Particle Dispersibility Improvement of Polyester Fibers with a New Line Injection

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In order to develop a new line injection system for spin draw yarn (FD SDY) fibers, the effect of various parameters in extrusion and melt line conditions on the dispersion and distribution of TiO_2 particles within FD PET fibers was investigated. As a result, the dispersibility of TiO_2 particles in a PET matrix is found to depend on the particle size and its surface characteristics. Surface modification of TiO_2 by dimethyl polysiloxane resulted in the improved dispersibility and affinity of TiO_2 particles in the PET matrix. Especially, residence time, mixing temperature, and mixing shear rate in the new line injection system under the SDY spinning process were very important parameters to minimize the agglomeration of TiO_2 particles. The FD SDY prepared by the new line injection system was superior to those using the polymerization process and the conventional masterbatch chip dosing process in the color-L and color-b values of the fibers.

Key Words: Line injection system, Polyethylene terephthalate, Fiber, Dispersibility, TiO_2

Introduction

Polyester fibers have excellent basic properties, such as mechanical properties and chemical resistance, antibiosis, easy care characteristics, and form stability, which make them special among synthetic fiber widely used in fibers, films, and various other areas.[1,2]

In the manufacturing process for polyester fibers, colorant, matting agent, cross-linking reagent, aromatic agent, deodorant, and flame retardant are used as functional characteristic additives to obtain the physical properties demanded from the application field.[3-10] Titanium dioxide is one additive that is widely used in polyester fibers, as it has stable chemical and physical properties, high reflexibility and index of refraction, and ideal particle size distribution.[11,12]

Masterbatch is a resin that contains a high concentration of pigments and additives, which use chips to form masterbatch to replace powder from pigments and additives. Masterbatch is able to improve the workplace process and obtain a high degree of dispersion.[13,14]

In the polyester fiber spinning process, the methods of adding the additive are divided into the dosing process and the line injection system. In the dosing process, additives and pigments are fed in solid chip form. However, a masterbatch of additives and pigments is supplied in a melted form in the line injection system.[15] Compared with the dosing method, the line injection method has excellent accuracy and broad application areas for pigments and additives. In the line injection system, it is important to design a static mixer to minimize layer separation of the polymer flow caused by laminar flow and heat decomposition derived by the fusion line stay.

In previous work, we reported the effects of injection conditions on the dispersibility of TiO_2 particles in the polymerization of poly(ethylene terephthalate) (PET).[16] In this study, the effect of various parameters in extrusion and melt line conditions on the dispersion and distribution of TiO_2 particles within spin draw yarn (FD SDY) fibers was investigated with several techniques.

Experimental

Materials. PET chips used in this study were supplied by Huvis Co. of Korea. These chips have an average molecular weight of 20000 g/mol and TiO_2 content of 1 wt % (super bright, SB), 0.35 wt % (SD), and 2.2 wt % (FD). TiO_2 was commercially available in four kinds of normal TiO_2, two kinds of inorganic coated TiO_2, and organic coated TiO_2, as shown in Table 1. Antimony trioxide and trimethyl phosphate were used as catalyst and antioxidant, respectively, and were supplied by Aldrich.

Synthesis of Co-PET. PET oligomer (40 g) was added to a 100 mL reactor equipped with a mechanical stirrer, thermometer sensor, and reflux condenser. The PET oligomer was heated to 250 °C and then TiO_2 (T-1-N), antimony trioxide (3 g) and trimethyl phosphate (1.5 g) were added to the reactor. The mixtures were gradually heated to 250 °C and reacted for 1 h. Antimony trioxide (3 g) and trimethyl phosphate (1.5 g) were added into mixtures. The mixtures were gradually heated to 280°C and reacted under a vacuum of 0.5 torr for 1 h. Finally, chip type

Table 1. Dosability of normal and surface-treated TiO_2

TiO_2	Average particle size (μm)	Surface type	Dosability (CV%)
T-1-N	0.36	Normal	3.74
T-2-N	0.39	Normal	3.65
T-3-N	0.41	Normal	3.41
T-4-N	0.42	Normal	3.4
T-5-C	0.36	SiO_2/Al_2O_3	3.13
T-6-C	0.39	SiO_2/Al_2O_3	1.91
T-7C	0.45	Polysiloxane	1.79
T-8-C	0.58	Epoxy silane	1.60

