Research Article

Using Rutile TiO$_2$ Nanoparticles Reinforcing High Density Polyethylene Resin

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The TiO$_2$ nanoparticles were used as a reinforcement to prepare nanocomposites with high density polyethylene (HDPE) by melt blending process. The original TiO$_2$ (ORT) was modified by 3-glycidoxypropyltrimethoxysilane (GPMS) to improve the dispersion into HDPE matrix. The FT-IR spectroscopy and FESEM micrographs of modified TiO$_2$ (GRT) demonstrated that GPMS successfully grafted with TiO$_2$ nanoparticles. The tensile test of HDPE/ORT and HDPE/GRT nanocomposites with various contents of dispersive particles indicated that the tensile strength and Young's modulus of HDPE/GRT nanocomposites are superior to the values of original HDPE and HDPE/ORT nanocomposites. At 1 wt.% of GRT, the mechanical properties of nanocomposites were optimal. In DSC and TGA analyses, with the presence of GRT in the nanocomposites, the thermal stability significantly increased in comparison with pure HDPE and HDPE/ORT nanocomposites. The better dispersion of GRT in polymer matrix as shown in FESEM images demonstrated the higher mechanical properties of HDPE/GRT nanocomposites to HDPE/ORT nanocomposites.

1. Introduction

Titania is one of the most popular photocatalysis which has many important technological applications: antibacterial, antiviral, fungicidal, proof, and self-cleaning glass [1]. Besides, applications of TiO$_2$ in nanocomposites have extensively attracted many researchers. In nature, nanotitanium dioxide exists in rutile, anatase, and brookite in which rutile phase exhibits high stiffness, UV light absorbability, high refractive index 2.7, and super hydrophilic. With such advantage aspects, nanocomposites based on thermoplastic and TiO$_2$ nanoparticles were expected to generate the new material class with superior properties such as excellent mechanical properties, light density, reduction UV, and thermal degradation. However, in nanocomposite fabrication, it is difficult to disperse the nanoparticles in polymeric matrices. Like the other nanoparticles, the nano-TiO$_2$ normally tends to get aggregation causing the effect on properties of nanocomposites. To overcome this problem, some methods have been considered, for example, melt processing [2, 3], chemical modification of nanoparticles surface [4, 5], in situ polymerization by dispersing the nanoparticles in a monomer, and then polymerizing the mixture [6] or high energy blending by ball milling [7], in which surface modification of nanoparticles is simple and conventional method and has been widely used to modify nanoinorganic particles. Normally, surface modification of TiO$_2$ nanoparticles was performed by the interaction of active sites on the surface with functional groups of coupling agent. Wang et al. [8] have reported dodecylamine-capped TiO$_2$ nanoparticles with –NH– which is bonded to TiO$_2$ surface. Wu et al. [9] proposed the mechanism of formation of the organo-capped TiO$_2$ nanoparticles which is to have competitive reactions between water and stearic acid. Misra and Liu [10] reported resorcinarene-capped TiO$_2$ nanoparticles. By the way, modified TiO$_2$ nanoparticles using silane-coupling agent are well

known, which is prepared by hydrothermal reaction between hydroxyl of TiO$_2$ surface and Si–OR groups of silane [11, 12]. They are one of main reasons that improved a dispersion property using organic surfactants of much quantity (in other words, using long chain alkyl surfactants).

Preparation of nanocomposites by dispersing TiO$_2$ into thermoplastic have been extensively investigated such as poly(vinyl chloride) [13, 14], polypropylene (PP) [15, 16], polystyrene (PS) [17], and polyethylene (PE) [18, 19]. In those works, the effects of photooxidation properties of anatase TiO$_2$ on polymer matrix have been studied. The obtained results showed that TiO$_2$ nanoparticles have promoted strongly photocatalytic degradation to polymeric matrix. Although the preparation of HDPE/TiO$_2$ nanocomposites has been studied, but the role of TiO$_2$ as reinforcement in HDPE matrix is still not clear in comparison with pure HDPE, especially with respect to the effect of n-TiO$_2$ on the physical and mechanical behaviors.

In order to evaluate the problems described above, the aim of this study is to investigate the effects of rutile TiO$_2$ nanoparticles contents with and without modification by 3-glycidoxypropyltrimethoxysilane on the behaviors of the physicomechanical, thermal properties, and structural morphology of HDPE/TiO$_2$ nanocomposites. FT-IR spectroscopy was used to elucidate effectiveness of the interaction between hydroxyl groups of TiO$_2$ and functional groups of 3-glycidoxypropyltrimethoxysilane.

