

Property Transitions in High-Density Polyethylene/Maleated Poly(ethylene–octene)/Calcium Carbonate Ternary Composites

Tingxiu Xie,¹ Hongzhi Liu,² Yuchun Ou,² Guisheng Yang^{1,2}

¹R&D Center, Shanghai Genius Advanced Materials Co., Ltd, Shanghai, 201109, People's Republic of China

²Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 24 November 2004; accepted 4 January 2006

DOI 10.1002/app.24029

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ternary composites of high-density polyethylene (HDPE)/maleated poly(ethylene–octene) (POE-g)/calcium carbonate (CaCO₃) were prepared by the melt extrusion process. Crystallization behavior investigation and mechanical properties study showed that there existed a transition in both crystallization temperature (T_c) and impact strength of ternary composites. These transitions were attributed to the development of morphology, with varia-

tion of concentration of POE-g in ternary composites. The strength of interfacial adhesion also influenced the property transitions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3361–3366, 2006

Key words: HDPE; ternary composites; transition; morphology; crystallization behavior

INTRODUCTION

Ternary composites of polymer/elastomer/inorganic filler have been drawn great attention because of their balance properties between stiffness and impact strength.^{1–9} In these composites, various microstructures could be obtained by control of processing condition and the chemical modification of polymer matrix or elastomer. In general, two extremes in phase structure can occur: (1) Elastomer particles and inorganic fillers are dispersed separately in polymer matrix and form the dispersed phase independently; (2) the elastomer encapsulates inorganic filler to form the “core-shell” structure of the elastomer as the shell and the filler as the core. It is known that the mechanical properties of various ternary composites depend on different microstructures. For a certain ternary composites, such as PP-elastomer-filler system, a separated microstructure can increase stiffness, while a core-shell microstructure can improve toughness of composites.

In our previous work,^{10,11} ternary composites of high-density polyethylene (HDPE)/poly(ethylene–octene)/calcium carbonate were prepared by reactive

extrusion process. For amino acid-treated calcium carbonate composites, the brittle–ductile transition occurred at lower maleated elastomer content than for untreated calcium carbonate composites because of stronger interfacial adhesion. An elastic interlayer was encapsulated on the surface of calcium carbonate to enlarge the effective volume of elastomer; thus, elastomer and calcium carbonate showed synergistic effects on toughness of HDPE.

The purpose of this study is to further investigate the morphology and the crystallization behaviors of ternary composites of HDPE/POE/CaCO₃. On the basis of this study, one can further understand the mechanism of toughness of HDPE with maleated POE and CaCO₃.

EXPERIMENTAL

Materials

HDPE was supplied by Panjin Petroleum Company under trade name HDPE5070EA with a melt flow index (MFI) of 23 g/10 min. Poly(ethylene–octene) elastomer (POE) was bought from Dupont Dow Chemical Elastomers (DE) with 9.5 wt % of octene and a MFI of 3.5 g/10 min. The maleated POE (POE-g) was prepared by maleic anhydride grafting of POE in a twin-screw extruder (SHJ-30, China), with a 30 mm diameter and an L/D ratio of 23.2. The grafting ratio of maleic anhydride is about 1% by weight. The CaCO₃ was obtained from Liaoning Heshan Chemicals Company with a particles size no less than 1250

Correspondence to: T. X. Xie (xietingxiu@hotmail.com), Y. C. Ou (ouyuchun@hotmail.com).

Contract grant sponsor: National Natural Science Key Foundation of China; contract grant number: 10032010.

mesh. The surface-treated CaCO_3 was prepared with amino acid (JL-GD02, provided by Nanjing University of Science and Technology) in a high-speed mixer for 15–30 min.

Sample preparation

The HDPE was first mixed with CaCO_3 and POE-g in a high-speed mixer for about 20 min. Then the mixture was extruded and pelletized on the twin-screw extruder. The extrusion-mixing process was performed at temperatures within the range of 190–200°C and a rotation speed of the screw of 200 rpm. As comparison, the binary blend of HDPE/POE-g (85/15 wt/wt) was also extruded and pelletized on the twin-screw extruder under the same conditions. The pellets were then dried and injection molded into standard testing samples in an injection-molding machine (SZ-160/80NB, China). The injection molding temperature was set at 200°C.

