Compatibilization and Toughening of Poly(2,6-dimethyl-1, 4-phenylene oxide)/Polyamide 6 Alloy with Poly(ethylene 1-octene): Mechanical Properties, Morphology, and Rheology

Xiaodong Wang, Wei Feng, Hangquan Li, Riguang Jin

School of Materials Science and Engineering, P.O. Box 61, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

ABSTRACT: Blends of a poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/polyamide 6 (PA 6) alloy toughened with a novel polyolefin elastomer poly(ethylene-1-octene) (POE) were prepared via melt extrusion. In order to improve the compatibilization between POE and the PPO/PA 6 alloy, POE was grafted with maleic anhydride (MA), which could react with the amine group of PA 6. The Izod impact strength of the blends exhibited an optimum when the extent of MA grafting of POE was changed, which is an order of magnitude higher than that of the untoughened blends. The morphology revealed that the size of the POE particles decreased with an increasing MA grafting ratio of POE. Studies on the tensile properties and rheology of the blends were also carried out. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3110–3116, 2003

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a high-strength engineering plastic with a high glass transition temperature (T_g) of 210°C and good dimensional stability.[1] However, deficiencies such as brittleness, poor processability, and solvent resistance prohibit it from broader usage.[2] Current research of PPO has been focused mainly on the alloys of PPO with polyamide 6 (PA 6).[3,4] The inherent properties of PPO and PA 6 suggest that a combination of PPO and PA 6 should provide the advantages of the individual components and give a useful blend with improved solvent resistance and processability.[5,6] However, PPO is incompatible with PA 6, and the simple melt blending of PPO and PA 6 generally shows a deterioration in impact and tensile properties.[7] Such a reduction in properties is frequently a reflection of poor interfacial adhesion between dispersed phase and continuous matrix that leads to rapid initiation and growth of cracks.[8,9] Thus, it is reasonable to expect that some form of compatibilization would be required to prepare a useful alloy. A large number of studies employed maleic anhydride (MA)-containing copolymers as compatibilizers for the alloy of PPO and PA 6.[10–15] Brown[16] reported that the reaction of an aryloxytriazine-functionalized PPO with PA 6 resulted in a copolymer, which was used as an *in situ* reactive compatibilizer for the PPO/PA 6 alloy. Jo and Kim[17] reported that a styrene–acrylic acid random copolymer with a high acrylic acid content was an effective interfacial linker for PPO/PA 6 blends. Lai[18] synthesized a PPO–PA 6-grafted copolymer with a well-defined structure and used this copolymer as the compatibilizer for PPO/PA 6 blends, which showed satisfactory mechanical properties except for tensile strength. Gallucci[19] compatibilized PPO/PA 6 blends with an MA-grafted SEBS and obtained improved toughness.

MA-grafted PPO (PPO-*g*-MA) was also reported as a good reactive compatibilizer for PPO/PA 6 alloys.[20–24] A PPO/PA6 blend with a weight ratio of 70/30 provided a notched impact strength of only 25 J/m[25]; however, when half of the PPO was replaced by PPO-*g*-MA, 49 J/m was achieved.[25] The improvement was moderate; however, it provided a basis for further toughening. In this article, a novel polyolefin elastomer, poly(ethylene-1-octene) (POE), was employed as the impact modifier. To improve the compatibility of POE with the PPO/PA 6 system, it was grafted with MA to various extents. All the investigation was based on a blend of PPO/PPO-*g*-MA/PA6 with a weight ratio of 35/35/30, which will, for simplicity, be denoted as PPO/PA6 blends. The effects of MA-grafted POE (POE-*g*-MA) on the mechanical properties, morphology, and rheology of the blends were also investigated.

