

Toughening of Polyethylene Terephthalate/Amorphous Copolyester Blends with a Maleated Thermoplastic Elastomer

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ABSTRACT: The toughening of polyethylene terephthalate (PET)/amorphous copolyester (PETG) blends using a maleic anhydride grafted mixture (TPEg) of polyethylene-octene elastomer and a semicrystalline polyolefin plastic (60/40 by weight) was examined. The TPEg was more effective in toughening PETG than PET, although the dispersion qualities of the TPEg particles in PET and PETG matrices were very similar. At the fixed TPEg content of 15 wt %, replacing partial PET by PETG resulted in a sharp brittle-ductile transition when the PETG content exceeded the PET content. Before the transition, PET/PETG blends were not toughened with the TPEg of 15 wt %, whereas after the transition, the PET/PETG blends with 15 wt % of TPEg, similar to the PETG/TPEg (85/15) binary blend, maintained a super-tough level. The impact-fractured surfaces of the

PET/PETG/TPEg blends were also evaluated. When PETG content was lower than PET content, the ternary blend showed a brittle feature in its impact-fractured surface, similar to the PET/TPEg (85/15) binary blend. While PETG content exceeded PET content, however, the impact-fractured surface of the ternary blend was very similar to that of PETG/TPEg (85/15) binary blend, exhibiting intensive cavitation and massive matrix shear yielding, which were believed to be responsible for the super-tough level of the blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 797–805, 2003

Key words: polyethylene terephthalate; copolyester; polyethylene-octene copolymer; toughness; blends

INTRODUCTION

In a previous paper¹, a maleated thermoplastic elastomer (TPEg) was developed, which was a maleic anhydride grafted mixture of polyethylene-octene elastomer (POE) and semicrystalline polyolefin plastic (60/40 by weight) prepared by radical grafting in a twin-screw extruder. The presence of the 40 wt % of polyolefin plastic greatly decreased the melt viscosity of POE elastomer and improved processability of the radical grafting of POE elastomer in the extruder. The TPEg was found to be very efficient for toughening nylon 6.^{1,2} Because of its lower melt viscosity, the TPEg had a finer dispersion in nylon 6 matrix than the maleic anhydride grafted polyethylene-octene elastomer (POEg) prepared with the same grafting conditions.

In another previous paper,³ the TPEg was employed to toughen poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) plastic (PETG), which is an amorphous thermoplastic copolyester. The “G” in the designation of PETG copolyester indicates a second

glycol, 1,4-cyclohexanedimethanol, incorporated in the polymer. Different from polyethylene terephthalate (PET), the PETG did not undergo crystallization on heating or on plasticisation by the dissolved species; the comonomer, cyclohexanedimethanol, was responsible for the completely amorphous nature of this polymer. PETG offered a range of processing parameters broader than that of normal crystallizable polymers and was useful for obtaining high clarity amorphous parts. Similar to ordinary PET, however, the PETG is also a pseudo-ductile polymer characterized by high crack-initiation energy and low-crack propagation energy, and consequently, by high unnotched and low notched impact-strength values. Its notched impact strength at ambient temperature and dry condition was just 23.5 J/m.³ The PETG was super-toughened by using the TPEg toughener. A sharp transition from brittle to ductile took place when the TPEg content was about 10 wt %. A similar transition was also occurred for PETG/POEg blends, but the POEg content for the transition was higher, i.e., 15 wt %. The TPEg showed a higher toughening efficiency than the POEg because of its better dispersion in the PETG matrix than that of the POEg.

Many works on PETG in the literature mainly focused on physical and mechanical properties of PETG.^{4–8} Papadopoulou et al.^{9,10} investigated the

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compatibility of PETG blended with PET or PBT over complete composition range. Saheb et al.¹¹ studied the crystallization and equilibrium melting behaviour of PBT/PETG blends and confirmed the miscibility of the PBT/PETG blends.

Because the TPEg efficiently toughened the PETG, we wondered whether the TPEg has similar effectiveness in toughening PET or PET/PETG blends. Hiltner and Baer^{12–14} investigated PET toughening with 5 wt % of a maleic anhydride grafted styrene-ethylene/butylene-styrene triblock copolymer (SEBS-*g*-MA). It was confirmed that graft copolymer was formed *in situ* by the reaction of PET hydroxyl end group with the anhydride occurred during melt extrusion, which acted as an emulsifier to decrease interfacial tension and reduce the tendency of dispersed particles to coalesce, and promoted interfacial adhesion between PET and SEBS-*g*-MA. Notched tensile tests were employed to characterize the toughening efficiency of SEBS-*g*-MA. Increasing the molecular weight of the SEBS and decreasing the hydroxyl-to-carboxyl ratio of the PET increased the effectiveness of the SEBS. In addition, numerous studies on PET/polyolefin blends with functionalised elastomers were reported in terms of compatibilization and toughening effectiveness.^{15–20} To our knowledge, a direct comparison of the toughening of PET and PETG has not been made using the same toughener and processing conditions. Therefore, the purpose of this study is to compare the toughening efficiencies of the TPEg toughener on PET and PETG in terms of mechanical properties and evaluate the impact-fractured surfaces.