Morphology observation

The freeze-fractured surfaces of injection-molded specimens were etched for 12 h with hydrogen chloride. Then they were washed with distilled water several times and dried under vacuum at 60°C. A scanning electron microscope (SEM) (Hitachi H800, Japan) was used to observe the surface morphology. The surfaces of samples were coated with gold prior to the SEM observation.

Thermal analysis

The melting and crystallization behaviors of the ternary blends were studied by differential scanning calorimetry (DSC-7, Perkin-Elmer) at cooling and heating rates of 10°C/min. Prior to a crystallization run, all samples were melted at 200°C and kept at this temperature for 5 min. For determination of crystallinity of HDPE component of the ternary composites, a value of 293 J/g was used as the heat of fusion of 100% crystalline polyethylene.¹² All testing samples used in thermal analysis were injection molded ones, and dried under vacuum before test.

Mechanical testing

The tensile and flexural tests were conducted on a universal tensile tester (Instron 1122) based on GB 1040–79 and GB 1042–78, respectively. The notched Izod impact strength was measured with an impact tester (XJU-22, Chengde Tester Manufactory, China) according to GB 1843–80. For all these tests, at least five specimens were used for each measurement.

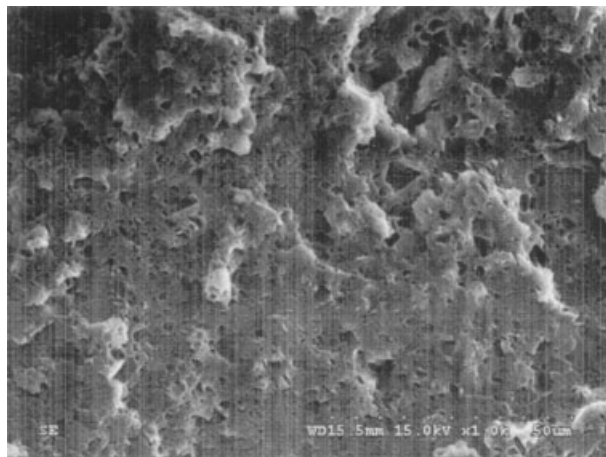


Figure 1 SEM micrographs of etched surface of HDPE/treated CaCO_3 (70/30) composite.

RESULTS AND DISCUSSION

Morphological development of ternary composites

In ternary composites of polymer/elastomer/inorganic filler, the dispersion status of elastomer and filler plays an important role in determination of properties of composites. To investigate the microstructures of this system, the cryogenic-fractured surfaces of samples were etched with hydrogen chloride for 12 h. If the elastomer and the calcium carbonate were dispersed separately, the calcium carbonate would be dissolved by hydrogen chloride. And the calcium carbonate could not be eliminated when the core-shell microstructures were formed. Figure 1 is the micrograph of the etched fractured surface of the binary composite of HDPE/treated CaCO_3 . The dark holes in picture represent CaCO_3 particles, which are dissolved out by hydrogen chloride. In this binary composite, the interfacial adhesion between HDPE and CaCO_3 is poor because of the high polarity of amino acid used to treat CaCO_3 , which leads to the naked CaCO_3 particles easily to be eliminated with strong acid.

Figure 2 shows the surface topology of the ternary composites. Here, "T" stands for treated calcium carbonate-based composites, "U" for untreated calcium carbonate-based composites. From these pictures, it clearly shows that the eliminated CaCO_3 particles decrease with increasing content of maleated POE (POE-g) for both series of composites. This result demonstrates that the introduction of POE-g can encapsulate the CaCO_3 particles to form core-shell structures to keep them from being dissolved by hydrogen chloride. The more POE-g is introduced, the more CaCO_3 particles are encapsulated and the fewer black holes are observed. When the POE-g reaches a certain concentration, the CaCO_3 particles are completely coated by POE-g to form core-shell structures and no black

