

Influence of Interfacial Adhesion on Toughening of Polyethylene–Octene Elastomer/Nylon 6 Blends

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ABSTRACT: Super-tough nylon 6 was prepared by using polyethylene–octene elastomer (POE) grafted with maleic anhydride as a toughener. The influences of maleating and a compatibilizer on interfacial adhesion and mechanical properties of nylon 6/POE blends were investigated in terms of mechanical testing, Molau tests, SEM observations, IR analyses, and rheological behavior. The results show that the unmodified POE has hardly any contribution to toughness of nylon 6, whereas the maleic anhydride-grafted POE (POE-*g*-MA) significantly improves the compatibility of POE with nylon 6 and sharply reduces its size in the nylon 6 matrix due to the *in situ* formation of a graft copolymer between POE-*g*-MA and nylon 6 during melt processing. With the POE-*g*-MA, a transition from brittle to ductile occurs. Besides, the use of a compatibilizer in nylon 6/POE-*g*-MA system shifts the brittle–ductile transition curve to a lower POE-*g*-MA content, which is attributed, in part, to the chain-extending effect of CE-96 on the nylon 6 matrix leading to further reduction of the sizes of POE-*g*-MA in the matrix, in part, to the coupling reaction of CE-96 between POE-*g*-MA and nylon 6. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1711–1718, 1998

Key words: super-tough nylon 6; elastomer; toughening; interfacial modifier; compatibilization

INTRODUCTION

The toughening of many engineering thermoplastics can be achieved by incorporation of a low-modulus second component.^{1–3} Super-tough nylon^{4–7} is one of the successful examples. The low-modulus phase incorporated in the nylon matrix usually is a maleated polyethylene–propylene binary rubber (EPR-*g*-MA) or a maleated polyethylene–propylene–diene ternary rubber (EPDM-*g*-MA). When highly dispersed, the rubbery phase acts as an effective stress concentrator and enhances both crazing and shear yielding in the ma-

trix. Because both processes can dissipate large amounts of energy, there is a significant increase in the toughness of nylon.⁵

Polyethylene–octene copolymer (POE) as a novel polyolefin elastomer was developed using a metallocene catalyst by the Dow Chemical Co. Compared with the conventional polyolefin elastomer EPDM, POE typically exhibits faster mixing and better dispersion when blending with polypropylene (PP). Van Oene⁸ investigated the influence of melt elasticity and particularly normal stresses on phase morphologies in polymer blends or alloys, and proposed that the normal stress can imbalance the interfacial energy over the interface in the melt state and determine the form of the dispersed phase. Because the ratio of viscosity to elasticity of POE is lower than that of EPDM,

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EPDM rubber often forms a spherical domain shape in the polymer matrix, whereas POE always forms an elliptic domain shape in the matrix. The nonspherical domain shape of dispersed phase helps dissipate more impact fracture energy than the spherical-dispersed phase does.⁸ Therefore, an attempt to substitute POE for EPDM to toughen nylon was made in our laboratory. However, semicrystalline nylons and rubbery POE are highly incompatible; they require some means to improve compatibility between them. One of the successful methods of improving the compatibility of polyolefin with nylon is maleic anhydride grafting.^{9–11} On the other hand, S. Wu⁴ pointed out that strong adhesion alone is not a necessary condition for toughening; Van der Waals attraction gives sufficient adhesion for toughening, and interfacial chemical bonding is not necessary. Even if there is interfacial chemical bonding, a polymer/rubber blend will still be brittle, if the interparticle distance is greater than the critical value.

The purpose of this article is to examine the possibility of developing super-tough nylon using POE grafted by maleic anhydride (POE-*g*-MA) as a toughener, and to investigate the contribution of interfacial modification to impact behavior. The toughening effectiveness of POE-*g*-MA and the contribution of a compatibilizer will be discussed in terms of composition, rheology, morphology, and interfacial adhesion.

