PROPERTIES OF POLYPROPYLENE/TiO_2 NANOCOMPOSITES: THE MELT RHEOLOGY, TENSILE STRENGTH AND ELECTRICAL CHARACTERISTICS

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Received 10 December 2010

Abstract

Titanium dioxide (TiO_2) in rutile crystal form with and without modification by 1 wt% of 3-glycidoxypropyl-trimethoxy silane were mixed with isotactic polypropylene (PP) at 180°C to prepare nanocomposites. Investigation of melt rheology of nanocomposites showed the relative melt viscosity increased with increasing levels of original TiO_2 (ORT) and modified TiO_2 (MRT). Tensile test of samples revealed that mechanical properties of PP/MRT nanocomposites have significantly improved in comparison with PP/ORT nanocomposites. The maximum value of tensile strength and Young's modulus of PP/MRT reached 42 MPa and 979 MPa, respectively, at 2 wt% of MRT. The investigation of accelerated weathering test of nanocomposites revealed the retention in tensile strength of PP/ORT and PP/MRT nanocomposites are higher than that of pure PP. The electrical properties of PP/ORT and PP/MRT nanocomposites were also studied. The results showed that both MRT and ORT decreased electric insulation of PP. However, electric insulation of PP/ORT nanocomposites is still higher than that of PP/MRT nanocomposites.

1. INTRODUCTION

Isotactic polypropylene (PP) is reasonable economic thermal plastic that has been widely used in industry and human life. Besides the good points like good thermal property, easy processing, low weight, and low cost…, PP possesses some limitations such as: low toughness and stiffness. In order to solve these problems, some researchers have dispersed nanoparticles into PP as reinforcing fillers. Composites using nanoparticles have gained much attention in recent years. The adding of nanoparticles in the polymeric matrix leads to improve mechanical, thermal and electrical properties of the nanocomposite materials [1 - 3]. These properties are affected by the dispersibility of nanoparticles into the polymeric matrix and the interaction between nanoparticles and polymer at nano scale.

Commonly, reinforcements added into PP are talc, calcium carbonate and clay etc… Among them, titanium dioxide (TiO_2) in crystal form of rutile can be one of the potential reinforcements in producing composites with high mechanical nature, high refractive index (2.7), UV light absorbability…[4]. With such advantages, the study of properties and structure of PP/TiO_2 nanocomposites are interesting and reasonable.

In previous work, we have successfully modified TiO_2 by using 3-glycidoxypropyl-trimethoxy silane (GPMS) and studied on structural characteristics of PP/TiO_2 nanocomposites [5, 6]. In this paper, we focus on melt rheological, mechanical and electrical properties of nanocomposites using TiO_2 with and without modification.

2. EXPERIMENTAL

2.1. Materials

Pure TiO_2 (ORT) nanoparticles in the crystal form rutile were provided by Polyplus Corporation (South Korea) with the purity of 99.4%, particles size is about 40-100 nm. 3-glycidoxypropyl-trimethoxysilane (98%) (GPMS) was purchased from Merck (Germany). Modified TiO_2 nanoparticles (MRT) were successfully grafted by using 1wt% silane [6]. Polypropylene (PP) with MFI = 2g/10 minutes/190°C/2.16 kg was purchased from Honam Petrochemical Corporation (South Korea).

2.2. Sample preparation

For nanocomposite preparation, PP pellets were melt blended in the addition of ORT and MRT 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

Imitation of relative melt viscosity while processing was carried out by using a software of Haake Polylab System (Germany). The tensile test was conducted and obtained the average value by measuring each sample piece five times at a crosshead speed of 50 mm/min in Zwick Tensiler 2.5 (Germany) according to ASTM D 638. The electric properties were measured by TR-10C instrument (Ando, Japan) according to ASTM D150. Accelerated weathering test was carried out on the UVCON (USA) according to ASTM G53 with cycles that include 8 hours in UV irradiation and 4 hours in condensation.

3. RESULTS AND DISCUSSION

3.1. Melt rheological study on PP/TiO_2 nanocomposites

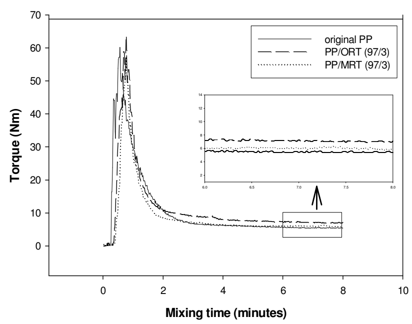

Fig. 1: Processing imitation of PP, PP/ ORT 97/3 and PP/MRT 97/3 nanocomposites

The rheological properties of PP/TiO_2 nanocomposites in melting state were carried out on internal Haake mixer by using imitational software. Fig. 1 describes the behavior of torque of PP, PP/ORT 97/3 and PP/MRT 97/3 nanocomposites. In the first two minutes of mixing process, the behavior of torque of PP and nanocomposites shows the loading peaks of materials. But in the latter sixth minutes, torque of mixture revealed clearly different values. The torque of PP/MRT nanocomposite (5.8 Nm) was higher than that of pure PP (5.4 Nm), but it still was lower than that of PP/ORT nanocomoposite (7.8 Nm). This can be explained that the addition of MRT and ORT might cause the increase of relative melt viscosity of mixture. However, because of the layer of silane on the MRT surface, the compatibility of MRT and polymeric matrix became easier than ORT. Thus, the torque of PP/MRT (97/3) nanocomposite slightly reduced.

