

# Toughening of Recycled Poly(ethylene terephthalate)/Glass Fiber Blends with Ethylene-Butyl Acrylate-Glycidyl Methacrylate Copolymer and Maleic Anhydride Grafted Polyethylene-Octene Rubber

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**ABSTRACT:** The aim of this study was to improve the toughness of recycled poly(ethylene terephthalate) (PET)/glass fiber (GF) blends through the addition of ethylene-butyl acrylate-glycidyl methacrylate copolymer (EBAGMA) and maleic anhydride grafted polyethylene-octene (POE-g-MAH) individually. The morphology and mechanical properties of the ternary blend were also examined in this study. EBAGMA was more effective in toughening recycled PET/GF blends than POE-g-MAH; this resulted from its better compatibility with PET and stronger fiber/matrix bonding, as indicated by scanning electron microscopy images. The PET/GF/EBAGMA ternary blend had improved impact strength and well-balanced mechanical properties at a loading of 8 wt % EBAGMA.

The addition of POE-g-MAH weakened the fiber/matrix bonding due to more POE-g-MAH coated on the GF, which led to weakened impact strength, tensile strength, and flexural modulus. According to dynamic rheometer testing, the use of both EBAGMA and POE-g-MAH remarkably increased the melt storage modulus and dynamic viscosity. Differential scanning calorimetry analysis showed that the addition of EBAGMA lowered the crystallization rate of the PET/GF blend, whereas POE-g-MAH increased it. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2795–2801, 2008

**Key words:** blends; compatibility; impact resistance; polyesters; reinforcement

## INTRODUCTION

For many years, poly(ethylene terephthalate) (PET) has been used extensively to manufacture soft drink bottles because of its expected properties, such as excellent chemical resistance and barrier properties. Recently, the recycling of PET has attracted the interest of researchers in view of potential economic and environmental advantages. However, the molecular weight of recycled PET decreased, probably because of thermal, oxidative, and hydrolytic degradations in the presence of retained moisture, high temperature, and/or contaminants.<sup>1–4</sup> As a result, recycled PET exhibits a much lower melt viscosity and poorer mechanical properties than ordinary PET. This property deterioration may be compensated for by the addition of reinforcing fillers and toughening modifiers.

Some elastomeric modifiers, such as maleic anhydride grafted styrene-ethylene-butadiene-styrene triblock copolymer (MA-g-SEBS), glycidyl methacrylate (GMA) grafted styrene-ethylene-butadiene-styrene, maleic anhydride grafted polyethylene-octene (POE-g-MAH) rubber, and ethylene-GMA copolymer,

have often been used to improve the fracture toughness of PET.<sup>5–9</sup> However, the rubber toughening of polymers has usually resulted in a severe reduction in the tensile properties (i.e., tensile modulus and tensile strength). Studies have shown that PET-modified glass fibers (GFs) have improved tensile strength, flexural modulus, notched impact strength, and thermal stability values.<sup>10–12</sup> Therefore, it is supposed that PET/GF blends incorporated with rubber should have better toughness. However, Fung and Li<sup>13</sup> reported that the existence of MA-g-SEBS rubber in the GF/rubber/PET blends did not improve the notched impact strength, and the tensile properties were adversely affected.

It was reported that the addition of ethylene-butyl acrylate-glycidyl methacrylate copolymer (EBAGMA), an epoxide-containing rubber, could lead to remarkable increases in the impact strength and elongation at break of poly(butylene terephthalate)/polycarbonate blends.<sup>14</sup>

The aim of this study was to improve the toughness of recycled PET/GF blends through the addition of functionalized EBAGMA and POE-g-MAH individually and to study in detail the morphology, mechanical properties, and crystallization behavior of the ternary blend. The effects of these two rubbers on the tensile strength, flexural modulus, Izod

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notched impact strength, and rheological behavior of PET/GF/rubber ternary blends were compared. The crystallization behavior of the blends was analyzed by differential scanning calorimetry (DSC). The morphology of the blends was characterized by scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

The recycled PET pellets, with an intrinsic viscosity of 0.65 dL/g, were purchased from Shenzhen Fushida Plastics Limited Co. (Shenzhen, China). First, the soft drink bottles were collected, cleaned, and milled; subsequently, granulates were obtained by extrusion with a single extruder at 260°C. EBAGMA (Elvaloy PTW), containing 5 wt % GMA, and POE-g-MAH (Fusabond N MN-493D), containing 0.5 wt % maleic anhydride, were supplied by Dupont. E-glass fibers were provided by Nanjing Fiberglass Research & Design Institute (Nanjing, China). The amine silane coupling agent was first allowed to hydrolyze into silanol in emulsion and was subsequently coated on the surface of the GFs. After drying, the silane-treated GFs were obtained.

