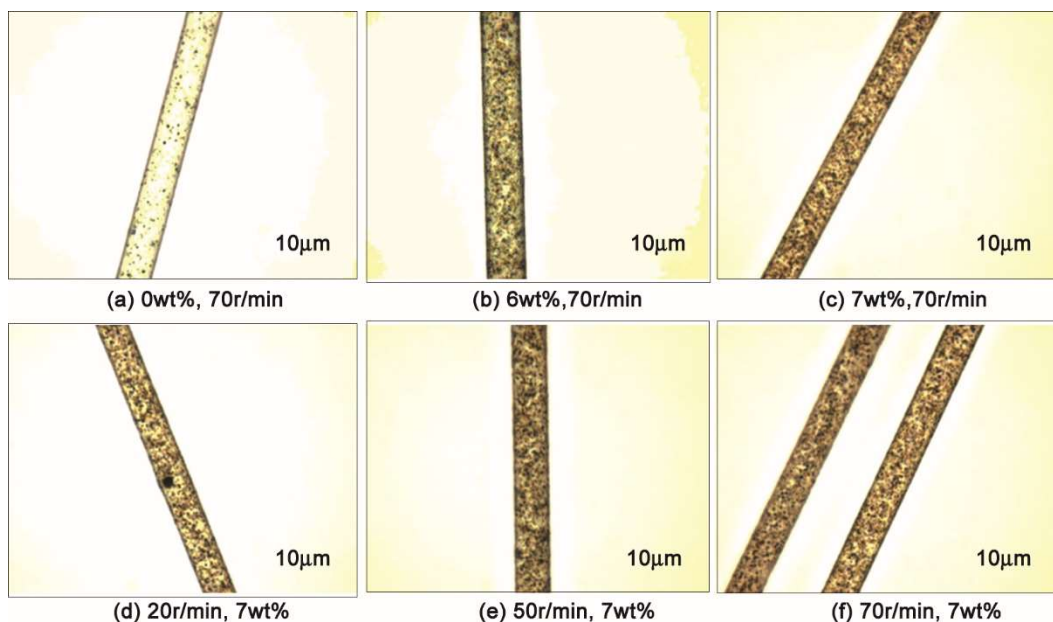

Fig.2 — OM images of POY with different masterbatch content and rotating speed [10μm]

Table 2 — Analysis results from image software

Fibre	Particle number	Average area μm^2	Heywood diameter μm	Image area μm^2	Area fraction %
0wt%	110	0.546	0.417	1212.700	5.0
6wt%	220	1.004	0.565	1694.329	13.0
7wt%	207	1.214	0.622	1422.585	17.7

between the density of inorganic particles and the PET matix. The addition of TiO2 particles changes fibre density. If TiO2 particles are unevenly dispersed, it will cause great volatility in density values. In addition, density gradient method can provide extremely high test accuracy, even accurate to the ten-thousandth.

The density values of POY fibres with 70r/min rotating speed and 6wt% masterbatch content are listed as follows:

$$\begin{pmatrix} 1.35459 & 1.35408 & 1.35398 & 1.35388 & 1.35378 \\ 1.35307 & 1.35297 & 1.35256 & 1.35246 & 1.35145 \\ 1.35145 & 1.35125 & 1.35104 & 1.35013 & 1.34983 \\ 1.34973 & 1.34952 & 1.34942 & 1.34882 & 1.35159 \\ 1.35415 & 1.35468 & 1.35382 & 1.35382 & 1.35403 \end{pmatrix} \qquad \dots (3)$$

The density values of POY fibres with 20r/min rotating speed and 7wt% masterbatch content are shown in following equation:

$$\begin{pmatrix} 1.34994 & 1.34983 & 1.35076 & 1.35209 & 1.35127 \\ 1.35260 & 1.35373 & 1.35321 & 1.35485 & 1.35496 \\ 1.35506 & 1.35537 & 1.35547 & 1.35547 & 1.35547 \\ 1.35557 & 1.35588 & 1.35428 & 1.35516 & 1.35593 \end{pmatrix} \qquad \dots (4)$$

The density values of POY fibres with 70r/min rotating speed and 7wt% masterbatch content are expressed as follows:

$$\begin{pmatrix} 1.34928 & 1.35282 & 1.3544 & 1.35469 \\ 1.35469 & 1.35489 & 1.35499 & 1.35489 \\ 1.35548 & 1.35538 & 1.35587 & 1.35617 \\ 1.35626 & 1.35572 & 1.35594 & 1.35682 \end{pmatrix} \qquad \dots (5)$$

Generally, mass fraction crystallinity (X_w) can be calculated from the measured filament density, using the following equation[11]:

$$X_w = \frac{\rho - \rho_{am}}{\rho_c - \rho_{am}} \times \frac{\rho_c}{\rho} \qquad \dots (6)$$

where ρ is the density of polymer; and ρ_c & ρ_{am}, the densities of fully crystalline and amorphous polymers

respectively. For PET, ρ_c of 1.455g/cm^3 and ρ_{am} of 1.335 g/cm^3 are used[12,13].

The mass fraction of inorganic particles can be analogied mass fraction crystallinity according to Eq. (6), which is presented in following equation:

$$\omega = \frac{\rho - \rho_m}{\rho_p - \rho_m} \times \frac{\rho_p}{\rho} \qquad \dots (7)$$

where ρ is the density of fibers; ρ_m, the density of PET matrix; and ρ_p, the density of TiO2 particles. For POY fibres of PET and TiO2 particles, ρ_m of 1.4 g/cm^3 and ρ_p of 3.8 g/cm^3 are employed[14] respectively.

