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学 位 記 番 号	博甲第８８５号
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学位授与の要件	課程博士（学位規則第４条第１項）
学位授与の題目	Study on Production Technology and High Functionalization of Polyester (ポリエステルの製造技術と高機能化に関する研究)
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Abstract

This project focused on the study of poly(ethylene terephthalate) (PET) with high functions and the thesis was divided into two parts. In the first part, a series of PET/ titanium dioxide (TiO_2) nanocomposites was synthesized via ***in situ*** polymerization utilizing a kind of commercial sol characterized with high stable nano dispersion. The incorporation of nano TiO_2 was found to improve the UV absorption property of PET matrix and have little damage on the transparency. The homogeneous dispersion of TiO_2 on nano-scale ensured the increasing of tensile strength as well as Young's modulus and tenacity. Meanwhile, the durability to the weather of nanocomposites was enhanced compared to neat PET. In the second part, a kind of hybrid processing technology was proposed for the production of PET. Theoretical analysis was carried out to predict the fluctuation of molten PET properties during hybrid processing in order to control the final product property.

Part I:
Preparation and characterization of PET/TiO_2 nanocomposites

Because of high surface area, nano particles are quite easy to aggregate to form larger size clusters, which will result in less even negative effect on the properties of polymer matrix. Therefore, one of the crucial problems for the study of nanocomposites is how to prepare samples with homogeneous nano dispersion.

I-1 Experimental

This work utilized a well-dispersed TiO_2 sol sample (STS-02) to pre-disperse TiO_2 in ethylene glycol (EG) suspension by replacing the dispersion medium. After pH adjustment, the suspension was dispersed by means of Wet Atomizing System. The *in situ* polymerization was carried out starting from the obtained EG/TiO_2 suspension to prepare PET/TiO_2 nanocomposites.

I-2 Results and discussion

EG/TiO_2 suspension

According to Fig. 1, the replacement of dispersion medium did not change the dispersion condition. Nano TiO_2 particles dispersed in EG suspension still owned sharp size distribution with average size as 58 nm. The re-dispersion by Wet Atomizing System could reduce the average size to 42 nm and make the distribution narrower. With pH increasing, the larger size particles generated due to the aggregation. From Fig. 2, it was found that the size exceeded 100 nm when pH was larger than 4.3. The distribution became wider. This was related to zeta potential as shown in Table 1. After the replacement of medium, the maintained high zeta potential ensured the stable dispersion in EG suspension. As pH increasing, the decreased zeta potential resulted in the aggregation behavior.

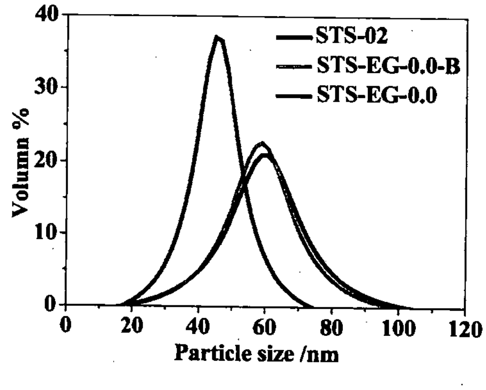

Fig. 1 Particle size distribution
(STS-EG-0.0-B: Before dispersion)

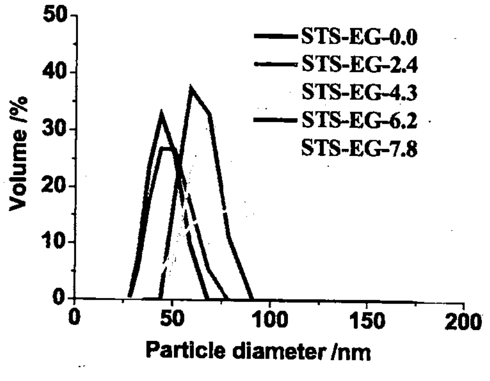

Fig. 2 Particle size distribution
depending on pH (EG)

Table 1 Information of EG/TiO_2 suspension samples

Sample	TiO_2 wt%	pH (EG)	Zeta potential (mV)
STS-02	10	1.7 (H_2O)	47.5
STS-EG-0.0	10	0.0	45.8
STS-EG-2.4	10	2.4	39.1
STS-EG-4.3	10	4.3	44.9
STS-EG-6.2	10	6.2	14.8
STS-EG-7.8	10	7.8	---

PET/TiO₂ nanocomposites

Fig. 3 shows the dispersion morphology of sample containing 1 wt% TiO_2 prepared from STS-EG-0.0. The TiO_2 particles (white spots) were homogeneously dispersed in the matrix within the nano-scale size. The strong electrical repulsive force prevented the re-aggregation behavior during the polymerization. With the increase of pH, the decreased zeta potential could not provide enough repulsive force to keep the particles away from each. Therefore, re-aggregation behavior happened during the polymerization. According to statistic results in Fig. 4, it can be concluded that the re-aggregation behavior deteriorated as pH of EG suspension increased. And more than 80% of particles was kept within 1~100 nm when pH (EG) equaled to 4.3.