Table 2. Representative physical properties of SD PET yarns prepared by polymerization and dosing process

Process	TiO$_2$	Yarn properties				
		Fineness (d)	Tenacity (g/d)	Elongation (%)	U (%)	Shrinkage (%)
Dosing	T-1-N	75.9	4.21	36.9	1.12	7.1
	T-2-N	76.4	4.12	40.0	1.02	7.3
	T-3-N	74.6	4.24	36.8	1.08	7.3
	T-4-N	76.3	4.24	38.3	1.10	7.6
	T-5-C	75.8	4.32	38.9	1.09	7.4
	T-6-C	75.3	4.40	39.4	1.07	7.2
	T-7-C	75.9	4.26	37.6	1.13	7.3
	T-8-C	76.0	4.02	38.3	1.37	7.2
Polymerization	T-1-N	76.9	4.38	34.6	1.21	7.4

melting materials were obtained (yield: 90.5%). FT-IR (KBr; v, cm^{-1}): 2970 (CH), 1725 (C=O), 1638 (C=C), 1620 (C=C), 1190 (C-O-C), 1062 (C-H), 988 (CH).

Line injection spinning. The SDY 75d/36f FD filaments were prepared using the new line injection system. The diameter of the main extruder is 30 mm, L/D: 32, screw pitch: 32, pitch width: 30 mm, screw type: full flight+pineapple, compression ratio (CR): 3.8/1. G/R-1 G/R-2 speeds were 1025 and 3780 m/min, respectively. G/R-1 G/R-2 temperatures were 87 and 120 $^{\circ}$C, respectively. Quenching speed was 0.8 *m/s*.

Masterbatch. An SB PET solid polymerization chip was used as a material chip. 7 wt % TiO$_2$-containing masterbatch was prepared using a twin screw extruder (ZSK-25) at melt mixing temperature of 260 $^{\circ}$C and screw speed of 200 rpm. Table 2 shows the characteristics of the TiO$_2$ masterbatch.

Characterization and measurements. Dosability (coefficient of variation, CV) shows the distribution of TiO$_2$ in the preparation of TiO$_2$ masterbatch chip, which is defined as the standard deviation of TiO$_2$ divided by the average.

$$CV\ (\%) = (\text{standard deviation/average}) \times 100 \quad (1)$$

TiO$_2$-coated films were prepared by dropping of 10% TiO$_2$/methanol solution on cover glass. Deionized water was selected as the testing liquid. The contact angle of the films was measured at a temperature of 20 $\pm$ 1 $^{\circ}$C and humidity of 65 $\pm$ 2% using a sessile drop method on a contact angle gonimeter (Erma Co., G-1 type). For each sample, every calculated contact angle was an average of ten measurements with a standard deviation below 1°.

TiO$_2$ was dispersed in EG with a concentration of 20% by a tooth disc type homogenizer, and the particle size of the TiO$_2$/EG slurry was measured using a light-scattering particle size analyzer (Malvern Co., Mastersizer X).

The viscoelasticity of the melt PET was investigated using a melt viscosimeter (Rheometric Scientific Co., RDA3) at a temperature range of 275 - 295. The diameter of the plate was 25 mm, and the gap between the plates was fixed at 1.1 mm.

Polymer fluids were assumed to be Poiseuille fluids, and as the fluids flowed through a cylindrical tube, the pressure drop (ΔP) was calculated by the following equation.

$$\Delta P = \frac{8 \eta L Q}{\pi R^4} \quad (2)$$

where η is the viscosity, Q is the flux, and L and R are the length and radius of cylindrical tube, respectively.

A tensile test was conducted using an Instron mechanical tester (Fafegraph-M and Textecho Co., Germany) at a temperature of 25 $^{\circ}$C and relative humidity of 65%. The specimen length was 100 mm and the tensile speed was 200 mm/min. All mechanical property values were obtained by averaging of ten experimental values.