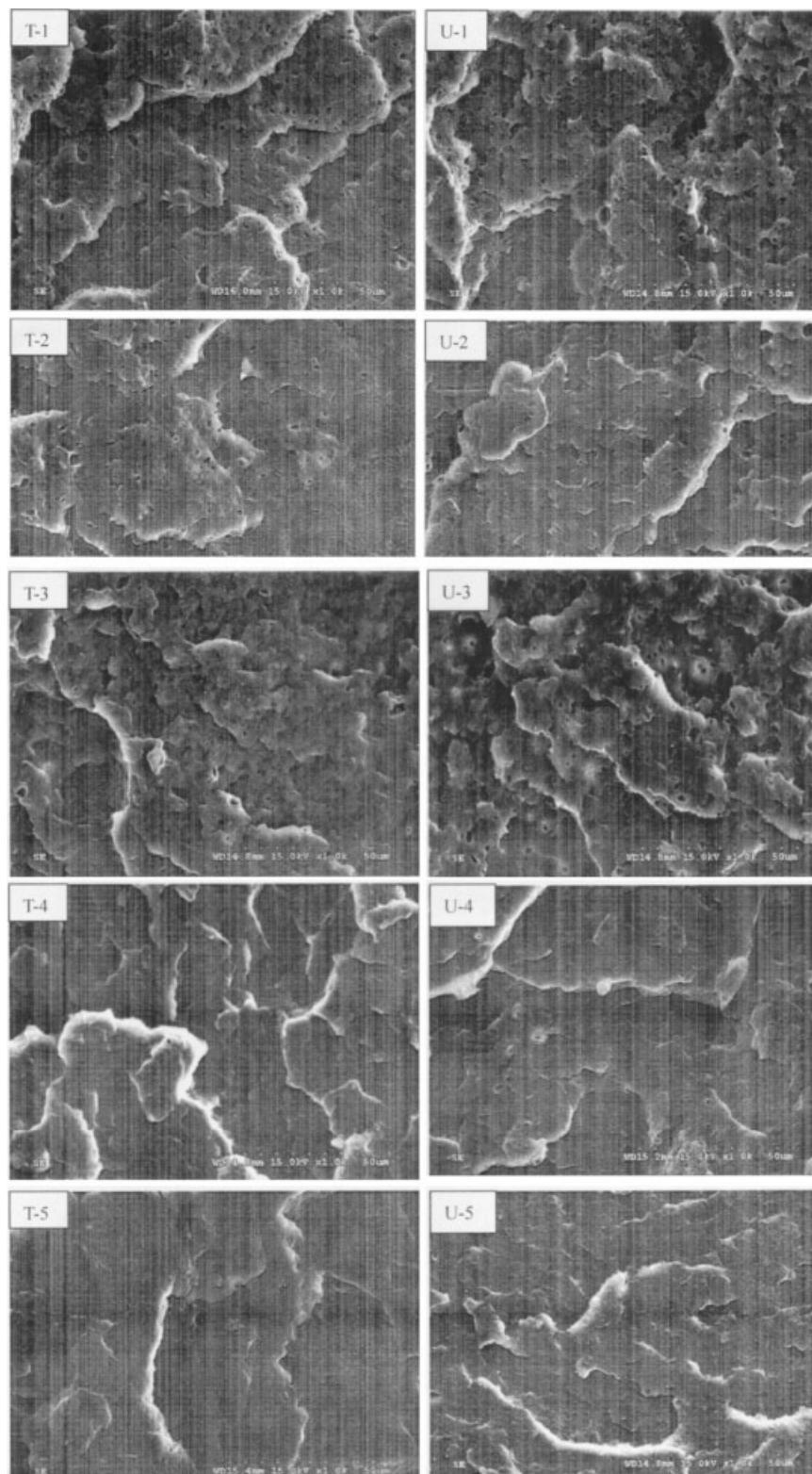


Figure 2 SEM micrographs of etched surfaces of ternary composites with different contents of POE-g: (1), 3.6%; (2), 7.2%; (3), 10.8%; (4), 14.4%; and (5), 18%. Here “T” stands for surface-treated CaCO_3 composites and “U” for untreated CaCO_3 composites.

hole is shown in SEM photographs. This microstructure leads to super toughness of ternary composite as described in latter mechanical properties section.

