Impact Fracture Morphology of Nylon 6 Toughened with a Maleated Polyethylene–Octene Elastomer

ZHONG-ZHEN YU,[1,2] YU-CAI KE,[1] YU-CHUN OU,[1] GUO-HUA HU[2]

[1] State Key Laboratory of Engineering Plastics, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Zhongguancun, P. O. Box 2709, Beijing 100080, China

[2] Laboratoire des Sciences du Genie Chimique, CNRS-ENSIC-INPL, 1 rue Grandville, B. P. 451, 54001 Nancy Cedex, France

ABSTRACT: This study aimed at using scanning electron microscopy to study the Izod impact fracture surface morphology of super-tough nylon 6 blends prepared by blending nylon 6 with a maleic anhydride-grafted polyethylene-octene elastomer (POE) in the presence of a multifunctional epoxy resin (CE-96) as compatibilizer. The fracture surface morphology and the impact strength of the nylon 6 blends were well correlated. The fracture surface morphology could be divided into a slow-crack-growth region and a fast-crack-growth region. Under low magnification, the fractured surface morphologies of the low-impact-strength nylon 6 blends appeared to be featureless. The area of the slow-crack-growth region was small. There were numerous featherlike geometric figures in the fast crack growth region. The fractured surface morphologies of the high-impact-strength nylon 6 blends exhibited a much larger area in the slow-crack-growth region and parabola markings in the fast-growth region. Under high magnification, some rubber particles of the low-impact-strength nylon 6 blends showed limited cavitation in the slow-crack-growth region and featherlike markings in the fast-crack-growth region. Rubber particles of high-impact-strength nylon 6 blends experienced intensive cavitation in the slow-crack-growth region and both cavitation and matrix shear yielding in the fast-crack-growth region, allowing the blends to dissipate a significant amount of impact energy. A nylon 6 blend containing 30 wt % POEgMA exhibited shear yielding and a great amount of plastic flow of the matrix throughout the entire slow-crack-growth region, thus showing the highest impact strength. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1285–1295, 2000

Key words: nylon 6; toughening; morphology; fracture surface; compatibilizer

INTRODUCTION

Nylon has been successfully toughened by different approaches.[1–8] The toughener usually used is a maleated ethylene propylene rubber (EPRgMA) or a maleated ethylene propylene diene rubber (EPDMgMA). When finely dispersed, the rubbery particles act as effective stress concentrators, initiating both crazing and shear yielding from many sites of the matrix, favoring the dissipation of large amounts of impact energy and slowing down the growth of cracks, hence increasing significantly the toughness of nylon.[5]

A copolymer of ethylene and octene (POE) was a novel polyolefin elastomer developed by Dow Chemical Co. (Midland, MI) by using a metallo-

cene catalyst. Unlike a conventional polyolefin elastomer such as EPDM, it typically exhibits faster mixing and better dispersion when blending with polypropylene (PP).[9] Therefore, an attempt to replace EPDM by POE to toughen nylon was made in our laboratories. However, the rubbery POE is highly incompatible with semicrystalline nylons. Therefore compatibilization methods had to be developed. Adding a maleic anhydride-modified polyolefin appeared to be very effective for compatibilizing polyolefin and nylon blends.[10–12]

The processes involved in the impact fracture of blends are reflected in the appearance of the fracture surface.[13–24] The objective of this article is to study the fracture topography and morphology of the nylon 6 toughened by a maleic anhydride-grafted POE (POEgMA), to evaluate the contribution of a multifunctional epoxy resin to the morphology, and to establish a relationship between the fracture morphology and the impact property.

EXPERIMENTAL

Materials

The nylon 6 used in this study was supplied by Shanghai Plastics production factory No. 18 (Shanghai, China); its relative viscosity is 2.6–2.9. The POE was obtained from Dow Chemical Co. (Engage 8445); its octene content and melt flow index were 9.5% and 3.5 g/10 min, respectively. The functionalization of the POE with maleic anhydride was carried out in a $\phi30$ twin-screw extruder (SHJ-30) with an L/D ratio of 23.2. The maleic anhydride content grafted onto the POE was about 1 wt %. The multifunctional epoxy resin (CE-96) was synthesized in our laboratories.[11]

Blend Preparation

Blends were prepared by melt extrusion in a $\phi30$ twin-screw extruder (SHJ-30) at 250 rpm. The barrel temperatures were $\sim$ 225–245°C. The pelletized materials were dried and injection-molded into standard Izod impact specimens in an injection-molding machine (SZ-160/80 NB).

Measurements

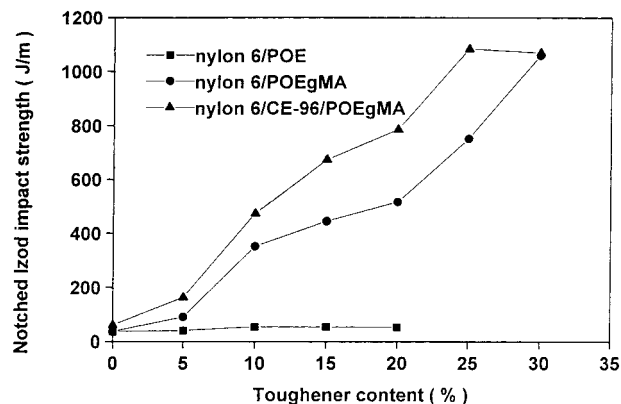The notched Izod impact strength of nylon 6 blends was measured with an impact test ma-

Figure 1 Effects of the maleic anhydride-modified POE (POEgMA) and a multifunctional epoxy resin (CE-96) on the notched Izod impact strength of nylon 6/POE blending systems.

chine (CSI-137C) according to National Standard Testing Methods GB 1843-80. The average values of at least five tests were reported. To study the morphology of the nylon 6 blends, the surfaces of impact-fractured specimens were gold-sputtered and then observed with a scanning electron microscope (S-530).

