

Enhanced Compatibility of PA6/POE Blends by POE-g-MAH Prepared Through Ultrasound-Assisted Extrusion

Tingting Xie,¹ Hong Wu,¹ Wenting Bao,¹ Shaoyun Guo,¹ Yong Chen,² Hua Huang,² Hongyu Chen,² Shih-Yaw Lai,² Jinder Jow³

¹The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

²The Dow Chemical (China) Company Limited, Shanghai 201203, People's Republic of China

³The Dow Chemical Company Limited, Freeport, Texas 77541

Received 16 December 2009; accepted 2 April 2010

DOI 10.1002/app.32547

Published online 7 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effects of POE-g-MAH, prepared through different methods, on morphology and properties of PA6/POE/POE-g-MAH blends are summarized in this article. The grafting degree of POE-g-MAH can be increased through the ultrasound-assisted extrusion. Experimental results showed that the addition of POE-g-MAH can increase the mechanical properties of the PA6/POE blend and decrease the particle size of POE dispersed phase in PA6 matrix due to the compatibilization by POE-g-MAH. The PA6/POE blend compatibilized by POE-g-MAH prepared through the ultrasound-assisted extrusion has smaller particle size of POE dispersed phase and higher

notched Izod impact strength than that by POE-g-MAH with similar grafting degree initiated only by peroxide. This result is ascribed to some anhydride rings attached to the chain terminus of POE due to ultrasound initiation. Rheological and Molau test results also showed enhanced compatibilization of POE-g-MAH prepared through the ultrasound-assisted extrusion on the PA6/POE blend due to a structural difference of POE-g-MAH. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1846–1852, 2010

Key words: polyolefin elastomer; maleic anhydride; polyamide; compatibility; ultrasound

INTRODUCTION

Poly(ethylene 1-octene) (POE) synthesized by metallocene catalyst technology is a family of polyolefin polymers produced by The Dow Chemical Company.^{1,2} They have good mechanical and processing performance and excellent resistance to heat-aging and are used directly as elastomer material³ and toughening modifier for polyolefin resin because of their good thermal stability, weather resistance, aging resistance, and excellent toughness.⁴ However, their nonpolar nature has limited the use as a modifier for polar polymers, e.g., poly(butylene terephthalate) (PBT) and Polyamide 6 (PA6).^{5–7}

To improve the miscibility between polar and nonpolar polymers, POE usually is graft-modified by polar monomers.^{8,9} Due to the high reactivity in successive reactions maleic anhydride (MAH), as one of the most commonly used monomers, has been successfully grafted onto POE in the presence of organic per-

oxide, either in the melt or in the solution state.^{8–10} Compared with solution graft copolymerization, the reactive-extrusion grafting has obvious advantages in term of energy and environment, such as reducing the production cost and tailoring polymer properties for special application.^{11,12} The grafting reaction of MAH may be accompanied by a free-radical-induced crosslink reaction due to the use of peroxide, resulting in gel formation, which is harmful to the miscibility of the graft copolymers.⁸ So it is important to find a new way to obtain the MAH-grafted copolymer with a higher grafting degree but lower gel content.

Over the past decades, ultrasound has been applied in the extrusion.^{13,14} It was shown that, during extrusion, ultrasound with high power can breakdown the molecular chain and rapidly breakup the three-dimensional network in vulcanized rubbers though the scission of C–S, S–S, and C–C bonds.^{15,16} Some studies show that ultrasound can cause the degradation of polymer melt.^{17–20} In recent years, Yuncan Zhang et al.^{21,22} studied the grafting reaction of MAH onto HDPE, LLDPE, PP, and EPDM in the presence of ultrasound during the extrusion. The results showed that the grafting degree (GD) of the product increased with increasing ultrasound power while the gel content was less than 0.7 wt %. The functionalized products obtained through ultrasound mainly consist of the products containing an anhydride ring attached to the

Correspondence to: H. Wu (nic7702@scu.edu.cn) or S. Guo (nic7702@scu.edu.cn).

Contract grant sponsor: Special Funds for Major State Basic Research Projects of China; contract grant number: 2005CB623800.