2. Experimental

2.1. Materials.
Titanium dioxide nanoparticles in the crystal form rutile were provided by Polyplus Corporation (Republic of Korea) with the purity of 99.4%; particles size is about 40–100 nm. 3-glycidoxypropyltrimethoxysilane (98%) (GPMS) was purchased from Merck (Germany). Ethanol (95%) and acetic acid using for modifying TiO$_2$ nanoparticles were bought from Shantou Xilong Company (China). High density polyethylene (HDPE) with MFI = 2 g/10 minutes/190°C/2.15 kg was purchased from Honam Petrochemical Corporation (Republic of Korea).

2.2. Sample Preparation.
GPMS grafting reaction onto the surface of TiO$_2$ nanoparticles was carried out in ethanol as follows: silane 1 wt.% in 100 mL ethanol solution (containing a few drops of acid acetic for controlling pH) was completely hydrolyzed for 1 hour with the aid of temperature at 50°C and stirring at 100 rpm. This silane concentration was selected because it showed the optimum content which was reported in our previous work [20]. Then, 20 g of original TiO$_2$ (ORT) powders was dispersed in these solutions with strong stirring at 250 rpm at 500°C for 3 hours. After that, the modified TiO$_2$ nanoparticles were filtered under low suction pressure. The residual of GPMS on the surface of nanoparticles after modifying was removed by soxhlet process during 5 hours in water : alcohol 1 : 1 solution. Finally, they were dried in a vacuum oven at 600°C for 8 hours to obtain modified rutile TiO$_2$ (GRT) nanoparticles.
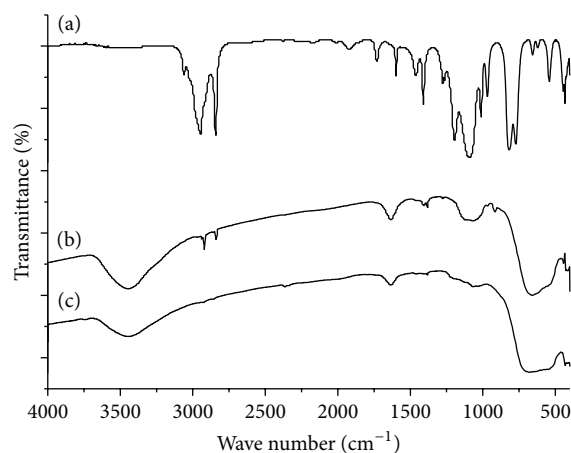

Figure 1: FT-IR spectra of (a) GPMS, (b) GRT, and (c) ORT.

For nanocomposite preparation, HDPE pellets were melt blended with the addition of ORT and GRT at several concentrations such as 0.5, 1, 1.5, 2, 3, and 5 wt.%. The processing was carried out in a Haake Intermixer (Germany) using Roller twin rotors at temperature of 180°C and mixing speed of 70 rpm for 7 minutes. The melt mixtures were then quickly transferred and molded by hot pressured instrument (Toyoseky, Japan) to form the samples for testing.

2.3. Characterizations.
The tensile test was conducted and obtained the average value by measuring each sample piece five times at a crosshead speed of mm/min in Zwick Tensiler 2.5 (Germany) according to ASTM D 638 standard. Thermogravimetric analysis (TGA) was conducted using TGA-50H (Shimadzu, Japan) at 10°C/min with heating from 25°C to 800°C in nitrogen. Differential scanning calorimetry (DSC) model of DSC 131 (Stream, USA) was used to determine the melting temperature of samples in nitrogen at 10°C/min with both heating and cooling systems. Field emission scanning electronic microscope (FESEM, model S-4500, Hitachi, Japan) was employed to examine the fracture surface of samples and also to investigate the dispersion of TiO$_2$ nanoparticles in the HDPE matrix. IR spectrum recording was carried out on Fourier transform infrared Nexus 670 (USA) with the following conditions: resolution 2 cm^{-1}; each sample was scanned 64 times in wavelength range from 4000 cm^{-1} to 400 cm^{-1}.