When one closely observes the photographs in Figure 2, it can be seen that only with 10.8% wt of POE-g, the CaCO_3 particles are almost completely encapsu-

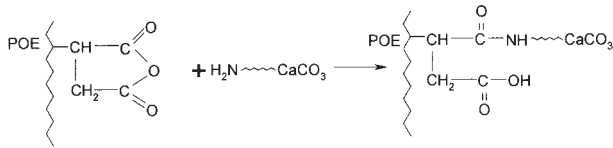


Figure 3 Chemical reaction between POE-g and treated CaCO_3 .

lated, as nearly no black hole can be seen in (T-3) for treated CaCO_3 composites. For untreated CaCO_3 composites, there is still many CaCO_3 particles not being coated with POE-g, as many black holes are shown in (U-3). Until up to 14.4% wt of POE-g, the CaCO_3 particles are completely encapsulated as indicated from (U-4). The differences in microstructures of the ternary composites can be attributed to the interaction between POE-g and treated/untreated CaCO_3 . Actually, POE-g can react with untreated CaCO_3 due to the interaction between maleic anhydride groups and CaCO_3 . Comparing with untreated CaCO_3 , the treated CaCO_3 is much easier to form bonded layer of POE-g related to the interaction between maleic anhydride groups and amino groups attached on the surfaces of CaCO_3 as demonstrated in Figure 3.¹³

Crystallization behavior

To study the influences of maleated POE and/or CaCO_3 on the crystallization and melting behaviors of the matrix of HDPE in composites, DSC studies of nonisothermal crystallization and melting behavior were carried out. The crystallization temperature (T_c) and melt temperature (T_m) were determined by the peak of crystallization curve and melting curve, respectively. The heat fusion of HDPE matrix, ΔH_m , was determined as follows:

$$\Delta H_{m(\text{HDPE})} = \frac{\Delta H_m}{W_{\text{HDPE}}}$$

where ΔH_m and $\Delta H_{m(\text{HDPE})}$ were the heat fusion of samples and HDPE respectively; W_{HDPE} was the weight fraction of HDPE in composites.

And heat of crystallization was determined as follows:

$$\Delta H_{c(\text{HDPE})} = \frac{\Delta H_c}{W_{\text{HDPE}}}$$

where ΔH_c and $\Delta H_{c(\text{HDPE})}$ were the heat fusion of samples and HDPE, respectively.

The crystallinity of HDPE in composites was calculated by $X\% = \frac{\Delta H_{m(\text{HDPE})}}{\Delta H_{m(\text{HDPE})}^0} \times 100\%$, where $\Delta H_{m(\text{HDPE})}^0$ was the heat of fusion of 100% crystalline polyethylene with a value of 293 J/g. The results of the DSC analysis were given in Table I.

From this table, it can be seen that only introduction of POE-g has little effect on the crystallization and melting temperatures as well as crystallinity of HDPE. On the contrary, the presence of CaCO_3 can increase the crystallization temperature and crystallinity of matrix. It clearly indicates that the CaCO_3 particles act as the nucleating agents in HDPE/ CaCO_3 composite, which quiet agrees on the results of research of Bartczak.¹⁴ But the inclusion of CaCO_3 influences the melting temperature (T_m) slightly, which indicates that the thickness of crystalline lamellae is nearly the same as in neat HDPE.

As the POE-g and CaCO_3 are involved simultaneously into the HDPE matrix, both T_m and crystallinity of HDPE in composites are lower than that of plain HDPE. In calculation of crystallinity of HDPE in composites, the POE-g component was considered as

TABLE I
DSC Crystallization and Melting Data (Cooling and Heating Rate, $dT/dt = 10^\circ\text{C}/\text{min}$)