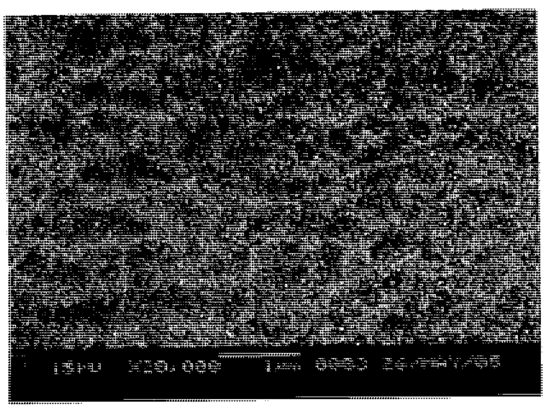

Fig. 3 Dispersion of TiO_2 in PET/TiO_2-1-0.0

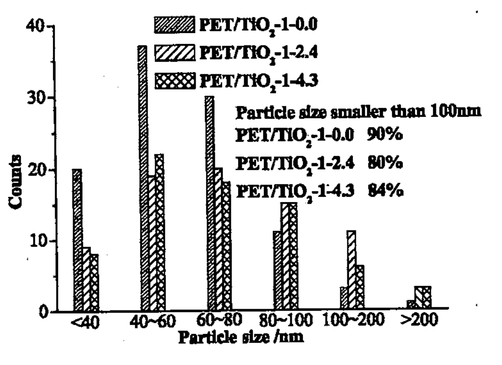

Fig. 4 Statistics of TiO_2 particles size distribution (PET/TiO_2-x-oo: PET incorporated x wt% TiO_2 and oo presents pH of EG suspension)

Fig. 5 is the UV/Vis spectra of PET and PET/TiO_2 nanocomposites. Table 4 gives the transmission under the wavelength of 320nm, 360nm and 570nm. The TiO_2 composite PET showed an absorption spectrum characterized with an extension to ultraviolet wavelength about 380nm. The absorption in ultraviolet wavelength region increased obviously when the concentration was larger than 0.5 wt%. Under the same content of TiO_2, the increasing pH had little effect on the absorption property as well as transparency even the dispersion condition became worse according to Fig. 4.

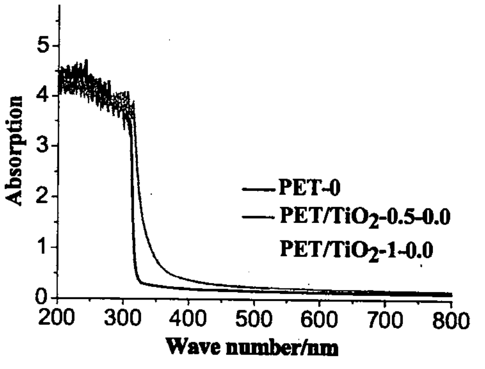

Fig. 5 The UV-Vis absorption property of samples

Table 4 Transmission of Samples depending on pH(EG)

Samples	Transmission (%)		
	320nm	360nm	570nm
PET-0	20.99	80.23	89.56
PET/TiO_2-1-0.0	0	6.87	76.97
PET/TiO_2-1-2.4	0	8.24	75.87
PET/TiO_2-1-4.3	0	7.17	79.03
PET/TiO_2-1-6.2	0	9.67	78.63

The effect of nano TiO_2 content on the tensile properties of the composites was given in Table 5. The simultaneous increasing of tensile strength, modulus and tenacity was found at the very low TiO_2 content. This was attributed to the nano size dispersed in PET matrix, which would benefit to form strong interaction between particle and polymer chains.

Table 5 Tensile performance for PET/TiO_2 nanocomposites and neat PET

Sample	TiO_2 wt%	IV dL/g	Strength at maximum (MPa)	Young's modulus (GPa)	Elongation at break %
Neat PET	0	0.60	37	1.3	220
PET/TiO_2-0.5-0.0	0.5	0.55	43	1.5	280
PET/TiO_2-1-0.0	1	0.55	44	1.5	260

Due to the homogeneous dispersion of nano TiO_2 in matrix, the appreciable degradation beneath surface layer decreased. The chain scission reaction was prevented and as a result, compared with neat PET, nanocomposites had a less loss of molecular weight under the same exposing time (Fig. 6).