EXPERIMENTAL

Materials

The polyethylene terephthalate resin was from Beijing Yanshan Petrochemical Co. (Beijing, China) with intrinsic viscosity of 0.82 dl/g. The amorphous copolyester of ethylene glycol, 1,4-cyclohexanedimethanol and terephthalic acid with a molar ratio of approximately 1 : 2 : 3,⁴ was a commercial product of Eastman Chemical Company (Rochester, NY) under the trade-name Eastar PETG 6763. Its number average molecular weight and intrinsic viscosity were 2.6×10^4 g/mol and 0.73 dl/g, respectively.⁹ The polyethylene-octene elastomer (POE) was a commercial product of Dupont Dow Elastomers (Wilmington, DE) under the trade-name Engage 8445. The radical grafting of mixture of POE elastomer/semicrystalline polyolefin (60/40, by weight) with maleic anhydride was carried out 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.

Blend preparation

Prior to blending, the PET was dried at 145°C under vacuum for at least 6 h. The PETG was also dried at

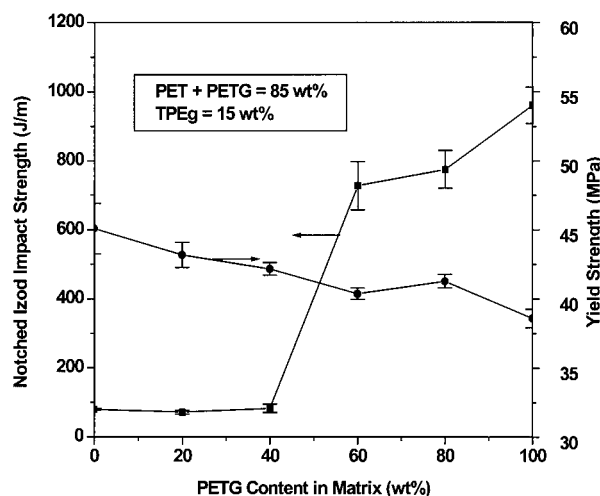


Figure 1 Notched Izod impact strength and yield strength as a function of PETG content in the matrix phase for PET/PETG blends with 15 wt % of TPEg.

70°C for 6 h under vacuum condition. Blends were prepared in the extruder at 15 wt % of TPEg plus 85 wt % PET/PETG mixture ranged from 0 to 100 wt % of PETG at four intervals. The screw speed and the barrel temperatures of the extruder were 250 rpm and 225–260°C, respectively. The extrudates were dried and injection moulded into standard tensile, flexural, and Izod-impact specimens in an injection-moulding machine (SZ-160/80 NB, China).

Mechanical testing

The tensile and flexural tests were carried out on an universal tensile tester (Instron 1122) according to the National Standard Test Methods of China, GB 1040-79 and GB 1042-79, respectively. They are very similar in sample dimensions and test conditions to ASTM D638 and ASTM D790, respectively. The notched Izod-impact strength was measured at ambient temperature using an impact tester (CSI-127C, USA) according to the National Standard Test Method of China GB 1843-80, which is similar to ASTM D256. For all these tests, at least five specimens were used for each measurement.

Morphology observation

The impact-fractured surfaces were observed with a scanning electron microscope (SEM) (Hitachi S-530, Japan) after they were splattered with gold.

RESULTS AND DISCUSSION

Toughening effect of TPEg

Figure 1 shows plots of notched Izod impact strength and tensile strength as a function of PETG content in the matrix for PET/PETG/TPEg ternary blends with a

fixed TPEg content of 15 wt %. Both PET and PETG are notch sensitive, and their notched Izod impact-strength values at room temperature and dry state are 25 and 23 J/m, respectively. After blending with 15 wt % of the TPEg, the impact strength of PET was increased more than 2-fold, i.e., 80 J/m. But the blend was still brittle as revealed from its impact-fractured surface shown below, whereas the 15 wt % of TPEg made the PETG super-tough, exhibiting a more than 40-fold increase in notched impact strength, i.e., 960 J/m.