EXPERIMENTAL

Materials

The matrix used was nylon 6, its relative viscosity is 2.6–2.9, supplied by Shanghai Plastics Production Factory No. 18. The rubber was polyethylene–octene copolymer (POE), Engage 8445, from Dow Chemical Co., its octene content and melt flow index are 9.5% and 3.5 g/10 min, respectively. The maleic anhydride grafting reaction of POE was carried out in a 30-diameter twin-screw extruder (SHJ-30) with an L/D ratio of 23.2, and the graft ratio is about 1% by weight. The compatibilizer (CE-96) with epoxy groups was made in our laboratory.

Blend Preparation

Blends were prepared by melt extrusion in a ϕ 30-diameter twin-screw extruder (SHJ-30) at 250

rpm. The barrel temperatures are 225–245°C. The pelletized materials were dried and injection molded into standard tensile, flexural, and Izod impact specimens in an injection-molding machine (SZ-160/80 NB).

Mechanical Testing

The notched Izod impact strength was measured with an impact testing machine (CSI-137C) according to National Standard Testing Methods GB 1843–80. The tensile and flexural testing were carried out on a universal tensile tester (Instron 1122) according to GB 1040–79 and GB1042–79, respectively. The tensile strength and elongation at break were measured at a crosshead speed of 50 mm/min; the flexural strength and modulus were measured at a crosshead speed of 2 mm/min. The average values of at least five tests are reported.

Rheology

The apparent viscosity was measured at 230°C as a function of apparent shear rate, using a capillary rheometer (XLY-1). The capillary die used was 0.5 mm in radius and 40 mm in length, with an L/D ratio 40. The Bagley and Rabinowitsch corrections were not made.

Morphology

To study the morphology of the nylon 6 blends, the specimens were fractured after immersion in liquid nitrogen, and observed by scanning electron microscope (S-530). A transmission electron microscope (Hitachi H800) was used to further observe the particle size of the dispersed phase in the nylon blend. An ultrathin sample was obtained by a microtoming-molded specimen using an ultramicrotome at about –80°C and stained with RuO₄ vapor for 100 min.

Molau Test^{12,13}

A Molau test was conducted by mixing about 0.4 g of the nylon 6/POE (80/20) blend with 10 mL of formic acid. The mixture was first shaken thoroughly in a beaker and then left alone in a test tube for 30 days. The same procedure was repeated with blends of nylon 6/POE-*g*-MA (80/20), and nylon 6/CE-96/POE-*g*-MA (80/0.3/20).

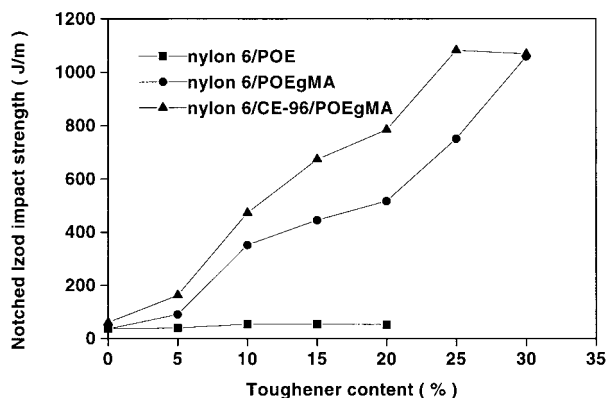


Figure 1 Effects of the maleating of POE and the use of CE-96 on notched Izod impact strength of nylon 6/POE blending systems.

Infrared Spectroscopy

The resulting insoluble part in the above Molau test was characterized by Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer 180); its interferometer resolution is 0.2 cm^{-1} .

RESULTS AND DISCUSSION

Mechanical Properties

The effects of the maleic anhydride grafting of POE and the compatibilizer (CE-96) on notched Izod impact strength of nylon 6/POE blends are shown in Figure 1. It is well known that nylon 6 belongs to a pseudoductile polymer that has a high crack initiation energy but a low crack propagation energy, and so has a high unnotched but a low notched impact strength.¹⁴ The addition of the unmodified POE almost has no contribution to notched impact strength of nylon 6. It should be pointed out that the blends containing the unmodified POE appeared as poor extrusion and pelletization due to a high incompatibility between nylon 6 and the unmodified POE. Especially, the blending components were hardly extruded beyond the POE content of 20% by weight. However, the maleic anhydride-grafted POE (POE-*g*-MA) significantly improves notched impact strength of nylon 6, and a transition from brittle to ductile occurs with increasing POE-*g*-MA content. Besides, the use of the compatibilizer (CE-96) promotes the toughening effectiveness of POE-*g*-MA and shifts the curve of brittle–ductile transition (BDT) to a lower POE-*g*-MA content.

