Effects of Injection Conditions on Dispersibility of TiO₂ in Polymerization of Poly(ethylene terephthalate)

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Received March 8, 2010, Accepted August 25, 2010

In this study, the optimal preparation conditions in the polymerization process of poly(ethylene terephthalate) (PET) were studied in detail. As a result, the dispersibility of TiO₂ was significantly improved by the addition of dispersant and steric hinderance additives into TiO₂/ethylene glycol (EG) slurry during the esterification step. The addition sequence of TiO₂/EG slurry and stirring also affected the dispersibility of TiO₂. The SEM results showed that some TiO₂ particles were agglomerated in the PET matrix. The full dull (FD) PET chip and fiber were prepared according to the optimal preparation conditions. The FD PET fiber exhibited a better dispersibility than that of the FD PET chip.

Key Words: Poly(ethylene terephthalate), Dispersibility, TiO₂, Chip, Fiber

Introduction

The history of polyesters began from synthesis research of aliphatic polyester.¹ Research on aromatic polyesters that used terephthalic acid as an acid component were performed in Germany and Great Britain.² In the early 1940, two kinds of polyester were prepared from terephthalic acid and butylene glycol, or terephthalic acid and ethylene glycol (EG). Polyesters have crystallinity, which exhibits a fiber formation ability. Poly(ethylene terephthalate) (PET) was invented by Whinfield and Dickson, and it was industrialized as clothing fibers. Polyester fibers have excellent basic properties, such as mechanical properties and chemical resistance, antibiosis, easy care characteristics, and form stability, and as synthetic fibers were rapidly developed after the 1970s.^{1,2}

In order to obtain the physical properties of the fibers demanded from the application fields, various functional characteristic additives, such as colorant, matting agent, cross-linking agent, aromatic agent, deodorant, and flame retardant, are used in the manufacturing process.^{3,4} In the selection of additives and the decision of additive amounts, one must consider cost and physical properties of the additives, compatibility with polymers, dispersion and distribution, thermal stability in the processing, and toxicity.⁵⁻⁹ Particularly, the dispersibility and distribution characteristic are major factors that affect color, mechanical properties, modulus of elasticity, luster, and conductivity of polymers in the fiber manufacturing process.

In this study, the effects of injection conditions, such as dispersant, addition sequence of TiO₂/EG slurry, stirring, and steric hinderance, on the dispersibility of TiO₂ in polymerization of PET were investigated. The FD PET chip and fiber were prepared according to optimal preparation conditions. The properties, such as dispersibility and average particle size of TiO₂, were characterized with several techniques.

Experimental

Materials. PET chips used in this study were supplied by

Huvis Co. of Korea, which have average molecular weight of 20000 g/mol and TiO₂ content of 0 wt % (super bright, SB), 0.35 wt % (SD), and 2.2 wt % (FD). The properties of SB and SD PET are shown in Table 1. Titanium dioxide was commercially available: four kinds of normal TiO₂, two kinds of inorganic-coated TiO₂, and two kinds of organic-coated TiO₂, as shown in Table 2. Antimony trioxide (ATO) and trimethyl phosphate (TMP) used as catalyst and antioxidant, respectively, and were supplied by Aldrich.

Synthesis of PET. PET oligomer (40 g) was added in a 100 mL reactor equipped with a mechanical stirrer, thermometer sensor, and reflux condenser. The PET oligomer was heated to 250 °C and then TiO₂, ATO (0.02 g), and TMP (0.02 g) were added into the reactor. The mixtures were heated to 280 °C gradually and reacted under vacuum of 0.5 torr for 1 h. Finally, chip-type melting materials were obtained (yield: 91.3%). FT-

Table 1. Specification of SB and SD PET

Grade	IV	-COOH (meq/kg)	T _g (°C)	T _m (°C)	TiO ₂ (%)
SB	0.64 ± 0.05	30 ± 10	79 ± 1	254 ± 1	0.35
SD	0.64 ± 0.05	30 ± 10	79 ± 1	254 ± 1	0

Table 2. Characteristics of TiO₂

TiO ₂	Particle size (μm)	Surface type
T-1-N	0.36	Normal
T-2-N	0.39	Normal
T-3-N	0.41	Normal
T-4-N	0.42	Normal
T-5-C	0.36	SiO ₂ /Al ₂ O ₃ , inorganic coating
T-6-C	0.39	SiO ₂ /Al ₂ O ₃ , inorganic coating
T-7-C	0.45	Polysiloxane, organic coating
T-8-C	0.58	Epoxy silane, organic coating

IR (KBr; ν , cm^{-1}): 2970 (CH), 1725 (C=O), 1638 (C=C), 1620 (C=C), 1190 (C-O-C), 1062 (C-H), 988 (CH).

Number of particle agglomeration. Five pieces of PET sample (about 1 - 2 mg) were placed on a slide glass, and the sample was heated above melting point. Then the sample was covered with the glass cover. The number of TiO_2 particle agglomeration was measured using an optical microscope, and the number was showed by number of 5 - 10 μM and above 10 μM TiO_2 . The agglomeration particle number values were obtained by averaging of five experimental values. The number was expressed as number/10 mg.