Wu²¹ postulated that the brittle-ductile behavior of polymers and blends may depend on two molecular parameters: entanglement density (ν_e) and characteristic ratio (C_∞) of the chain of polymer matrix. As demonstrated in many pseudo-ductile polymer/elastomer blends, the brittle-ductile transition was controlled by critical surface-to-surface interparticle distance (τ_c). The mechanism appeared to involve the cavitation of elastomer particles, which relieved the hydrostatic stresses, and thus allowed thin matrix ligaments ($\tau < \tau_c$) to yield locally.²² When the thin matrix ligaments were interconnected to form a pervasive network, the yielding process could then propagate and pervade over the entire deformation zone. When this occurred, a blend would exhibit a ductile behavior. So far, the τ_c values reported in literatures are 0.3 μm for nylon 66/EPDM-g-MA blends,^{22,23} 0.15 μm for isotactic PP/EPDM blends,²⁴ 0.33 μm for PBT/POE-g-MA blends,²⁵ 0.6 μm for both HDPE/EPDM and HDPE/calcium carbonate blends,^{26,27} and 0.44 μm for PETG/elastomer blends.²⁸ It should be pointed out that τ_c is dependent on stress state, rate, temperature, and interfacial adhesion.²⁹⁻³⁵

It is believed that the polymer matrix with more flexible molecular chain will be easier to be toughened. As shown in the following SEM photographs, the dispersion qualities of the TPEg particles in PET and PETG matrices were very similar, as revealed by the same average diameter of approximately 0.68 μm . As such, the difference of the TPEg in toughening PET and PETG with the same specimen dimensions and testing conditions should be attributable to the intrinsic property difference between PET and PETG. The presence of the second glycol, 1,4-cyclohexanedimethanol, in the PETG made the molecular chain of aromatic polyester flexible. It would be reasonable that the τ_c value for PET/elastomer blends would be smaller than that for PETG/elastomer blends. Up to now, no τ_c value for PET/elastomer blends has been reported.

At the fixed TPEg content, replacing partial PET by PETG hardly increased the impact strength of the blends as long as PETG content was less than PET content. In this range of PETG content, PET played a dominant role in determining the toughening effectiveness of the TPEg in the ternary blends. Once the PETG content exceeded the PET content, the impact

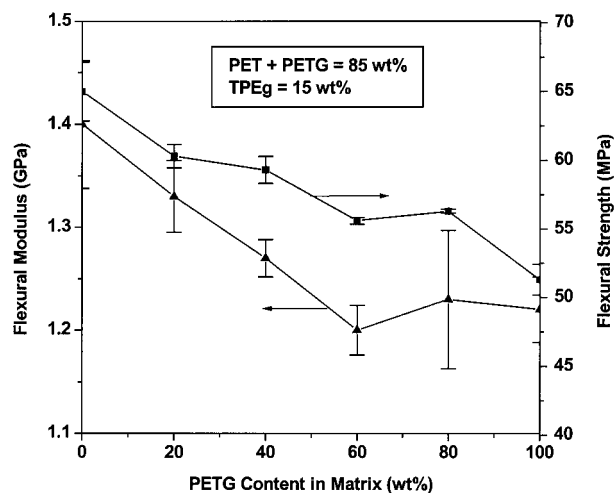


Figure 2 Flexural modulus and flexural strength as a function of PETG content in the matrix phase for PET/PETG blends with 15 wt % of TPEg.

strength of the ternary blends was drastically increased about 10-fold, thus exhibiting a sharp transition from brittle to super-tough. Further increasing the content of PETG only led to a limited further increase in the impact-strength value of the ternary blends. In other words, replacing partial PETG with PET caused only a slight decrease in impact strength of the PETG/TPEg blend and the ternary blends were still at the super-tough level, as long as the PET content was less than PETG content. In this case, PETG dominated the toughening effectiveness of TPEg in the ternary blends.

An investigation of the properties of PET/PETG binary blends over entire composition range will be useful in explaining the sharp brittle-ductile transition of the PET/PETG blends with the fixed TPEg content. Papadopoulou et al.¹⁰ found that the PET/PETG binary blends exhibited miscibility in an amorphous state as evidenced by the single composition-dependent glass transition temperature. The annealed PET/PETG blends were miscible when the PETG content $\phi \geq 0.50$. The change in miscibility of the PET/PETG blend was well consistent with the brittle-ductile transition of the PET/PETG/TPEg blends occurred at the same PETG content. When PETG content was lower than PET content, the PET/PETG blend behaved like PET, the toughening effectiveness of TPEg was limited; whereas, after the PETG content exceeded the PET content, the PET/PETG blend behaved like PETG, 15 wt % of TPEg exhibited remarkable toughening efficiency on the PET/PETG blend.

The influences of varying levels of the PET and the PETG on other mechanical properties of the PET/PETG/TPEg blends with the fixed TPEg content of 15 wt %, such as yielding strength, flexural strength, and modulus, are shown in Figures 1 and 2. The presence of the second glycol caused lower tensile strength and