### Blending

PET was dried at 120°C *in vacuo* for 4 h before blending. A corotating twin-screw extruder (Werner & Pfleiderer ZSK-25, Niederbieger, Germany) was used to blend the recycled PET pellets with the GFs (30 wt %) and toughening agents. In the extrusion process, barrel temperatures were set at 255°C, and the practical melt temperature was about 265°C. The extrudate was cooled in a water bath, pelletized, and dried in an air oven for 4 h at 80°C. Specimens were prepared via a plastic injection-molding machine (HTB125, China) for the testing of their tensile (ISO R527, thickness = 4 mm), flexural (ISO 178, thickness = 4 mm), and impact (ISO 180, thickness = 4 mm) properties. The barrel temperature for injection molding was 280°C, and the mold temperature was 80°C. The compositions for all of the blends are listed in Table I.

### Testing and characterization

#### Mechanical properties

The tensile and flexural tests were carried out at room temperature with an Instron 4466 testing machine (Norwood, MA) at speeds of 50 and 2 mm/min, respectively. The Izod impact test was conducted on a CEAST impact machine (Charlotte, NC). The notches (depth = 2.54 mm, mean radius = 0.25 mm) for the impact test were cut at least 24 h before the test.

**TABLE I**  
Compositions of All of the Blends

Sample	PET	EBAGMA	POE-g-MAH	GF
0	70	—	—	30
A1	66	4	—	30
A2	62	8	—	30
A3	58	12	—	30
A4	54	16	—	30
B1	66	—	4	30
B2	62	—	8	30
B3	58	—	12	30
B4	54	—	16	30

### Dynamic rheology analysis

The sample was tested on a Bohlin VOR-HTC rheometer with parallel plates (diameter = 25 mm) (Malvern, Worcestershire, UK) at 265°C in nitrogen. The gap between the plates was 1.0 mm. The sample was dried *in vacuo* at 120°C for 4 h before testing. The sample was heated to 265°C and maintained at that temperature until thermal equilibrium was established between the plate and the melt. The temperature of the sample was measured with a thermocouple probe located in the center of the top plate.

### Crystal behavior

The crystal behavior of the blend was tested on a PerkinElmer DSC (Pyris 1) (Waltham, MA). The samples were first heated at a rate of 20°C/min from room temperature to 300°C, maintained for 2 min to remove the thermal history, and then cooled at a rate of 10°C/min to 100°C to obtain the crystallization temperature ( $T_c$ ). Crystallinity was estimated with the following equation:

$$\text{Crystalline degree} = \Delta H_C / \Delta H^\circ$$

where  $\Delta H_C$  is the exothermic heat caused by the PET crystallization.  $\Delta H^\circ$  is the fusion heat of fully crystallized PET, and the value of 117.6 J/g was adopted.<sup>15</sup>  $\Delta H_C$  values were normalized by the PET weight percentage to obtain the crystallinity. The half-value width of the crystallization peak ( $\Delta T$ ) was determined from these exotherms.

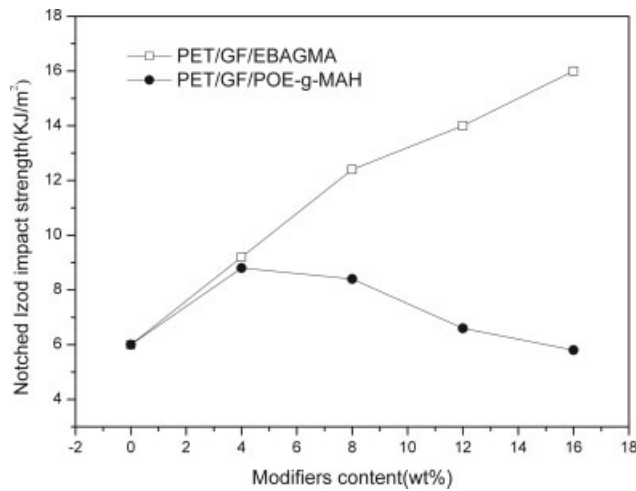
### Morphology

The impact-fractured surfaces of the samples were observed with a scanning electron microscope (FEI XL-30) (Hillsboro, OR) after they were coated with gold.

