In Situ Preparation Of Poly(Ethylene Terephthalate)/ Titanium Dioxide Nanocomposites

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ABSTRACT

This study deals with the synthesis and characterization of poly(ethylene terephthalate)(PET)/TiO_2 nanocomposites. Commercial stable TiO_2 sol was used to prepare ethylene glycol (EG)/TiO_2 suspension while keeping the average particle size as 60nm. PET incorporated with different content of TiO_2 nanoparticles was prepared via in situ polymerization and characterized by scanning electron microscopy (SEM). The homogeneous dispersion in nano-scale was found for nanocomposites when the content of TiO_2 is less than 2 wt%. Tensile performance shows that the nanoparticles can simultaneously provide PET improvement in modulus, strength and elongation at break at a rather low filler content. The addition of nano TiO_2 to PET matrix also produces a broader UV absorption. © 2006 Trade Science Inc. - INDIA

INTRODUCTION

Inorganic particles have been used as filler in polymer for a long time on commercial production primarily for the reason of stiffness enhancement and cost reduction. One of the most notable instances is the incorporation of C-black in rubber to improve the anti-abrasion property of a tyre. However, in order to bring positive effects for such blends of polymer and micro-sized particles, high filler content, typically higher than 20% by volume, is general required, which would detrimentally affect some other important properties such as processibility, toughness, transparence and density.

In recent years, with the development of nano technology, the design and preparation of nanocom

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posites produced by inorganic nanoparticles filled polymer have gained increasing attention. Because of the high surface area and the strong surface energy, nanoparticles facilitate creating a great amount of interphase and a tighter adhesive strength with polymer matrix, therefore, it is expectable to achieve the modification purpose under a rather low filler content with nanoparticles. The remarkable improvement in mechanical properties has been found in some nanocomposites such as polypropylene (PP)/nano-silica (SiO_2)[1,2] and epoxy/nano-titanium (TiO_2)[3], and it is especially worth noting that the Young's modulus of PP/SiO_2 increased with the decreasing size of filler[4]. However, the opposite effects have also been observed in some composite systems[5]. As a matter of fact, the resulting mechanical property of polymer/nanoparticles composites significantly depends on the dispersion state and the microstructure homogeneity of the filler. Unfortunately, a homogenous dispersion of nanoparticles in a polymer matrix is very difficult due to the strong agglomerate tendency of the nanoparticles with high surface energy and the high viscosity of the polymer matrix. Many attempts have been exploited to overcome this dilemma. One of the mostly used method is the surface treatment of the nano filler prior to the compounding[5,6]. Another notable method is the so-called in situ polymerization, which means the dispersing nanoparticles in a liquor monomer with relatively low viscosity before polymerization[7-9].

Han et al.[10] demonstrated the good UV absorption of polyethylene terephthalate (PET) nanocomposites incorporated with TiO_2. But the detail about the preparation method was not given. Moreover, it was reported that the addition of 1-2 wt% TiO_2 results in the decrease of tensile strength as well as elongation-to-break and modulus of PET composites fiber. In this work, the authors would present details about the preparation of PET/TiO_2 nanocomposites and study the effect of nanoparticles on the tensile properties. The filler nano-TiO_2 was a commercial product which originally dispersed in aqueous colloid state, and before the polymerization the colloid was changed into ethylene glycol (EG)/ TiO_2 suspension by replacing of water with EG. Because of the good dispersion of TiO_2 in nano scale,

the mechanical properties were expected to be enhanced at rather low filler content. Meanwhile, the addition of nano TiO_2 should play a positive role on the UV absorption of nanocomposites.

EXPERIMENTAL

Materials

The nano TiO_2 dispersed in water (STS-02, TiO_2% = 30%, pH =1.5, anatase) was commercially produced by Ishihara Sangyo Co. Ltd. Ethylene glycol (EG) used for the substitution of dispersion medium was purchased from Kanto Kagaku Co.Ltd. Dimethyl terephthalate (DMT) and EG for polymerization of PET were industrial reagents and not purified before use. The neat PET (PET-0, IV=0.60) used for the comparison of physical properties was supplied by Toyobo Co.Ltd.

Pre-dispersion of nano TiO_2 in EG

STS-02 and EG were sufficiently mixed with magnetic stirring and the water was distilled by vacuum distillation at 85°C. The distillation was continued until no further distillate could be collected. The observation of dispersion morphology and the analysis of particle size distribution (PSD) were performed on transmission electron microscopy (H-7600, Hitachi, Ltd.) and LS13 320 Multi-wavelength Particle Size Analyzer (Beckman Coulter, Inc.), respectively.