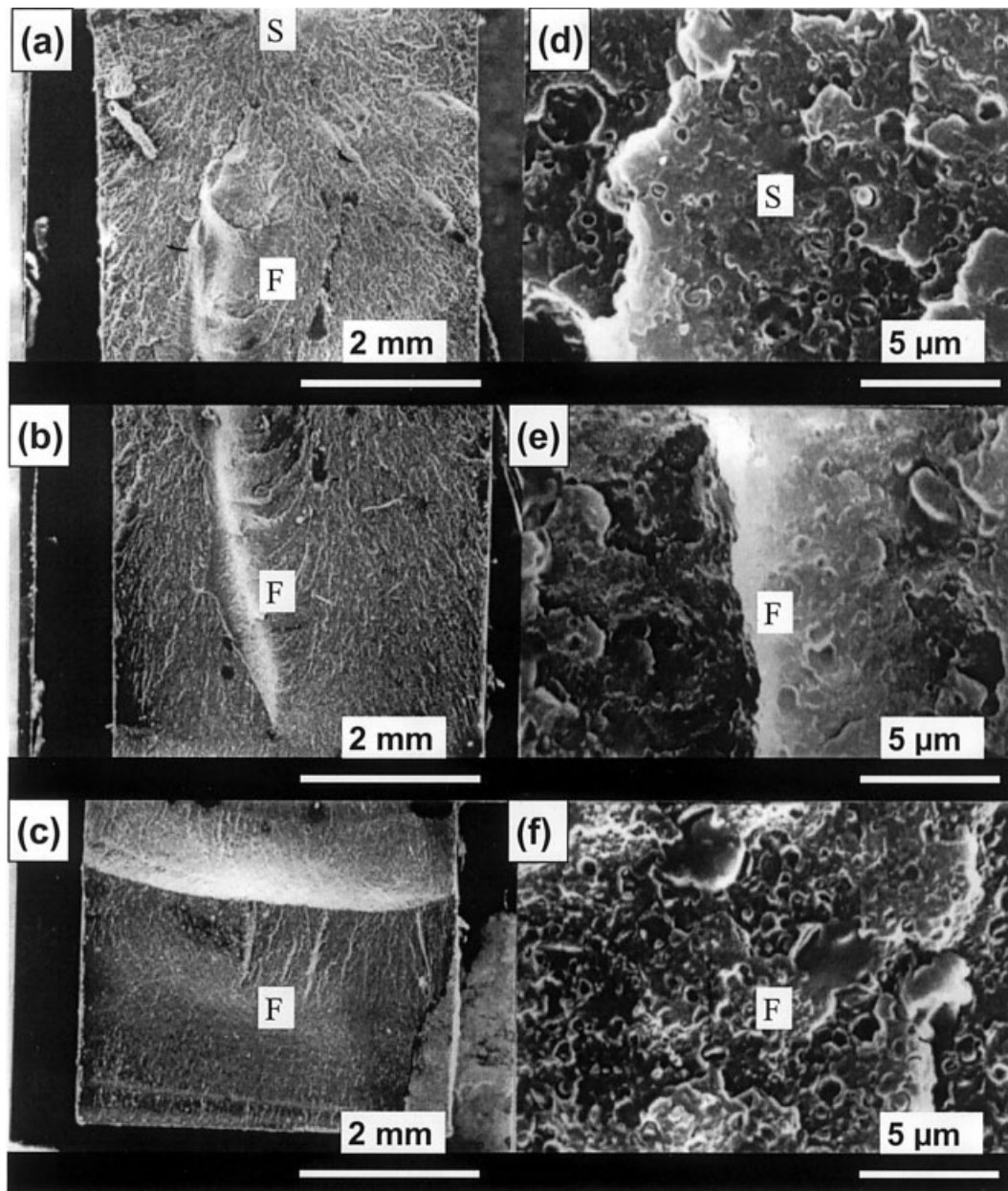


Figure 3 SEM photographs of impact-fractured surface of PET/TPEg (85/15) blend under low (a, b, and c) and high (d, e, and f) magnifications. S and F denote the slow and fast crack growth regions, respectively.

modulus of PETG itself as compared to those of PET. Consequently, the PETG/TPEg (85/15) blend exhibited lower tensile strength and modulus than the PET/TPEg (85/15) blend did. For the PET/PETG/TPEg ternary blends, with the increase of PETG content, the tensile strength and modulus of the ternary blends decreased gradually, although the notched impact strength showed a sharp jump when the PETG content exceeded PET content.

Evaluation of impact-fractured surfaces

Observation of the fracture surface helped researchers to understand the involved impact energy dissipation mechanisms upon fracturing.^{14,36–40} Figure 3 shows

the SEM fractographs of the impact-fractured surfaces of the PET/TPEg (85/15) blend. The fracture surface exhibited a region of slow crack growth (denoted as S) at the notch root followed by a region of fast crack growth (denoted as F), as shown in the low magnification fractographs [see Figs. 3(a,b,c)]. The slow crack growth region was near the notch root. In this region, the crack propagation was believed to be slow because of the blunt notch given before impact testing. The area of the slow crack growth region was obviously enlarged compared to the pure polymer.³⁹ However, as shown in the high-magnification fractograph of Figure 3(d), no elastomer cavitation and matrix shear yielding appeared in the slow crack growth region and the fracture surface showed a brittle failure.