Figure 2 shows plots of elongation at break versus toughener content for the nylon 6/POE, nylon 6/POE-*g*-MA, and nylon 6/CE-96/POE-*g*-MA blending systems, respectively. The elongation at break of the blends containing the unmodified POE evidently decreases with increasing POE content; however, that of the blends containing POE-*g*-MA only has slight changes up and down with POE-*g*-MA content. It is interesting that, in comparison with nylon 6/POE-*g*-MA blends, the use of CE-96 in these blends results in significant reduction of the elongation at break in the range of toughener contents investigated, which may be caused by the chain-extending reactions of CE-96 with the terminal $-\text{NH}_2$ group of nylon 6, and the coupling reaction at the interface of the POE-*g*-MA and nylon 6 matrix. These reactions will be confirmed by the following experimental results.

Figure 3 shows plots of the yield strength (σ_y) and break strength (σ_b) versus toughener content for nylon 6/POE, nylon 6/POE-*g*-MA, and nylon 6/CE-96/POE-*g*-MA blending systems, respectively. σ_y is always larger than σ_b for the blends containing unmodified POE. The latter two blending systems, however, show interesting orders of σ_y and σ_b with the contents of POE-*g*-MA: $\sigma_y > \sigma_b$ at low POE-*g*-MA contents, whereas $\sigma_y < \sigma_b$ at high POE-*g*-MA contents. These results conform to the BDT competition theory developed by Ludwik, Davidenkov, and Orowan (LDO).^{15,16} Based on the yield strength data in Figure 3, Figure 4 shows plots of yield strength (σ_y) versus toughener content for the above three blending systems for the purpose of comparing the effects of the maleating of POE and the use of CE-96. Compared with the unmodified POE blend, the

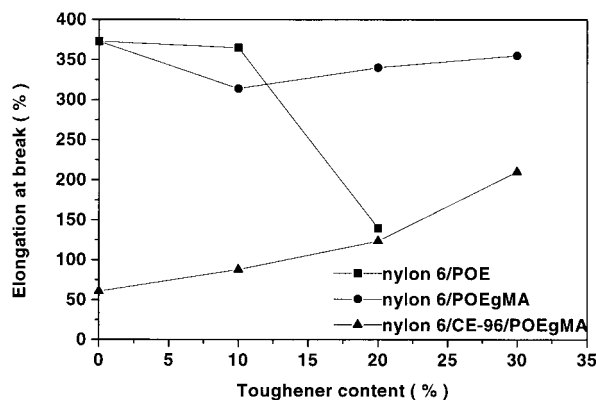


Figure 2 Plots of elongation at break versus toughener content for nylon 6/POE, nylon 6/POE-*g*-MA, and nylon 6/CE-96/POE-*g*-MA blends, respectively.