RESULTS AND DISCUSSION

Mechanical Properties

The influences of adding the POEgMA and/or the multifunctional epoxy resin (CE-96) on notched Izod impact strength of nylon 6/POEgMA blends are shown in Figure 1. Nylon 6 is a pseudoductile polymer, exhibiting a high crack initiation energy but a low crack propagation energy. Therefore, it has a high unnotched but a low notched impact strength.[4] Adding the nonreactive POE had virtually no contribution to the notched impact strength of the nylon 6. Moreover, the nylon 6 blends containing the nonreactive POE were difficult to extrude and pelletize because of poor compatibility between nylon 6 and the POE. This occurred particularly when the amount of the POE in the blend was > 20 wt %. However, when the POE was replaced by the POEgMA, there was not any problem for extruding and pelletizing the blend. Additionally, its presence allowed the great improvement in the notched impact strength of the nylon 6. This latter increased with increasing POEgMA content. Adding CE-96 as a
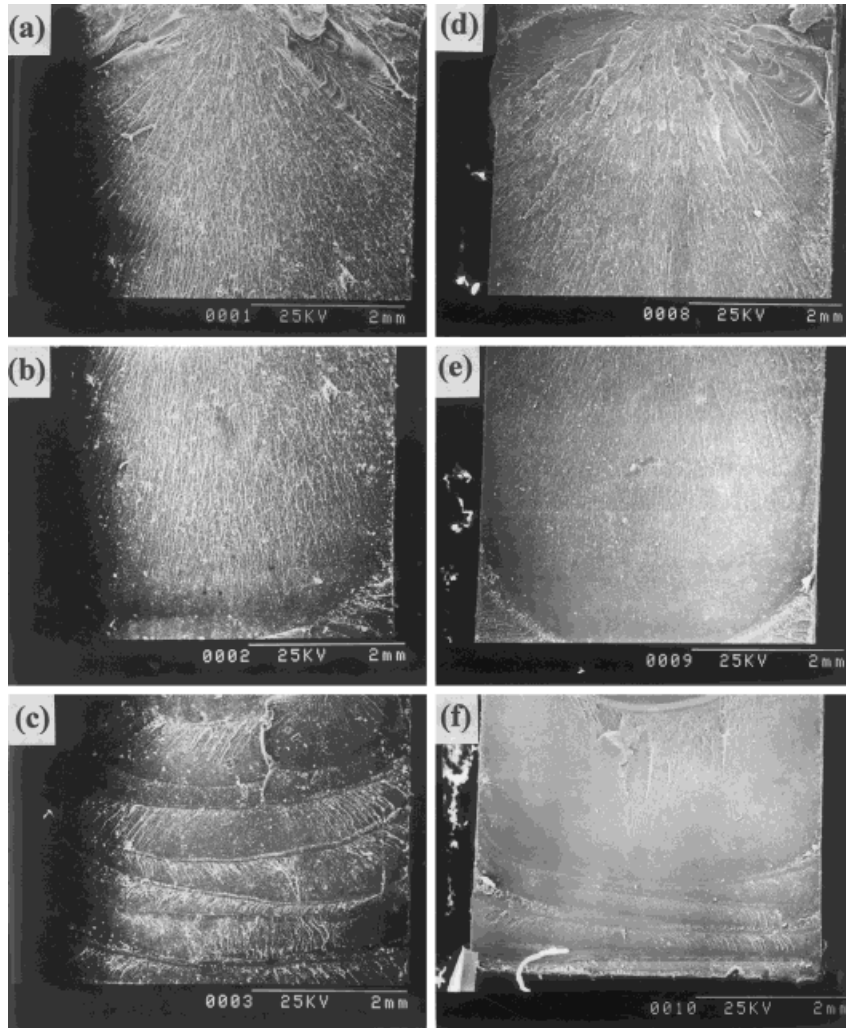
Figure 2   Low-magnification SEM photographs of the pure nylon 6 (a, b, and c) and its blend with 5 wt % POEgMA (d, e, and f).

compatibilizer further increased the notched impact strength of the nylon 6/POEgMA blend. This is because the CE-96 is capable of reacting with the nylon 6 increasing therefore its viscosity and reducing the viscosity mismatch between the nylon 6 and the rubber phase. Moreover, it can react with the nylon 6 and the POEgMA at the same time leading to the formation of a copolymer at the interfaces between the nylon and POEgMA. This copolymer serves to reduce the interfacial tension and the coalescence.