## RESULTS AND DISCUSSION

### Mechanical properties

Figure 1 shows the curves of the notched impact strength versus the modifier content for the PET/

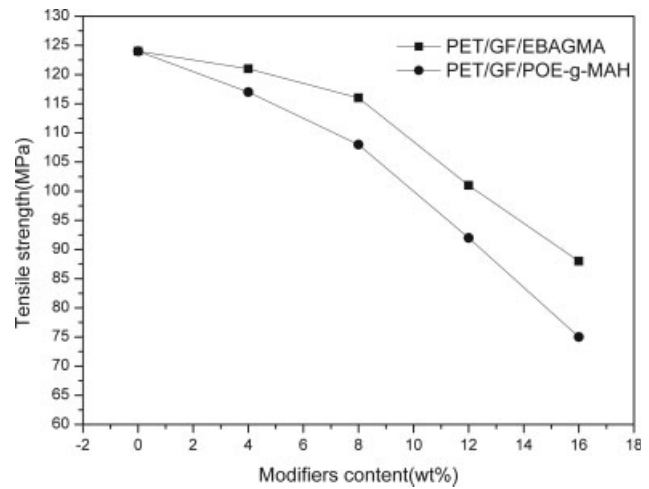


**Figure 1** Curves of the notched impact strength versus the modifier content for the PET/GF/EBAGMA and PET/GF/POE-g-MAH blends.

GF/EBAGMA and PET/GF/POE-g-MAH blends. As shown in Figure 1, the impact strength of the PET/GF blend was as low as  $6.0 \text{ kJ/m}^2$ , and it improved after EBAGMA or POE-g-MAH was introduced. The impact strength of the PET/GF/EBAGMA blend increased with increasing EBAGMA, whereas the impact strength of PET/GF/POE-g-MAH decreased with increasing POE-g-MAH after a maximum value at a loading of 4%. As the addition of modifier increased to 16 wt % POE-g-MAH, the impact strength of the PET/GF/EBAGMA blend increased to  $16 \text{ KJ/m}^2$ , whereas at the same content of modifier, that of PET/GF/POE-g-MAH dropped to  $5.8 \text{ kJ/m}^2$ , which was even lower than that of the PET/GF binary blends. We concluded that EBAGMA showed much better toughening effects for the PET/GF blend than did POE-g-MAH.

Figure 2 shows the tensile strength versus the modifier content for the PET/GF/EBAGMA and PET/GF/POE-g-MAH blends. Similar to common rubber-toughened plastics, the tensile strength of both ternary blends decreased with increasing modifier content. When the loading of the modifier was lower than 8%, the tensile strength of the two blends showed just a slight drop and, thereafter, decreased drastically with more modifier. The PET/GF/EBAGMA blends presented higher tensile strengths than the PET/GF/POE-g-MAH blends at the same modifier content.

A balance of toughness and stiffness for toughened blends are required for structural materials. Figure 3 reveals the relationship of the notched Izod impact strength and the flexural modulus of the PET/GF/EBAGMA and PET/GF/POE-g-MAH blends. The PET/GF/EBAGMA blends exhibited a higher impact strength in the case of the same required flexural modulus and a higher flexural modulus in

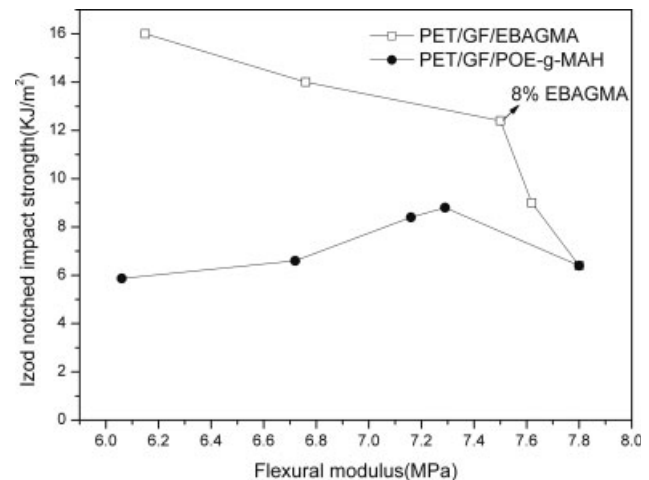


**Figure 2** Plots of the tensile strength versus the modifier content for the PET/GF/EBAGMA and PET/GF/POE-g-MAH blends.