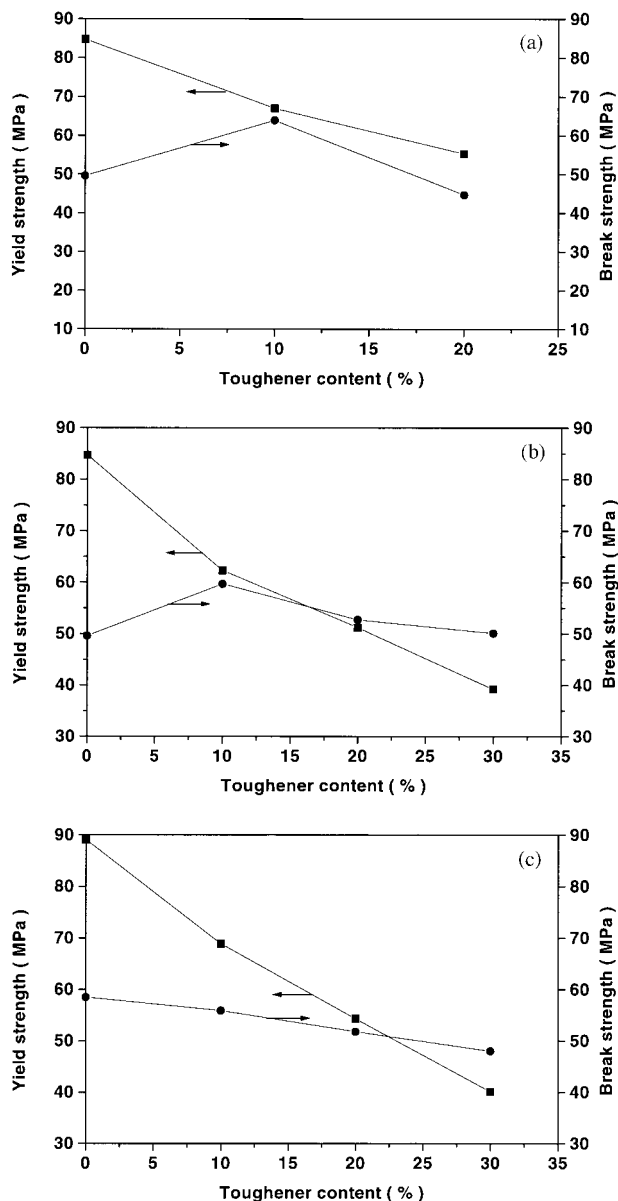


Figure 3 Plots of yield strength (σ_y) and break strength (σ_b) versus toughener content for (a) nylon 6/POE blends; (b) nylon 6/POE-*g*-MA blends; and (c) nylon 6 CE/96/POE-*g*-MA blends.

blend containing POE-*g*-MA has a lower yield strength. This is attributable to the changes of both morphology of the blends and crystallization of nylon 6 caused by the graft modification of POE. Moreover, the use of CE-96 clearly improves the yield strength of nylon 6/POE-*g*-MA blends.

Figures 5 and 6 show plots of flexural modulus and flexural strength versus toughener content for the above three blending systems, respectively. It can be seen that the flexural modulus

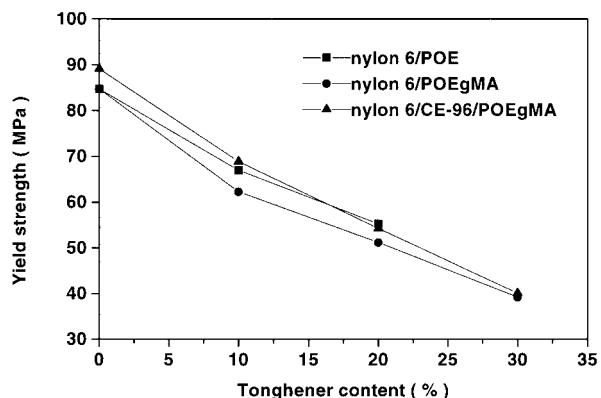


Figure 4 Plots of yield strength versus toughener content for nylon 6/POE, nylon 6/POE-*g*-MA, and nylon 6/CE-96/POE-*g*-MA blends, respectively.

and the flexural strength of all blends, whether POE was grafted and CE-96 was added or not, decrease gradually with increasing toughener contents. It is also seen that the maleating of POE decreases the flexural strength and flexural modulus of nylon 6/POE blends due to the improved compatibility, whereas the use of CE-96 increases the flexural modulus and flexural strength of nylon 6/POE-*g*-MA blends because of the chain-extending effect of CE-96 and its coupling effect at the interface of the blend. The effects of the POE maleating and CE-96 on flexural properties are similar to those on yield strength (see Fig. 4).