Fracture Topography

Effects of the POEgMA

The fracture surface of a solid polymer material is often an indication of how the material frac-

tures.[25] Figures 2 and 3 show low-magnification SEM fractographs of the pure nylon 6 and its blends. As observed in the typical fracture surface of glassy polymers such as poly(methyl methacrylate) (PMMA),[13–15] polystyrene (PS),[16,17] polycarbonate (PC),[18] and also in rubber-toughening plastics,[19–22] the fractographs of the pure nylon 6 and its blends exhibit two regions with a distinct boundary between them: a slow-crack-growth region (stress-whitened zone) and a fast-crack-growth region. The slow-crack-growth-region is near the notch. It is smooth and featureless under low magnification. Some authors attempted to relate the fracture morphology to the crack velocity.[26–28] In this slow-growth region, the crack propagation rate is much smaller. Because the crack reaches a critical length for the applied
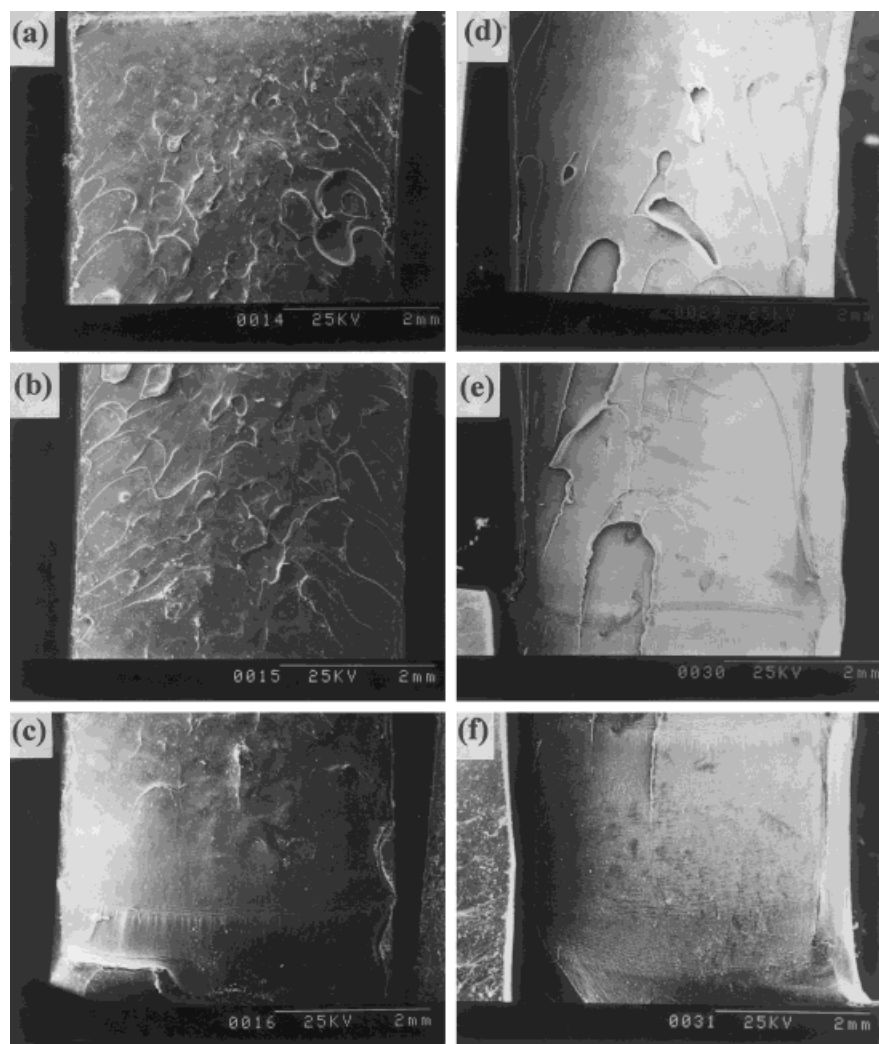
Figure 3 Low-magnification SEM photographs of nylon 6 blends with 20 (a, b, and c) and 30 wt % (d, e, and f) POEgMA, respectively.

stress while in the fast-growth zone, it becomes unstable and propagates very rapidly and the higher stress is sufficient to actuate flaws well in advance of the main crack front. In other words, these flaws are activated by the advance stress wave and become sources of the secondary cracks. A number of featherlike, parabola geometric markings are produced by the intersection of the main crack front with secondary cracks propagating radially from the flaws on different planes. As pointed out by Wolock and Newton,[25] the formation of these markings is a direct indication of the energy required for crack propagation and also determined by both the main-crack-front velocity (V_m) and the secondary-crack-front velocity (V_s). If $V_m \gg V_s$, a featurelike marking is formed. If V_m