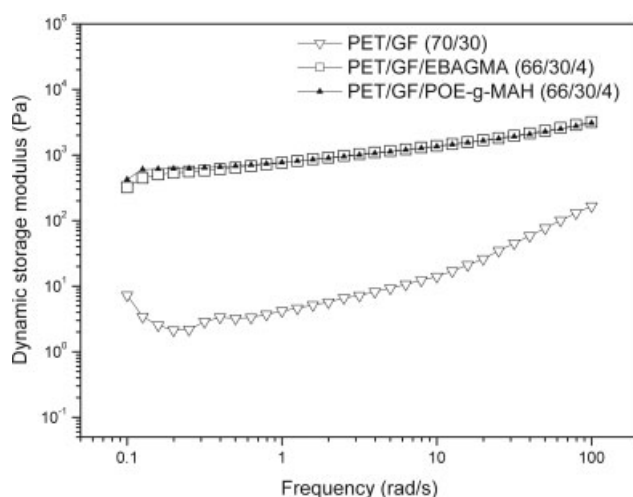
the case of the same required impact strength, compared with the PET/GF/POE-g-MAH blend. Therefore, the PET/GF/EBAGMA blend reached a better balance of toughness and flexural modulus than the PET/GF/POE-g-MAH blend. This again proved that EBAGMA showed better modifying effects in the PET/GF/rubber ternary blends than POE-g-MAH. It is here recommended for PET/GF/EBAGMA ternary composites that a EBAGMA content of 8% can give the best balanced mechanical properties.

### Dynamic rheological behavior analysis

The dynamic rheology reflects the viscoelastic properties of a polymer during deformation. It is an



**Figure 3** Relation of the notched Izod impact strength and flexural modulus of the PET/GF/EBAGMA and PET/GF/POE-g-MAH blends.

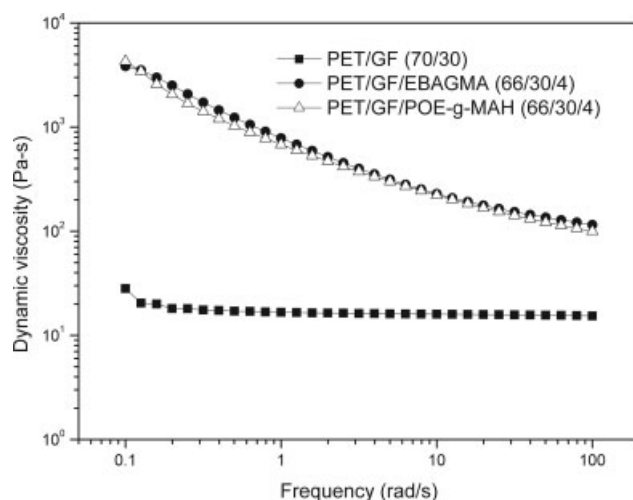


**Figure 4** Relation of the dynamic storage modulus and frequency for the PET/GF (70/30), PET/GF/EBAGMA (66/30/4), and PET/GF/POE-g-MAH (66/30/4) blends.

effective method for investigating the microstructure of multicomponent polymer blends.<sup>16</sup>

Figure 4 shows the relationship of the dynamic storage modulus and frequency for the PET/GF (70/30), PET/GF/EBAGMA (66/30/4), and PET/GF/POE-g-MAH (66/30/4) blends. The addition of both EBAGMA and POE-g-MAH remarkably increased the melt dynamic storage modulus of the PET/GF blend. The dynamic storage modulus of both PET/GF/EBAGMA and PET/GF/POE-g-MAH slightly increased with the rising frequency. The dynamic storage modulus of the blend was increased more than 10 times by the addition of 4 wt % EBAGMA or POE-g-MAH.

Figure 5 shows the relationship of the dynamic viscosity and frequency for the PET/GF (70/30),



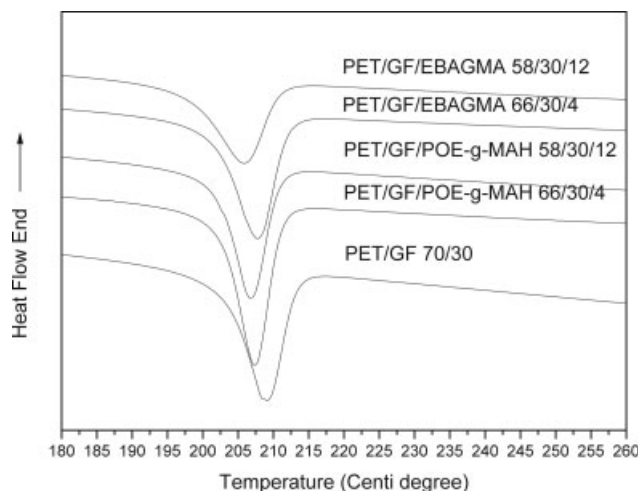
**Figure 5** Relation of the dynamic viscosity and frequency for the PET/GF (70/30), PET/GF/EBAGMA (66/30/4), and PET/GF/POE-g-MAH (66/30/4) blends.