EXPERIMENTAL

Materials

PPO (646-111 grade) was purchased from the GE Plastics Co. Ltd., Moka, Japan, which had an intrinsic

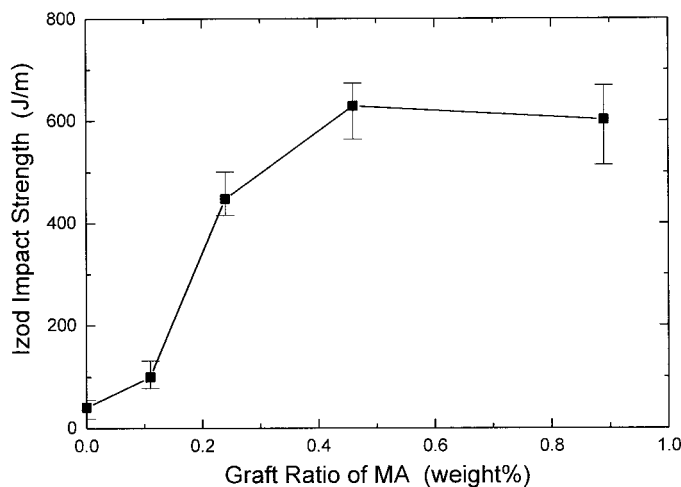*Correspondence to:* X. Wang (wangxd@mail.buct.edu.cn).

Figure 1 Effect of MA graft ratio on Izod impact strength of PPO/PA 6/POE-*g*-MA (70/30/15) blends.

viscosity of 0.43 dL/g measured in chloroform at 25°C. Polyamide 6 (1013B), with a number-average molecular weight (M_n) of 25,000, was supplied by the UCB Chemical Co., Ltd. (Tokyo, Japan). POE (Engage 8150) was supplied by the Dupont–Dow Elastomer Co. Ltd., Wilmington, DE. Its octene content and melt-flow index were 25 wt % and 0.5 g/10 min, respectively. MA and dicumyl peroxide (DCP) were commercial reagents AR.

Preparation of PPO-*g*-MA and POE-*g*-MA

PPO was grafted with MA via reactive extrusion to obtain a graft ratio of 0.78 wt % based on a reported method.[20–22] POE-*g*-MA was prepared as follows: Powders of POE, MA, and DCP was tumble-mixed for 1 h and, subsequently, the mixture was extruded using a ZSK 30-mm twin-screw extruder (Werner & Pfleidere Corp.) with a length/diameter ratio (*L/D*) of 35. The temperature was increased from 280°C at the barrel to 300°C at the die. The feed rate was between 30 and 50 g/min, and the rotation speed of the screw was 120 rpm. Four kinds of POE-*g*-MA were prepared with graft ratios of 0.11, 0.24, 0.46, and 0.89 wt %, respectively, which were determined by acid–base titration.

Preparation of blends

The pellets of all materials were dried in a vacuum oven at 90°C overnight. The components were mixed using an extruder that was described in the preceding section. All the ingredients were tumble-blended before being fed into the throat of the extruder. The temperature increased from 310°C at the barrel to 320°C at the die, and the rotation speed of the screw was 200 rpm. The extruder was equipped with a highly efficient vacuum vetting to remove unreacted species and reaction by-products. The blends passed through a cooling water bath and were pelletized. All

the extrusion parameters were changed as little as possible from one formulation to another.

Mechanical properties test

Tensile and impact bars were molded at 310°C using a reciprocating screw injection-molding machine (M-20-55). Tensile properties were measured with an Instron universal testing machine (Model 1130) according to ASTM D638. Notched Izod impact strength was measured with a SUMITOMO impact tester according to ASTM D256. The thickness of the Izod impact specimens was 1/8 in., and the impact energy was 4 J. All tests were carried out at room temperature. Five measurements were done for each data point in all mechanical property tests.

Scanning electron microscopy (SEM)

The fractured surface of the tested Izod impact bars was coated with a thin film of an Au/Pd alloy and subsequently observed and photographed using a Cambridge S250 SEM at an accelerating voltage of 20 kV.

Transmission electron microscopy (TEM)

The morphology was determined by TEM. Samples were cryogenically microtomed from Izod impact bars perpendicular to the flow direction using a diamond knife. The PPS segment in blends was stained with ruthenium tetroxide (RuO_4). A Hitachi H-800 transmission electron microscope was used to view and photograph these samples which were only of an order of nanometers in thickness.