$> V_s$, the primary front will completely enclose it and an ellipse will result. If both velocities are equal, a parabola is formed. For the pure nylon 6, the area of the slow crack growth is very small as shown at the top of Figure 2(a) and the fast-growth region exhibits a number of featherlike geometric markings that are the classic fracture markings of brittle polymers, as shown in Figure 2(b). The addition of 5 wt % POEgMA does not change much the fracture topography of the nylon 6 except that the area of the slow growth region is slightly larger [see the top of Fig. 2(d)]. This implies that 5 wt % of POEgMA is not enough to improve the toughness of the nylon 6. As shown in Figure 3, 20 wt % POEgMA greatly modifies the fracture topography of the nylon 6. The area of
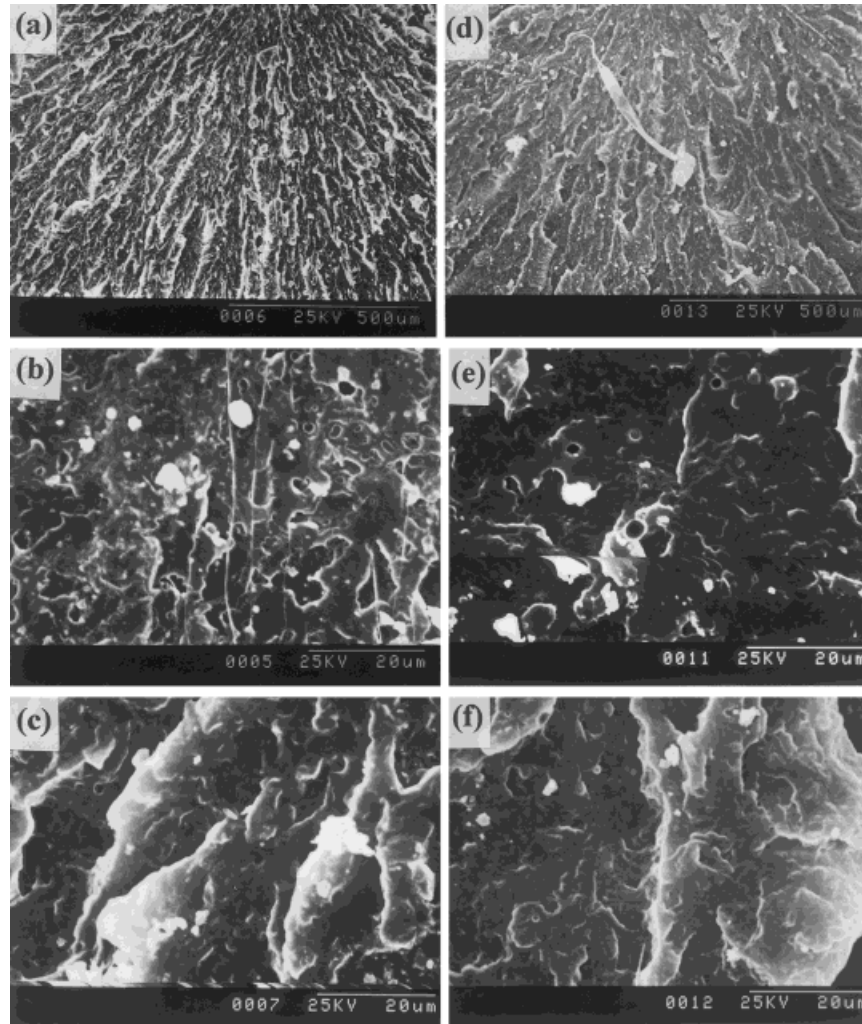
Figure 4   High-magnification SEM photographs of the pure nylon 6 (a, b, and c) and nylon 6 blend with 5 wt % POEgMA (d, e, and f).

the slow-crack-growth region [at the top of Fig. 3(a)] is much greater and the fast-growth region exhibits geometric markings resembling a parabola [Fig. 3(b) and the bottom of Fig. 3(a)]. When the POEgMA content reaches 30 wt %, the fracture surface of the blend is very smooth and the slow growth region (or the stress-whitened region) is enlarged significantly and occupies almost the entire surface except for a few parabola markings [Fig. 3(d–f)]. Each parabola contains a flaw or pit at the focus, at which secondary fracture is initiated. In addition, several ribs or stick–slip lines[29] are present at the bottom of the fracture surfaces of the pure nylon 6 [Fig. 2(c)]. They probably correspond to another case of the discontinuous mode of fracture propagation. The stick–

slip transition may result from a sudden expenditure of stored impact energy and its associated stress relief, and a following delay of propagation when stored impact energy reaches the required level.[30] With increasing the POEgMA content, the ribs rapidly decrease in number and resolution [Fig. 3(c)]. This is particularly true when the POEgMA content is more than 20 wt %. In fact, the ribs could not be observed anymore because the bottom of the impact specimen was not broken completely.