Effects of the maleating of POE and the use of CE-96 on the apparent viscosity of virgin nylon 6 and nylon 6 blends are shown in Figure 7. It is seen that CE-96 is effective in improving the melt viscosity of virgin nylon 6, which is due to the chain-extending reaction between the epoxy

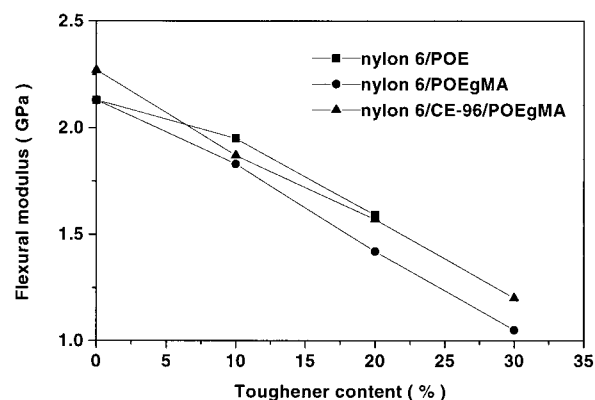


Figure 5 Plots of flexural modulus versus toughener content for the above three blending systems, respectively.

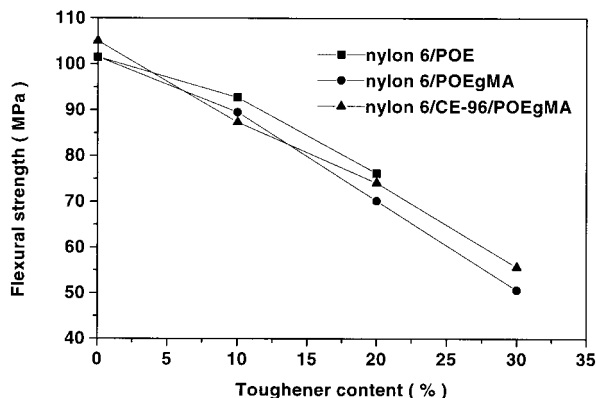


Figure 6 Plots of flexural strength versus toughener content for the above three blending systems, respectively.

groups of CE-96 and the terminal $-\text{NH}_2$ group of nylon 6.¹⁷ It is also seen that the maleating of POE increases the apparent viscosity of the nylon 6/POE system, which is owing to the enhanced interfacial adhesion resulting from the chemical reaction of the anhydride of the POE-*g*-MA with the terminal $-\text{NH}_2$ group of nylon 6.^{16,17} Besides, CE-96 can further improve the apparent viscosity of the nylon 6/POE-*g*-MA system. It is attributable, in part, to the chain-extending effect on nylon 6, in part, to the coupling reaction between POE-*g*-MA and nylon 6, which will be confirmed by the following experiments.

Interfacial Interaction

Morphology

To investigate the effects of the maleating of POE and the use of CE-96 on dispersion of POE and interfacial adhesion of the three nylon 6/POE blend systems, SEM and/or TEM were used to examine the morphological structures. Figure 8 shows SEM micrographs of the freeze-fractured surface under liquid nitrogen of the three systems, and a TEM micrograph of nylon 6/POE-*g*-MA blend cryogenically microtomed from injection-molded bars and stained with RuO_4 . It is clearly seen from Figure 8(a) that the domain sizes of the unmodified POE and their distribution of sizes are rather large (from 0.8 to 3.0 μm), and that, upon fracture, the dispersed particles were pulled off from nylon 6 matrix, indicating that no chemical interaction took place, during melt blending between POE and nylon 6. Figure 8(b) and (d) shows the influence of the maleating of POE on the morphology of the nylon 6/POE-*g*-

MA blends. It is seen that the domain size of the POE-*g*-MA is fairly small (less than 0.6 μm on the average) and the POE-*g*-MA is uniformly dispersed in nylon 6 matrix. The fracture surface does not show sharp edges, clearly showing that chemical reaction have taken place between POE-*g*-MA and nylon 6.^{18–20} Compared with Figure 8(b) and (d), Figure 8(c) shows that CE-96 greatly decreases the domain size of POE-*g*-MA (about 0.2 μm on the average), and the boundaries of the dispersed phase and matrix have not clear interface, indicating that CE-96 is effective in improving the dispersion and the interfacial interaction of the nylon 6 blends.