The torque of PP/ORT and PP/MRT nanocomposites are shown in the Fig. 2. With increasing concentration of ORT and MRT, relative melt viscosity of nanocomposites was clearly enhanced. The results showed that the concentration of ORT and MRT influenced on fluid plasticity of PP. In particular, the increases of equilibrium of torque of PP/ORT nanocomposites can be observed clearly than PP/MRT nanocomposites. The addition of TiO_2 nanoparticles in polymeric matrix might cause the increase of internal friction during mixing process. However, in the case of MRT, the surface treatment of TiO_2 nanoparticles formed siloxane layer. The layer has improved compatibility between PP molecules and reinforcement; it led to reduce the viscosity of mixture. Thus, equilibrium of torque of PP/MRT nanocomposites is lower than that of PP/ORT.

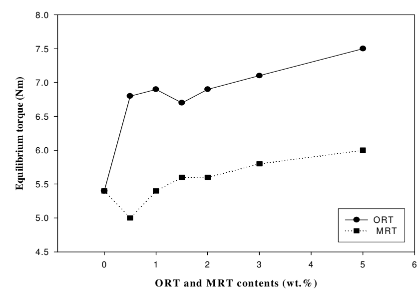

Fig. 2: Equilibrium torque of PP/ORT and PP/MRT nanocomposites

3.2. Tensile properties

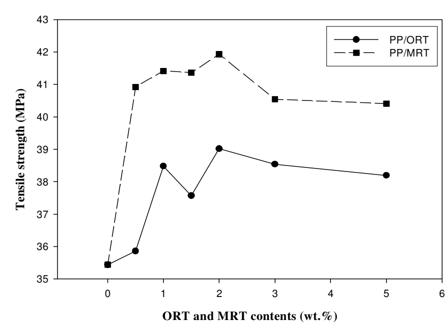

Fig.3: Effect of ORT and the MRT contents on tensile strength of nanocomposites

Fig. 3 exhibits the tensile strength of PP/MRT and PP/ORT nanocomposites. Tensile strength of pure PP is 35.4 MPa and the tensile strength of PP/MRT nanocomposites is higher than that of PP/ORT nanocomposites. When the content of MRT and ORT increased, tensile strength of the nanocomposites have tendency to clearly increase. The maximum value of PP/MRT and PP/ORT reached to 42 and 39.1 MPa at MRT and ORT level of 2 wt%, respectively. However, when the content of reinforcement excess 2 wt%, tensile strength of nanocomposites tend to gradually decrease but still higher than that of the pure PP. The obtained result can be explained that the slightl increase in the tensile strength of PP/ORT nanocomposites is probably due to the poor interfacial adhesion between the hydroxyl groups on the surface of TiO_2 nanoparticles and the PP matrix. In contrast to PP/ORT nanocomposites, by adding MRT, the mechanical properties of PP/MRT samples significantly increased (increased by 18.5 % in comparison with pure PP). This is understandable that the siloxane layer on TiO_2 nanoparticles have strongly improved the compatibility of MRT and polymeric matrix, causing fine dispersion and good adhesion between phases.

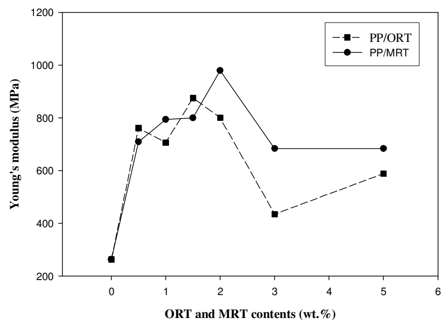

Fig.4: Effect of ORT and MRT contents on Young's strength of nanocomposites

Fig. 4 shows Young's modulus of PP/MRT and PP/ORT nanocomposites. The presence of the TiO_2 nanoparticles within the PP matrix obviously increased the rigidity of the nanocomposites. Moreover, PP samples were mixed with MRT nanoparticles showed the higher Young's modulus than those using ORT. The maximum value of PP/MRT nanocompsite is 979 MPa at MRT of 2wt% content. Whereas, Young's modulus of PP/ORT nanocomposite gave maximum value of 875 MPa at the 1.5 wt% content. It is obviously that MRT exhibited a better reinforcement on the properties of nanocomposites than ORT, especially at higher contents of 2 wt%. Surface modification of TiO_2 by GPMS has improved the higher dispersion, as well as better compatibility of MRT with PP matrix than ORT. These obtained results of Young's modulus of PP/TiO_2 are suitable with report of Pitt Supaphol et al. The same result showed that modified TiO_2 nanoparticles have enhanced the stiffness of PP samples better than non-modified TiO_2 [6].