Figures 4 and 5 show high-magnification SEM fractographs of the nylon 6 and its blends. The slow-crack-growth region of the pure nylon 6 is relatively smooth [Fig. 4(b)] and its fast-crack-growth region exhibits featherlike markings [Fig.
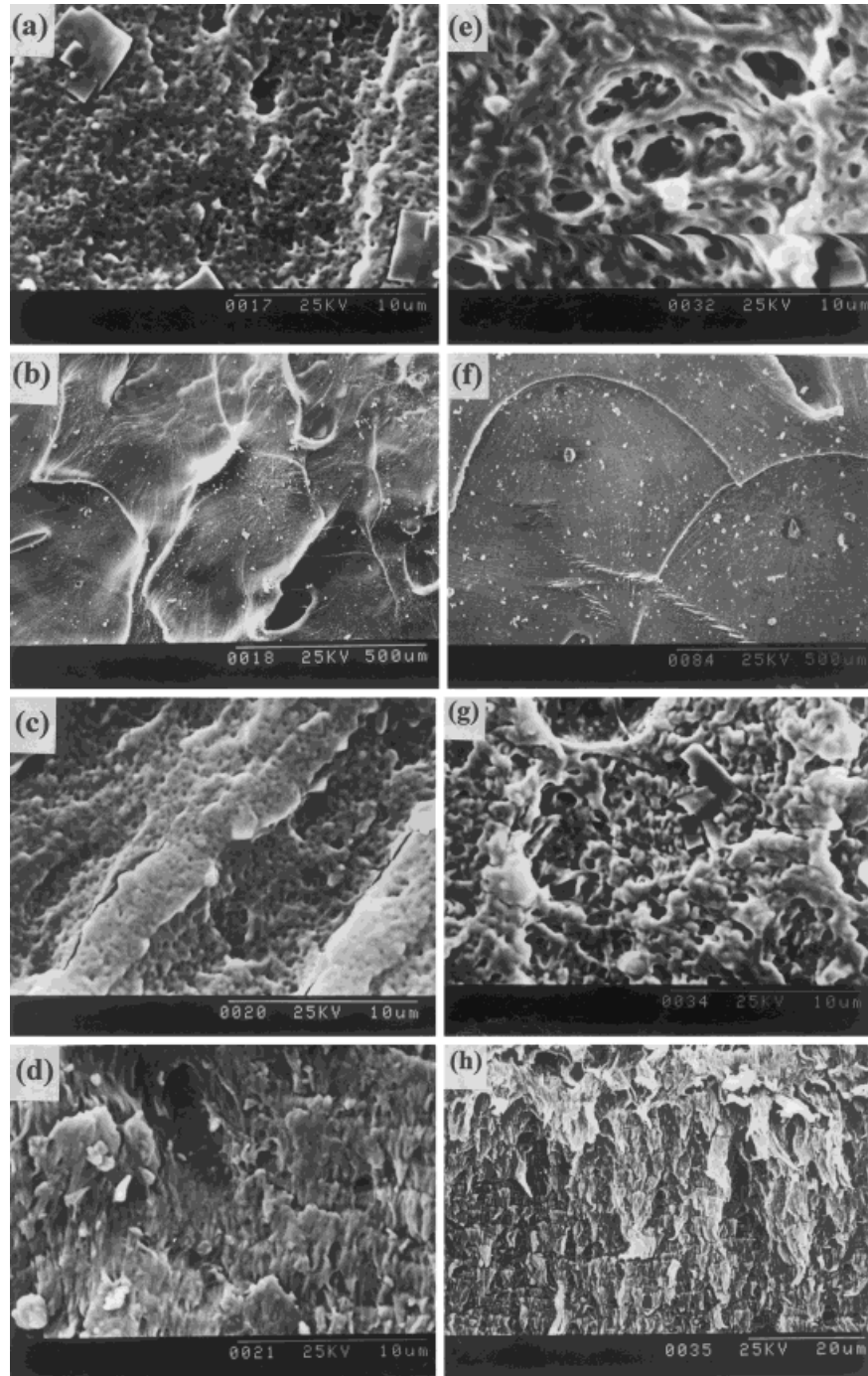
Figure 5 High-magnification SEM photographs of nylon 6 blends with 20 (a, b, c, and d) and 30 wt % (e, f, g, and h) POEgMA, respectively.

4(a) and (c)], indicating a brittle feature. The addition of 5 wt % POEgMA to nylon 6 showed limited cavitation of some rubber particles in the slow-crack-growth region [Fig. 4(e)] and feather-like markings in the fast-crack-growth region

[Fig. 4(d) and (f)]. This implies that its notched impact strength would not be much improved. Adding 20 wt % POEgMA resulted in extensive cavitation of the rubber particles in the slow-crack-growth region [Fig. 5(a)] and both cavita-
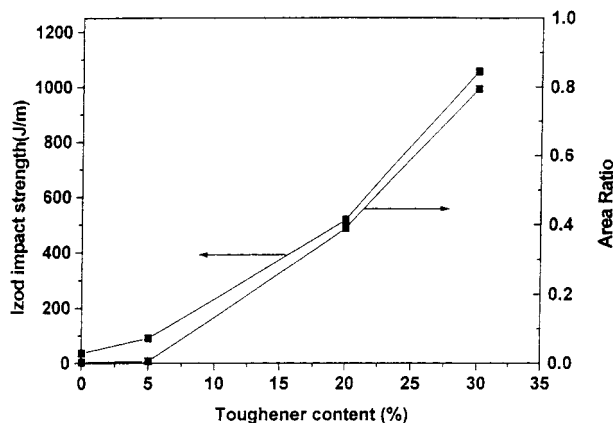
Figure 6 Plots of impact strength with the area ratio *S* for nylon 6/POEgMA blends.

tion and matrix shear yielding in the fast-crack-growth region [Fig. 5(b–d)]. Such cavitation and shear yielding led to a large amount of plastic deformation, thereby dissipating a significant amount of impact energy. Finally, with further increasing POEgMA content, shear yielding and extensive plastic flow of the matrix are seen throughout the entire slow crack growth region as shown in Figure 5(e–h). Thus the blend containing 30 wt % POEgMA should exhibit the highest impact strength.

The boundary between the slow- and fast-crack-growth zones can be easily identified. This allows the evaluation of the area of the slow-crack-growth zone. In fact, the area ratio (*S*) of the area of slow crack growth zone to that of the entire fracture surface was used to analyze the impact energy absorption mechanisms.[19] Figure 6 shows the variation of the notched impact strength and that of the area ratio as a function of the POEgMA content for the nylon 6/POEgMA blend. It appears that similar to the impact strength of the nylon 6 blends, the area ratio also shows a brittle–tough transition with increasing POEgMA content. It may be concluded that generally speaking, the larger the area of the slow crack growth, the greater the impact energy dissipated during Izod impact testing.