3. Results and Discussion

3.1. Investigation of Surface Modification of ORT and GRT.
FT-IR infrared spectroscopy of TiO$_2$ initial silane GRT is shown in Figure 1. FT-IR spectra of ORT showed that the peak appearing in 3406 and 1639 cm^{-1} is the characteristic of vibrations of OH groups of hydrogen bonding on the surface of TiO$_2$ ORT. In addition, the wide spectrum from 680 to 420 cm^{-1} is the variation of bonding Ti–O–Ti. Compare to the infrared spectroscopy of ORT, the infrared spectroscopy showed that matched samples GRT
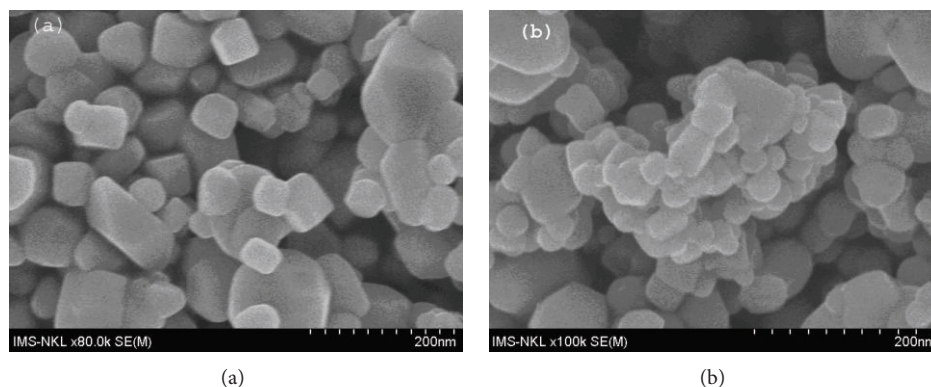
(a)

(b)

FIGURE 2: FESEM images of (a) ORT and (b) GRT.

many new peak shows the reaction between functional groups of OH groups of TiO_2 with silane happened. Peak at wavelengths 2925 and 2839 cm^{-1} is the valence vibrations of alkyl groups [$-(CH_2)n-$] [21]. Figure 1(a) shows the peak specific methyl groups ($-CH_3$) at wave numbers 2936 and 1472 cm^{-1}. However, IR spectrum of the GRT on the peak is not appearing. As shown in Figure 1(b), Si–O–C link appears on the spectrum with the characteristic vibrations at 1096.5 cm^{-1} for sharp peak. Special variation of the Si–O–linked Ti appears at 910 cm^{-1} showing that silane grafting reaction with OH groups on the surface of TiO_2 particles was successful [22]. The above results demonstrated that the reaction of hydrolysis and condensation has occurred and formed on the surface layer of silicon GRT.

The morphology of GRT and ORT samples is introduced in Figure 2. The FESEM images with higher resolution showed that the ORT particles with diameters from 40 to 100 nm are discretely dispersed. After modifying, GRT particles tended to link together by silane layer formed on the GRT surface.

3.2. Mechanical Properties of HDPE/TiO_2 Nanocomposites.

Figure 3 exhibits tensile strength versus the ORT and GRT contents of nanocomposites. The tensile strength of HDPE is 32.9 MPa. By adding the ORT in polymeric matrix, the tensile strength slightly increased at sample containing 0.5 wt.% of ORT and reached the highest value at 33.2 MPa. However, tensile strength of HDPE/ORT nanocomposites decreased rapidly with the increase of TiO_2 contents. It can be explained that nature of TiO_2 is superhydrophilic while HDPE was structured by many long hydrophobic hydrocarbon chains. Therefore, in the melt blending process, compatibility of ORT in polymer matrix was difficult and generated separated phases in nanocomposites leading to the reduction of mechanical properties. On the other hand, TiO_2 nanoparticles possess large interfacial area causing the formation of the big TiO_2 clusters in the polymer matrix by the strong surface force. So, introducing TiO_2 into polymer without modifying surface is a difficult process.