Nanocomposites preparation and characterization

PET/TiO_2 nanocomposites were synthesized from dimethyl terephthalate (DMT) and EG/TiO_2 suspension (EG/DMT=2.2 mol ratio). According to the conventional transesterification method, a torque recorder was used to monitor the viscosity of the reaction melt during the polycondensation. The reaction was terminated when the torque increased by the same fixed value.

Intrinsic viscosity

The intrinsic viscosity determinations were made using an Ubbelohde viscometer. The dilution solution of the composites in 60/40 (wt/wt) phenol/ tetrachloroethane mixing solvent were filtrated be-

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fore measurement.

$\overline{M}_w$ of the samples was calculated by means of the Mark-Houwink equation[11] K and a are 4.68×10^{-4} and 0.68, respectively [12].

$$\eta = K[\overline{M}_w]^{\alpha}$$

Dispersion morphology

Scanning electron microscopy (SEM, JOEL-5600LV, Japan) was used to study the dispersion morphologies of TiO_2 in PET matrix. SEM photos with magnification as 50K were randomly selected to carry out the statistics of TiO_2 particles size distribution in PET matrix.

Tensile test

Room temperature tensile testing of the composites was conducted on a Universal Tensile Tester (Toyo Measuring Instron. Co. Ltd.) with crosshead speed as 10mm/min. Three samples were tested for each case. The fractured surfaces of the samples were observed with SEM. Before performance, all the samples were prepared with film using hot press at 275°C and then quenched in chilled water. The thickness of the film was kept within 0.3±0.02mm. X-ray patterns of film samples were measured on Rigaku/RINT 2000 X-ray diffractometer with Cu Ka radiation (l=0.13263 °A, 30KV, 20mA). Both neat PET and nanocomposites were scanned with rate of 2°/min and scope from 6 to 40°.

UV-Vis absorption property

The optical properties of the nanocomposites and the neat PET were examined by Lambda 35 UV/VIS Spectrometer (Perkin Elmer) and the thickness of film samples was kept as 0.3±0.02mm.

RESULTS AND DISCUSSION

Pre-dispersion condition of nano TiO_2 in EG

The average size and size distribution of TiO_2 particles for STS-02 and D-STS2-EG are shown in figure 1. It could be found that the average size and the particle size distribution keep almost the same after replacing water with EG. The average particle size of TiO_2 in EG suspension is 60nm and the par-
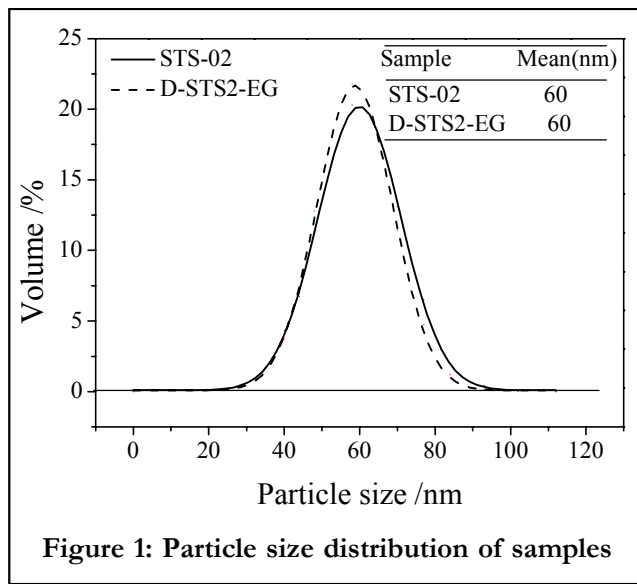

Figure 1: Particle size distribution of samples

ticles distribute in the range from 0 to 100nm. The amounts of particles with size less than 80nm reaches 98 vol% for both water and EG suspension. The observed particles in TEM photos exhibit 40-100nm in diameter (Figure 2). From TEM photos (Figure 2), the particles are homogeneously dispersed in the observed field. Most of them exhibit 40~100nm in diameter. No obvious change was found for the dispersion morphology between water and EG suspension.