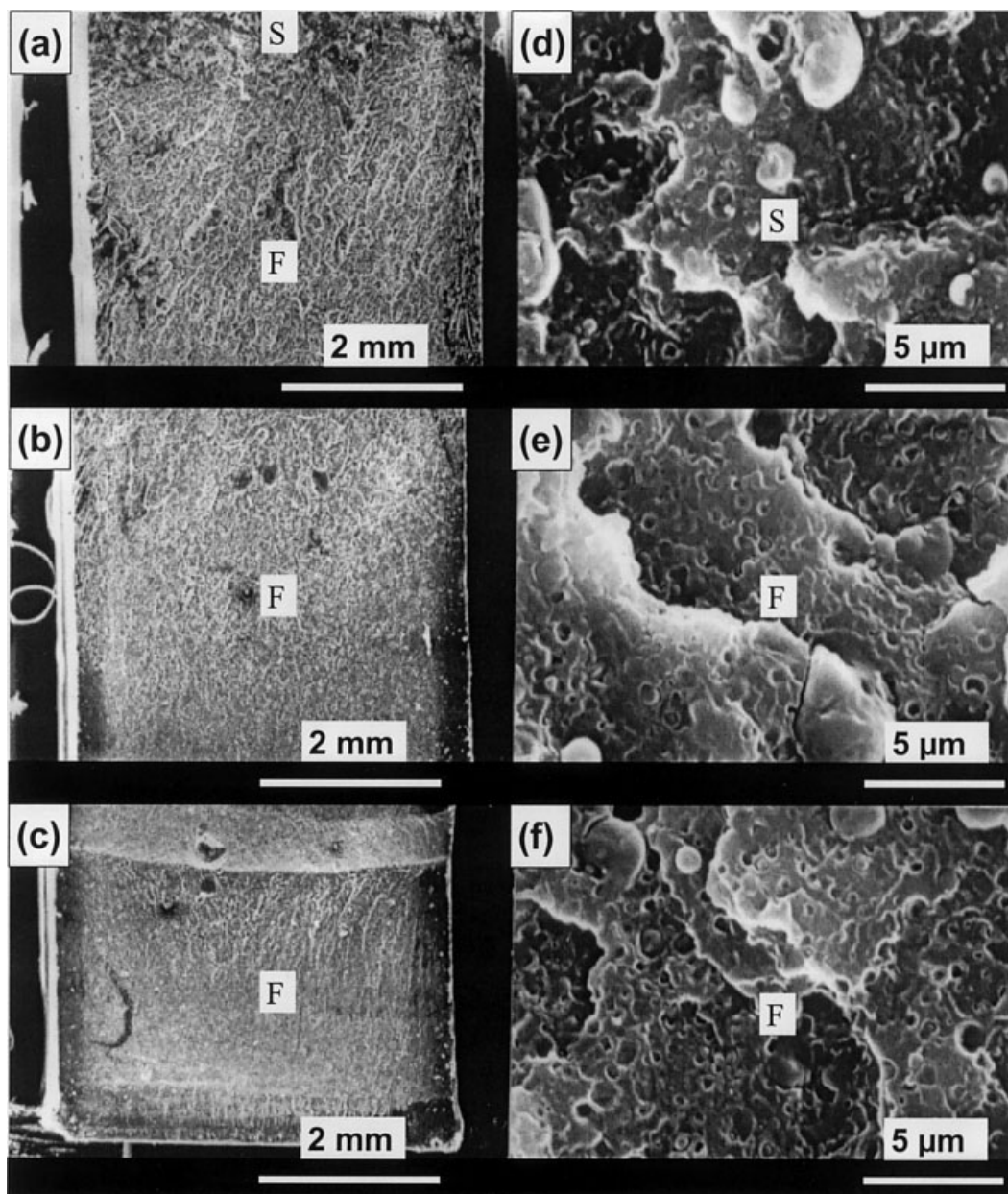


Figure 4 SEM photographs of impact-fractured surface of PET/PETG (60/40) blend with 15 wt % of TPEg under low (a, b, and c) and high (d, e, and f) magnifications. S and F denote the slow and fast crack growth regions, respectively.

When the crack reached a critical length for the applied stress, it became unstable and propagated very rapidly and the higher stress was sufficient to actuate flaws well in advance of the main crack front. In other words, these flaws were activated by the advanced stress wave and became sources of the secondary cracks. In the fast crack growth region, the secondary cracks propagated radially from the flaws. The intersection of the main crack front with the secondary cracks on different planes generated a number of featherlike or parabolic markings, which were indicative of secondary cracks. The formation of these markings was determined by both the main crack front rate and secondary crack propagation rate.^{41,42} The fast crack growth region of the PET/TPEg (85/15)

blend exhibited a number of featherlike markings that were the classic fracture markings of brittle polymers as shown in Figure 3(a–c). The high magnification fractograph of this region also showed brittle fracture feature. Also, the dispersion of TPEg particles was relatively homogeneous as revealed from Figure 3(d–f). The number average diameter of the TPEg particles was about $0.68 \mu\text{m}$ in PET matrix, which was the same as the diameter of the TPEg particles for PETG/TPEg (85/15) blend.⁴³ It was believed that the anhydride group of the TPEg reacted with the hydroxyl end group of the PET to generate a chemical linkage, forming *in situ* a PET-co-TPEg copolymer during melt extrusion. Tanrattanakul et al.⁴⁴ confirmed the chemical reaction between PET and SEBS-g-MA at high temper-