Contract grant sponsor: The Dow Chemical Company.

TABLE I
Grafting Degree of POE Grafted Samples with Different Monomer Concentration

Samples	POE	MAH	DCP	St	Ultrasound power (W)	Grafting degree (%)
POE-g-MAH _a	100	1	0.1	1	0	0.38
POE-g-MAH _b	100	1	0.1	1	200	0.57
POE-g-MAH _c	100	2	0.1	2	0	0.60

terminus of macromolecular chain; however, the product prepared through peroxide initiation mainly contains an anhydride ring grafted on the side chain. Therefore, if POE grafted with MAH (POE-g-MAH) with similar GD induced by ultrasound and peroxide in melt state processing are used to toughen PA6, respectively, then the properties of the corresponding blends should be different due to the structural difference of POE-g-MAH.

To confirm the above hypothesis, preparation of POE-g-MAH with different GD through different initiation methods and the compatibilization effect of POE-g-MAH on the PA6/POE blend, will be studied in this article. Morphology, mechanical, and rheological properties of the corresponding blends also will be studied. The objective is to develop a new method to prepare functionalized POE for better processability than the traditional peroxide-initiation grafting method.

EXPERIMENTAL

Materials

ENGAGE™ 8150 POE was supplied by The Dow Chemical Company, with a density of 0.868 g/cm³ and a melt flow index of 0.5 g/10 min (180°C, 2.16 Kg). The PA6 used in this study was supplied by Guangdong Xinhui Meida Nylon Co. (China), with a density of 1.14 g/cm³ and a melt flow index of 11 g/10 min (230°C, 2.16 Kg). All other chemicals including MAH, dicumyl peroxide (DCP), and styrene (St), were of reagent grade and were used without further purification.

Samples preparation

The grafting reactions were carried in a single-screw extruder with 25 mm diameter and a length to diameter ratio $L/D = 30$ and a die connected to a generator of ultrasound.²³ The maximum power output and fixed frequency of the generator were 300 W and 20 kHz. The POE was mixed with MAH, DCP, and St which were dissolved in acetone before extrusion. The temperatures of the extruder barrel and the ultrasonic power were controlled, and the temperature profile from feed zone to die zone was set at 80, 180, 185, and 185°C, respectively. The screw rotation speed was fixed at 10 rpm to maintain extrusion rate.

Table I lists the experimental conditions used in this study. The monomer concentrations in POE-g-MAH_a and POE-g-MAH_b were the same while POE-g-MAH_b was prepared in the presence of 200 W ultrasound. Compared with POE-g-MAH_a and POE-g-MAH_b, the concentration of MAH and St in POE-g-MAH_c was doubled.

The blends of PA6/POE and PA6/POE/POE-g-MAH were prepared through melt mixing in a twin-screw extruder (SHJ-20, Nanjing Giant Machinery Co., Nanjing, China). The PA6 pellets were dried at 80°C overnight before mixing. The temperature profile from the feed zone to die zone was set at 200, 230, 240, 240, 240°C. The extrudates were then dried and molded into impact and tensile bars by using an injection molding machine (K-TEC40, Milacron, Malterdingen, Germany) with the injection temperature set at 240°C.

Measurements and characterization

To determine the MAH graft ratio on POE, the method of chemical titration was employed. A 2-g portion of the POE-g-MAH extrudate was heated in 200 mL of refluxing xylene for 1 h, then filtered through into 400 mL acetone, resulting in a precipitate of POE-g-MAH polymer. The precipitated polymer was concentrated in a Rotavaporator for 8 h by acetone, and the residual polymer was dried in at 50°C for 12 h. The MAH content of the soluble polymers was determined by heating a 0.2-g portion in 50 mL of refluxing xylene for 30 min, followed by cooling to 80°C. About 5 mL of 0.25 mol/L solution of potassium hydroxide (KOH)/ethanol standard solution was added, then heated under reflux for 15 min. A 0.1% phenolphthalein/ethanol solution was added as the indicator and a known excess of KOH/ethanol was added, resulting in a blue solution. The hot solution was then back titrated with 0.25 mol/L acetic acid/xylene solution. The MAH graft degree (GD) was calculated by the following equation:

$$\text{Grafting degree (wt \%)} = \frac{(V_0 - V_1) \times N}{2 \times W \times 1000} \times M \times 100\% \quad (1)$$