Rheological property measurement

The mixing torque of the blend samples was measured with a Brabender mixer (Plasti-Corder model PLE 330)
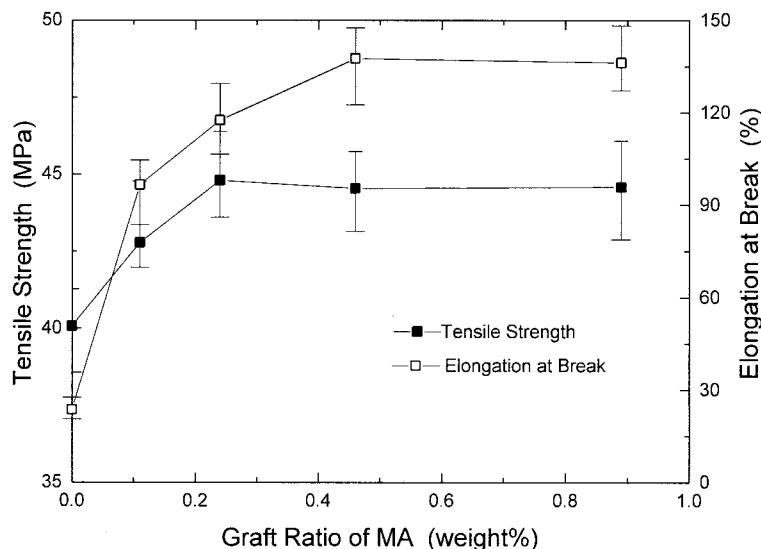
Figure 2 Effect of MA graft ratio on tensile strength and elongation at break of PPO/PA 6/POE-*g*-MA (70/30/15) blends.

at 300°C for 20 min, and the rotational speed was set at 50 rpm. The torque was recorded as a function of time. The apparent viscosities at various shear rates were measured using an Instron capillary rheometer. The capillary diameter was 1.262 mm and the *L/D* ratio was 60.51. The experiments were carried out at 300°C under shear rate ranging between 1 and 10^3 s^{-1}.

RESULTS AND DISCUSSION

Effect of MA graft ratio of POE on mechanical properties

Figure 1 presents the notched Izod impact strengths of PPO/PA6/POE-*g*-MA blends against the graft ratio of MA, which shows that the grafting of MA had a major effect on the impact strength. The impact strength of the blend based on ungrafted POE is 49 J/m; it increased dramatically to 630 J/m when the graft ratio of MA increased to 0.46 wt %, which constituted an optimum value. Further increasing of the graft ratio of MA resulted in a slight decrease of the impact strength; however, it still remained much higher than that of the ungrafted POE-based blend. The MA graft can modify the blends in two ways: First, the polarity of POE was increased. The solubility parameters of PPO and POE were 8.6 and 8.4 (cal/cm^3)$^{1/2}$, respectively,[26] and the difference between the two was not large enough to result in a remarkable toughening. The MA graft imparts to POE a higher polarity and, thus, a greater difference in the solubility parameters of PPO and POE-*g*-MA. As a result, more effective toughening is obtained. Second, and more importantly, the MA grafts react with the amine groups on PA 6, which generates bridges between the two polymers. However, a high graft ratio of MA had a negative effect on the toughness: Because the difference of the solubility parameter between POE and PPO be-

came too large, the increasing incompatibility caused the impact strength to decrease.

Figure 2 presents the effect of the MA graft ratio on the tensile strength and the elongation at break of the blends. The tensile strength and the elongation at break of the PPO/PA 6 alloy are 64.6 MPa and 11.2%, respectively. It was noticed that the graft ratio of MA had a moderate effect on the tensile strength. The increase of MA groups on POE did create bridges between POE and PA6; however, since POE was a flexible elastomer, its presence in the blends would largely soften the material. As seen in Figure 2, the maximum tensile strength (at a graft ratio of about 0.22 wt %) was much lower than that of the PPO/PA 6 alloy.