The investigation of tensile strength of HDPE/GRT nanocomposites obtained remarkable results. Tensile
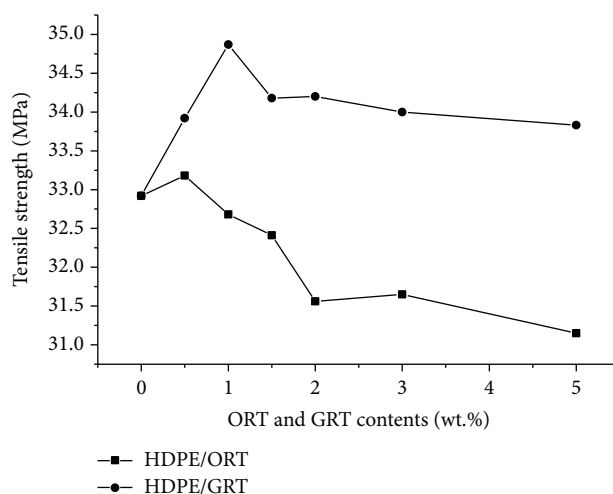
FIGURE 3: The effect of TiO_2 contents on tensile strength of HDPE/TiO_2 nanocomposites.

strength of nanocomposites is further increased than that of pure HDPE. The highest tensile strength was 34.9 MPa samples containing 1 wt.% of GRT. The results pointed out that the presence of GRT in HDPE matrix has enhanced significantly tensile strength in comparison with HDPE. In this part, silane layer on the TiO_2 surface played an important role to reduce interfacial interaction of dispersed nanoparticles. Through the interaction of the hydrocarbon chain with alkyl groups in the silane layer, the interfacial adhesion between HDPE and TiO_2 has strongly improved and created homogenous morphology of material. Therefore, mechanical properties of HDPE/TiO_2 have been enhanced. However, when the contents of nanoparticles reached the saturation level, only a part of the GRT particles took part in the interaction with HDPE and the excess has tent to agglomeration in the matrix affecting its homogeneity and consequently the mechanical properties of the nanocomposites. For instance, at the highest concentration of 5 wt.%, the value of tensile strength was
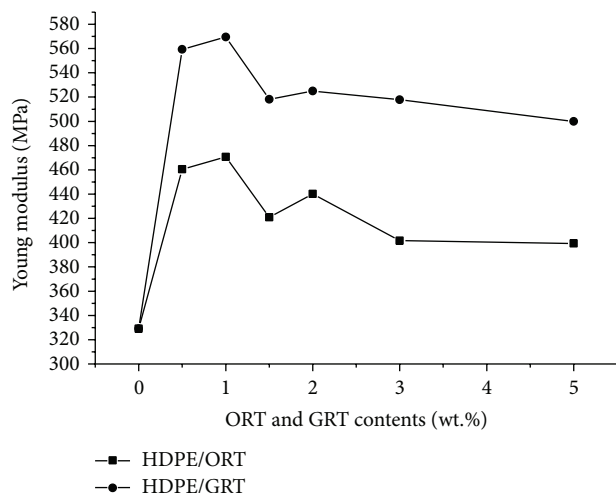
FIGURE 4: Effect of TiO$_2$ contents on Young's modulus of HDPE/TiO$_2$ nanocomposites.

TABLE 1: The melting temperature (T_m) of HDPE/TiO$_2$ nanocomposites was obtained from the DSC analysis.

Contents (wt.%)	T_m (°C) HDPE/TiO$_2$ nanocomposites	
	ORT	GRT
0	130.0	130.0
0.5	131.0	131.0
1.5	131.4	132.9
3	129.9	132.0

down to 33.8 MPa; however this value is still higher than that of pure HDPE [23, 24].

Young's modulus reflected the stiffness of nanocomposites. Figure 4 shows the tensile modulus of HDPE, HDPE/ORT, and HDPE/GRT nanocomposites. Through the testing samples, tensile modulus of HDPE/GRT nanocomposites was higher than that of nanocomposites containing ORT. The tensile modulus of HDPE/GRT gave maximum value of 569.6 MPa at 1 wt.% of GRT content of and then slowly decreased with increasing GRT content. It is obvious that GRT played a role as reinforcement of composites better than that of ORT. It can explain that silane layer on the surface of TiO$_2$ play a role as compatibilizer of dispersive phase and long HDPE chains. This enhances dispersion of TiO$_2$ in the matrix, so the confinement effect of GRT could restrict the motion of polymer chains and result in the increase of Young's modulus of nanocomposites.