Figure 7 shows the SEM micrographs of the impact fracture surface of the nylon 6/POE blend. Its slow-crack-growth zone is very small as shown at the top of the Figure 7(a), whereas its fast-crack-growth zone shows featherlike markings [Fig. 7(b) and (c)]. The high-magnification photo-

graphs in the slow growth zone [Fig. 7(d)] and in fast growth zone [Fig. 7(e) and (f)] of the blend show that the nonreactive POE rubber particles were poorly dispersed. Moreover, the interfacial adhesion between the nylon 6 matrix and the POE particles is weak. Thus, the presence of the POE has little contribution to the impact toughness of the nylon 6.

Effect of the Multifunctional Epoxy Resin

Figures 8 and 9 show typical high-magnification SEM micrographs of the impact fracture surfaces of the nylon 6/CE-96 and nylon 6/POEgMA/CE-96 blends. The addition of CE-96 modifies slightly the fracture morphologies of nylon 6 and nylon 6/POEgMA blends. Comparison of Figure 8(a) with 2(a) shows that the addition of CE-96 into nylon 6 enlarges the area of the slow crack growth of nylon 6 and exhibits a few tearing bands at the fast-crack-growth region [Fig. 8(d)]. Incorporation of 5 wt % POEgMA and 0.3 phr CE-96 to the nylon 6 apparently did not modify its morphology in the fast crack growth region [Fig. 8(e) and (g) versus Fig. 8(a) and (c)]. However, tearing bands in the slow crack region [Fig. 8(f)] and limited cavitation of the dispersed phase in the bottom of the impact fracture surface [Fig. 8(h)] are observed. It was confirmed[8] that the addition of CE-96 increased the melt viscosity of the nylon 6 matrix and improved the compatibility between the POEgMA and the nylon 6. Consequently, the domain size of POEgMA was reduced and the notched impact strength of the nylon 6/POEgMA blends further improved. When the POEgMA content exceeded 20 wt %, the morphologies of the nylon 6 blends changed greatly, regardless of whether or not CE-96 was added. The blend containing 20 wt % POEgMA and 0.3 phr CE-96 was very tough, showing cavitation in the slow-crack-growth region [Fig. 9(a)] and both cavitation and matrix shear yielding in the fast-crack-growth region [Fig. 9(c) and (d)]. When the POEgMA content reached 30 wt %, extensive shear yielding of nylon 6 matrix was observed over the entire impact fracture surface [Fig. 9(e), (g), and (h)].

It is also interesting to note that although parabolic markings were observed under a low magnification in the fast-crack-growth zones of the nylon 6 blends containing 20 and 30 wt % POEgMA, respectively [Fig. 9(b) and (f)], they exhibited different features under high magnification. The fracture surface of the nylon 6 blend
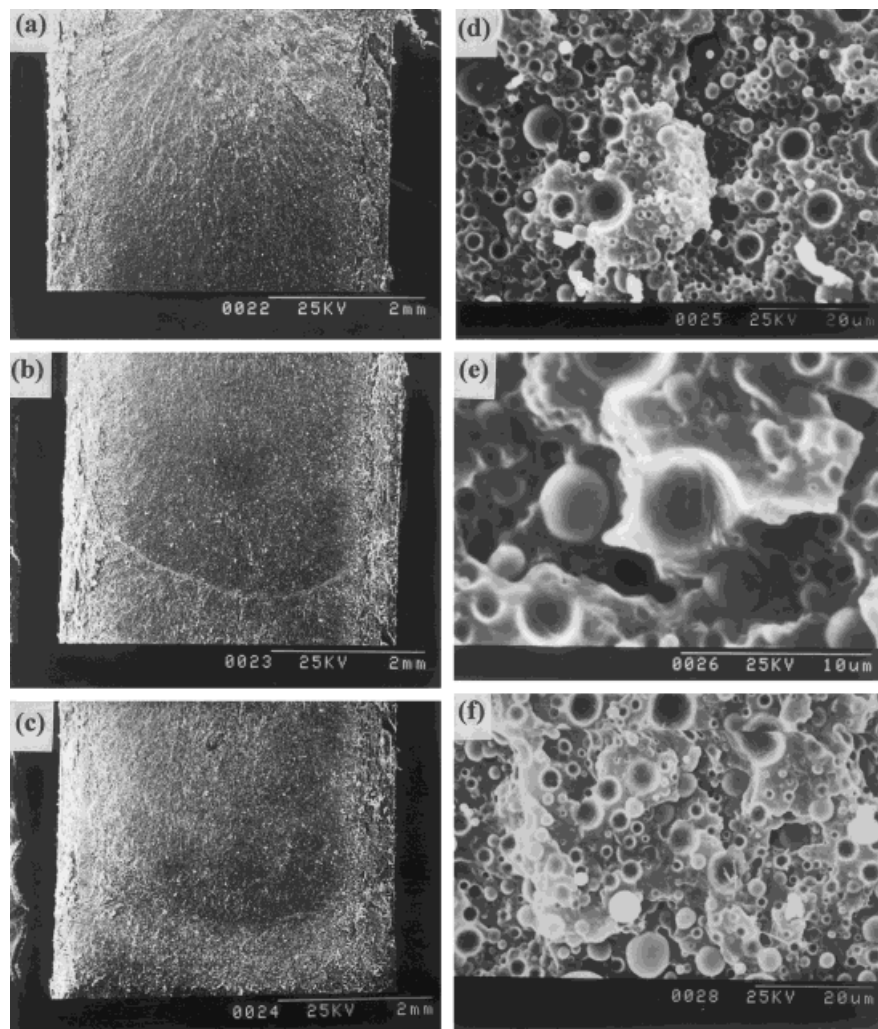
Figure 7 SEM photographs of the impact fracture surface of nylon 6/POE (80/20) blend at low (a, b, and c) and high (d, e, and f) magnifications.