The fibers were made into a hoop form and hung on a clip of 0.7 g, and then the length (L_1) of the hoop was measured. The hoop was added into a glass tube in a damp contraction percentage measurement device and dipped at 100 $\pm$ 1 $^{\circ}$C for 30 min. After taking the hoot out of the tube for 2 h, the length (L_2) of the hoop was measured. The shrinkage was calculated according to the following equation.

$$\text{Wet shrinkage ratio (\%)} = \frac{L_1 - L_2}{L_1} \times 100 \quad (3)$$

Evenness (U) was measured using an evenness tester (Keisokki Kogyo) at a speed of 250 mm/min. The evenness values were obtained by the averaging of five experimental values.

The surface of the PET samples was treated with plasma etching, and the particle distribution of the TiO$_2$ was investigated using a scanning electron microscope (HITACHI S-3000N).

Results and Discussion

Effect of dosing conditions. Table 1 shows the dosability of the TiO$_2$ according to the particle size and the surface treatment process. As can be seen, the dosability increased with increasing particle size of TiO$_2$. The dosability also increased according to the surface treatment of the TiO$_2$ with inorganic and organic compounds, due to the improved fluidity of the TiO$_2$ powders.

Figure 1 shows the contact angle and average particle size of TiO$_2$ prepared from different kinds of TiO$_2$. As a result, the contact angle for T-1-N~T-4-N increased with increasing aver-
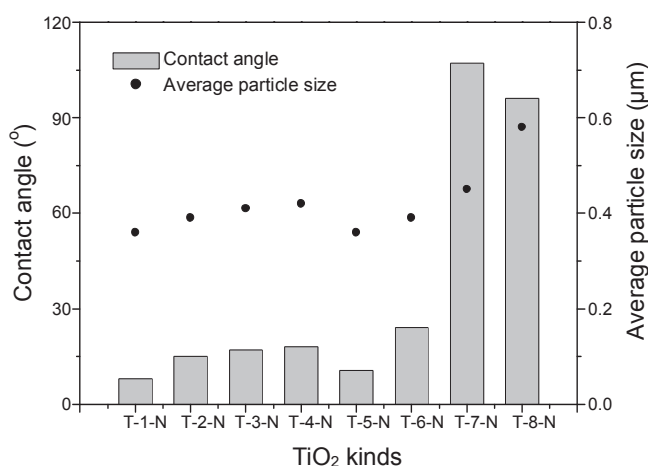
Figure 1. Contact angle and average particle size of TiO_2 prepared from different experimental conditions.
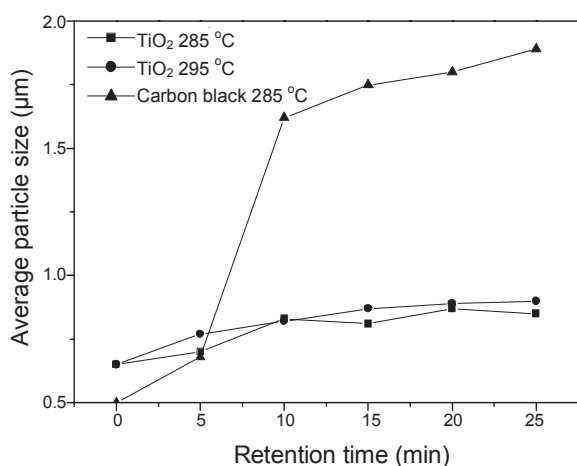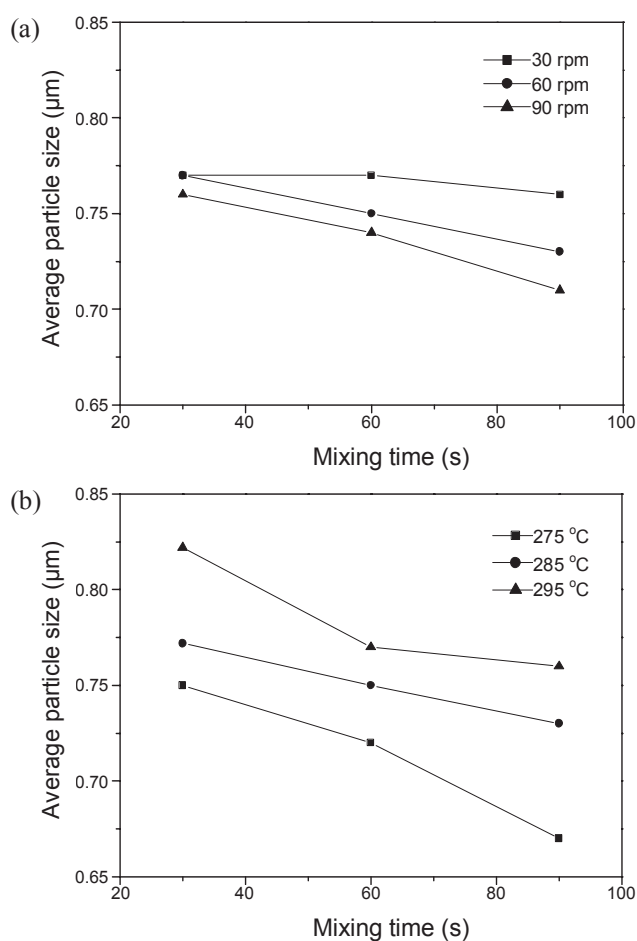