According to Eqs (7), Eqs (3)–(5) can be translated to corresponding mass fraction, which are described below:

$$\begin{pmatrix} 1.66378 & 1.60623 & 1.59494 & 1.58364 & 1.57235 \\ 1.49212 & 1.48081 & 1.43444 & 1.42312 & 1.30874 \\ 1.30874 & 1.28607 & 1.26226 & 1.15900 & 1.12492 \\ 1.11356 & 1.0897 & 1.07833 & 1.01010 & 1.32461 \\ 1.61413 & 1.67393 & 1.57687 & 1.57687 & 1.60058 \end{pmatrix} \qquad \dots (8)$$

$$\begin{pmatrix} 1.13742 & 1.12492 & 1.23050 & 1.38124 & 1.28834 \\ 1.43896 & 1.56670 & 1.50795 & 1.69310 & 1.70551 \\ 1.71678 & 1.75172 & 1.76299 & 1.76299 & 1.76299 \\ 1.77425 & 1.80916 & 1.62880 & 1.72805 & 1.81479 \end{pmatrix} \qquad \dots (9)$$

$$\begin{pmatrix} 1.06242 & 1.46385 & 1.64234 & 1.67506 \\ 1.67506 & 1.69761 & 1.70889 & 1.69761 \\ 1.76411 & 1.75285 & 1.80804 & 1.84181 \\ 1.85194 & 1.79115 & 1.81592 & 1.91493 \end{pmatrix} \qquad \dots (10)$$

The average value and standard deviation of density and mass fraction for UV-resistance fibres are listed in Table 3. As the mixer speed raises, the fibre density and mass fraction of TiO2 particles increase, while the standard deviation decreases, indicating that at the same content of masterbatch, the dispersion of TiO2 particles is improved with the increasing in mixer speed. When the content of masterbatch is 6wt%, theoretical content of TiO2 particles in the fibre is 1.4wt% containing 1.2wt% from the masterbatch and 0.2wt% from semi-dull PET melt. While the calculated value according to Eq. (7) is 1.3984wt%, which is very close to the theoretical value. At the same rotating speed of mixer, the mass fraction of TiO2 particles for

fibres containing 7wt% masterbatch is 0.3wt% greater than that of fibres containing 6wt% masterbatch, similar to the theoretical value of 0.2wt%. Therefore, by the aid of direct melt spinning with on-line addition, TiO_2 particles are still in good dispersion at high content of 6wt% and 7wt% masterbatch. Among other things, the formula of mass fraction of inorganic particles in fibre has been deduced on the basis of crystallinity, and the calculated value is consistent with theoretical value.

3.2 Tensile Properties of Micro/Nano Fibres

When masterbatch content is 7wt%, the properties of fibres from direct melt spinning with on-line addition and chip spinning are illustrated in Table 4. The tenacity of fibres from melt-direct spinning increases by 13.87%, the CV value decreases by 75.19% and Heywood diameter of TiO_2 particles decreases by 13.97%. In addition, the OM images show that at the same masterbatch content the fibres from

Table 3 — Density of fibre and mass fraction of TiO_2

Samples	Density, g·cm⁻³		Mass fraction of TiO_2, %	
	Average value	Standard deviation	Average value	Standard deviation
70r/min, 6wt% POY	1.3515	0.0041	1.3984	0.2117
20r/min, 7wt% POY	1.3538	0.0021	1.5794	0.2319
70r/min, 7wt% POY	1.3549	0.0018	1.6977	0.1994

Table 4 — Performance comparison of fibres from melt direct spinning and chip spinning

Parameter	POY from melt spinning	POY from chip spinning
Linear density, dtex	135.2	151.5
Linear density, CV %	0.10	0.23
Tenacity, cN/dtex	1.97	1.73
Tenacity, CV %	2.55	10.28
Elongation at break, %	121.2	134.71
Elongation at break, CV %	2.52	6.76
Heywood diameter, μm	0.622	0.723
Area fraction,%	17.7	2.2

Table 5 — UV-resistance performance of fabrics

Samples	Plain weave fabric		Knitted pile fabric A		Knitted pile fabric B	
	0wt%	7wt%	0wt%	7wt%	0wt%	7wt%
UVA Transmittance, %	25.1	3.2	12.5	0.1	17.9	1.3
UVB Transmittance, %	21.2	0.1	7.6	0.1	12.8	0.1
UPF values	5	326	12	935	7	589

direct melt spinning with on-line addition have more particle numbers and smaller particle size than that of fibres from chip spinning. Therefore, the comparison results of direct spinning and chip spinning show that the former presents better dispersion of inorganic particles and superior performance.

3.3 Ultraviolet Protection Factor

Draw textured yarn (DTY) fibres at masterbatch content of 7wt% and 0wt%, with 70r/min rotating speed of the mixer, were woven into plain weave fabric, and knitted pile fabrics A and B respectively. The UPF values of various fabrics are shown in Table 5, which indicates that UPF values of the fabrics are much greater than the standard "UPF>40,T(UVA)<5%".

4 Conclusion

4.1 At the mixer rotating speed of 70r/min, Heywood equivalent diameters of TiO_2 particles in fibres with addition of 0wt%, 6wt% and 7wt% masterbatch are 0.417μm, 0.565μm and 0.622μm respectively. The formula of mass fraction of inorganic particles in fibre is deduced on the basis of crystallinity and fibre density.

4.2 Compared with chip spinning fibres, the fibres prapared by direct melt spinning with on-line addition presents better dispersion of inorganic particles and superior mechanical properties. When 7wt% masterbatch is empolyed, the tenacity of fibres from melt-direct spinning increases by 13.87%, the CV value decreases by 75.19% and Heywood diameter of TiO_2 particles decreases by 13.97%.

4.3 The UPF values of fabrics made from UV-resistance micro/nano fibres are found much greater than the standard of UV-resistance fabric.

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