PET/GF/EBAGMA (66/30/4), and PET/GF/POE-g-MAH (66/30/4) blends. As shown in Figure 5, the melt of the PET/GF (70/30) blend retained a stable and low dynamic viscosity at the different frequency, whereas the melts of the PET/GF/EBAGMA and PET/GF/POE-g-MAH blends showed gradually decreased viscosity with increasing frequency. Furthermore, there was no difference in the dynamic viscosity between the previous two ternary blends.

Both EBAGMA and POE-g-MAH are rubbery with high viscosity and good elasticity values, so the introduction of rubber improved the melt strength and dynamic viscosity of the PET/GF blend. As reported by Busse,<sup>17</sup> the better the melt elasticity of the polymer is, the higher the melt strength is.

### DSC analysis

Figure 6 shows the DSC cooling thermograms curves of the PET/GF, PET/GF/EBAGMA, and PET/GF/POE-g-MAH blends, and the resulting parameters are shown in Table II. As shown in Table II, the addition of EBAGMA and POE-g-MAH showed the opposite effects on the crystallization behavior of the PET/GF blend. Compared with the PET/GF blend, when the addition level of EBAGMA increased, the  $T_c$ ,  $\Delta H_C$ , and crystallization degree of the PET/GF/EBAGMA blend decreased, but  $\Delta T$  was widened, which indicated that the crystallization of the PET/GF blend was weakened. However, for the PET/GF/POE-g-MAH blends,  $\Delta H_C$  and the crystallization degree increased, but  $\Delta T$  became narrow, which demonstrated that the introduction of POE-g-MAH promoted the crystallization of the PET/GF blend. A similar result was found in the PBT/PC/EBAGMA and PBT/PC/POE blends by Bai.<sup>14</sup> In that research, it was reported that EBAGMA could inter-



**Figure 6** DSC cooling thermograms curves of the PET/GF, PET/GF/POE-g-MAH, and PET/GF/EBAGMA blends.

**TABLE II**  
**DSC Results for the PET/GF, PET/GF/POE-g-MAH, and PET/GF/EBAGMA Blends**

Content of rubber	$T_c$ (°C)	$\Delta T$ (°C)	$\Delta H_C$ (J/g)	Crystalline degree (%)
None	209.0	10.17	42.04	35.70
4% EBAGMA	207.7	10.44	41.67	35.46
8% EBAGMA	208.1	11.73	40.32	34.32
12% EBAGMA	205.9	13.22	37.93	32.28
4% POE-g-MAH	207.3	8.61	43.33	36.88
8% POE-g-MAH	207.8	9.12	46.13	39.26
12% POE-g-MAH	206.9	8.95	45.17	38.44

ferre with PBT crystallization and cause a greater fraction of amorphous PBT in PBT/PC/EBAGMA blends, whereas POE could promote the crystallization of PBT in PBT/PC/POE blends. The two rubbers' different effects on the crystallization behavior was mainly attributed to the better compatibility of EBAGMA with PET than with POE-g-MAH.

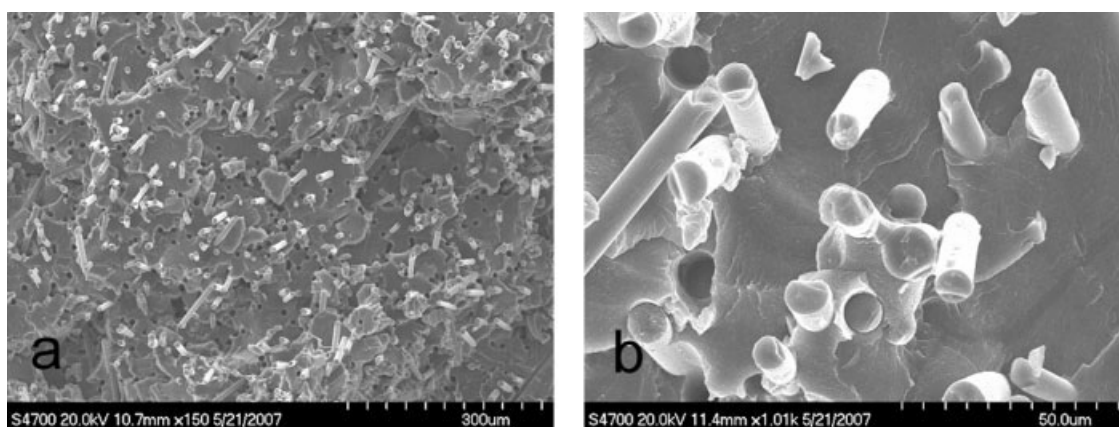
### Morphology

The mechanical properties of reinforced materials such as PET/GF are closely related to the intrinsic characteristics of both the matrix and the fiber and to the nature of the fiber/matrix interface.<sup>10,18,19</sup> The latter should allow the efficient transfer of mechanical stress within the blended material.