Figure 2. Dispersibility of TiO_2 and carbon black as a function of retention time.

Figure 3. (a) Effect of mixer rpm on dispersibility of TiO_2 at 285 °C; (b) Effect of mixing temperature on dispersibility of TiO_2 at 60 rpm of rotor speed.
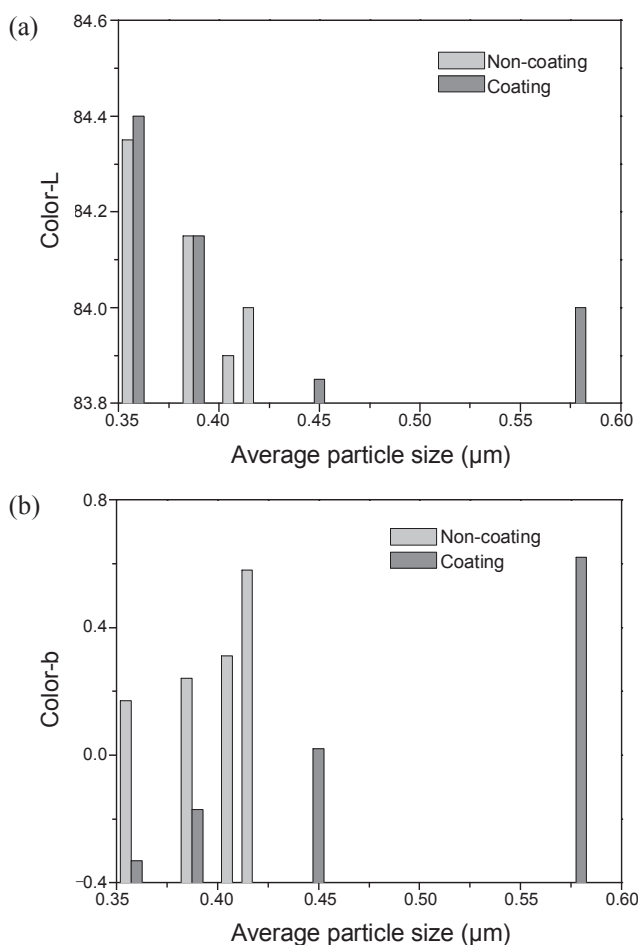
$$\text{Shear rate} = k \times \text{rotor speed (rpm)} \quad (4)$$

where k is the geometrical factor of rotor and head.

According to Equation 1, the shear rate is directly proportional to the rotor speed. In order to investigate the effects of dispersion time and shear rate on the dispersibility of TiO_2, the average particle size of TiO_2 as a function of rotor speed was measured. Figure 3(a) shows the effect of rotor speed on the dispersibility of TiO_2 at 285 °C. As can be seen, the dispersibility increased with increasing rotor speed and mixing time. From this result, it is clear that the increase of shear rate is an effective method to increase the dispersibility of TiO_2.

Figure 3(b) shows the effect of mixing temperature on the dispersibility of TiO_2 at a rotor speed of 60 rpm. As a result, the dispersibility of TiO_2 increased with decreasing mixing temperature, which was due to the increased melt viscosity of the polymer melts.