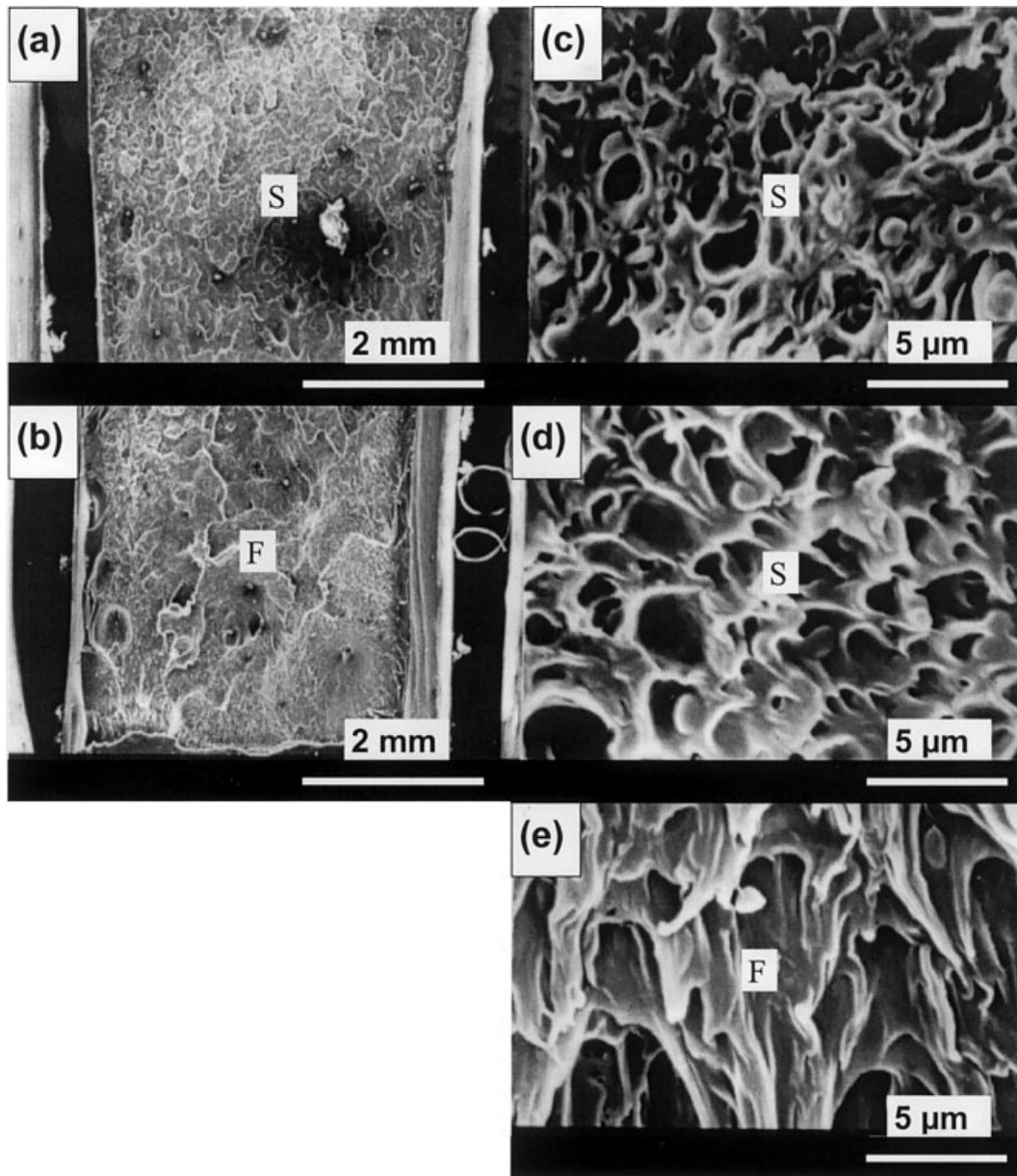


Figure 5 SEM photographs of impact-fractured surface of PET/PETG (40/60) blend with 15 wt % of TPEg under low (a and b) and high (c, d, and e) magnifications. S and F denote the slow and fast crack growth regions, respectively. The specimen did not break completely.

ature. In their work, blends of PET with grafted SEBS-*g*-MA and non-grafted SEBS were extracted by tetrahydrofuran (THF) in an attempt to isolate an SEBS-*g*-MA component that had chemically reacted with PET. THF is a good solvent for SEBS and SEBS-*g*-MA, but a non-solvent for PET. The THF-insoluble fraction was characterized by photo acoustic FTIR, which showed that it contained un-extracted SEBS-*g*-MA by strong absorbance of SEBS in the C—H stretching region. This unextracted SEBS-*g*-MA had to be chemically linked to the PET in order not to be extracted by the THF solvent. The chemical reaction between the anhydride and hydroxyl groups was also confirmed in PBT/ethylene-propylene elastomer grafted maleic an-

hydride (EPR-*g*-MA) blend by Cecere et al.⁴⁵ The *in situ* formation of a PET-co-TPEg copolymer should be responsible for the homogeneous dispersion of the TPEg.