containing 20 wt % POEgMA was characterized by the cavitation of the rubber particles and the localized matrix yielding around these particles [Fig. 9(c) and (d)]. When the POEgMA content was 30 wt %, an extensive matrix yielding was observed within the parabolic features [Fig. 9(g) and (h)]. This was responsible for the higher impact strength obtained in this particular blend.

CONCLUSION

The impact fracture surface of polymers exhibits certain characteristic features formed during the impact fracture process. The slow-crack-growth region of the pure nylon 6 is relatively smooth and its fast-crack-growth-region exhibits featherlike markings, indicating a brittle appearance. The addition of 5 wt % of a maleic anhydride copolymer of ethylene and octene (POEgMA) to the nylon 6 shows limited cavitation of some rubber particles in the slow-crack-growth region and featherlike markings in the fast-crack-growth region, implying that its notched impact strength is not improved. Adding 20 wt % POEgMA results in extensive microvoid or cavitation of the rubber particles in the slow crack growth region and both cavitation and matrix shear yielding in the fast-crack-growth region. Such cavitation and shear yielding led to a large amount of plastic deforma-
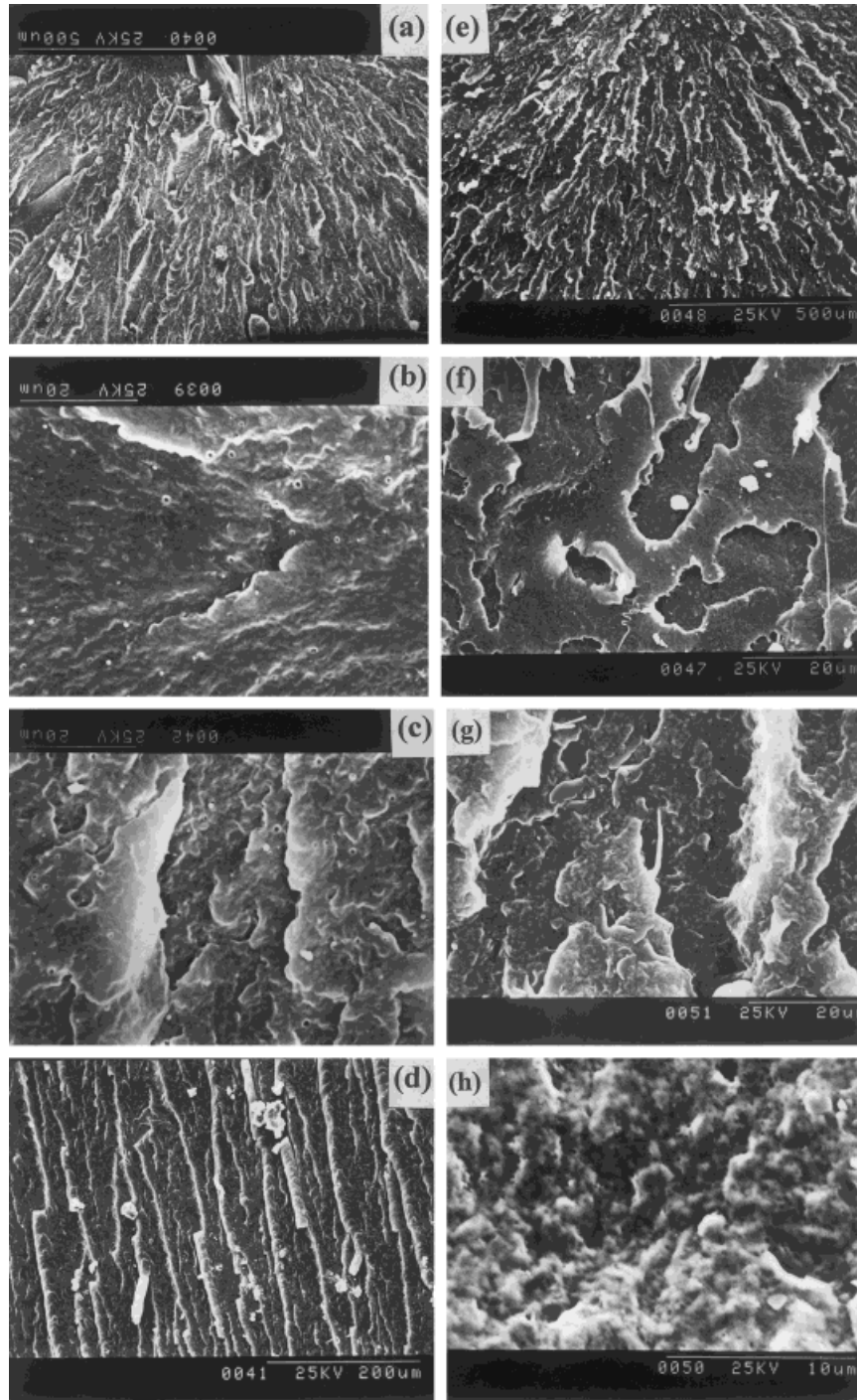
Figure 8 High-magnification SEM photographs of nylon 6/CE-96 (0.3 phr) blends without (a, b, c, and d) and with (e, f, g, and h) 5 wt % POEgMA, respectively.