Where V_0 (mL) is the volume of acetic acid/xylene solution used in a blank assay, V_1 (mL) is the volume of acetic acid/xylene solution used by titration,

TABLE II
Mechanical Properties of the Blends

Samples		Elongation at break (%)	Stress at break (MPa)	Notched Izod impact strength (KJ/m ²)
PA6	100	155 ± 8	42.6 ± 1	10.1 ± 0.5
PA6/POE	70/30	55 ± 5	31.9 ± 0.8	9.6 ± 0.4
PA6/POE/POE- <i>g</i> -MAH _a	70/20/10	230 ± 10	34.4 ± 0.6	28.8 ± 0.8
PA6/POE/POE- <i>g</i> -MAH _b	70/20/10	250 ± 9	35.1 ± 0.5	74.1 ± 1.2
PA6/POE/POE- <i>g</i> -MAH _c	70/20/10	259 ± 11	35.6 ± 0.6	68.3 ± 1.5

N (mol/L) is the concentration of acid/xylene solution, M (98.06) is the molecular weight of MAH, and W (g) is the quantity of sample.

The tensile bars conformed to GB1040-79 and stress-strain behaviors were measured by using a tension machine (CMT4104, Shenzhen Sans Material Testing Co., Shenzhen, Shenzhen, China). The speed of the crosshead in the tensile test was 50 mm/min. According to GB1843-80, the impact bars were used to measure the notched Izod impact strength by using an impact testing machine (XJU-22, Chengde Dahua Testing Machine Co., Chengde, China) at the temperature of 20°C. The average values of at least five tests were reported.

Viscoelastic properties of the blends were determined with a Rheometer system Gemini 200 rheometer (Malven Co., Worcestershire, UK) at 240°C using a parallel plate configuration. The disks of the specimens with 25 mm diameter and 1 mm thickness were prepared through the compression molding. Frequency sweep tests were performed for each blend from 0.01 Hz to 100 Hz, and the strain is 1% within the linear viscoelastic region. All experiments were carried out under a dry nitrogen atmosphere.

The samples were cryogenically fractured in liquid nitrogen, then etched in xylene at 70°C for 4 h to extract the elastomeric POE phase. The samples were coated with gold prior to morphology observation under the electron beam. The fracture surface of the impact specimens and phase morphology of the blends were studied by using scanning electron microscopy (SEM, JSM-5900, JEOL, Tokyo, Japan). The analysis of particle size and particle size distribution in the blends was carried out by using a computerized image analyzer. The number-average diameters of the POE domains were determined according to the following relationship:

$$D_i = \frac{\sum N_i D_i}{\sum N_i} \quad (2)$$

where N_i is the number of dispersed POE domains with a diameter of D_i counted from the SEM images. The total number of particles used in the analysis was ca 300–400.

The Molau test was used to evaluate the interfacial interaction between PA6 and POE. A 0.2 g sam-

ple of PA6/POE and PA6/POE/POE-*g*-MAH was added into 10 mL formic acid. The photo was taken after the solution was hold for 24 h.

RESULTS AND DISCUSSION

Grafting degree of POE-*g*-MAH

Two approaches were used here to increase the grafting degree of POE-*g*-MAH. The first one was through the ultrasound-assisted extrusion. The second one was by increasing concentration of MAH and St monomers. Table I shows that the grafting degree of POE-*g*-MAH_b is higher due to the use of ultrasound. Compared with POE-*g*-MAH_a, which has the same concentration of the monomers as POE-*g*-MAH_b. It is ascribed that more POE macroradicals are formed during ultrasound-assisted extrusion since ultrasound can break the macromolecular chains to form the macro-radicals. Therefore, the higher concentration of macro-radicals is available to react with maleic anhydride, which results in the increase of the grafting degree.