3.3. Thermal Behavior of Pure HDPE and HDPE/TiO$_2$ Nanocomposites.
T_m was measured by DSC analysis while heating the samples from room temperature to 250°C at heating rate of 10°C/min. Table 1 shows T_m of pure HDPE, HDPE/ORT, and HDPE/GRT. With presenting reinforcements, the T_m of nanocomposites appears higher than that of pure HDPE. At a same content, T_m of HDPE/GRT nanocomposites is normally higher than that of HDPE/ORT nanocomposites. These results showed that the GRT and ORT increased the crystallization of HDPE due to at the nanoscale, nanoparticles might carry out as likely as not the crystalline centers which could excite earlier crystallization in the structure of nanocomposite. Among them, obviously, the GRT dispersed finer in matrix than the ORT. The increase of crystalline part/amorphous part ratio can improve the physicomechanical properties and thermal stability of nanocomposites. Obviously, by the existence of silane layer on the surface, GRT showed the dispersibility and interfacial

adhesion with HPDE matrix better than ORT. However, at higher contents, the dispersion of ORT and GRT became difficult during melt blending, thus leading to agglomeration of nanoparticles in matrix; crystalline part is reduced; therefore, T_m temperature of nanocomposites trended down as shown in Figure 5.

The thermogravimetric analysis in this research was carried out under N$_2$ atmosphere to avoid the oxidation of samples by O$_2$. Figure 6 shows the weight loss of pure HDPE, HDPE/ORT 98.5/1.5, and HDPE/GRT 98.5/1.5 nanocomposites that is measured as a function of temperature at a constant rate. It can be seen that the onset decomposition temperature of pure HDPE occurs nearly around 416°C. This value is significantly lower than onset decomposition temperature of HDPE/ORT and HDPE/GRT nanocomposites, which are 438 and 442°C, respectively. However, during decomposing, TGA curves of HDPE were showed by high slope; it seems to indicate that decomposing of HDPE occurs more rapidly than that of nanocomposites. At 485°C, the decomposition of HDPE was completed, but the weight of HDPE/ORT and HDPE/GRT nanocomposites remained 8.7 and 12.9%, respectively. The results demonstrated that adding ORT and GRT in the HDPE matrix has improved thermal stability of nanocomposites and HDPE/GRT nanocomposites exhibit the better characteristic than HDPE/ORT.