Properties of filaments prepared by masterbatch process. In order to investigate the effect of average particle size of TiO_2 on the color of filaments, 57d/36f SD PET filaments were prepared from a 7 wt % TiO_2-containing masterbatch chip and SB PET. Figure 4 shows the effect of average particle size in non-coating and coating type TiO_2 on the color-L (visual lightness) and color-b (yellowness to blueness) values of filaments.

age particle size of TiO_2. The average particle size of inorganic-coated T-5-C (or T-6-C) is similar to that of T-1-N (or T-2-N), whereas the contact angle of T-5-C (or T-6-C) is higher than that of T-1-N (or T-2-N). The organic-coated T-7-C and T-8-C showed the highest values of contact angle in this study. The increased contact angle indicated that the decrease of surface free energy, and the supply a uniform particle size of TiO_2 improved the affinity between the hydrophobic PET and SiO_2.

Distribution and agglomeration charateristics of TiO_2 particles. Figure 2 shows the effect of retention time on the dispersibility of TiO_2 and carbon black. As can be seen, the average particle size of TiO_2 increased from 0.65 μm to 0.86 μm after 25 min at 285 °C. The average particle size of TiO_2 at 295 °C is slightly higher than that at 285 °C. However, the average particle size of carbon black increased from 0.50 μm to 1.88 μm under the same conditions, which indicates that a serious particle agglomeration occurred. This can be attributed to the fact that the increased fluidity is derived from the low viscosity of polymers and the increased PH value is derived from the decomposition of polymers.

The shear rate of the Brabender mixer was calculated from the following equation.

(a)

(b)

Figure 4. Effect of average particle size in non-coating type and coating type TiO$_2$ on color L and b values of filaments.

As shown in Figure 4(a), the L value and whiteness increased with decreasing average particle size of TiO$_2$. The b value and yellow index decreased with decreasing average particle size of TiO$_2$, as shown in Figure 4(b).

Table 2 shows the physical properties of SD PET yarns prepared by dosing and polymerization processes. Giving comprehensive consideration to the dispersibility of TiO$_2$, color, and physical properties of yarns, T-4-N and T-7-C were used as TiO$_2$ in the masterbatch of dosing and line injection processes.

Rheological properties of FD PET. Temperature and shear rate are important factors in the improvement of the dispersibility of TiO$_2$. Figure 5 shows the melt viscosity of FD PET as a functions of shear rate and temperature. As can be seen, the melt viscosity decreased with increasing temperature and shear rate. Table 3 lists the rheological values, i.e., melt viscosity, store elastic modulus, and loss elastic modulus, of FD PET at various temperatures and a shear rate of 100 rad/s.

The shear rate can expressed as a function of shear speed.

$$\tau_w = k(\gamma_w)^n \tag{5}$$

$$\eta = \tau_w / \gamma_w \tag{6}$$
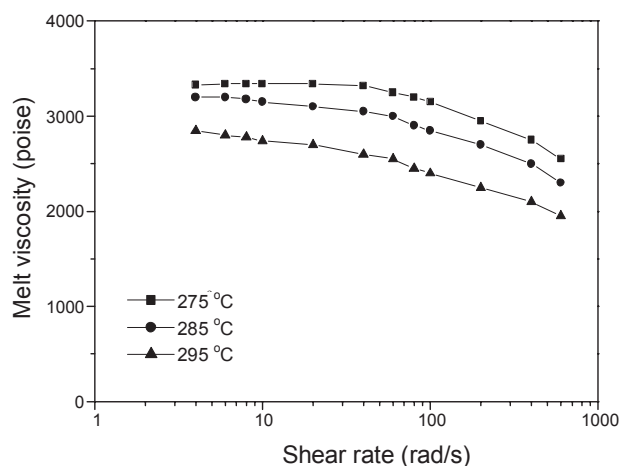
Figure 5. Mel viscosity of melt FD PET as a function of shear rate at various temperatures.