Image analyzer. The samples were prepared according to the agglomeration TiO_2 particle number measurements, and the particle size of the samples was measured using an image analyzer. The average particle size and the content of above 2 μm were calculated from the experimental data.

TiO_2 distribution. Ten pieces of PET (5 g) were added to a furnace and the PET ash was obtained at 450 $^\circ\text{C}$. The TiO_2 content and standard deviation of the ash were measured.

Inherent viscosity measurements. The specimens was dissolved in phenol/tetrachloroethane (60/40 weight ratio) mixture solvent at 130 $^\circ\text{C}$. The concentration was measured using Ubbelohde viscosimeter 1C type at 30 $^\circ\text{C}$, and inherent viscosity (IV, $[\eta]$) was calculated from Solomon-Ciuta equation.

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{\frac{1}{2}} \quad (1)$$

where η_{sp} is the specific viscosity, η_r is the relative viscosity, c is concentration of polymer solution.

Scanning electron microscope. The surface of the PET samples was treated with plasma etching, and the particle distribution of TiO_2 was examined using a scanning electron microscope (HITACHI S-3000N).

Results and Discussion

Dispersibility of TiO_2 slurry. In order to prevent agglomeration and improve dispersibility of TiO_2 , potassium tripolyphosphate (KTPP) used as a dispersant was added to TiO_2/EG slurry. The KTPP content varied from 0 to 0.3 wt %, and the concentration of TiO_2/EG slurry was 20 wt %. Figure 1 shows the precipitation level of TiO_2/EG slurry as functions of KTPP content and ageing time. As a result, the precipitation level of TiO_2/EG slurry increased with increasing ageing time. The dispersibility improved obviously with increasing KTPP content.¹⁰ When the KTPP content was above 0.15 wt %, the inorganic particles stabilized and were well dispersed in the EG after 30 days. KTPP significantly affected the polymerization of PET above 0.2 wt % KTPP. Thus, the optimal KTPP content is 0.15 wt %.

Addition stage of TiO_2 slurry. In order to investigate the effect of addition point on the dispersibility of TiO_2 , terephthalic acid (TPA)/EG slurry of ambient temperature was mixed with oligomer (250 $^\circ\text{C}$) after esterification-1 (ES-1) stage reaction and oligomer (250 $^\circ\text{C}$) after ES-2 stage reaction, and the dispersibility (TiO_2 content: 0.35 wt %) was measured. Figure 2 shows the agglomeration particle number of TiO_2 for TiO_2/EG slurry

Figure 1. Precipitation level of 20 wt % TiO_2/EG slurry prepared with different KTPP contents as a function of aging time.

Figure 2. Effect of TiO_2/EG slurry injection step on TiO_2 dispersibility in polymerization process (ES: esterification, PC: polycondensation).

in the polymerization process. As can be seen, the dispersibility of TiO_2/EG slurry mixed with oligomer after ES-2 stage reaction is better than that of oligomer after ES-1 stage reaction. This result can be attributed to the fact that the acidity of oligomer of ES-2 stage (0.27 meq/g) is lower than that of ES-1 stage (0.87 meq/g). It is understood that OH group charged positive charge at low PH reaction system, and charged negative charge at high PH reaction system. Thus, negative charged TiO_2 reduces repulsion force between the particle surfaces and increases particle agglomeration at high PH reaction system.¹¹

Figure 3 shows the dispersibility of TiO_2 particle obtained from esterification reaction and polycondensation process examined by an optical microscope. As a result, many agglomeration phenomenon of TiO_2 were observed after addition of TiO_2/EG slurry to oligomer after esterification reaction, as shown in Figure 3 (a). The dispersibility of TiO_2 particles improved with increasing reaction time, which was due to the increased melt viscosity of PET and mixing effect. Figure 4 shows the SEM images of 0.35 wt % TiO_2 -containing SD PET chip after poly-

Figure 3. Dispersibility of TiO₂ particles obtained from different steps: (a) esterification reactor and (b) polycondensation reactor.

Figure 4. SEM images of TiO₂ particles with different magnification in PET matrix: (a) ×2000, (b) ×10000, and (c) ×10000.

Table 3. TiO₂/EG slurry injection conditions in polymerization process

Step	1	2	3	4	5
Condition-1	TiO ₂ , Sb ₂ O ₃ , TMP	PC ^a start	-	-	-
Condition-2	TiO ₂ , Sb ₂ O ₃ , TMP	Agitation (5 min)	PC start	-	-
Condition-3	TiO ₂	Agitation (5 min)	Sb ₂ O ₃ , TMP	Agitation (5 min)	PC start
Condition-4	Sb ₂ O ₃ , TMP	Agitation (5 min)	TiO ₂	Agitation (5 min)	PC start

^aPC: polycondensation

condensation. As can be seen, some TiO₂ particles agglomerated in the PET matrix.^{12,13}

Effects of catalyst, heat stabilizer, and stirring. It is important to prevent secondary agglomeration of TiO₂ in the polymerization process. In particular, esterification catalyst and heat stabilizer work as agglomeration agents for TiO₂. The TiO₂/EG slurry injection conditions in the polymerization process are shown in Table 3. Figure 5 shows the effect of TiO₂/EG slurry

Figure 5. Effect of TiO₂/EG slurry injection conditions on TiO₂ dispersibility in polymerization process.