Molau Test

In our investigation, the Molau test was applied to examine the state of interface of the three nylon 6/POE blend systems. In our case, the blend is placed in formic acid, which is a solvent for nylon 6 and a nonsolvent for the toughener used. Figure 9 shows the results of the Molau test. A phase separation was observed in the nylon 6/POE blend [see Fig. 9(a)], the lower part of the test tube (the dark area) represents a solution consisting of formic acid and nylon 6, and the upper part of the same test tube (the white area) represents a suspension of POE, whereas Figure 9(b) shows a milky, colloidal suspension persisted in the solution containing the nylon 6/POE-*g*-MA blend, which is undoubtedly attributed to the emulsifying effect of a graft copolymer *in situ* formed during melt processing.¹⁸ Surprisingly, for the nylon 6/CE-96/POE-*g*-MA blend [see Fig. 9(c)], a phase separation was also observed. The

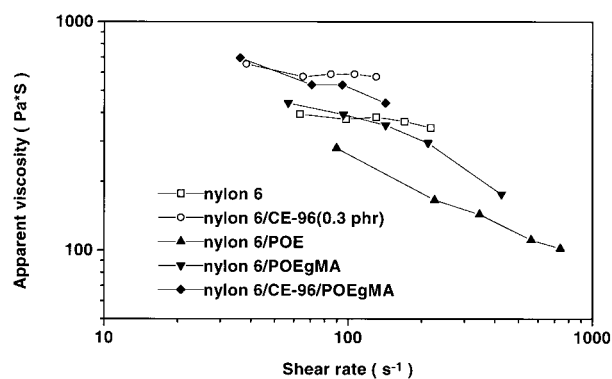


Figure 7 The apparent viscosity versus shear rate for: (□) virgin nylon 6; (○) nylon 6/CE-96 (100/0.3); (▲) nylon 6/POE (80/20); (▼) nylon 6/POE-*g*-MA (80/20); (◆) nylon 6/CE-96/POE-*g*-MA (80/0.3/20) at 230°C.