Table 3. Representative rheological values and power law index of melt FD PET at various temperature and a shear rate of 100 rad/s

Temperature	275 °C	285 °C	295 °C
Melt viscosity (P)	3106	2811	2352
G' (dyne/cm^2)	5.07×10^5	4.73×10^5	3.98×10^5
G" (dyne/cm^2)	3.06×10^5	2.77×10^5	2.32×10^5
tan δ	6.05	5.86	5.83
k	3536	3392	3076
n	0.965	0.953	0.938

From Equations (5) and (6), η can expressed as follows:

$$\eta = k(\gamma_w)^{n-1} \tag{7}$$

Taking a log on both sides of Equation 7,

$$\log\eta = \log k + (n-1)\log(\gamma_w) \tag{8}$$

where τ_w is the shear rate, γ_w is the shear speed, η is the viscosity, n is the power law index of fluids, and k is the constant, which is the viscosity at $\gamma_w = 1$.

The power law index k and n for line injection spinning simulation were calculated by plotting $\log\eta$ as a function of $\log(\gamma_w)$. The results are shown in Table 4. As can be seen, k and n decreased with increasing temperature.

Effect of static mixer. The pressure rising rate of the spinning pack was evaluated by measurements of time for pressure rise to 100 kgf/cm^2. Figure 6 shows the effect of the number of static mixer elements on the pack life time. As a result, the pack life time increased with the increasing number of static mixer elements.

Figure 7 shows the effect of the number of static mixer elements and the process method on the dispersibility of TiO$_2$. As can be seen, the pressure drop of FD PET prepared from polymerization, dosing process, and static mixer and dosing process after 60 min are 97 kgf/cm^2, 31 kgf/cm^2, and 10 kgf/cm^2, res-

Table 4. Dispersibility and mechanical properties of FD SDY yarns prepraed by masterbatch process and conventional polymerization process

Process		Polymerization	Dosing	Line injection	
Base resin		-	SD PET	SD PET	SB PET
Dispersion	Average size (μm)	0.79	0.73	0.73	0.75
	Above 2 μm (%)	0.33	0.58	0.08	0.61
Distribution	Average weight (wt %)	2.23	2.25	2.21	2.22
	Standard deviation	0.07	0.05	0.02	0.02
Properties	Tenacity (g/d)	4.17	4.28	4.21	4.33
	Elongation (%)	35.6	35.4	34.8	29.8
	U (%)	1.07	0.96	1.09	1.14
	Color-b	2.95	2.64	2.71	2.31
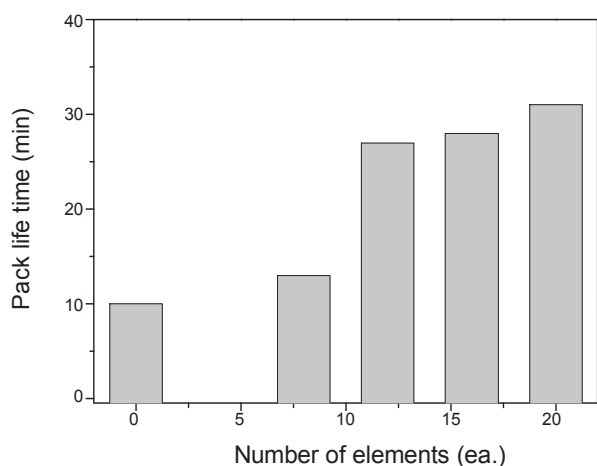
Figure 6. Effect of number of static mixer elements on dispersibility and pack life time.
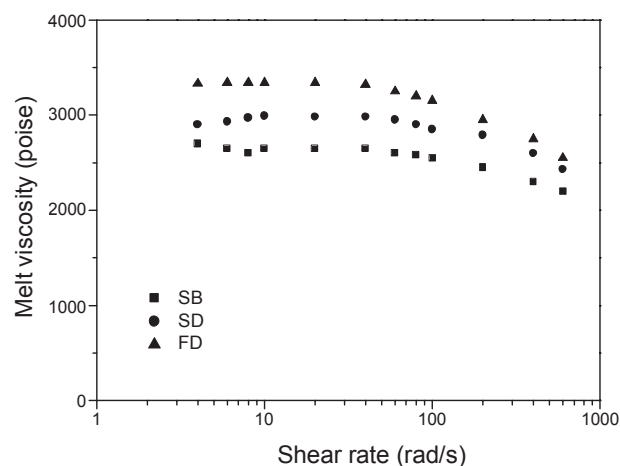
Figure 8. Mel viscosity of melt PET as a function of shear rate at various TiO_2 content.
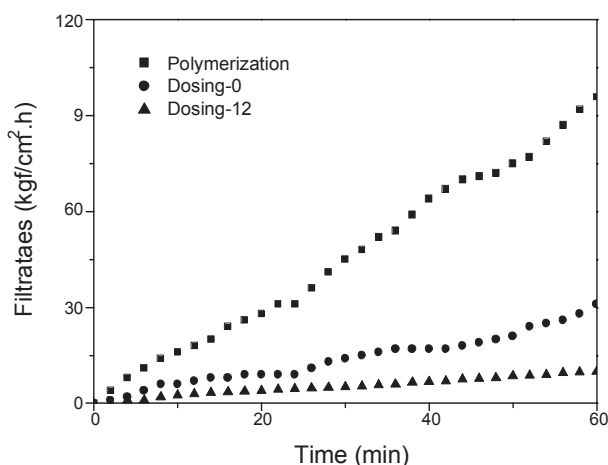
Figure 7. Effect of number of static mixer elements and process method on dispersibility of TiO_2 and pack life time.