The presence of an elastomer increased the mobility of the plastic chains, resulting in a high elongation at break. As will be shown later, the reaction between the MA grafts and the amine groups on the PA 6 extended the chain length; as a result, the elongation at break kept increasing as the graft ratio of POE increased. However, the amount of MA should match that of the amine groups on PA 6. If the amount of MA exceeded a limit (in the present case, 0.46 wt %), further improvement could not be observed. As in the case of impact strength, the elongation at break even decreased slightly with increasing incompatibility with PPO.

Effect of POE-*g*-MA content on mechanical properties

Notched Izod impact strengths of the the PPO/PA 6 alloy toughened with POE-*g*-MA blends are plotted against the amount of POE-*g*-MA in Figure 3. The POE-*g*-MA was dispersed in the plastic matrix as fine particles, which may induce shear and craze yielding
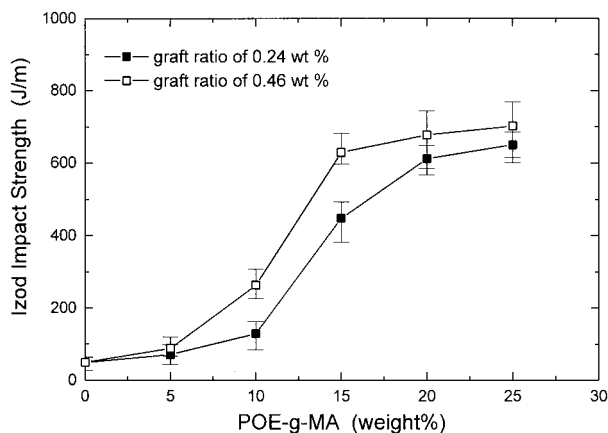
Figure 3 Content of POE-*g*-MA on Izod impact strength of PPO/PA 6 (70/30) alloys.

Figure 4 Content of POE-*g*-MA on tensile strength of PPO/PA 6 (70/30) alloys.

of the plastic phase, causing an increase in toughness. In other words, they activated the plastic layer surrounding them; the motion of the plastic segments consumed a major part of the external energy, resulting in toughening. If the amount of the elastomer particles was low, the thickness of the activated layer was much smaller than the average half-distance between the particles and the toughening was moderate. When the thickness of the activated layer approached the average half-distance between the particles, a brittle–ductile transition occurred. In the range of the transition, the toughness increased dramatically, as seen in Figure 3. If the amount of the elastomer was beyond the transition range, only a moderate further increase in toughness can be observed. In Figure 3, the toughening effects of two kinds of POE-*g*-MA are presented. The blend based on POE-*g*-MA with a graft ratio of 0.46 wt % was tougher than that of 0.24 wt % for the reasons already mentioned. The brittle–ductile transition of the former took place at a range of POE-*g*-MA content between 5 and 15 wt %, and of the latter, between 10 and 20 wt %. This indicates that the former possessed a higher activating effect on the plastic matrix.

Figures 4 and 5 show the effect of the POE-*g*-MA content on the tensile strength and elongation at break, respectively. As expected, as the content of POE-*g*-MA increased, the tensile strength decreased and the elongation at break increased. The reasons were already discussed in the preceding section.

Morphology

The morphology of the PPO/PA 6/POE-*g*-MA systems could be identified with the aid of RuO$_4$ staining. Although PA 6, PPO, and POE all can be stained with RuO$_4$, the staining rates are very different. It was found that the staining rate of PA6 was the fastest and that of POE was the slowest; PPO was the medium. When controlling the staining time, PA 6 appears in
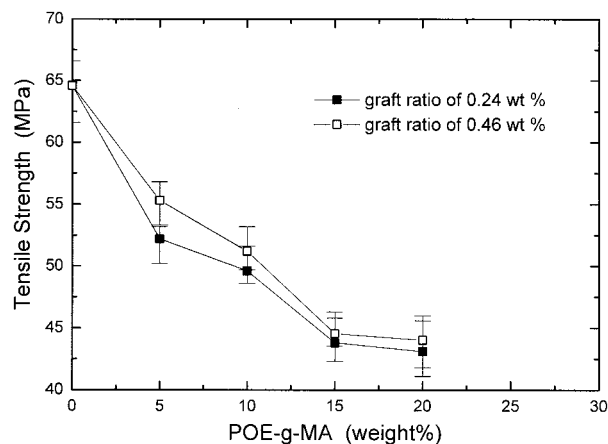
micrographs as black regions, PPO as dark gray, and POE as white.