As comparison with POE-*g*-MAH_a and POE-*g*-MAH_b, POE-*g*-MAH_c has the same concentration of DCP but twice concentration of MAH and St, while the grafting degree of POE-*g*-MAH_c is similar with that of POE-*g*-MAH_b. The next question is whether these two different methods have the grafted products with different structure, although the grafting degrees of POE-*g*-MAH_c and POE-*g*-MAH_b are similar. The POE-*g*-MAH_c prepared through peroxide initiation should mainly contain anhydride rings grafted on the side chains while POE-*g*-MAH_b prepared through both ultrasound and DCP initiation should contain some anhydride rings attached to the chain terminus. Therefore, morphology and properties of the blends should be different, when the grafted products with a similar grafting degree but different structure are used to compatibilize the PA6/POE blend.

Mechanical properties of the blends

Tensile properties and notched Izod impact strength of PA6, PA6/POE binary blend, and different PA6/

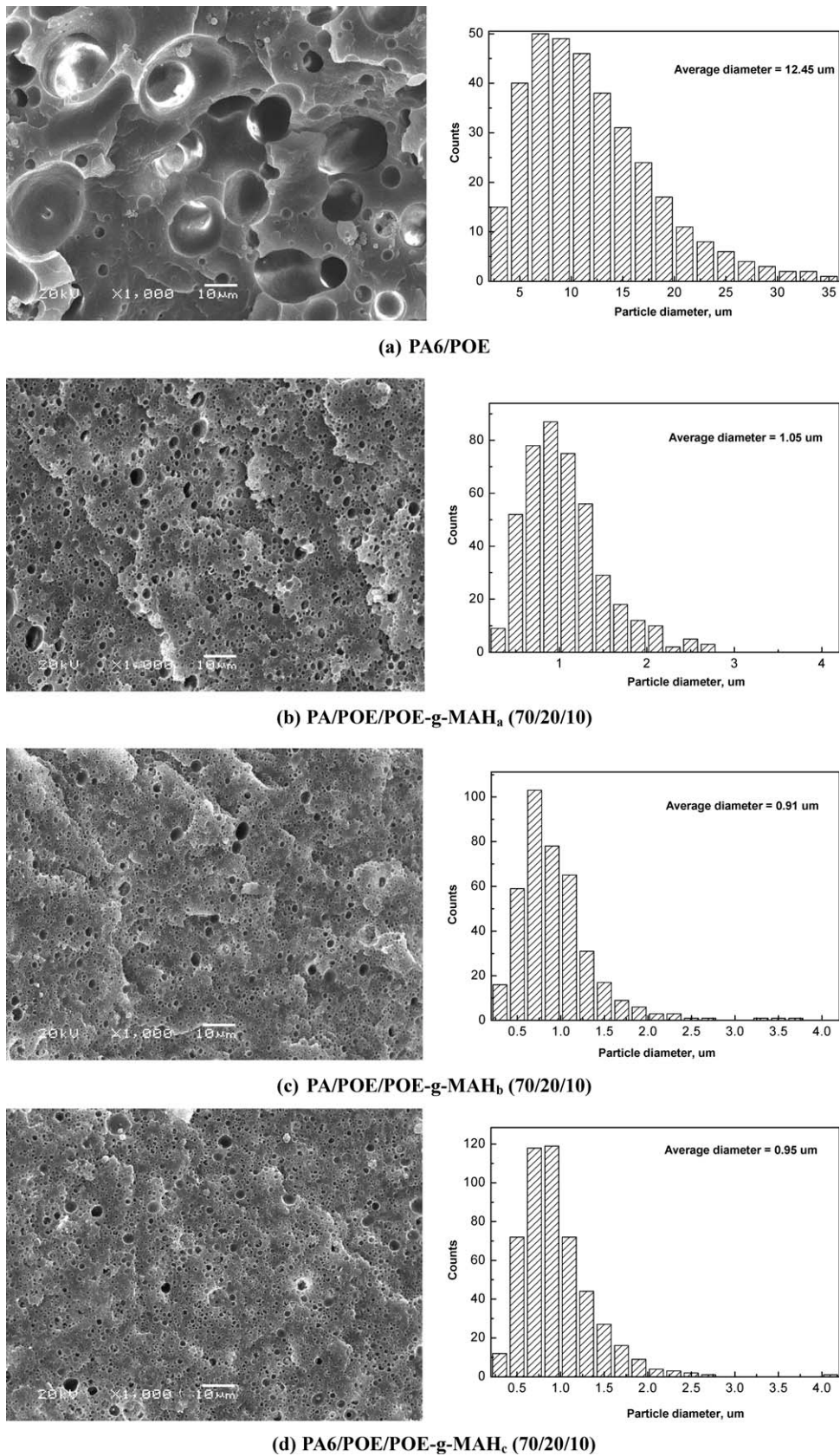


Figure 1 SEM images and particle size distribution of PA6/POE/POE-g-MAH blends.

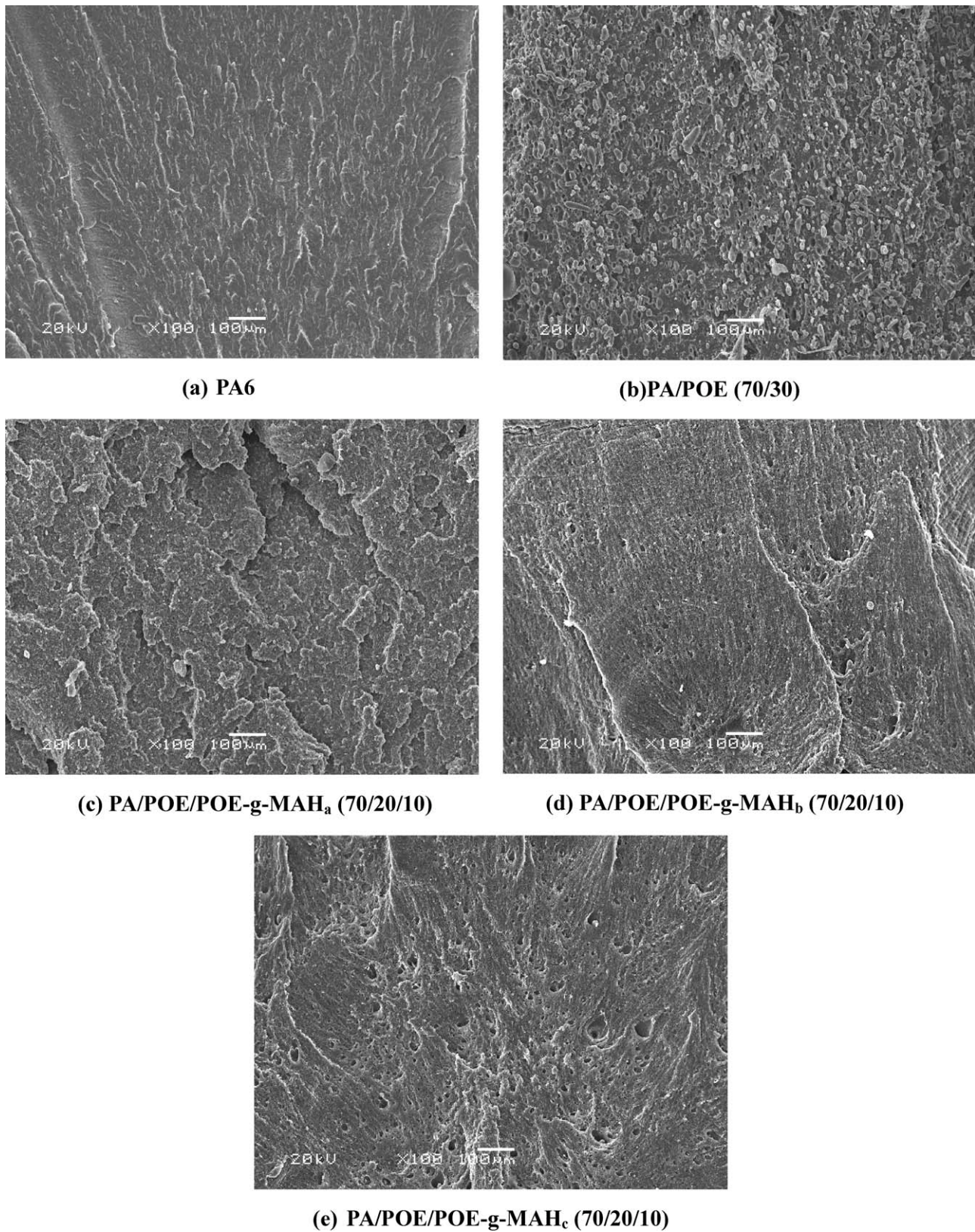


Figure 2 SEM photos of impact-fractured surfaces of PA6/POE/POE-g-MAH blends.