Because of strong acidity, in original water sol, there is larger amount of H^+ absorbed on the surface of TiO_2 particles to form the surface potential[13]. And it is due to the electrical repulsion force between particles that the aggregation could be prevented. According to the above results, it is thought that the good dispersion of TiO_2 in EG suspension is ascribed to the hardly broken electrical repulsion force.

Characterization of PET/TiO_2 nanocomposites

Intrinsic viscosity

In this study, PET/TiO_2 nanocomposites were prepared via in situ formation. The polymerization results are summarized in TABLE 1. It can be observed that the TiO_2 has an effect on the intrinsic viscosity and therefore, the molecular weight of the resulting PET, depending on the TiO_2 contents. During the polycondensation, the incorporation of nano particles cause higher melting viscosity of poly-
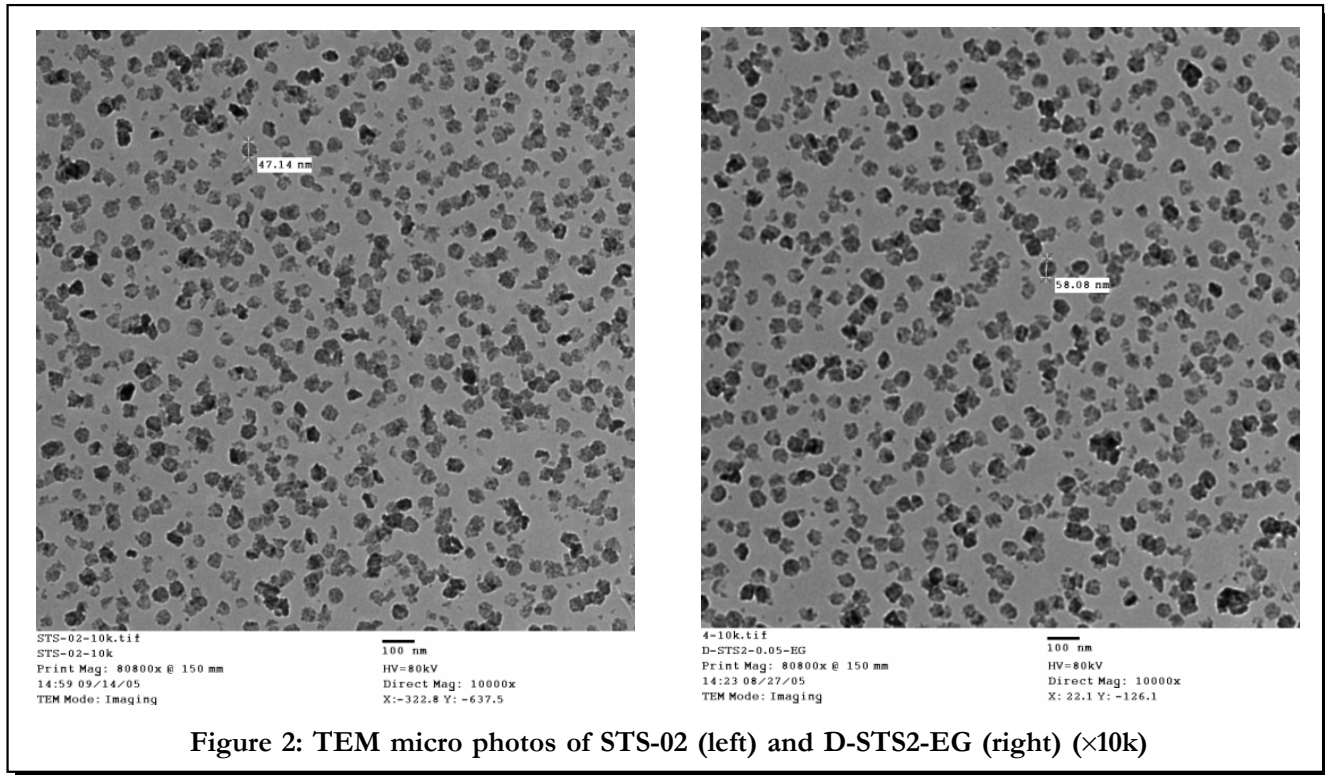
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Figure 2: TEM micro photos of STS-02 (left) and D-STS2-EG (right) (×10k)

TABLE 1: Samples information

Samples	TiO₂ wt%	IV (η/dl g^{-1})	$\overline{W}_X$ (^{o}10^4)
PET/TiO₂-0[*a]	0	0.65	4.1
PET/TiO₂-0.5	0.5	0.55	3.2
PET/TiO₂-1	1	0.55	3.2
PET/TiO₂-2	2	0.50	2.8
PET/TiO₂-3	3	0.42	2.2
PET-0[*b]	0	0.60	3.7