Figure 7(a) displays the overall SEM micrographs of the impact-fractured surfaces of the recycled PET/GF binary blends. The fractured surface was flat, which was evidence of brittle break. Also, many holes were left because of the pulled-out GFs detached from the matrix under impact loading. This may have dissipated part of the energy and led to the improvement of impact strength. High-magnification SEM micrographs for the pulled-out fibers on the impact-fractured surfaces are shown in Figure 7(b). As shown in Figure 7(b), although the fiber surface was relatively smooth, some traces of polymers

could be seen attaching to the fiber surface, and no gap around the fibers was observed. This indicated that the GF was strongly bonded to the PET matrix, which resulted from the reactivity of the end carboxyl group of PET and the amine group of the silane coupling agent coated on the GFs. Even though the interface of fibers and matrix was good, the recycled PET/GF appeared to be brittle due to the very poor toughness of the recycled PET matrix.

Figures 8 and 9 show the SEM micrographs of the PET/GF/EBAGMA (66/30/4) and PET/GF/POE-g-MAH (66/30/4) blends. As shown, although the PET/rubber matrix still fractured in a brittle manner, more "steps" were formed on the fracture surfaces. This indicated that the incorporation of 4 wt % EBAGMA or POE-g-MAH improved the toughness of the PET/GF blends, as shown previously in Figure 1. By comparing Figure 8 with Figure 9, we concluded that EBAGMA showed better compatibility with the PET matrix than POE-g-MAH, in that some spherical traces were left due to the detachment of the dispersed POE-g-MAH from the matrix, as shown in Figure 9(b). Two main reasons could have accounted for this. On one hand, the epoxy group included in EBAGMA could have reacted with the end carboxyl of PET and the amine group of the silane coupling agent coated on the GFs, whereas maleic anhydride of POE-g-MAH may have preferred



**Figure 7** SEM micrographs of the impact-fractured surfaces of the recycled PET/GF binary blends.

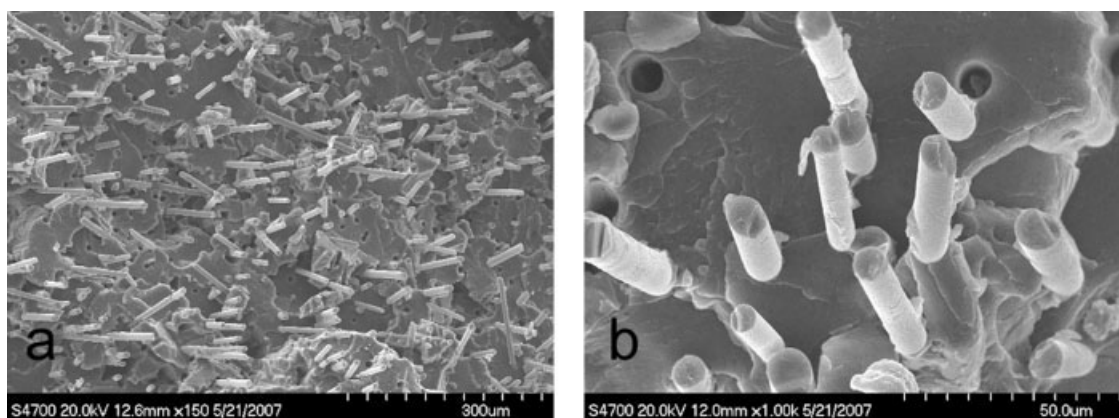


Figure 8 SEM micrographs of the PET/GF/EBAGMA (66/30/4) blend.

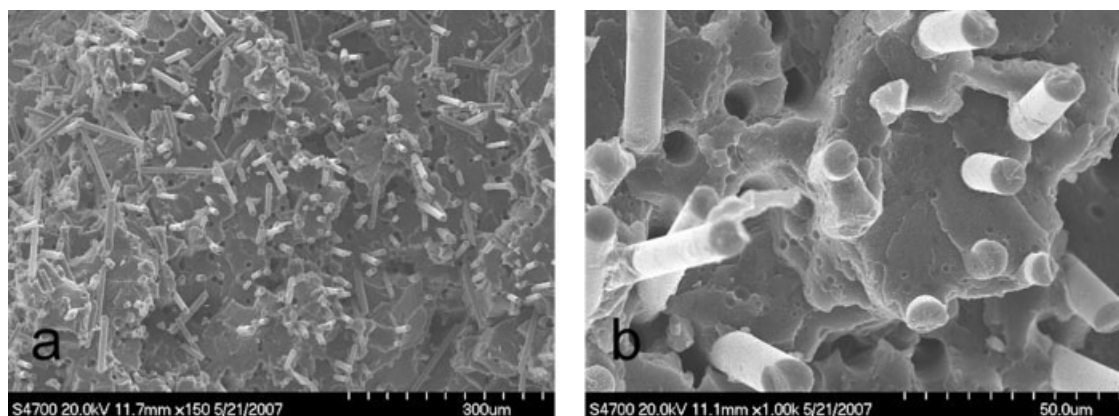


Figure 9 SEM micrographs of the PET/GF/POE-g-MAH (66/30/4) blend.