3.4. Morphologies of Fracture Surface of HDPE/TiO$_2$ Nanocomposites.
In order to investigate the dispersion of TiO$_2$ in the polymer matrix, the FESEM analysis has been performed on the tensile fracture surfaces of samples. Figure 7 shows FESEM micrographs fracture surface of HDPE/ORT 99/1, HDPE/GRT 99/1, and HDPE/GRT 95/5 nanocomposites. In the case of HDPE/ORT 99/1 nanocomposite, there are some parallel fracture lines in the direction of stress. The formation of agglomerates of ORT nanoparticles can be clearly observed on surface of nanocomposites. Obviously, the interfacial adhesion between ORT and polymer matrix is not strong enough therefore leading to create the defect during fabrication of nanocomposites. This explains why the material mechanical properties of HDPE/ORT samples decrease rapidly with increasing ORT contents. Figure 7(b) shows the fracture surface of the HDPE/GRT 99/1 nanocomposite. After fracturing nanocomposite by a strong impact force, the GRT is still covered by polymeric matrix. This proves the
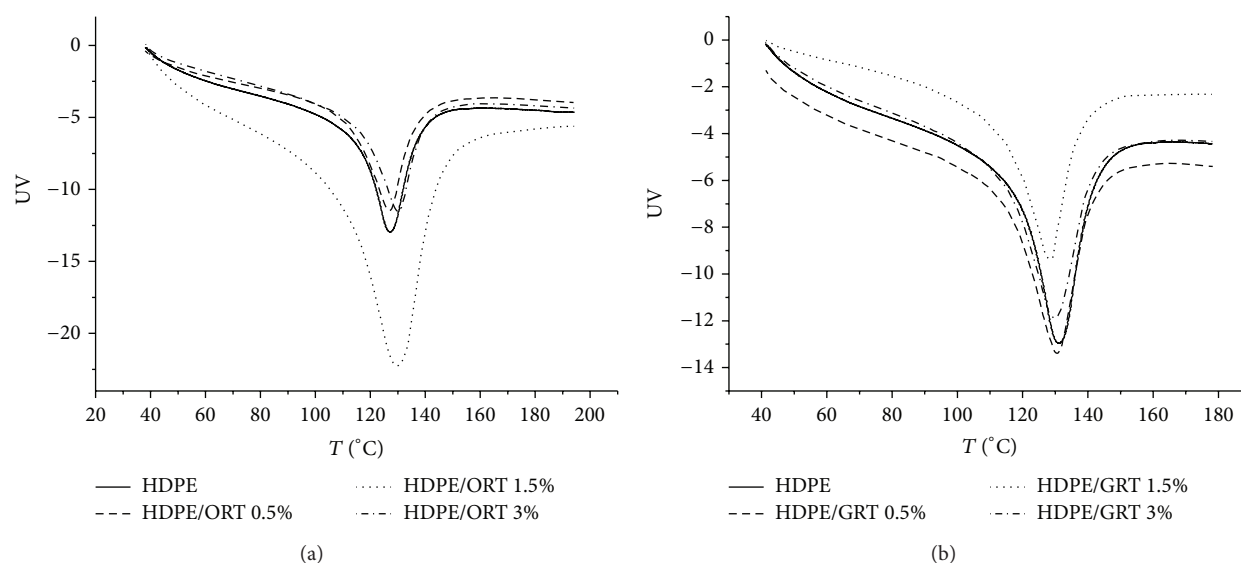
Figure 5: Melting temperatures of (a) HDPE/ORT and (b) HDPE/GRT nanocomposites.
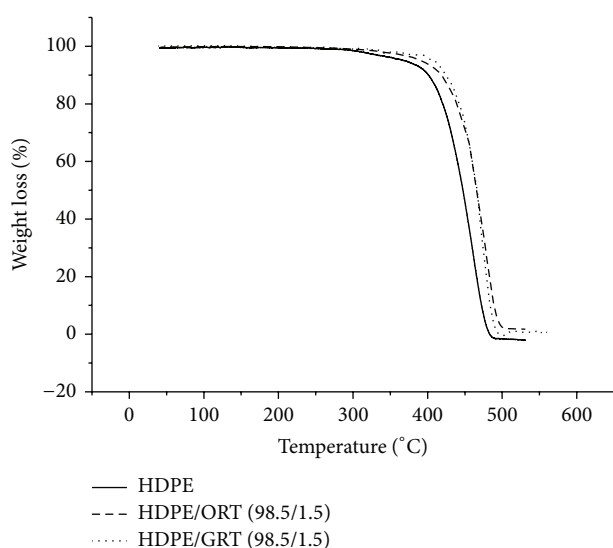

Figure 6: TGA curves of pure HDPE, HDPE/ORT 98.5/1.5, and HDPE/GRT 98.5/1.5 nanocomposites.

good adhesion of GRT into polymeric matrix owing to the bonding of silane coupling agent between GRT and HDPE. These results demonstrated the better mechanical properties of HDPE/GRT nanocomposites in comparison with HDPE/ORT nanocomposites.

However, when the amount of GRT nanoparticles increases up to 5 wt.% (Figure 7(c)), the large cluster of GRT with their diameters of several micrometer can be observed. These defects usually occur on the fracture surface when applying a strong force to specimen and deteriorate the mechanical properties of nanocomposites.