pectively. This result indicates that the dispersibility and the distribution characteristics are significantly improved by the use of a static mixer.

Properties of FD PET yarns prepared by line injection process. Table 4 shows the dispersibility, distribution, and mechanical properties of FD SDY yarns prepared by masterbatch process

and by conventional polymerization process. As can be seen, the FD PET prepared through the masterbatch process showed better dispersibility, distribution, and color (b value) than that done through the conventional polymerization process. In the line injection process, the physical properties of yarns based on the SD PET yarns is similar to that of SB PET yarns, whereas the dispersibility and distribution characteristics of SD PET yarns are better than those of SB PET yarns. This situation can be explained by the melt viscosity of PET as a function of shear rate, as shown in Figure 8. When the SD PET was used as a base resin, TiO_2 dispersed uniformly in the resin and increased the melt viscosity, resulting in an improvement of the dispersibility and distribution characteristics of TiO_2 particles.

Table 5 shows the dispersibility, distribution, and mechanical properties of FD SDY yarns with different TiO_2 contents prepared by the line injection process and by the conventional polymerization process. As can be seen, the dispersibility and distribution increased with increasing TiO_2 content. However, the TiO_2 content did not significantly affect the mechanical properties.

Table 6 shows the dispersibility, distribution, and mechanical properties of FD SDY yarns with different TiO_2 masterbatch types prepared by the dosing process and conventional polymerization process. As a result, the average particle size of the yarns prepared from surface-treated TiO_2 is lower than that from

Table 5. Dispersibility and mechanical properties of FD SDY yarns with different TiO_2 contents prepared by line injection process and conventional polymerization process

Process		Polymerization		Line injection	
TiO_2 addition (wt %)		2.2	2.2	2.4	2.6
Dispersion	Average size (μm)	0.79	0.73	0.77	0.83
	Above 2 μm (%)	0.33	0.08	0.08	0.61
Distribution (content)	Average weight (wt %)	2.23	2.21	2.24	2.64
	Standard deviation	0.07	0.02	0.02	0.02
Properties	Tenacity (g/d)	4.17	4.21	4.20	4.23
	Elongation (%)	35.6	34.8	33.8	35.9
	U (%)	1.07	1.09	0.84	1.00
	Color-b	2.95	2.71	2.59	2.71

Table 6. Dispersibility and mechanical properties of FD SDY yarns with different TiO_2 masterbatch type prepared by dosing process and conventional polymerization process

Process		Polymerization	Line injection		
Master batch	TiO_2 type	T-1-N	T-4-N		T-7-C
	TiO_2 content (wt %)	-	30	50	50
Dispersion	Average size (μm)	0.79	0.77	0.73	0.67
	Above 2 μm (%)	0.33	0.26	0.08	0.09
Distribution (content)	Average weight (wt %)	2.23	2.15	2.21	2.18
	Standard deviation	0.07	0.02	0.02	0.02
Properties	Tenacity (g/d)	4.17	4.28	4.21	4.22
	Elongation (%)	35.6	42.0	34.8	38.3
	U (%)	1.07	1.07	1.09	1.09
	Color-b	2.95	2.85	2.71	1.95

Figure 9. Relationship between TiO_2 dispersibility (ΔP) and CV of tenacity.