to react with the amine group on the GFs. On the other hand, EBAGMA had a stronger molecular polarity than POE-g-MAH, which contained only 0.5 wt % MAH.

Figure 10 shows the SEM micrographs of the PET/GF/EBAGMA (58/30/12) blend. From the micrographs of the impact-fractured surface, an

obvious ductile break was observed around some pulled-out GFs, as mentioned earlier. Moreover, some undetached GFs were found standing on the impact-fractured surface, which further demonstrated that the interfacial shear strength between the GF and PET/rubber matrix was strong enough to bear a larger impact loading. Therefore, the PET/

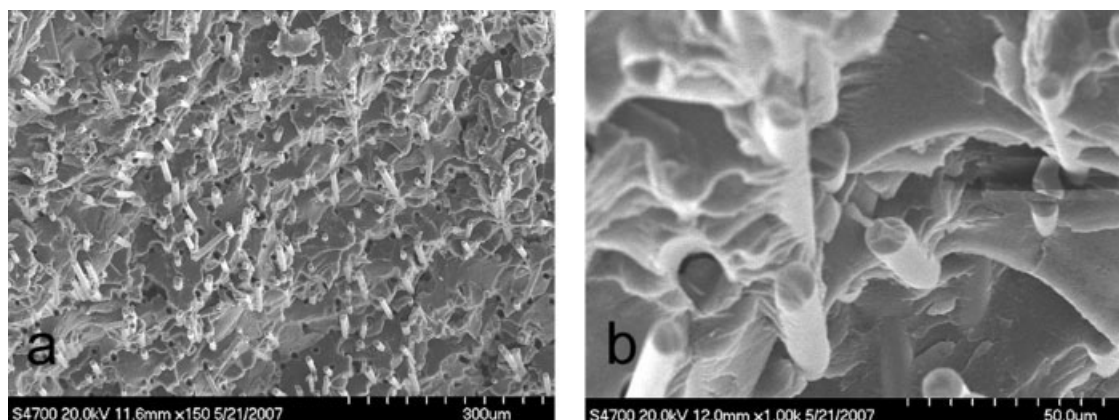


Figure 10 SEM micrographs of the PET/GF/EBAGMA (52/30/12) blend.

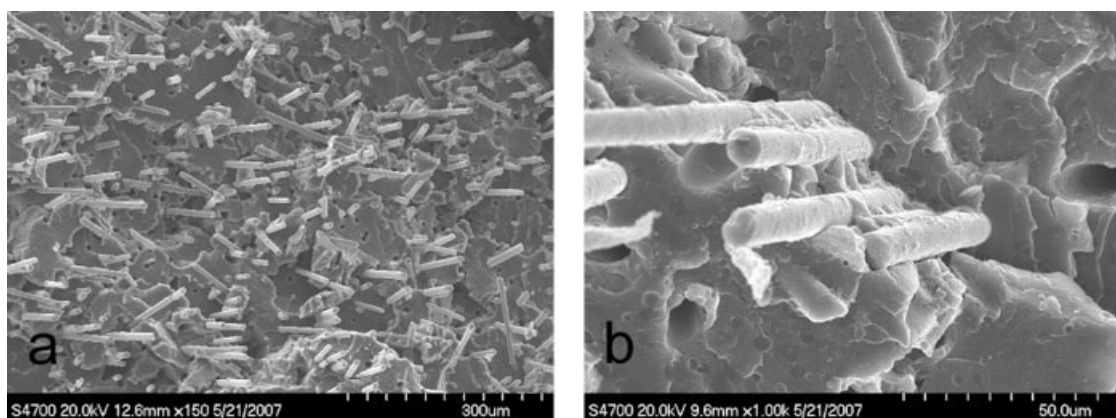


Figure 11 SEM micrographs of the PET/GF/POE-g-MAH (52/30/12) blend.

GF blend was effectively toughened by the increasing content of EBAGMA.