tion, thereby dissipating a significant amount of impact energy. Finally, with further increasing POEgMA content, shear yielding and extensive plastic flow of the matrix are seen throughout the entire slow-crack-growth region. Thus, the blend containing 30 wt % POEgMA exhibits the highest impact strength. The addition of CE-96 further improves the notched impact strength of nylon 6
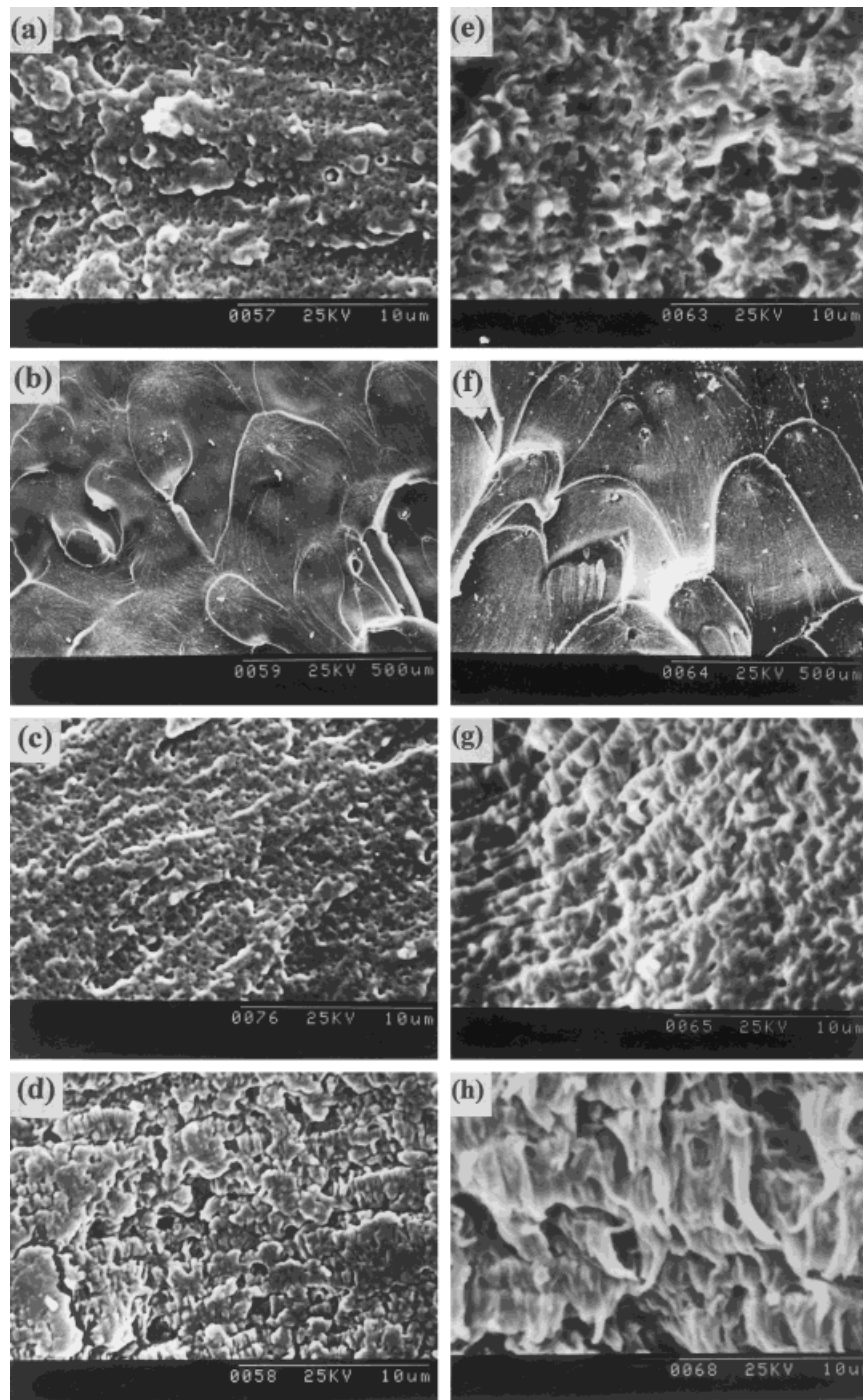
Figure 9   High-magnification SEM photographs of nylon 6/POEgMA/CE-96 (0.3 phr) blends with 20 (a, b, c, and d) and 30 wt % (e, f, g, and h) POEgMA, respectively.

blends, but its contribution is slightly reflected from the fracture morphologies of nylon 6 blends.

For the nylon 6/nonreactive POE blend, its slow-crack-growth zone is very small and its fast-crack-growth-zone appears featherlike figures.

The high-magnification photographs both in slow-growth zone and in fast-growth zone of the blend show that the POE rubber particles have poor dispersion and interfacial adhesion with nylon 6 matrix. These are responsible for the fact that the

nonreactive POE can hardly improve the impact toughness of nylon 6.

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