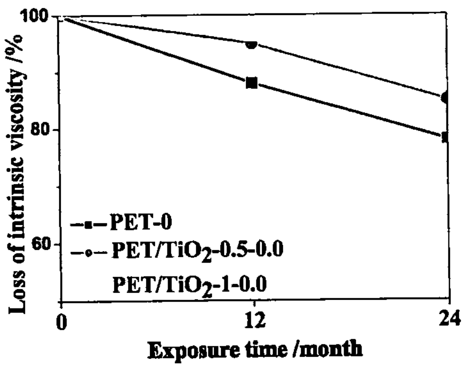

Fig. 6 Intrinsic viscosity (IV) loss depending on exposure time

I-3 Conclusions

The high zeta potential and nano particle size were maintained by replacing the dispersion medium with EG. The stable EG/TiO_2 suspension ensured the final good dispersion of nanoparticles in PET matrix. The incorporation of TiO_2 improved UV absorption properties of PET while transparency had less affected. Because of nano size and homogenous dispersion, the tensile performance as well as durability to weather of PET/TiO_2 nanocomposites was found to be enhanced compared to neat PET.

Part II:

Theoretical analysis of production technology

In order to reduce the manufacturing cost, a new method was proposed in this part called hybrid processing technology. That is, the molten PET synthesized in several batch reactors (RA) is stored in a large tank (Pool Tank) to bring about a continuous processing, such as spinning. Fig. 7 shows a diagram of hybrid process. The equivalent of component j that flows from ith reactor into Pool Tank in unit time is X_j^i (eq/hr). C_j (eq/kg) and X_j (eq) are the concentration and equivalent of j in Pool Tank, respectively. W (kg) is the total weight of polymer in Pool Tank while F_d (kg/hr) is the rate of flow at the exit of Pool Tank. The hybrid process not only decreases manufacturing cost, but assures the homogeneous quality of polymer from N of batch reactors.

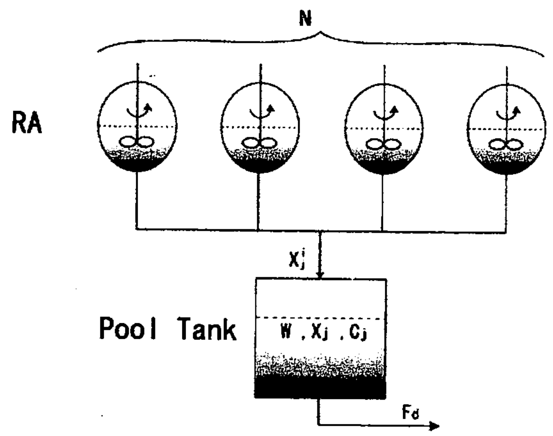

Fig. 7 Diagram of Hybrid Process

The theoretical calculation was carried out according to the following equation to simulate the fluctuation of properties of molten PET during the processing. For the sake of controlling final product property, the hybrid processing technology could be optimized by theoretical simulation.

Runge Kutta method

$$\frac{dX_j}{d\theta} = X_j^i - \frac{X_j}{W} F_d + W \frac{dC_j}{d\theta}$$

Here, θ is the residual time in Pool Tank;

DCT is time for polymer flowing RA to Pool Tank;

CT is time for completely replacing polymer in RA.

学位論文審査結果の要旨

郝立飛氏より提出された学位論文に関して、各審査委員によって個別に審査をした後、審査員による予備審査会を実施すると共に、平成 19 年 2 月 2 日に開催された口頭発表の結果を踏まえて、同日に論文審査委員会を開催して協議を行った。その結果、以下のように判定した。

ポリエステルは優れた物性と機能から繊維、フィルム、ボトル、成形品等の生活に密着した用途に幅広く使用されている。このポリエステル繊維の不透明性、紡糸性や滑り性などを向上させるために、ミクロンからサブミクロンオーダーの酸化チタン粒子を添加することは古くから行われていた。一方、透明性を重視したフィルムなどの分野では、繊維で用いられていた酸化チタンの添加はほとんど行われてこなかった。近年、この酸化チタンの有する紫外線吸収特性や抗菌性などの優秀な特性が発見され、酸化チタンの利用が様々な方面で検討されている。透明な酸化チタン含有のポリエステル開発にはナノオーダーの微粒子のポリエステル中への均一分散技術が必要であるが、このような微粒子は凝集しやすく極めて困難であった。氏は新たな重合法を見出して、酸化チタン微粒子を含有した透明なポリエステルを開発し、その力学的特性、熱的特性、耐候性、紫外線吸収特性等を評価し、その特性が優秀であることを確認している。

一方、このような機能性ポリエステルは小ロット生産されることが多く、その品質安定化を図るために、回分プロセスと連続プロセスを組み合わせたプールタンク方式という新たな重合プロセスを提案している。

以上のように、本研究は、学術面のみならず、ポリエステルの製造の工業化に対する重要で画期的な指針を与え、当該分野に大きく寄与するものである。従って、本論文は博士（工学）の学位に値するものと判断する。