[*a]: neat PET obtained under the same polymerization condition in this work [*b]: neat PET obtained from Toyobo Co. Ltd.

mer matrix [14] and the time for the torque increasing by the same value is shortened compared to the neat PET. Therefore, the untimely end of reactions results in the lower molecular weight.
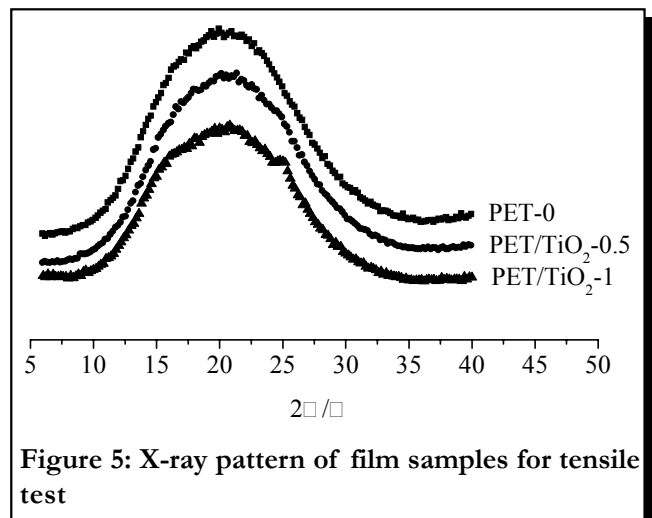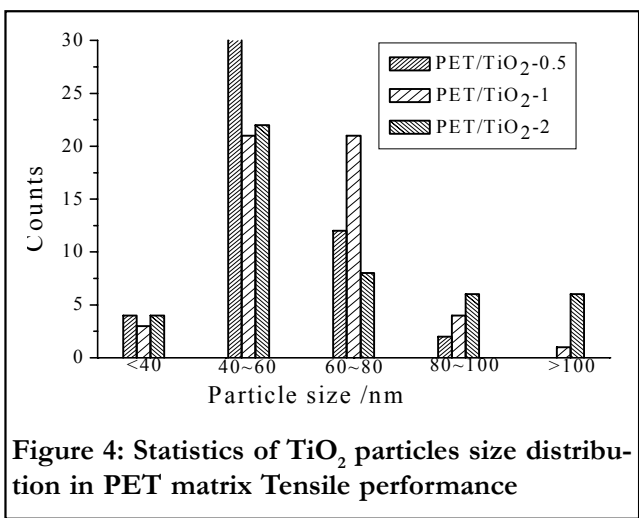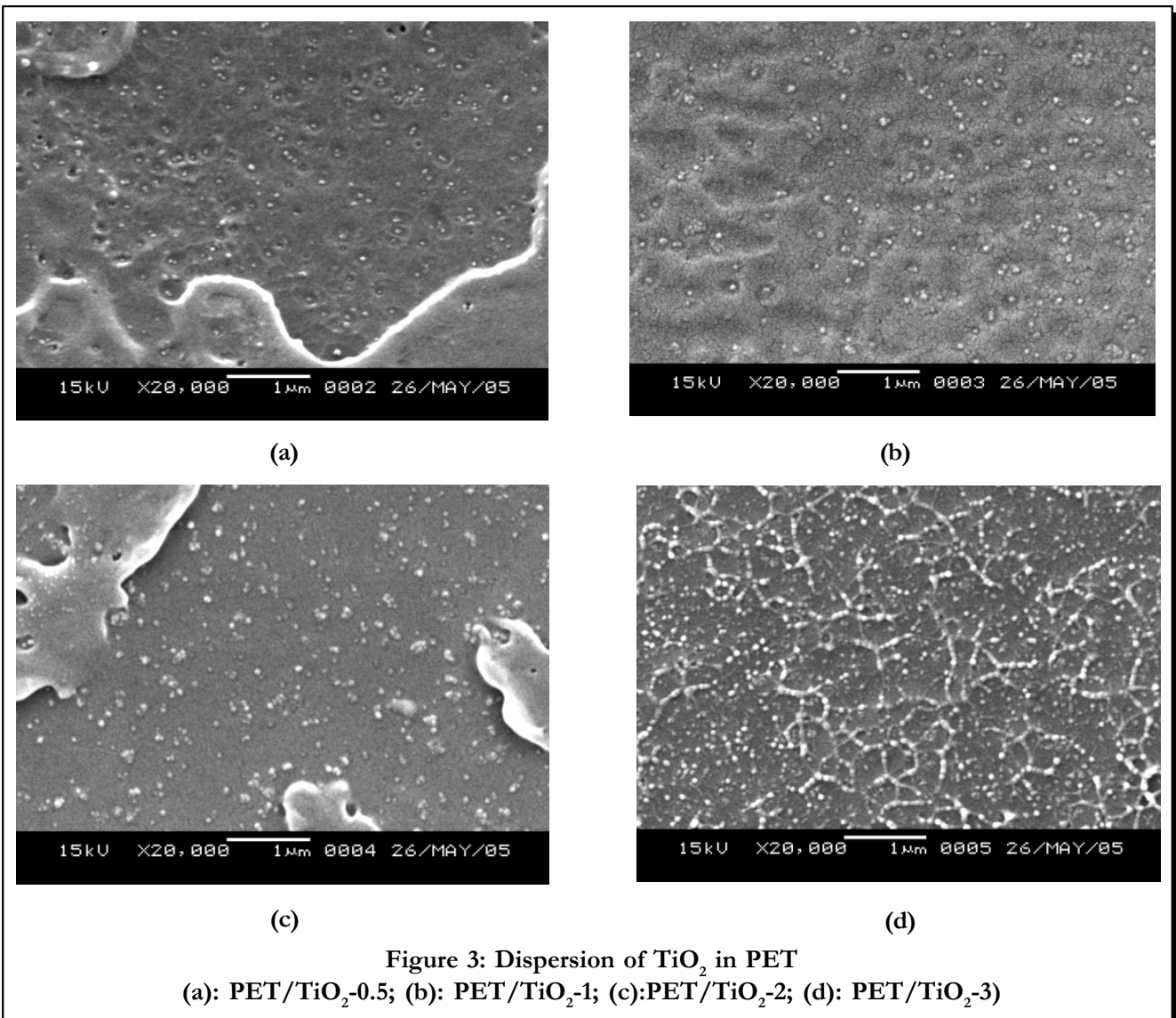
Dispersion morphology
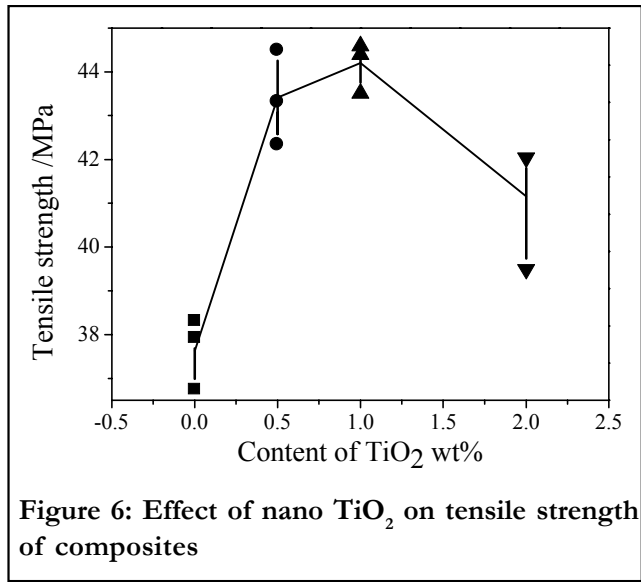
Figure 3 shows the cross section morphology of PET/TiO₂ nanocomposites. The TiO₂ particles (white spots) are homogeneously dispersed in the matrix with the nano-scale size when the concentration of TiO₂ is less than 2 wt%. With more concentration of TiO₂, for example 3 wt%, there is a trend for TiO₂ particles to combine together and form the