Figure 4 shows the SEM fractographs of the impact-fractured surfaces of the PET/PETG (60/40) blend with 15 wt % of TPEg. Replacing the 40 wt % of PET with PETG did not change much of the topography of the impact-fractured surface, which corresponded with its low notched impact strength value. The fractured surfaces in both slow and fast crack growth regions exhibited the feature of brittleness. In addition, by comparing Figure 4(d–f) with Figure 3(d–f), it was seen that the dispersion quality of TPEg particles

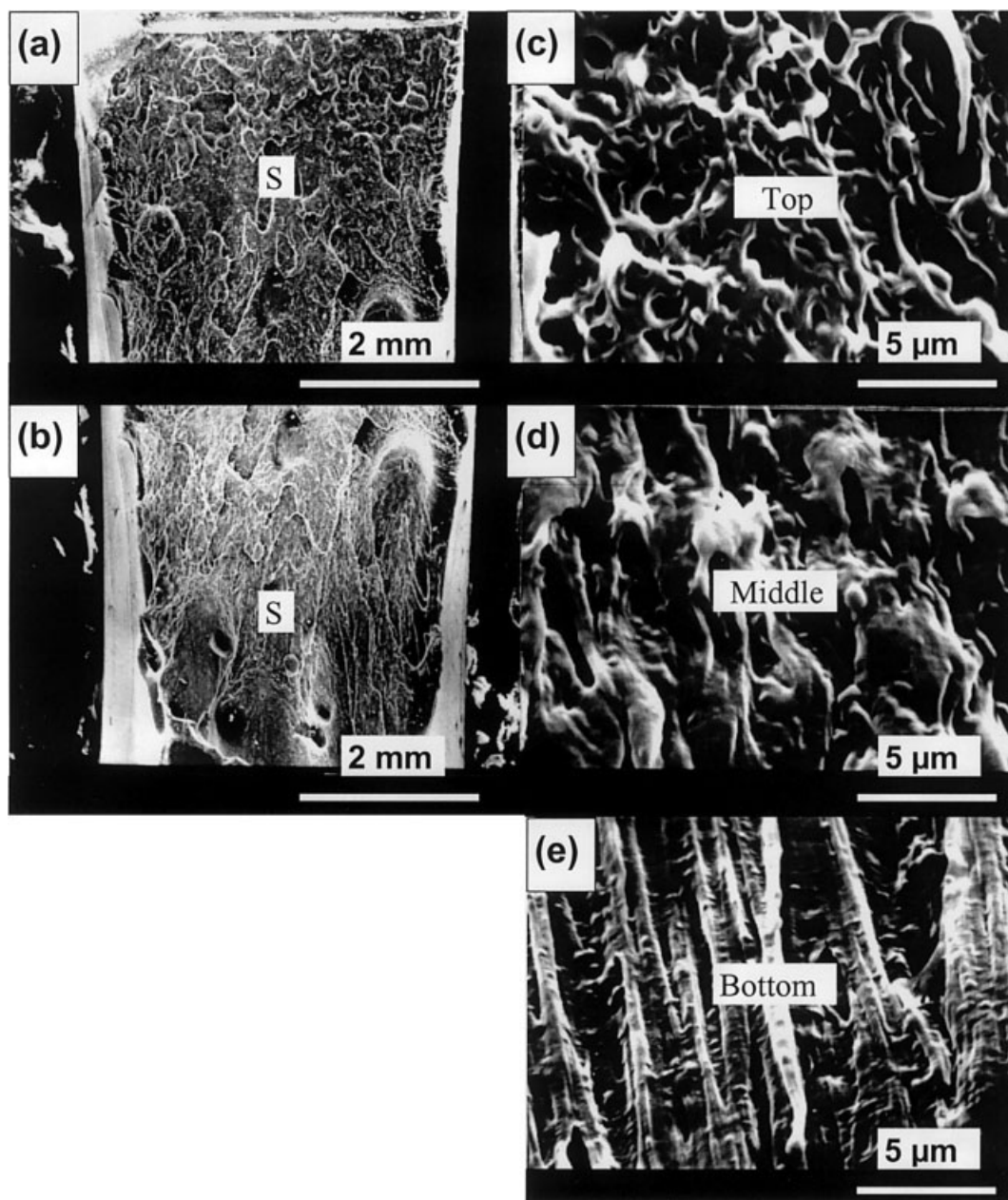


Figure 6 SEM photographs of impact-fractured surface of PETG/TPEg (85/15) blend under low (a and b) and high (c, d, and e) magnifications. The specimen did not break completely.

in the ternary blend was not affected by the replacing of PET with PETG, and was very similar in diameter and distribution to that in PET/TPEg (85/15) binary blend.