Table 4. Average particle size of TiO₂, TPA, and oligomer powders

Particle	Average particle size (μM)
TiO ₂	0.36
TPA	85.7
Oligomer powder	99.6

injection conditions on the dispersibility of TiO₂ particles in the polymerization process. As a result, the dispersibility of the slurry prepared from condition 2 is better than that of condition 1, which was due to stirring effect. From the result of condition 3, the respective addition of TiO₂, ATO, and TMP can improve the dispersibility of the slurry. The result of condition 4 indicated that the addition of TiO₂ to the slurry after addition of ATO and TMP can also improve the dispersibility in the slurry.¹⁴

Effect of steric hinderance additives. The agglomeration of TiO₂ was often happened at the stage for addition of TiO₂/EG slurry to melt oligomer of 150 - 260 °C. At this stage, the EG (boiling point: 198 °C) evaporated instantaneously, and the agglomeration between the TiO₂ particles occurred. Thus, TPA and oligomer powders were used as steric hinderance additives in this study. The average particle size of TiO₂, TPA, and oligomer powders measured with particle size analyzer is listed in Table 4. Figure 6 shows the effect of steric hinderance of TPA oligomer powders on the dispersibility of TiO₂. As can be seen, the slurry exhibited a maximum dispersibility at 0.1 wt % TPA, which was due to the slurry showing an appropriate acidity at this condition, whereas, after which the dispersibility of TiO₂ in TiO₂/EG slurry decreased, which was due to the increased acidity of TiO₂/EG slurry.¹⁵

Figure 7 shows the effect of steric hinderance of PET oligomer powders on the dispersibility of TiO₂. As a result, the dispersibility of the slurry increased with increasing PET content and exhibited a constant value above 0.05 wt % PET.

Optimal preparation conditions of FD PET chip. From above experimental results, optimal preparation conditions for FD PET polymerization were determined, and the conditions are summarized in Table 5. FD PET chip and fiber were prepared

Figure 6. Effect of steric hindrance of TPA powders on TiO_2 dispersion.

Figure 7. Effect of steric hindrance of PET oligomer powders on TiO_2 dispersion.

according to the optimal conditions, and the results are also shown in Table 5. As can be seen, the dispersibility of FD PET chip prepared in condition 4 is better than that of condition 1, which was due to the effects of dispersant and steric hindrance. Table 6 shows the dispersibility of TiO_2 for FD PET chip and fiber. As a result, the average particle size of TiO_2 in FD PET chip is $0.83 \mu\text{M}$, whereas the average particle size of TiO_2 in FD PET fiber is $0.70 \mu\text{M}$. The standard deviation and TiO_2 content of above $2 \mu\text{M}$ for the fiber are lower than that of the chip. From these results it is confirmed that the dispersibility of FD PET fiber is higher than that of FD PET chip.

Conclusions

The effects of injection conditions, such as dispersant, addition stage of TiO_2/EG slurry, stirring, and steric hindrance, on the dispersibility of TiO_2 in polymerization of PET were investigated. As a result, the TiO_2/EG slurry showed a better dispersi-

Table 5. Experimental conditions for FD PET polymerization

	T-1	T-2
TiO_2 content (wt %/PET)	2.2	2.2
Dispersant (KTPP, wt %/ TiO_2 slurry)	0	0.15
Steric hindrance (TPA, wt %/PET)	0	0.1
TiO_2 injection condition	Condition 1	Condition 4
TiO_2 agglomerates (ea./10 mg)	98.2	36.8
	5 ~ 10 μM	36.5
	Above 10 μM	16.0

Table 6. Dispersibility of TiO_2 in FD PET chip and fiber prepared by polymerization process

Materials	Chip	Fiber
Average particle size (μM)	0.83	0.70
Standard deviation	0.183	0.044
Above $2 \mu\text{M}$	3.10	0.29

bility after 30 days above 0.15 wt % KTPP. The dispersibility of TiO_2/EG slurry mixed with oligomer after ES-2 stage reaction was better than that of oligomer after ES-1 stage reaction. The SEM images showed that some TiO_2 particles were agglomerated in the PET matrix. The slurry exhibited a maximum dispersibility at 0.1 wt % TPA and 0.05 wt % PET. The optimal preparation conditions for FD PET polymerization were determined, and the FD PET chip and fiber were prepared according to the conditions. The FD PET fiber showed a small average size compared with the FD PET chip.

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