Figure 6 shows TEM micrographs of the PPO/PA6/POE-*g*-MA blends based on POE with various graft ratios of MA, in which white and black particles are distributed in a gray background. This indicates that PPO constituted the continuous phase, and PA 6 and POE-*g*-MA were the dispersed phase. While the size of the PA 6 particles (black) remained unchanged, that of the POE-*g*-MA (white) decreased obviously with the increasing of its MA graft ratio. As mentioned above, the MA grafts improved the compatibility via increasing the polarity and via chemical reactions with the amine group on PA 6. When the graft ratio of MA was 0.46 wt %, the average size of the POE-*g*-MA particles was less than 1 μm, which resulted in a high toughness.

Figure 7 shows SEM micrographs of the fractured surface of various blends, which shows the dispersion of the elastomer particles and the activating effect caused by them. From Figure 7(b), which is based on
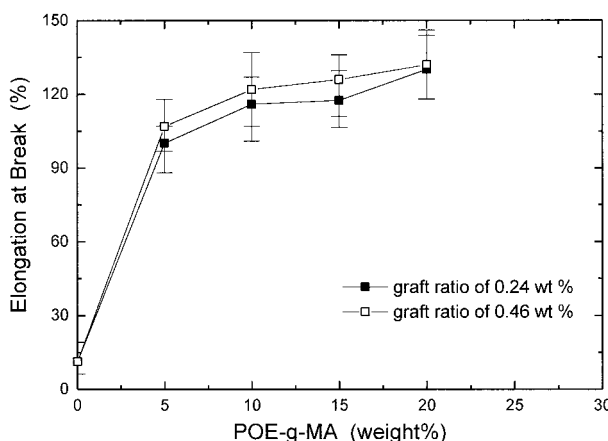

Figure 5 Content of POE-*g*-MA on elongation at break of PPO/PA 6 (70/30) alloys.