network morphology. The statistics of particle size as shown in figure 4 displays that the amount of particles with size below 80nm reaches 96% for PET/TiO₂-0.5, which is quite approximate to that of EG suspension. With TiO₂ content increasing, larger size aggregates gradually form. For PET containing 2 wt% TiO₂, the amount of agglomerates with size larger than 100nm is 12%. After all, generally speaking, a good dispersion of TiO₂ in PET matrix on a nano scale has been achieved when TiO₂ content is less than 2 wt% in this study.

Many researchers have demonstrated that the nanoparticles can act as nucleating agents and therefore, accelerate the crystallization rate of polymer matrix[8, 15-16]. In order to eliminate the possible effect of different crystallinity on mechanical properties, the film samples for tensile test were prepared by quenching into chilled water from melt. figure 5 shows the X-ray patterns of neat PET as well as nanocomposites before the tensile test. The curves are smooth and have no obvious diffraction peaks at around 16.8, 22.4 and 25.2^o, which are correspondent respectively to the (010), (1$\bar{1}$0) and (100) diffraction planes of PET[17-18]. Therefore, it is thought

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(a)

(b)

(c)

(d)

Figure 3: Dispersion of TiO$_2$ in PET
(a): PET/TiO$_2$-0.5; (b): PET/TiO$_2$-1; (c):PET/TiO$_2$-2; (d): PET/TiO$_2$-3)

Figure 4: Statistics of TiO$_2$ particles size distribution in PET matrix Tensile performance

Figure 5: X-ray pattern of film samples for tensile test

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Figure 6: Effect of nano TiO$_2$ on tensile strength of composites

Figure 7: Effect of nano TiO$_2$ on elongation at break


Figure 8: Effect of nano TiO$_2$ on Young's modulus

that the film samples for tensile test are of amorphous state.