Figure 10. SEM images of FD PET prepared by polymerization system (a: bulk-PET, b: fiber) and a new line injection system (c: bulk-PET, d: fiber).
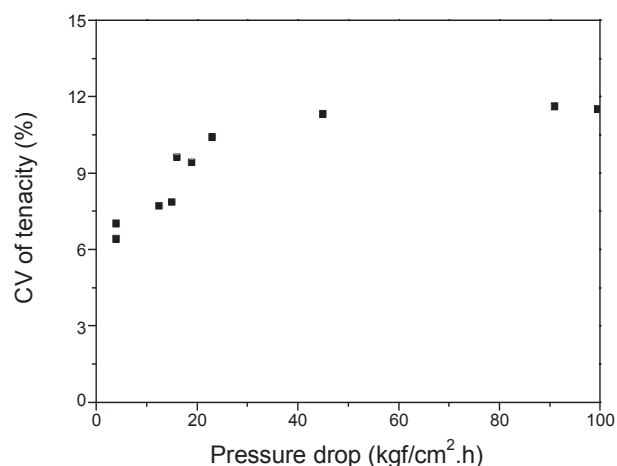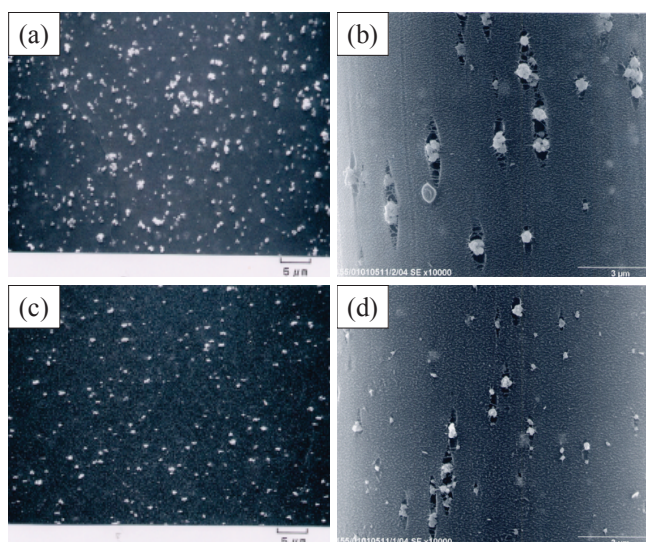
normal TiO_2, which indicates that the surface-treated TiO_2 dispersed easily in the PET. The mechanical properties was not largely affected by the TiO_2 content in the masterbatch process.

Figure 9 shows the relationship between the dispersibility (pressure drop) of TiO_2 and the CV of tenacity for FD SDY 75d/36f yarns. As a result, the pressure drop increased and the tenacity decreased with the decreasing dispersibility of TiO_2.

Morphology. Figure 10 presents SEM images of FD PET prepared by polymerization and line injection system. As can be seen, the agglomeration of TiO_2 particles for FD PET prepared by the polymerization system is larger than that for FD PET prepared by the line injection system. These results indicate that the dispersibility of FD PET prepared by the new line injection system is better than that of FD PET prepared by the polymerization system.

Conclusions

A new line injection system was developed by investigation

of the effect of various parameters on the dispersion and distribution of TiO_2 particles within FD PET fibers. The dosability increased with increasing particle size of TiO_2 and by the surface treatment of TiO_2 with inorganic and organic compounds. The average particle size of TiO_2 at 295 °C is slightly higher than that at 285 °C. The average particle size of TiO_2 was lower than that of carbon black. The L value and whiteness increased and the b value and yellow index decreased with decreasing average particle size of TiO_2. The SEM results indicated that the dispersibility of FD PET prepared by the new line injection system was better than that of FD PET prepared by the polymerization system. In conclusion, the production of FD SDY fibers using the new line injection system was successfully introduced to improve properties such as dispersion, distribution, fiber quality, and spinning processability, which are essential for applications in the commercial field.

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