POE/POE-g-MAH ternary blends are listed in Table II. It clearly shows that the PA6/POE blend has lower elongation at break and notched Izod impact

strength than PA6 due to the immiscibility between PA6 and POE. However, notched Izod impact strength and elongation at break of the blends are

improved, obviously, when POE is partially substituted by POE-*g*-MAH. When the grafting degree of MAH in the POE-*g*-MAH increases from 0.38 wt % to 0.57 wt %, notched Izod impact strength increased from 28.8 to 74.1 KJ/m², and elongation at break of the PA6/POE/POE-*g*-MAH_b blend (250%) is a little higher than that of the PA6/POE/POE-*g*-MAH_a blend (230%). It should be attributed to the improved compatibility between the PA6 matrix and the POE dispersed phase, resulting from the chemical reaction of anhydride groups of MAH with the NH₂ groups of PA6.

On the other hand, the notched Izod impact strength of PA6/POE/POE-*g*-MAH_b is higher than that of PA6 /POE/POE-*g*-MAH_c, as expected, though it is not marked, and the elongation at break does not change very much. The increase of notched Izod impact strength may be attributed to the structural difference of grafted products. It is much easier for some anhydride rings attached to the chain end of POE in POE-*g*-MAH_b to react with the terminal groups of PA6, resulting in better compatibility between POE and PA6, compared with anhydride rings grafted only on the side chains of POE in POE-*g*-MAH_c.

Morphological characterization

It is well known that the morphology and particle size of the rubber or elastomer as the dispersed phase has been shown to be critical for improving the toughness of blends. The SEM micrograph and particle size distribution of blends shown in Figure 1 reveals the compatibility between PA6 and POE due to the addition of different POE-*g*-MAH. In Figure 1(a), holes where POE as dispersed phase has been extracted from the PA6 matrix can be seen, and the edges of the holes are very smooth. The POE particles (with average diameter >12 μm) are large and the distribution of particle size is broad. It confirms that there is the weak interfacial adhesion between two phases. Due to the addition of POE-*g*-MAH to partially replace POE, the morphology of the PA6/POE/POE-*g*-MAH_a blend in Figure 1(b) showed completely different from the morphology of the PA6/POE blend. The particle size is reduced obviously and the distribution of POE particle size in PA6/POE/POE-*g*-MAH_a is narrower than that in the PA6/POE blend. It showed improved interfacial adhesion between PA6 and POE-*g*-MAH, resulting in good compatibility between two phases. Figure 1(b,c) clearly demonstrates the influence of MAH grafting degree on the morphology of the blends. With increasing the grafting degree from 0.38 wt % (POE-*g*-MAH_a) to 0.57 wt % (POE-*g*-MAH_b) due to the use of ultrasound, POE particles in PA6 matrix become significantly smaller and more uniformly

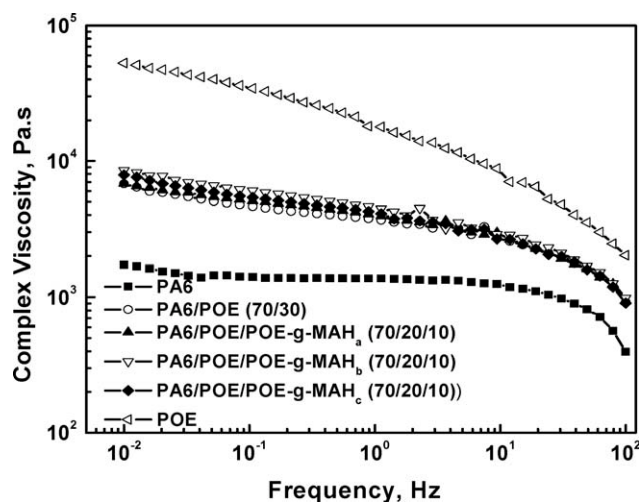


Figure 3 Complex viscosity of PA6, POE and their blends.