The effect of nano TiO$_2$ content on the tensile properties of the composites is given in figure 6~8. The strength, tenacity and modulus of PET increase after adding nano TiO$_2$ particles. Moreover, an optimum value will appear under a relatively low filler loading, and further increasing TiO$_2$ content results in a decrement. This result is consistent with the effect of TiO$_2$ content on the impact strength of TiO$_2$ filled epoxy (EP/TiO$_2$) nanocomposites reported by Wetzel et al.[3] that the highest value is found at 4-5 vol% TiO$_2$ loading and then becomes low with more TiO$_2$ addition. As we known, because of the small size, there exists a large amount of unsaturated atoms on the surface of the nanoparticles. These unsaturated atoms are highly active and liable to establish strong Van der Waals interaction with the polymer chains. Therefore, nanoparticles act as a fine modifier for the lacunae of the polymer. When a force imposed on such a polymer/nanoparticles composite, the particles play a role of jointer of the polymer chain and the whole composite is able to bear large external force than neat polymer material. But, the mechanical properties become poor with the increasing TiO$_2$ content, which should be owing to the agglomerate of nanoparticles. As shown in TABLE 1, though molecular weight is the same, compared to PET/TiO$_2$-0.5, the addition of 1 wt% TiO$_2$ gives slight effect on the tensile strength and causes the decreasing of tenacity as well as modulus. It can not
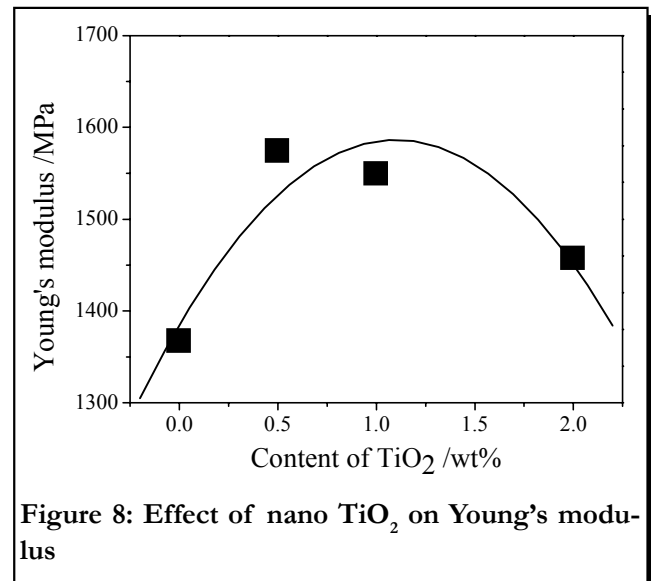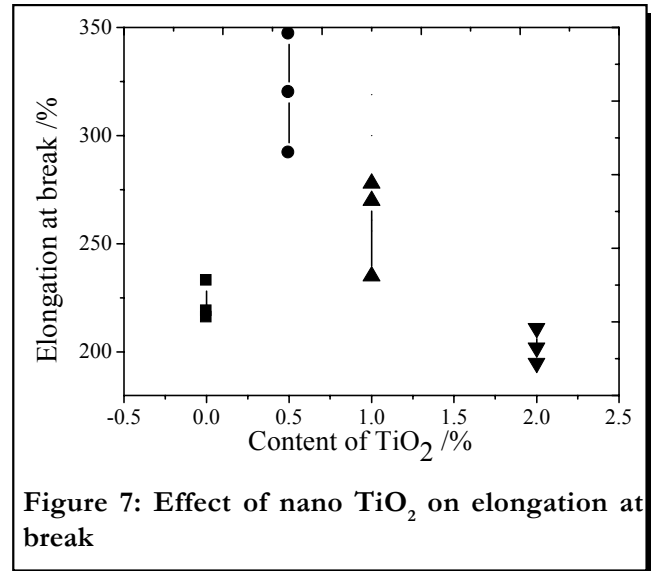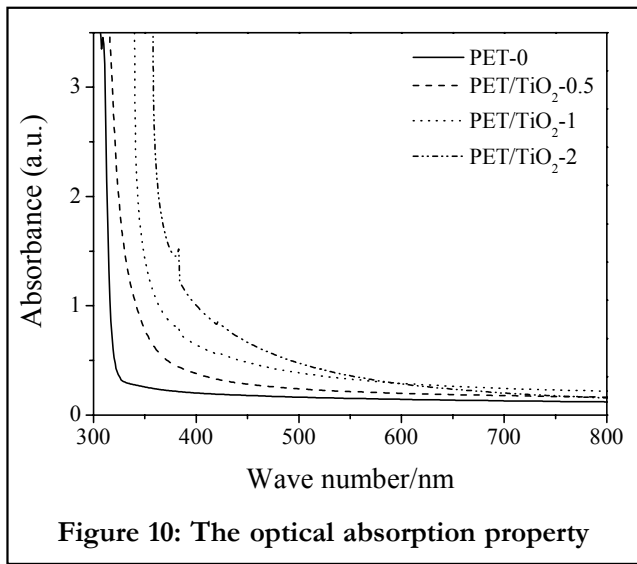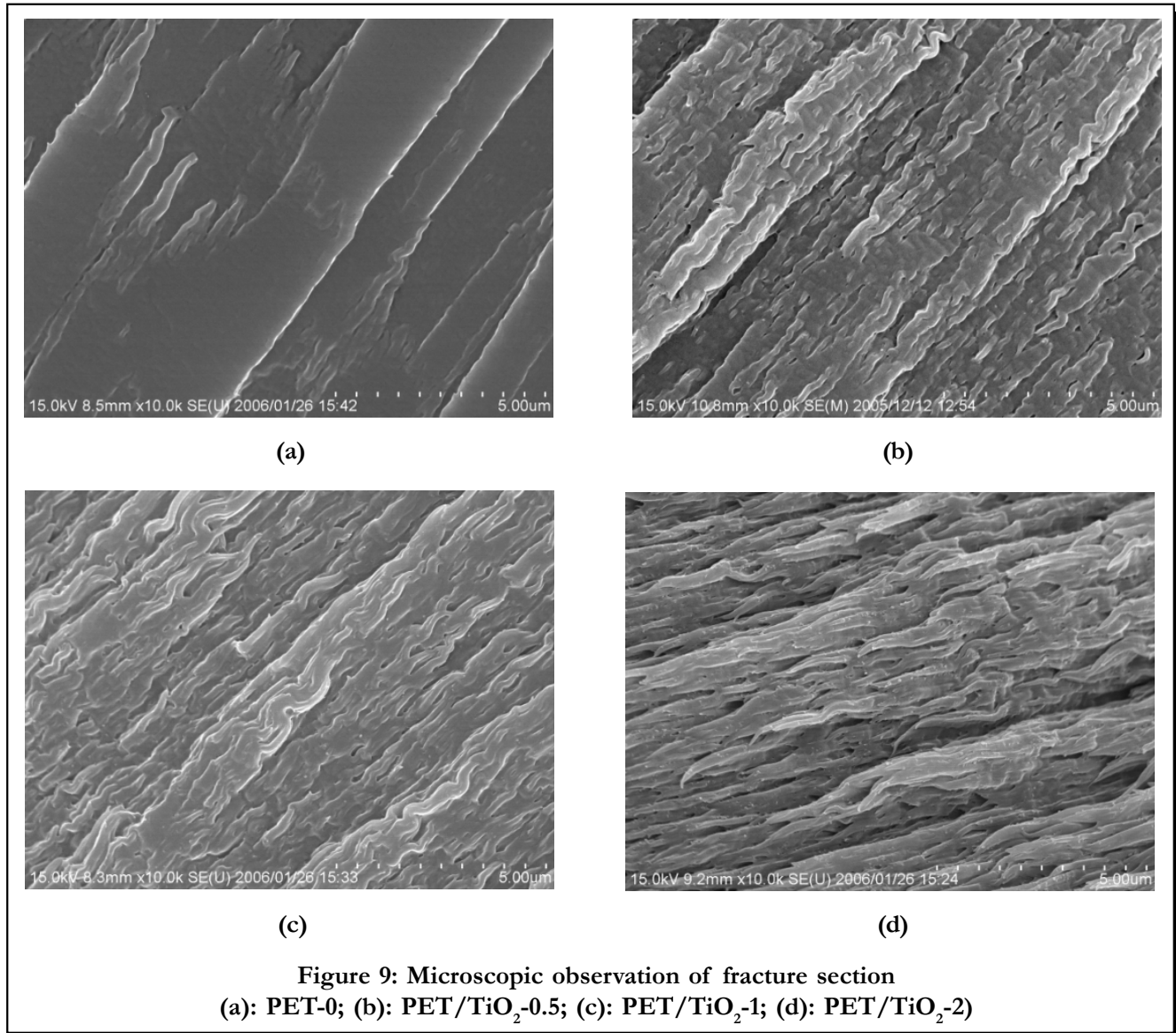
be expected that those relatively larger particle clusters can bear the imposed force. Meanwhile, less interface adherence between larger particles and polymer is responsible for the decreasing of tenacity as well as modulus. And the relatively decrement of mechanical properties of nanocomposite with 2 wt% TiO$_2$ should be the result related to both the poor dispersion condition and low molecular weight.