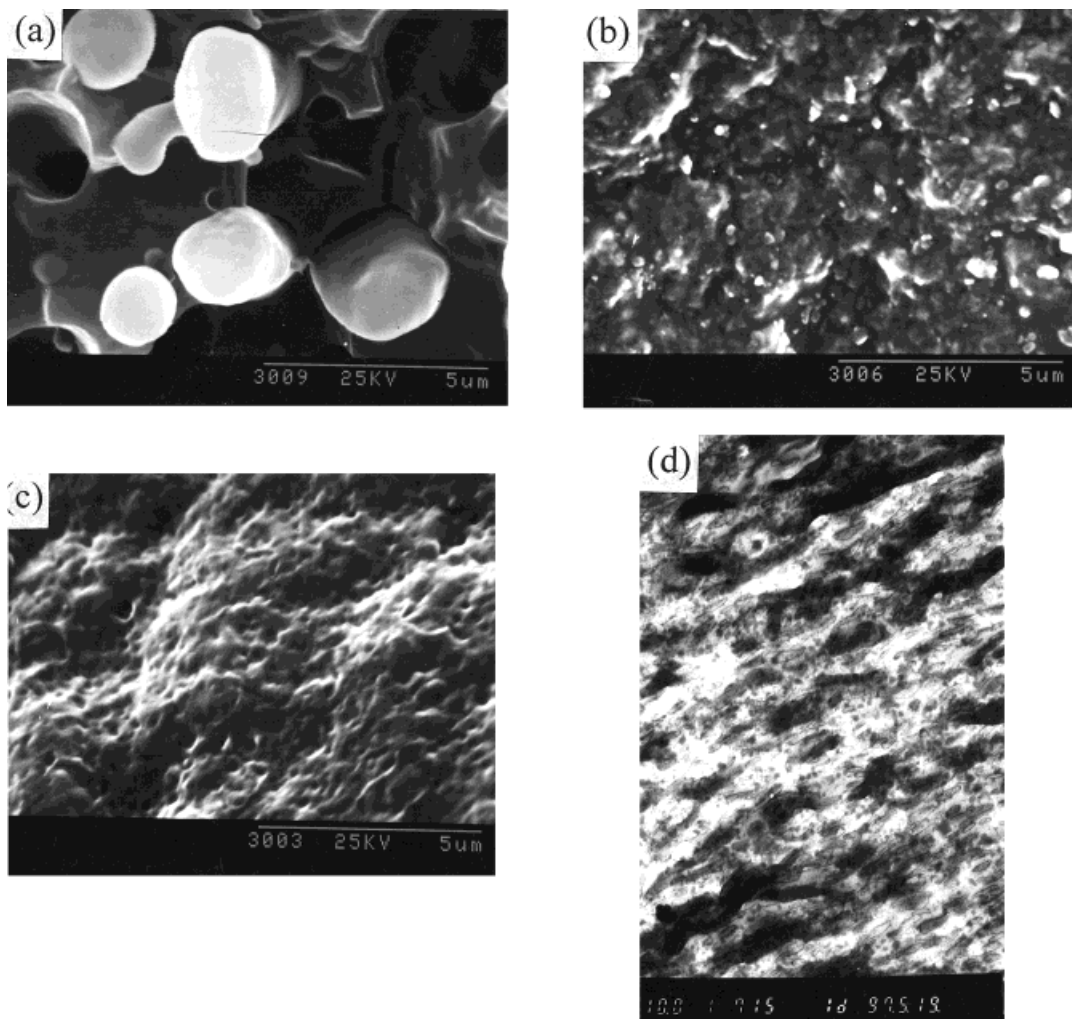


Figure 8 SEM micrographs of the freeze fracture surfaces under liquid nitrogen of (a) nylon 6/POE (80/20), (b) nylon 6/POE-*g*-MA (80/20) and (c) nylon 6/CE-96/POE-*g*-MA (80/0.3/20); and TEM one of (d) nylon 6/POE-*g*-MA (80/20). The TEM sample was cryogenically microtomed from injection-molded bars and stained with RuO₄.

lower part of the tube presents a slight milky solution showing this part containing POE-*g*-MA molecules; and the upper part of the same tube also arises a white suspension, similar to the tube (a) containing the unmodified POE blend. It should note that the white insoluble fraction in tube (c) does not have a milky colloidal suspension, but a suspension that is composed of a lot of insoluble macroscopical particles. This phenomenon can be interpreted by the facts that CE-96 can not only react with the anhydride group of POE-*g*-MA and terminal —NH₂ group of nylon 6, respectively, but also couple at the interface between them. The occurrences of these reactions during melt processing result in the formation of a semiinterpenetrating network in the blend, so that formic

acid solvent is difficult to solute it completely, the insoluble fraction consisting of POE-*g*-MA and nylon 6 can only be suspended at the top of the tube as in the form of macroscopical particles. This conjecture will be supported by the IR analysis below.

Infrared Spectroscopy Characterization

Figure 10 shows the IR spectra of the insoluble fraction (POE component) extracted from the formic acid solution of the nylon 6/POE and the nylon 6/CE-96/POE-*g*-MA systems. It should be pointed out that, for the nylon 6/POE-*g*-MA system, the POE component can hardly be extracted by centrifuging. As a matter of fact, turbidity

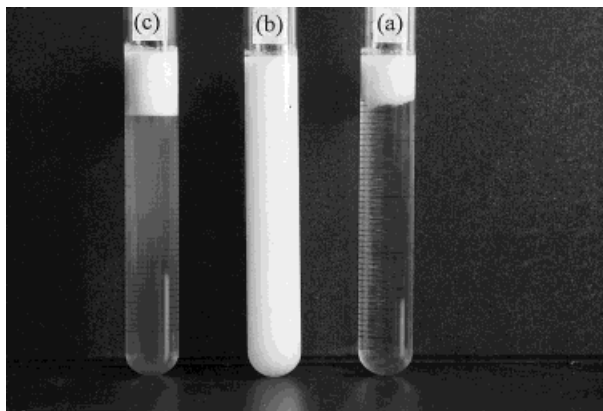


Figure 9 Molau test solutions consisting of formic acid and each of the following blend: (a) nylon 6/POE (80/20); (b) nylon 6/POE-*g*-MA (80/20); (c) nylon 6/CE-96/POE-*g*-MA (80/0.3/20).