distributed, indicating that enhanced adhesion between the two phases as a result of more possible chemical reactions between PA6 and POE-*g*-MAH makes POE particles smaller and more finely dispersed in the PA6 matrix. Therefore, the PA6/POE/POE-*g*-MAH_b blend exhibits superior impact strength than PA6/POE/POE-*g*-MAH_a. Though the grafting degree of POE-*g*-MAH_b and POE-*g*-MAH_c are similar, the particle size and dispersion of POE in PA6/POE/POE-*g*-MAH_b is smaller than that in PA6/POE/POE-*g*-MAH_c as expected due to the structural difference in POE-*g*-MAH.

The fracture surface of a polymer material usually indicates how the material fractures. SEM micrographs of PA6 and its blends are shown in Figure 2. It is clearly found that the impact-fractured surface of PA6 is very smooth, showing typical brittle fracture. For the PA6/POE blend, POE particles can be seen in and on the surface while the matrix is also smooth, indicating the brittle fracture. When the blend added with POE-*g*-MAH, shear yielding of the matrix appears. With increasing the grafting degree of POE-*g*-MAH, the shear yielding occurs and runs entirely within the PA6 matrix, which becomes the main impact energy dissipation mechanism.

Rheological properties

Rheological properties of the polymer blends are frequently studied to indicate phase compatibility and structure formation, because the dynamic viscoelastic response is very sensitive to the changes of structure and morphology of the polymer blends. Figure 3 shows that in the studied frequency range, all the systems show typical nonNewtonian behavior, and ρ^* of blends are between those of pure PA6 and POE. PA6/POE shows a significant increase in ρ^* than PA6 by adding POE. Due to the addition of

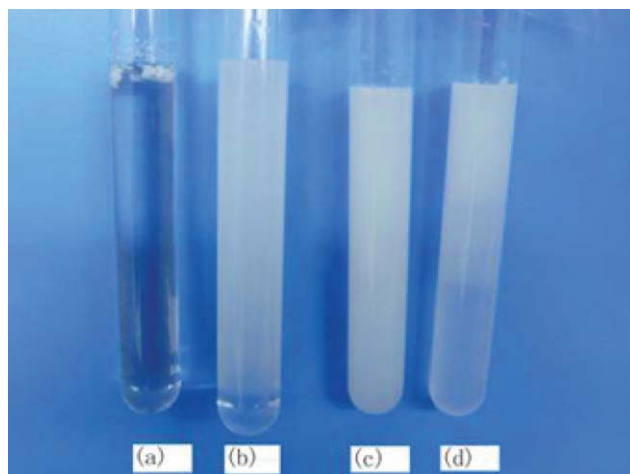


Figure 4 Molau test results of the samples in formic acid: (a) PA6/POE, (b) PA6/POE/POE-*g*-MAH_a, (c) PA6/POE/POE-*g*-MAH_b, and (d) PA6/POE/POE-*g*-MAH_c. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

POE-*g*-MAH, PA6/POE/POE-*g*-MAH_a shows a more significant increase in ρ^* than PA6/POE, indicating an enhanced interfacial adhesion between PA6 and POE. Comparing with ρ^* of the blends with the grafted product prepared through two different initiation methods, ρ^* of PA6/POE/POE-*g*-MAH_b are higher than that of PA6/POE/POE-*g*-MAH_c, especially at low angular frequencies. This is a qualitative evidence for a structural difference between POE-*g*-MAH_b and POE-*g*-MAH_c. Because of chemical reaction between anhydride group of POE-*g*-MAH and the terminal $-\text{NH}_2$ group of PA6, MAH grafted on the end of POE chains could diffuse more easily from the POE phase to the interface between POE and PA6 phases, and then more MAH groups could react with PA6, which lead to chain extension of PA6 and stronger interfacial adhesion between PA6 and POE, thus ρ^* increases.