Corresponding to the jump of the notched impact-strength value when the PETG content exceeded PET content, however, the topography of the impact-fractured surface was essentially changed. Figure 5 shows the SEM fractographs of the impact-fractured surfaces of the PET/PETG (40/60) blend with 15 wt % of TPEg. It was interesting to note that the ternary blend was too tough to break completely under the severe notch impact testing. Besides, lateral contraction of the specimen sides and subsurface whitening were visible as

shown in the low magnification graphs of Figure 5(a,b), which were typical features of super-toughened polymer blends.⁴⁶ In the low magnification graphs, the area of the slow crack region was greatly enlarged [Fig. 5(a)] and the fast crack growth region exhibited parabolic markings rather than featherlike ones [Fig. 5(b)]. Each parabola contained a flaw at the focus, at which secondary fracture was initiated. At high magnification, both the slow and fast crack growth regions showed profuse cavitation and extensive matrix shear yielding. Now, it is generally believed that the shear yielding mechanism constitutes cavitation of the elastomer particles followed by shear yielding throughout the matrix.^{47–50} The cavitation of the elastomer parti-

cles explained the observed stress whitening as light scattering occurred which was enhanced by the holes enlarging. Cavitation is followed by the onset of shear yielding, because on cavitation in the elastomer particles the buildup of hydrostatic tension is locally relieved and the yield stress is lowered. After cavitation the constrained conditions, triaxial stresses, disappear and the matrix behaves as if it is under plane stress conditions. Shear yielding deformations occur more readily under a biaxial stress state rather than the craze-favoring triaxial state.⁴⁷ Although cavitation of the elastomer particles does involve energy absorption, the enhanced shear yielding of the matrix is the major energy absorbing mechanism.⁴⁷⁻⁵⁰ As the extensive cavitation and matrix shear yielding, TPEg dispersed phase was hardly recognized from Figure 5, and thus no diameter value of the TPEg particles in the ternary blend was given here.

When the PET was completely replaced with PETG, the matrix shear yielding of PETG/TPEg (85/15) blend was more extensive. Figure 6 shows the SEM fractographs of the impact-fractured surfaces of the PETG/TPEg (85/15) blend. The fracture surface was mainly occupied by the slow crack growth region with some parabolic markings caused by secondary cracks. The blend was not broken completely and showed obvious lateral contraction of the specimen sides. The top part adjacent to the notch root exhibited uniform and profuse cavitation and highly drawn matrix ligaments. The elongated cavitation and the extensive matrix plastic flow appeared in the middle part of the fracture surface. Compared to the bottom part of the PET/PETG (40/60) blend with 15 wt % TPEg [Fig. 5(e)], the bottom part of the PETG/TPEg (85/15) blend, as shown in Figure 6(e), showed more intensive matrix plastic flow and the matrix was stretched to be many parallel fibrils along the fracture direction.

CONCLUSIONS

The maleated thermoplastic elastomer (TPEg) was more effective in toughening PETG than PET, although the dispersion qualities of the TPEg particles in the PET and PETG matrices were very similar, revealed by the same average diameter of approximately 0.68 μm . 15 wt % of TPEg made PETG super-tough. However, the notched impact strength of PET was only increased 2-fold with 15 wt % of TPEg. It was believed that the presence of the second glycol, 1,4-cyclohexanedimethanol, incorporated in the PETG caused the molecular chain of aromatic polyester flexible and made the PETG easier to be toughened than PET.

At the fixed TPEg content of 15 wt %, replacing partial PET by PETG resulted in a sharp brittle-ductile transition when the PETG content exceeded PET content. Before the transition, PET/PETG blends were not toughened with the TPEg of 15 wt %, their notched

impact-strength values were very similar to that of the PET/TPEg (85/15) blend. After the transition, however, the PET/PETG blends with 15 wt % of TPEg, similar to the PETG/TPEg (85/15) binary blend, maintained a super-tough level with a notched impact strength of more than 10-fold.

The fracture morphologies of the PET/PETG blends with 15 wt % of TPEg exhibited that, when PETG content was lower than the PET content, the impact-fractured surface of the blends showed a small area of the slow crack growth region and numerous feather-like markings in the fast crack growth region, thus indicating a brittle failure mode. While the PETG content exceeded the PET content, the impact-fractured surfaces of the blends were dramatically changed. Massive cavitation and extensive matrix shear yielding were the main mechanisms of the impact energy dissipation upon impact testing.

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