Figure 11 shows the SEM micrographs of the PET/GF/POE-g-MAH (58/30/12) blend. The overall micrograph of the impact-fractured surfaces [Fig. 11(a)] showed an obvious brittle break. A thicker coating was found on the pulled-out fibers [Fig. 11(b)], compared with those observed in Figure 9(b). Some similar spherical traces were also observed. As discussed earlier, in addition to the poor compatibility of POE-g-MAH and PET, POE-g-MAH was inclined to adhere to the GFs because of the reactivity of the maleic anhydride of POE-g-MAH and the amine group of the silane coupling agent coated on the GFs, which resulted in more POE-g-MAH coated on the GFs with increasing POE-g-MAH. Meanwhile, many fibers were found lying down on the impact-fractured surface, and debonding cracks were formed between the fibers and matrix. This indicated that the fiber/POE-g-MAH/PET bonding was weakened, even worse than that of PET/GF when more POE-g-MAH was incorporated. As a result, the stress could not be effectively transferred on the fibers, which led to poor impact resistance. On the other hand, the addition of POE-g-MAH could improve the impact strength of the PET matrix to some degree. These two competitive effects determined the toughness of the PET/GF/POE-g-MAH blend. The higher the loading amount of POE-g-MAH was, the worse the interface of the fiber/matrix was and the worse the impact strength was.

## CONCLUSIONS

Both EBAGMA and POE-g-MAH were evaluated for toughening recycled PET/GF blends. EBAGMA was more effective in toughening recycled PET/GF blends than POE-g-MAH, which resulted from its better compatibility with PET and the stronger fiber/matrix bonding. As a result, the PET/

EBAGMA/GF ternary blend possessed improved impact strength and well-balanced mechanical properties at a loading of 8 wt % EBAGMA. The addition of EBAGMA slowed down the crystallization of the PET/GF blend, whereas POE-g-MAH promoted the crystallization of the PET/GF blend and led to an increase in the crystallization degree and a decrease in  $\Delta T$ . Dynamic rheological behavior analysis showed that both EBAGMA and POE-g-MAH remarkably increased the melt storage modulus and dynamic viscosity of the PET/GF blends.

## References

1. La Mantia, F. P.; Vinci, M. *Polym Degrad Stab* 1994, 45, 121.
2. Tsiourvas, D.; Tsartolia, E.; Stassinopoulos, A.; Barrell, M.; Bontemps, J. *Adv Polym Tech* 1995, 14, 227.
3. Milana, M. R.; Denaro, M.; Arrivabene, L.; Maggio, A.; Gramiccioni, L. *Food Addit Contam* 1998, 15, 355.
4. Paci, M.; La Mantia, F. P. *Polym Degrad Stab* 1998, 61, 417.
5. Yu, Z. Z.; Yang, M. S.; Dai, S. C.; Mai, Y. W. *J Appl Polym Sci* 2004, 93, 1462.
6. Tanrattanakul, V.; Hiltner, A.; Baer, E.; Perkins, W. G.; Massey, F. L. *Polymer* 1997, 38, 2191.
7. Tanrattanakul, V.; Hiltner, A.; Baer, E.; Perkins, W. G.; Massey, F. L. *Polymer* 1997, 38, 4117.
8. Pawlak, A.; Perkins, W. G.; Massey, F. L.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 1999, 73, 203.
9. Tanrattanakul, V.; Perkins, W. G.; Massey, F. L.; Moet, A.; Hiltner, A.; Baer, E. *J Mater Sci* 1997, 32, 4749.
10. Ronkay, F.; Czigany, T. *Polym Adv Technol* 2006, 17, 830.
11. Quintanilla, L.; Alonso, M.; Rodriguez-Cabello, J. C.; Pastor, J. M. *J Appl Polym Sci* 1996, 59, 769.
12. Yoshihara, N. *J Polym Eng* 2006, 26, 547.
13. Fung, K. L.; Li, R. K. Y. *J Mater Sci* 2006, 41, 6123.
14. Bai, H. Y.; Zhang, Y.; Zhang, Y. X.; Zhang, X. F.; Zhou, W. *J Appl Polym Sci* 2006, 101, 54.
15. Mehta, A.; Gaur, U.; Wunderlich, B. *J Polym Sci Polym Phys Ed* 1978, 16, 289.
16. Utracki, L. A. *Polymer Alloys and Blends*; Hanser: New York, 1981; p 131.
17. Busse, W. F. *J Polym Sci Part A-2: Polym Phys* 1967, 5, 249.
18. Bergeret, A.; Bozec, M. P.; Quantin, J. C.; Crespy, A. *Polym Compos* 2004, 25, 12.
19. Frenzel, H.; Bunzel, U.; Haessler, R.; Pompe, G. *Adhes Sci Technol* 2000, 14, 651.