lasted for several months, until the solution was discarded. It is mainly because of the excellent emulsifying effect of the graft copolymer *in situ* formed during melt processing. For the unmodified POE blend, besides the characteristic absorption peaks of $-\text{CH}_2$ and $-\text{CH}_3$ at 2925.4, 2847.9, 1461.7, and 716.3 cm^{-1} , the characteristic absorption peaks of nylon 6 also appeared. This part of nylon 6 may be a result of physical entanglements and/or mechanical grafting between nylon 6 and POE, and is difficult to be removed completely by formic acid. For the blend containing CE-96, as

shown in Figure 10, the presence of the strong characteristic absorption peaks of nylon 6^{2,21} at 3428.9, 1644.6, and 1543.0 cm^{-1} ($-\text{CONH}-$) indicates that CE-96 indeed couples nylon 6 to POE-*g*-MA.

CONCLUSIONS

The maleic anhydride grafting of POE results in significant improvements of compatibility and interfacial adhesion between nylon 6 and POE and a sharp reduction of the particle sizes of the dispersed phase due to the *in situ* formation of a graft copolymer during melt processing. Besides, the addition of CE-96 not only increases the viscosity of the nylon 6 matrix, but also further improves the interfacial adhesion of nylon 6 with POE-*g*-MA and the dispersion of POE-*g*-MA in the matrix.

The use of POE-*g*-MA significantly improves notched Izod impact strength of nylon 6/POE blends so as to reach a level of super tough, whereas the unmodified POE has hardly any contribution to toughness of nylon 6. Furthermore, the addition of CE-96 promotes the toughening effect of POE-*g*-MA and shifts the brittle-ductile transition to a lower POE-*g*-MA contents.

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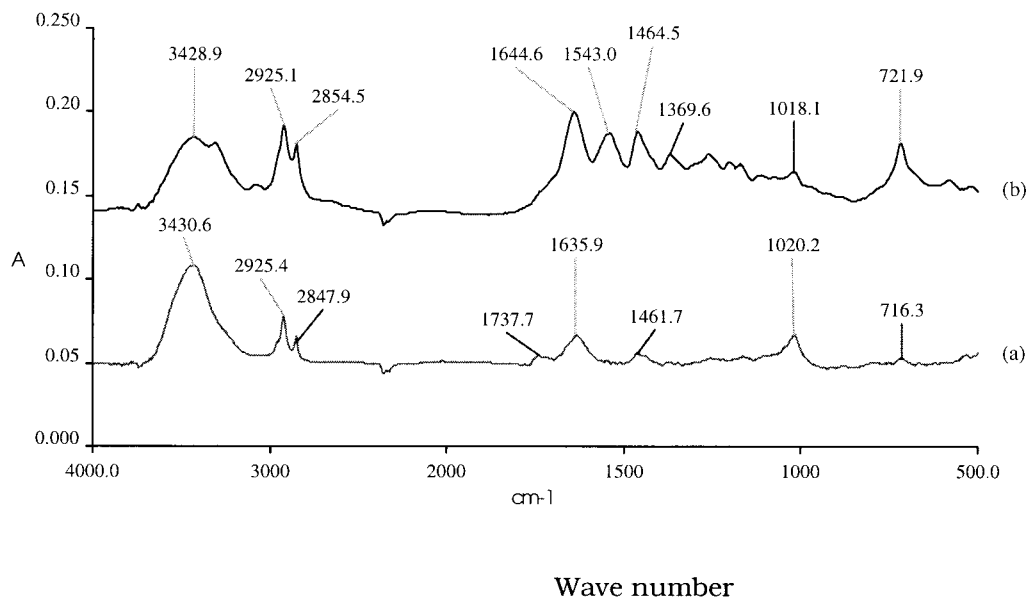


Figure 10 Infrared spectra of (a) nylon 6/POE (80/20), and (b) nylon 6/CE-96/POE-*g*-MA (80/0.3/20) after noncoupled nylon 6 removed with formic acid.

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