4. Conclusions

Nanocomposites based on high density polyethylene and rutile TiO_2 nanoparticles were prepared by melt blending method. To enhance the dispersal ability of TiO_2 nanoparticles into polymer matrix, the ORT was grafted with GPMS (1 wt.%) by hydrothermal reaction between hydroxyl of TiO_2 surface and Si–OR groups. By FT-IR analysis, the special variation of the Si–O–Ti bonding appeared at 910 cm^{-1} demonstrated that GPMS successfully grafted with the surface of TiO_2 particles through OH groups. Moreover, the FESEM micrographs of the morphological surface of TiO_2 nanoparticles showed that GRT particles tended to link together by silane layer formed on the surface. Tensile test of HDPE/TiO_2 samples exhibited that the tensile strength and the tensile modulus of nanocomposites containing GRT are higher than that of HDPE/ORT and HDPE. The highest tensile strength and Young' modulus of HDPE/GRT nanocomposites are 34.9 and 569.6 MPa, respectively. The investigation of thermal properties of HDPE/TiO_2 by DSC and TGA analysis indicated that the thermal stability of nanocomposites have improved in comparison with the original HDPE. At the temperature which HDPE completely decomposed (485°C), the weight of HDPE/ORT and HDPE/GRT nanocomposites remained 8.7 and 12.9%, respectively. The observation of morphological surface of nanocomposites showed that GRT exhibited higher dispersion and better adhesion with HDPE matrix than the ORT at same 1 wt.% content. Obviously, TiO_2 nanoparticles have played a role as an effective reinforcement of nanocomposites and GRT exhibited better properties than that of ORT.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
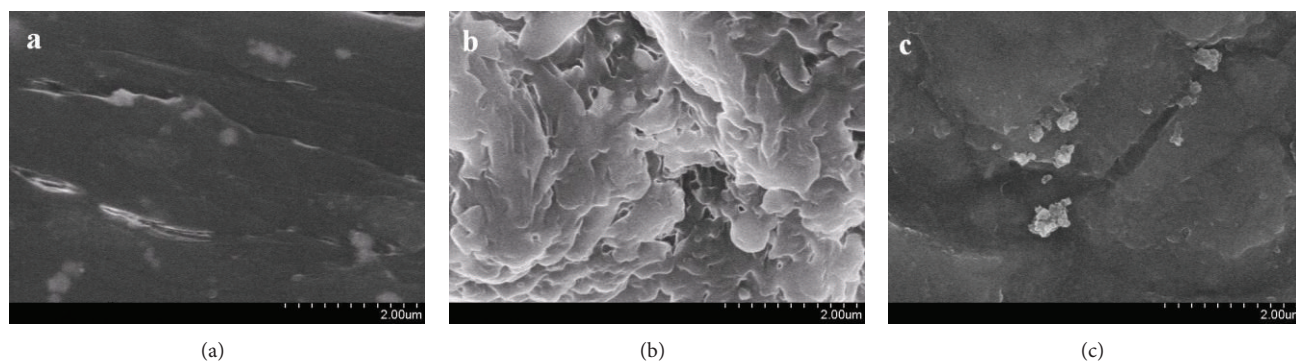
(a)　　　　　　　　　　　　　　　　　(b)　　　　　　　　　　　　　　　　　(c)

FIGURE 7: FESEM images of surfaces of nanocomposites: (a) HDPE/ORT 99/1; (b) HDPE/GRT 99/1; and (c) HDPE/GRT 95/5.

Acknowledgment

References

[1] M. Kaneko and I. Okura, *Photocatalysis Science and Technology*, Spinger, New York, NY, USA, 2002.

[2] A. Chandra, L.-S. Turng, P. Gopalan, R. M. Rowell, and S. Gong, "Study of utilizing thin polymer surface coating on the nanoparticles for melt compounding of polycarbonate/alumina nanocomposites and their optical properties," *Composites Science and Technology*, vol. 68, no. 3-4, pp. 768–776, 2008.

[3] A. Chandra, L.-S. Turng, S. Gong, D. C. Hall, D. F. Caulfield, and H. Yang, "Study of polystyrene/titanium dioxide nanocomposites via melt compounding for optical applications," *Polymer Composites*, vol. 28, no. 2, pp. 241–250, 2007.

[4] M. Yang and Y. Dan, "Preparation and characterization of poly(methyl methacrylate)/titanium oxide composite particles," *Colloid and Polymer Science*, vol. 284, no. 3, pp. 243–250, 2005.

[5] M. Z. Rong, M. Q. Zhang, Y. X. Zheng, H. M. Zeng, R. Walter, and K. Friedrich, "Structure-property relationships of irradiation grafted nano-inorganic particle filled polypropylene composites," *Polymer*, vol. 42, no. 1, pp. 167–183, 2001.

[6] E. Reynaud, T. Jouen, C. Gauthier, G. Vigier, and J. Varlet, "Nanofillers in polymeric matrix: a study on silica reinforced PA6," *Polymer*, vol. 42, no. 21, pp. 8759–8768, 2001.

[7] D. Olmos, C. Domínguez, P. D. Castrillo, and J. Gonzalez-Benito, "Crystallization and final morphology of HDPE: effect of the high energy ball milling and the presence of TiO$_2$ nanoparticles," *Polymer*, vol. 50, no. 7, pp. 1732–1742, 2009.

[8] Y. Wang, S. Zhang, and X. Wu, "Synthesis and optical properties of mesostructured titania-surfactant inorganic-organic nanocomposites," *Nanotechnology*, vol. 15, no. 9, pp. 1162–1165, 2004.