3.3. Electrical properties

Study on electrical properties of nanocomposites is one of the indirect methods to examine the dispersion of TiO_2 nanoparticles in the polymer, as well as the interconnectivity of TiO_2 into PP. Electrical properties of material are characterized by dielectric constant, loss dielectric and volume resistivity. Table 1 showed the volume resistivity of nanocomposites as a function of contents of TiO_2. Volume resistivity of PP/MRT nanocomposites decreased by 3 orders of magnitude of resistivity when MRT content changed from 0 to 5 wt.% (volume resistivity of pure PP is 9.1×10^{12} Ω.cm). It is similar to PP/ORT samples, however, their volume resistivity only decreased in about 10^2 times of magnitude at the maximum ORT content. Besides, the dielectric constant and loss dielectric increased with increasing ORT and MRT contents as listed in table 1. The significant differences of electrical parameters between nanocomposites using ORT and MRT, in which MRT proved the efficient role of surfactant on the improvement of dispersion of TiO_2. Moreover, by using a polar surfactant such as GPMS also improved the electrical conductivity of nanocomposites.

Table 1: Electrical properties of PP/MRT and PP/ORT nanocomposites

TiO_2 Contents, wt%	PP/ORT composites			PP/MRT composites		
	Volume resistivity, Ω.cm	Dielectric constant, ε	Loss dielectric, tgδ	Volume resistivity, Ω.cm	Dielectric constant, ε	Loss dielectric, tgδ
0.0	9.1×10^{12}	1.91	0.002	9.1×10^{12}	1.91	0.002
0.5	6.0×10^{12}	1.94	0.002	5.0×10^{12}	1.98	0.002
1.0	4.0×10^{12}	2.06	0.002	1.0×10^{12}	2.03	0.003
1.5	5.0×10^{11}	1.95	0.003	5.0×10^{11}	2.06	0.003
2.0	3.0×10^{11}	1.96	0.003	2.5×10^{11}	2.07	0.003
3.0	1.1×10^{11}	1.93	0.004	2.3×10^{10}	2.07	0.007
5.0	5.2×10^{10}	1.99	0.005	3.2×10^{9}	2.12	0.008

3.4 The photo-thermal oxidation of PP/TiO_2 nanocomposites by accelerated weathering test

Table 2 shows the retention of tensile strength after 144h accelerated weathering test. Without TiO_2, the percentage of retention in tensile strength of pure PP shows much lower value in comparison with nanocomposites. From these results, rutile TiO_2 nanoparticles play a role as photo stabilizer to prevent UV irradiation destroying the structure of PP [7].

At low content of TiO_2, the retentions in tensile strength are similar to PP/MRT and PP/ORT nanocomposites. When the loading of nanoparticles increased, the retention in tensile strength PP/MRT nanocomposites was higher than that of PP/ORT nanocomposites. For instance, at TiO_2 content of 5 wt.%, the tensile strength PP/MRT nanocomposite remain at 78.84%, but PP/ORT nanocomposite reached only 69.37%. It can be explained that at high contents, ORT became more difficult and tended to agglomerate that can form big clusters in polymeric matrix. This strongly reduced the UV absorbability of dispersion phase. Whereas, MRT still exhibited fine dispersibility in PP matrix through interaction between ankyl groups of silane and PP chains. That led to the high retention in tensile strength of PP/MRT nanocomposites. Therefore, the role of MRT and its dispersion in PP could create higher resistance to UV irradiation than PP/ORT nanocomposites and pure PP.

Table 2: Variations in tensile strength of PP and PP/TiO_2 nanocomposites

TiO_2 contents, wt%	Tensile strength of samples before testing, MPa		Tensile strength of samples after testing, 144 h, MPa		Percent of retention in tensile strength, %	
	MRT	ORT	MRT	ORT	MRT	ORT
0.0	35.44	35.44	23.20	23.2	64.46	64.46
0.5	40.92	35.86	30.30	29.19	74.04	81.40
1.0	41.41	35.48	30.84	28.6	74.47	74.32
1.5	41.36	37.57	30.95	28.69	74.83	76.36
2.0	41.93	39.02	29.76	27.4	70.98	70.23
3.0	40.54	38.54	32.68	27.06	80.61	70.21
5.0	40.41	38.20	31.86	26.5	78.84	69.37

4. CONCLUSION

The effects of adding contents of ORT and MRT on the melt rheology, physico-mechanical, electrical properties of PP/ORT and PP/MRT nanocomposites were studied. The results of melt rheological study of nanocomposites indicated that the increase in MRT contents enhanced the equilibrilium torque of PP/MRT nanocomposites. The investigation of physico-mechanical properties showed that MRT exhibited the best reinforcement at about 2 wt% content. The study of accelerated weathering test of nanocomposites revealed that PP/ORT and PP/MRT nanocomposites exhibited stable than pure PP under UV irradiation. Electrical property measurement showed that the conductivity of nanocomposites can be enhanced by adding MRT.

Acknowledgements. *This work has been financially supported by Vietnam National Foundation for Science and Technology Development (NAFOSTED, 104.04.37.09).*

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