1 μ m   **(a)**   **(b)**   **(c)**

(d)   **(e)**   **(f)**

Figure 6   TEM photographs of PPO/PA 6/POE and PPO/PA 6/POE-*g*-MA blends: (a) PPO/PA 6/POE = 70/30/15; (b) PPO/PA 6/POE-*g*-MA (0.11 wt %) = 70/30/15; (c) PPO/PA 6/POE-*g*-MA (0.24 wt %) = 70/30/10; (d) PPO/PA 6/POE-*g*-MA (0.24 wt %) = 70/30/15; (e) PPO/PA 6/POE-*g*-MA (0.46 wt %) = 70/30/10; (f) PPO/PA 6/POE-*g*-MA (0.46 wt %) = 70/30/15.
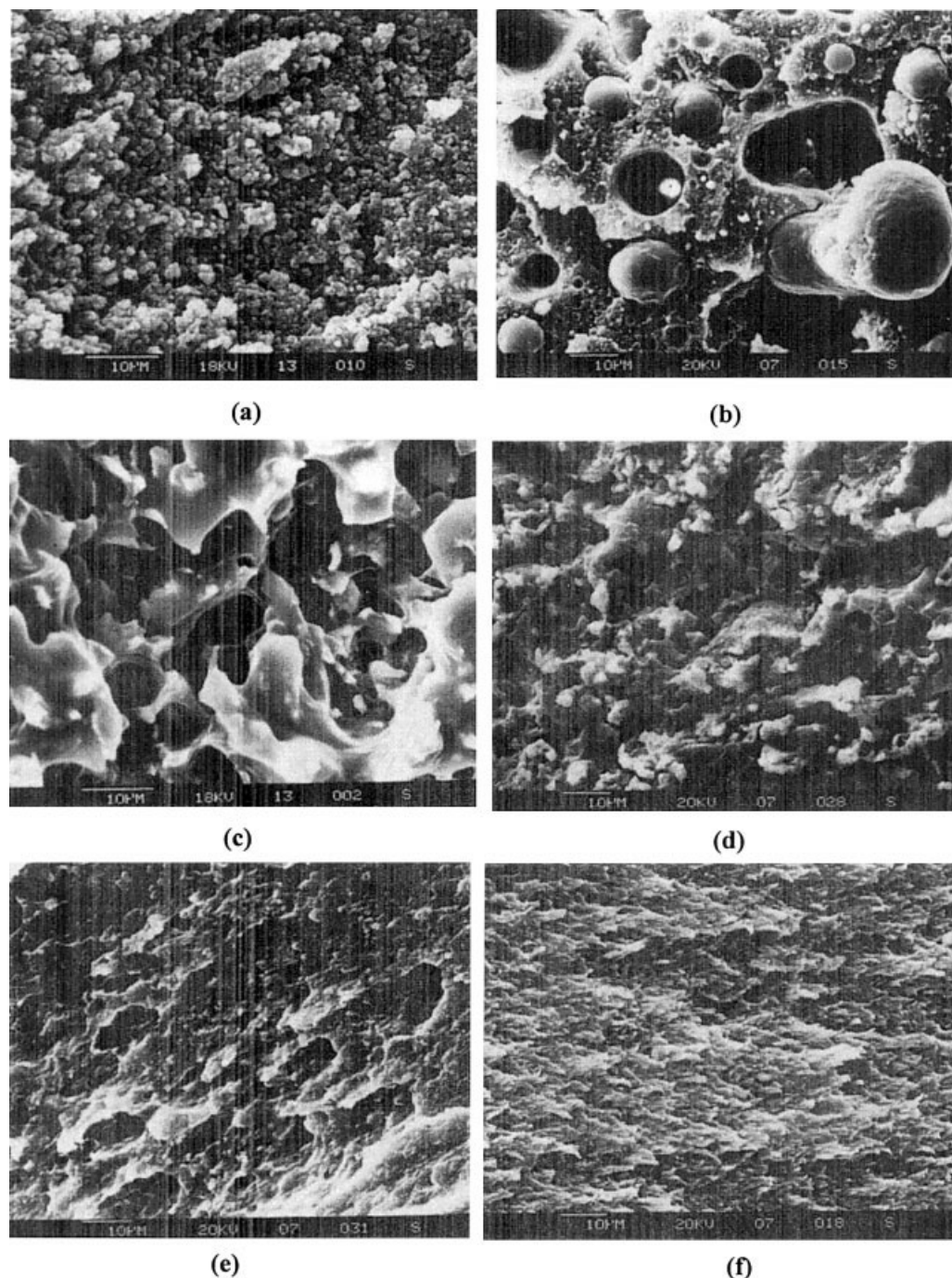
Figure 7 SEM photographs of PPO/PA 6 alloy and its blends toughened by POE-*g*-MA: (a) PPO/PA 6 = 70/30; (b) PPO/PA 6/POE = 70/30/15; (c) PPO/PA 6/POE-*g*-MA (0.11 wt %) = 70/30/15; (d) PPO/PA 6/POE-*g*-MA (0.24 wt %) = 70/30/15; (e) PPO/PA 6/POE-*g*-MA (0.46 wt %) = 70/30/10; (e) PPO/PA 6/POE-*g*-MA (0.46 wt %) = 70/30/15.

ungrafted POE, one sees big particles of POE and the holes left by them when the sample was broken. It is clear that no deformation of the matrix occurred during the break, that is, the plastic phase was inactivated. Figure 7(c–e) shows that the particle size became increasingly smaller with increasing graft ratio of MA of POE, and the fractured surfaces exhibited a larger deformation. In Figure 7(f), the deformation was so severe that a threadlike structure was observed.