[9] X. Wu, D. Wang, and S. Yang, "Preparation and characterization of stearate-capped titanium dioxide nanoparticles," *Journal of Colloid and Interface Science*, vol. 222, no. 1, pp. 37–40, 2000.

[10] T. K. Misra and C.-Y. Liu, "Synthesis, isolation, and redispersion of resorcinarene-capped anatase TiO$_2$ nanoparticles in non-aqueous solvents," *Journal of Colloid and Interface Science*, vol. 310, no. 1, pp. 178–183, 2007.

[11] H. Tada, O. Nishio, N. Kubo et al., "Dispersion stability of TiO$_2$ nanoparticles covered with SiO$_x$ monolayers in water," *Journal of Colloid and Interface Science*, vol. 306, no. 2, pp. 274–280, 2007.

[12] L. Gamble, M. A. Henderson, and C. T. Campbell, "Organofunctionalization of TiO$_2$(110): (3,3,3-trifluoropropyl)trimethoxysilane adsorption," *Journal of Physical Chemistry B*, vol. 102, no. 23, pp. 4536–4543, 1998.

[13] S. Cho and W. Choi, "Solid-phase photocatalytic degradation of PVC-TiO$_2$ polymer composites," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 143, no. 2-3, pp. 221–228, 2001.

[14] H. Hidaka, Y. Suzuki, K. Nohara et al., "Photocatalyzed degradation of polymers in aqueous semiconductor suspensions I: Photooxidation of Solid Particles of Polyvinyl chloride," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 34, pp. 1311–1316, 1996.

[15] T. J. Turton and J. R. White, "Effect of stabilizer and pigment on photo-degradation depth profiles in polypropylene," *Polymer Degradation and Stability*, vol. 74, no. 3, pp. 559–568, 2001.

[16] B. Ohtani, S. Adzuma, H. Miyadzu, S.-I. Nishimoto, and T. Kagiya, "Photocatalytic degradation of polypropylene film by dispersed titanium dioxide particles," *Polymer Degradation and Stability*, vol. 23, no. 3, pp. 271–278, 1989.

[17] L. Zan, L. Tian, Z. Liu, and Z. Peng, "A new polystyrene-TiO$_2$ nanocomposite film and its photocatalytic degradation," *Applied Catalysis A: General*, vol. 264, no. 2, pp. 237–242, 2004.

[18] K. Miyazaki and H. Nakatani, "Preparation of degradable polypropylene by an addition of poly(ethylene oxide) microcapsule containing TiO$_2$," *Polymer Degradation and Stability*, vol. 94, no. 12, pp. 2114–2120, 2009.

[19] Y. Zhu, G. C. Allen, J. M. Adams, D. Gittins, P. J. Heard, and D. R. Skuse, "Statistical analysis of particle dispersion in a PE/TiO$_2$ nanocomposite film," *Composite Structures*, vol. 92, no. 9, pp. 2203–2207, 2010.

[20] N. V. Giang and M. D. Huynh, "Study on the surface modification of rutile titanium dioxidenanoparticles using silane coupling agent," *Journal of Analytical Sciences*. In press.

[21] N. Nakayama and T. Hayashi, "Preparation of TiO$_2$ nanoparticles surface-modified by both carboxylic acid and amine: Dispersibility and stabilization in organic solvents," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 317, no. 1–3, pp. 543–550, 2008.

[22] R. K. Dey, A. S. Oliveira, T. Patnaik, V. K. Singh, D. Tiwary, and C. Airoldi, "Grafting of organosilane derived from 3-glycidoxypropyltrimethoxysilane and thiourea onto magnesium phyllosilicate by sol-gel process and investigation of metal

adsorption properties," *Journal of Solid State Chemistry*, vol. 182, no. 8, pp. 2010–2017, 2009.

[23] N. V. Giang, D. Q. Tham, and T. S. Ha, "Mechanical, electrical properties and morphology of high-density polyethylene/multi-walled carbon nanotubes composites," in *Proceedings of the 1st International Workshop on Functional Materials and The 3rd International Workshop on Nanophysics and Nanotechnology*, pp. 151–154, Ha Long City, Vietnam, December 2006.

[24] N. V. Giang and V. D. Son Tho, "Morphological characterization correlation in resistivity of high-density polyethylene/multi-walled carbon nanotubes composites," *Journal of Science and Technology*, vol. 3, pp. 64–70, 2009.