Composites	Composition (wt %)	Crystallization		Melting		X (%)
		T_c ($^\circ\text{C}$)	ΔH_c (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	
HDPE	—	117.8	-207.8	134.1	214.5	73.2
HDPE/POE-g	85/15	118.7	-207.5	133.9	214.8	73.3
HDPE/T- CaCO_3	70/30	121.5	-231.4	134.4	224.1	76.5
HDPE/POE-g/T- CaCO_3^a	66.4/3.6/30	121.5	-206.2	133.6	209.8	71.3
	62.8/7.2/30	121.4	-213.5	133.4	210.5	71.8
	59.2/10.8/30	121.0	-211.3	133.9	212.5	72.5
	55.6/14.4/30	121.0	-205.0	133.3	196.2	66.9
	52.0/18.0/30	120.8	-195.0	132.8	190.6	65.1
HDPE/POE-g/U- CaCO_3^a	66.4/3.6/30	121.6	-203.2	133.6	204.9	69.9
	62.8/7.2/30	121.3	-209.9	133.3	208.9	71.3
	59.2/10.8/30	121.3	-206.3	132.3	196.9	67.2
	55.6/14.4/30	120.8	-201.6	132.8	204.4	69.8
	52.0/18.0/30	120.7	-193.2	132.0	192.2	65.6

^a In calculation of ΔH_c and ΔH_m for these composites, the POE-g was considered as amorphous with a crystallinity of 0%.

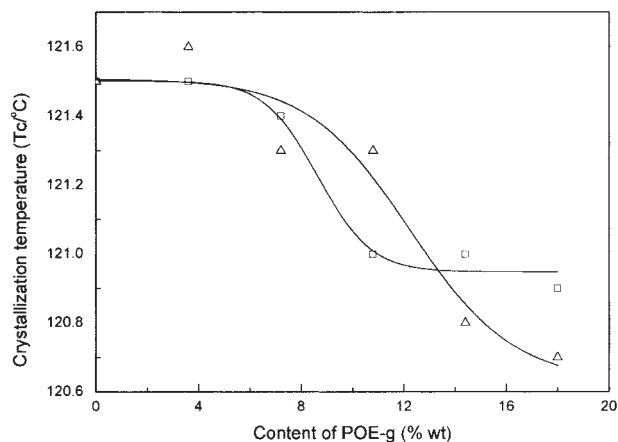


Figure 4 The relationship of crystallization temperatures via content of POE-g at the fixed weight fraction of CaCO₃ of 30%. (□), treated CaCO₃-based composites and (△), untreated CaCO₃-based composites.

amorphous. Actually, the POE-g was still crystallized in some degree. In consideration of this, the crystallinity of HDPE in composites was much lower. As demonstrated by Premphet,^{5,9,15,16} the changes of crystallization behaviors could also reveal the phase morphology in multiphase composites. The introduced POE-g in HDPE/CaCO₃ can form a thin layer around the CaCO₃ particle due to the interaction between POE-g and treated/untreated CaCO₃ particles. This formed outer layers will reduce the nucleation of CaCO₃-based composites, and decrease the crystallization temperatures. Figure 4 shows the relationship of crystallization temperature of HDPE via content of incorporated POE-g with a constant weight fraction of CaCO₃ at 30%. There exists a transition of crystallization temperature at 9% wt of POE-g for treated CaCO₃-based ternary composites, and 12% wt of POE-g for untreated CaCO₃-based ones. Comparing with the development of morphology with content of POE-g in ternary composites as earlier being studied, the transitions in T_c are corresponding to the complete encapsulation of CaCO₃ with POE-g in ternary composites, which leads to the significant reduction of nucleation of CaCO₃.

Mechanical properties

The relationships of tensile strength with content of maleated POE for both treated and untreated CaCO₃-based ternary composites are shown in Figure 5. The tensile strength of treated CaCO₃-based composites is higher than that of untreated CaCO₃-based composites with corresponding content of POE-g. These results imply that the stronger interfacial adhesion between matrix and CaCO₃ in treated CaCO₃-based composites than untreated CaCO₃-based composites at the same content of POE-g. The different strength of