Microscopic observation of fracture section (Figure 9) of neat PET and the nanocomposites with 0.5-2.0wt% TiO$_2$ addition shows that the neat PET has a relatively smooth fracture surface in association with less fibril formation, while in the case of PET/TiO$_2$, the fracture surface becomes rougher and with more thinner fibril formation than that of neat

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(a)

(b)

(c)

(d)

Figure 9: Microscopic observation of fracture section
(a): PET-0; (b): PET/TiO$_2$-0.5; (c): PET/TiO$_2$-1; (d): PET/TiO$_2$-2)

Figure 10: The optical absorption property

PET., which implies the good interface adherence between PET and nano-TiO$_2$ particles. It is well known that a good interface adherence is necessary for the particles to control the generation and development of the craze. If the interface adherence intensity is less than critical stress of craze, the interface will be disassembled and this can promote the destruction of the whole material. However, if the interface is strong enough, the polymer will craze before the disassembly of interface and the viscoelastic deformation of matrix will consume more energy. Therefore, the tenacity of the composites increases, which results in a rough fracture surface.

UV-Vis absorption property

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The absorption of the composites increases with the increasing filler content in the UV-A region, that is, in the wavelength range of 315~400nm. PET/ TiO_2-0.5 shows almost the same absorption as the intrinsic absorption of the neat PET in the visible wavelength region, which implies that the dispersion size of TiO_2 particles is much lower than the wavelength of 400~800nm. This result is consistent with that observed in figure 3. With the increasing load of filler, the agglomerate of the TiO_2 makes the resulting size of cluster particles to be more comparable with the wavelength of UV (200~400nm). Therefore, a strong random diffusion of incidence UV ray will occur and the detected absorption increases rapidly.

CONCLUSIONS

The commercial stable water suspension containing nano TiO_2 was utilized and by vacuum distillation, TiO_2 was pre-dispersed in EG through replacement of water. The obtained EG/TiO_2 suspension still keeps narrow particle size distribution and the average size of 60nm attributed to the maintained electrical repulsive force between particles. PET/ TiO_2 nanocomposites with different TiO_2 loading were prepared via in situ polymerization. The homogeneous dispersion of TiO_2 particles in nano-scale was found for PET composites with 0.5-1 wt% TiO_2. A simultaneous improvement in modulus, strength and elongation at break was found for PET/TiO_2 nanocomposites when TiO_2 loading is less than 2 wt%, which is hard to be observed in conventional micro-sized particulate composites. The decreasing in tensile strength as well as elongation at break for nanocomposites with 2 wt% TiO_2 is ascribed to the aggregation and inhomogeneous dispersion of particles.

ACKNOWLEDGMENTS

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