Molau test

The Molau test results are shown in Figure 4. PA6 can be absolutely dissolved in formic acid, thus the solution is transparent. Phase separation can be clearly found for the PA6/POE blend in formic acid since the POE phase forms the white deposits. However, the POE phase can be well distributed in formic acid to form the stable emulsion due to the addition of POE-*g*-MAH, indicating that the interfacial tension between PA6 and POE is decreased due to the compatibilization of POE-*g*-MAH on PA6-*g*-POE by the interfacial interaction between POE-*g*-MAH and PA6. Compared with the other POE-*g*-

MAH, the addition of POE-*g*-MAH_b is more beneficial to form uniform emulsion, indicating that POE-*g*-MAH_b with some anhydride rings attached to the chain end, which can compatibilize the PA6/POE blend more effectively.

CONCLUSIONS

In this article, POE-*g*-MAH was prepared through three different methods, and the grafting degree of POE-*g*-MAH was increased by increasing the concentration of MAH and St or through ultrasound initiation. The addition of POE-*g*-MAH prepared through ultrasound-assisted extrusion as a compatibilizer to the PA6/POE blend can decrease the particle size of POE dispersed phase in PA6 matrix and increase the notched Izod impact strength more than POE-*g*-MAH at a lower GD or similar GD at twice monomer concentrations, both initiated without ultrasound. The enhanced compatibility of the PA6/POE blend by POE-*g*-MAH prepared through ultrasound-assisted extrusion should be ascribed to some anhydride rings attached to the chain end of POE due to ultrasound initiation. The enhanced compatibility can also be found from the rheological and Molau test results.

References

- Xu, Z. *Mod Chem Ind* 2004, 24, 23.
- Lancaster, G. M. *Applications of INSITE Technology in the Rubber/Elastomer Market*, Technical Information; The Dow Chemical Company, US, 1996.
- Xue, P.; Zhang, X.; Zhou, Y. *Eng Plast Appl* 2003, 31, 67.
- Wang, D.; Li, Y.; Li, L.; Meng, L. *China Plast* 2000, 14, 12.
- Li, Y. *Plast Additives* 2006, 3, 21.
- Yu, Z. Z.; Ou, Y. C.; Hu, G. H. *J Appl Polym Sci* 1998, 69, 1711.
- Zhang, J. *Plast Sci Technol* 1999, 2, 5.
- Feng, W.; Wu, D. *J Beijing Univ Chem Technol* 1998, 25, 33.
- Yu, Z.; Zhen, Y.-C. *J Appl Polym Sci* 1998, 36, 1987.
- Huang, H.; Cheng, Y.; Zhang, Y. *China Plast* 2000, 14, 74.
- Xu, C.; Guo, Q.; Wang, X.-M. *Plastics* 2006, 35, 54.
- Huang, F. R. *Chem Ind Press* 2000, 1, 11.
- Ivanov, A. V.; Bogush, A. L. *Khirurgiya* 1985, 6, 122.
- Isayev, A. I.; Mandelbaum, S. *Polym Eng Sci* 1991, 31, 1051.
- Isayev, A. I.; Chen, J. *US Patent* 5,284,625, 1994.
- Isayev, A. I.; Chen, J.; Tukachmsky, A. *Rubber Chem Technol* 1995, 68, 267.
- Kim, H.; Lee, J. W. *Polymer* 2002, 43, 2585.
- Li, Y. T.; Li, J.; Guo, S. Y.; Li, H. L. *Ultrason Sonochem* 2005, 12, 183.
- Li, J.; Guo, S. Y.; Li, X. L. *Polym Degrad Stab* 2005, 89, 6.
- Li, J.; Liang, M.; Guo, S. Y.; Lin, Y. *Polym Degrad Stab* 2004, 86, 323.
- Zhang, Y. C.; Li, H. L. *Polym Eng Sci* 2003, 43, 774.
- Zhang, Y. C.; Chen, J. Y.; Li, H. L. *Polymer* 2006, 47, 4750.
- Wu, H.; Guo, S. Y.; Chen, G. S.; Lin, J.; Chen, W.; Wang, H. T. *J Appl Polym Sci* 2003, 90, 1873.