Rheological property

The rheology behavior of a blend is a reflection of the change in molecular weight and the interaction among the components. In Figure 8, the mixing torque of the melt is plotted against the mixing time for systems with various compositions. The PPO/PA 6 alloy exhibited a low torque, and the torque of the PPO/PA 6/POE blends was even lower, which constituted ev-

idence of incompatibility. When, however, POE-*g*-MA was employed, the torque increased. Indeed, as shown by Figure 8, the greater the graft ratio of MA on POE, the higher was the torque. The increase in torque was due mainly to the reaction of MA moieties on POE with the amine groups of nylon 6. The reactions increase the molecular weight and the degree of branching, and both increase the torque of the blends.

The relationship of melt viscosity and shear rate for the PPO/PA6/POE-*g*-MA system is plotted in Figure 9. It is found that the melt viscosity of the PPO/PA6/POE blend is lower than that of PPO/PA6; however, the greater the extent that POE was grafted with MA, the higher was the viscosity. The changes in the melt viscosity confirmed the explanation for the torque above. Figure 9 also shows that the higher the shear rate, the less sensitive was the viscosity to grafting of POE, which could be explained by the entanglement of the segments. During the flow of a polymer melt, the molecular chains are disentangled by shear and reentangled by thermomotion. If the rate of the former is less than that of the latter, the viscosity is low. At low shear rates, the high molecular weight caused by the reactions between MA and amine groups is responsible for the high viscosity. However, when the shear rate is high enough, the rate of disentanglement is greater than that of the entanglement and the viscosity is much lower. For these reasons, at high shear rates, the viscosity increment caused by the grafting is smaller than that at low shear rates.

CONCLUSIONS

POE, a novel polyolefin elastomer, when grafted with MA, can be employed as an impact modifier for the PPO/PA 6 alloy. The particle size of the POE-*g*-MA in the plastic matrix can be controlled by the MA graft ratio, which is below 1 μm when the graft ratio is 0.46 wt %, resulting in effective toughening. Notched im-
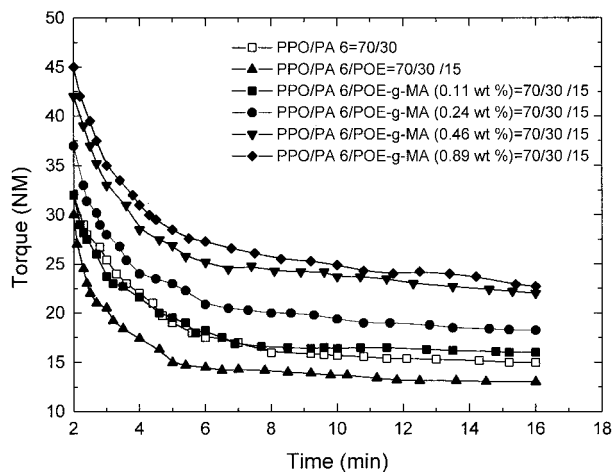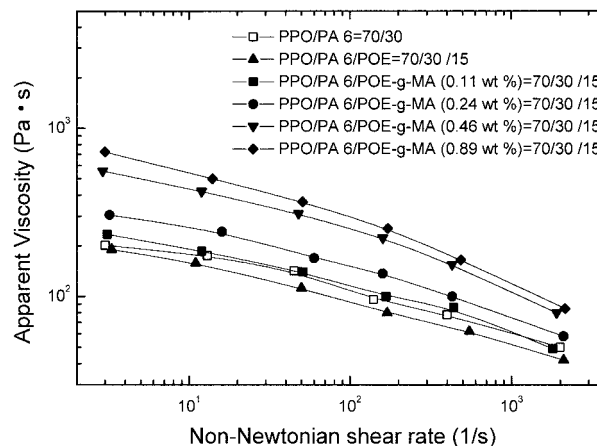
Figure 9 Melt viscosity versus non-Newtoina shear rate for the PPO/PA 6 alloy and its blends with POE and POE-*g*-MA.

pact strength of the PPO/PA 6/POE-*g*-MA blend achieved an optimum value of 630 J/m. The introduction of MA to POE increased the torque and melt viscosity of the PPO/PA 6/POE blends.

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Figure 8 Plots of torque versus time for the PPO/PA 6 alloy and its blends with POE and POE-*g*-MA.