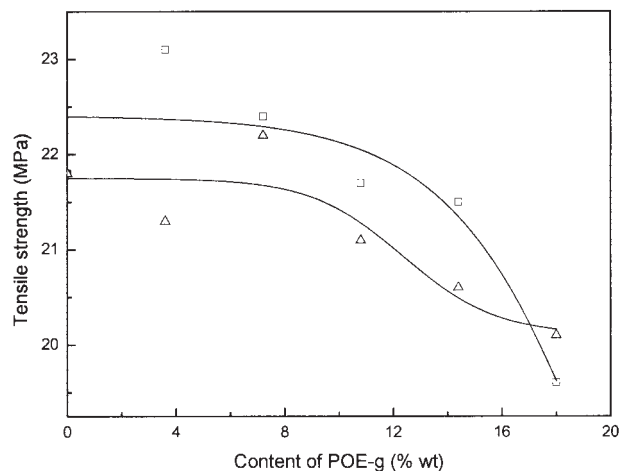


Figure 5 Tensile strength versus content of POE-g for ternary composites of HDPE/POE-g/CaCO₃. (□), treated CaCO₃-based composites and (△), untreated CaCO₃-based composites.

interfacial adhesion is also demonstrated in rheological properties. The treated CaCO₃ composites with stronger interfacial strength showed higher dynamic modulus and viscosity in contrast with untreated CaCO₃ composites at the same concentration of POE-g.¹⁰ Whereas for flexural strength and flexural modulus of ternary composites, the interfacial adhesion shows little influence as shown in Figures 6 and 7. These results are much similar to other ternary composites as many researchers studied.^{1,4}

Figure 8 presents the notched Izod impact strength as a function of POE-g content at a fixed concentration of CaCO₃ of 30%. In this figure, a definite brittle-ductile transition can be seen for both treated and untreated CaCO₃-based ternary composites.

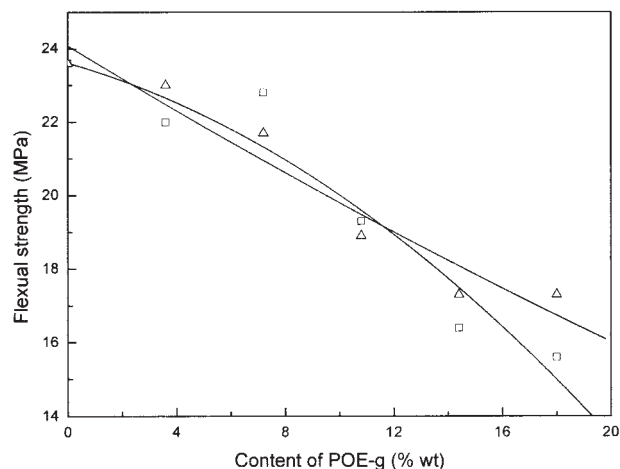


Figure 6 Flexural strength versus content of POE-g for ternary composites of HDPE/POE-g/CaCO₃. (□), treated CaCO₃-based composites and (△), untreated CaCO₃-based composites.

However, the brittle–ductile transition of treated CaCO_3 -based composites occurs at lower concentration of POE-g than that of untreated CaCO_3 -based composites. The transition appears at about 9% content of treated CaCO_3 and 12% content of untreated CaCO_3 , respectively. The transitions in both impact strength and crystallization temperatures show much agreement, which happens at the same concentration of POE-g with a fixed CaCO_3 content.

In consideration of morphological development with concentration of POE-g at the fixed CaCO_3 content, it can be concluded that the transitions occurred in both crystallization temperatures and impact strength of ternary composites HDPE/POE-g/ CaCO_3 can be attributed to the evolution of the formation of the core-shell structures. The interfacial adhesion effects the encapsulation of CaCO_3 particles with POE-g.

CONCLUSIONS

In this article, ternary composites of HDPE/POE-g/ CaCO_3 were prepared by melt extrusion process. Morphology, crystallization behavior, and mechanical properties of these composites were studied. Whatever the treated or untreated CaCO_3 used, there existed a transition in both crystallization temperatures and impact strength. These transitions were the results

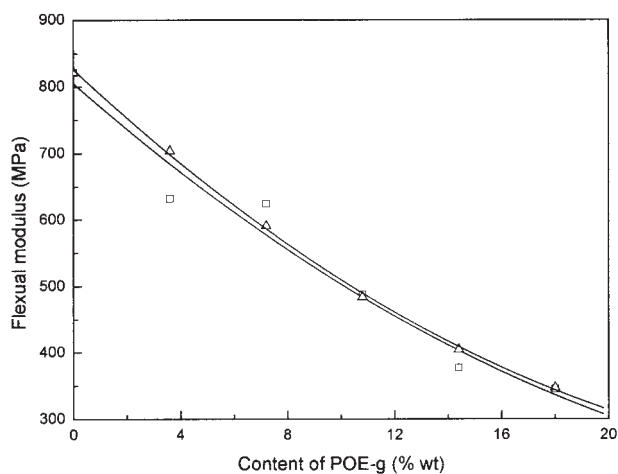


Figure 7 Flexural modulus versus content of POE-g for ternary composites of HDPE/POE-g/ CaCO_3 . (\square), treated CaCO_3 -based composites and (\triangle), untreated CaCO_3 -based composites.

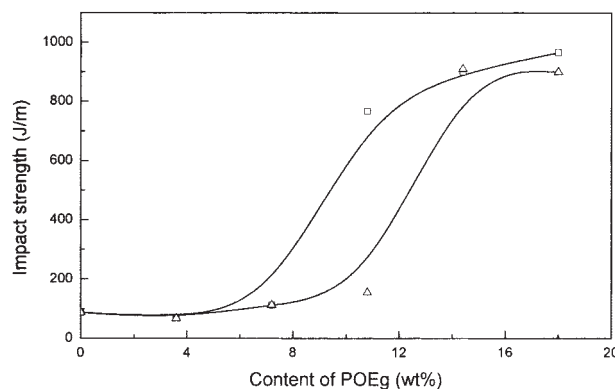


Figure 8 The relationship of impact strength via content of POE-g at a fixed weight fraction of CaCO_3 of 30%. (\square), treated CaCO_3 -based composites and (\triangle), untreated CaCO_3 -based composites.

of the development of morphology in ternary composites as the increase of content of maleated POE (POE-g). The transition also was related with the interaction between POE-g and CaCO_3 . With the stronger interaction for treated CaCO_3 -based ternary composites, transition occurred at relatively lower weight fraction of POE-g when the content of CaCO_3 was kept constant.

References

1. Yu, Z. Z.; Lei, M.; Ou, Y. C.; Hu, G. H. *J Polym Sci Part B: Polym Phys* 1999, 37, 2664.
2. Ou, Y. C.; Guo, Q. T.; Fang, X. P.; Yu, Z. Z. *J Appl Polym Sci* 1999, 74, 2397.
3. Long, Y.; Shanks, R. A. *J Appl Polym Sci* 1996, 62, 639.
4. Premphet, K.; Horanont, P. *J Appl Polym Sci* 1999, 74, 3445.
5. Premphet, K.; Preechachon, I. *J Appl Polym Sci* 2003, 89, 3557.
6. Li, Z.; Guo, S. Y.; Song, W. T.; Yan, Y. *J Polym Sci Part B: Polym Phys* 2002, 40, 1804.
7. Zheng, M. J.; Li, H. L. *J Appl Polym Sci* 2004, 91, 1635.
8. Gao, X. L.; Qu, C.; Zhang, Q.; Peng, Y.; Fu, Q. *Macromol Mater Eng* 2004, 289, 41.
9. Stricker, F.; Mülhaupt, R. *J Appl Polym Sci* 1996, 62, 1799.
10. Xie, T. X.; Liu, H. Z.; Ou, Y. C.; Yang, G. S. *J Polym Sci Part B: Polym Phys* 2005, 43, 3213.
11. Xie, T. X.; Liu, H. Z.; Ou, Y. C.; Yang, G. S. *Acta Polym Sinica* 2006, 1, 53.
12. Wunderlich, B.; Cormier, C. M. *J Polym Sci Part A-2: Polym Phys* 1967, 5, 987.
13. Wang, Y.; Lu, J.; Wang, G. H. *J Appl Polym Sci* 1996, 64, 1275.
14. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. *Polymer* 1999, 40, 2347.
15. Hornsby, P. R.; Premphet, K. *J Appl Polym Sci* 1998, 70, 587.
16. Premphet, K.; Horanont, P. *Polymer* 2000, 41, 9283.