

Influence of heat treatment on toughening of polyethylene-octene copolymer (POE)/poly(ethylene terephthalate) (PET) blends

CHEN JUN, YANG WEI, LIU ZHENGYING, HUANG RUI*

College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, Sichuan, People's Republic of China
E-mail: chen_jun_cj@163.com

Poly(ethylene terephthalate) (PET) is a low cost, high-performance thermoplastic. Its major use is in fabrics and soft drink bottles, due to its excellent chemical resistance, good optical and barrier properties. However, the most serious shortcoming of this material is its very low impact strength. Rubber toughening without seriously compromising other properties has developed impact-modified versions of these thermoplastics. In the quest of toughening engineering thermoplastics, polycarbonate and polyamides, especially nylon6, 6 and nylon6, have received more attention than polyesters. Furthermore, most of the studies of polyesters have focused on poly(butylene terephthalate) (PBT) rather than on PET [1, 2]. It can be anticipated that the same general aspects of toughening will also apply. However, the structural difference between both materials will inevitably result in differences regarding their overall physical behaviors, i.e., processing temperatures, compatibilization efficiency, crystallization kinetics, and it is of interest to examine specifically the issue in toughening PET.

The addition of elastomers results in an improved overall toughness, provided that the rubber phase is finely dispersed, on the submicron level, in the PET matrix. Because of the high interfacial tension between the polar polyesters and the apolar elastomers, the use of reactive compatibilization becomes necessary in order to obtain the desired dispersed phase morphology. In the literatures, different types of elastomers and functional groups have been explored. Ethylene-propylene rubber grafted with maleic anhydride (EPR-g-MA) and ethylene-propylene-diene rubber grafted with maleic anhydride (EPDM-g-MA) are two of the most frequently added components [3, 4]. Compared with the conventional polyolefin elastomer EPDM and EPR, polyethylene-octene copolymer (POE) as a novel polyolefin elastomer obtained using metallocene catalysts has a well-defined structure, a homogeneous comonomer distribution and narrow molecular weight distribution. The incorporation of the comonomer significantly decreases the degree of crystallinity, and highly branched chains may promote molecular segregation, both of which influence the thermal and mechanical properties of the ethylene copolymers [5]. The effect of the addition of POE grafted by maleic anhydride (POE-g-MA) on the mechanical properties of

polar polymer has been reported previously [6, 7]. In this report, preliminary results on the toughening effectiveness of PET by POE-g-MA are presented; in addition, a comparative fundamental study was performed regarding the notched impact strength and tensile strength of PET/POE-g-MA blends, before and after heat treatment of samples.

The PET used is a condensation polymer produced from dimethyl terephthalate and ethylene glycol with a bulk density of 1400 kg/m³ and an intrinsic viscosity of 0.08 m³/kg, obtained from the Wuliangye group Push Company under the name PET resin Wp-56151.

To improve the impact strength of the PET, the blends were prepared containing polyester, and the maleic anhydride grafted ethylene-octene-copolymer (POE-g-MA) contained 0.85 wt% MA, which was supplied by HuaDu Company under the name MOE-800.

The PET was dried at 120 °C for 24 h and the POE-g-MA dried at 60 °C for 24 h before melt blending in a corotating twin-screw extruder, with the temperature profile ranging from 200 to 270 °C. The screw rotation was usually 100 rpm, unless stated otherwise. The melt blends were extruded through a 3 mm die, quenched in water and pelletized. The pellets were dried at 120 °C for 24 h and stored in a desiccator.

The pellets were injection molded into dumbbell-shaped specimens (used for the tensile test) and bar-shaped specimens (used for impact test) on an injection molding machine with the temperature of barrel, nozzle, mould of 275, 270 and 25 °C respectively, and the injection pressure and back pressure were 56 and 1 MPa.

The tensile strength of dumbbell samples was evaluated following ASTM D638 using a typical testing machine at a deformation rate of 50 mm/min. An Izod impact tester was used to evaluate the Izod impact resistance of V-notched samples following ASTM D256 method. One half of the specimens were heat treated at 120 °C for 3 h while the others were not, to find out the influence of heat treatment on the toughening of PET/POE blends, and all the specimens were placed at 23 °C and 50% relative humidity for one day before testing. At least five specimens were tested in each case and the average value is reported in this paper.

The toughening ability of the elastomeric dispersed phases is evaluated by notched impact strength

*Author to whom all correspondence should be addressed.

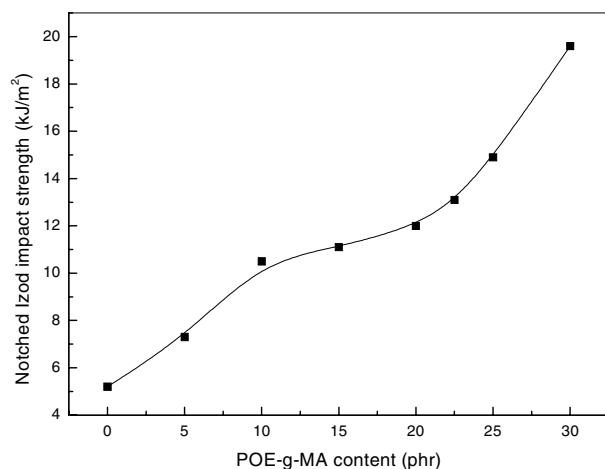


Figure 1 Influence of POE-g-MA content on notched Izod impact strength.

measurements at room temperature. The impact strength of pure semicrystalline PET was established at 4.9 kJ/m². The sample clearly fractured in a brittle manner, displaying only a microscopically sized stress-whitened zone and a complete separation of the sample halves.

The non-compatible polyester/POE blends do not display any improvement of the impact strength. This is caused by the high degree of incompatibility between both blends components, leading to large particle sizes without any significant interfacial adhesion [8]. However, the maleic anhydride grafted POE (POE-g-MA) can improve the notched impact strength of PET. Fig. 1 shows plot of notched Izod impact strength versus toughener content for the PET/POE-g-MA blending system. It can be seen that the impact strength increases gradually with increasing POE-g-MA content. This is attributed to the maleic anhydride group reacting with the terminal carboxyl group or hydroxyl group of the PET chain at high temperature. In addition, the increase of polarity, which is induced by grafting maleic anhydride, reduces the interfacial tension between POE and PET.

Although POE-g-MA can enhance the notched impact strength of PET, the blends still fail in a brittle manner, even if the modified elastomer concentration in the blend is 30 phr, the transition from brittle to ductile still does not occur. After heat-treating these samples, it is observed that the impact strength of blends changes astonishingly. The experiment, which was repeated several times, confirmed the results were not an occasional phenomenon. The effects of the heat treatment on notched Izod impact strength of PET/POE-g-MA blends are shown in Fig. 2. After heat treatment, the impact strength of each sample increased to different extents, especially, when the POE-g-MA concentration in the blend was 22.5 phr, the impact resistance increased significantly and the blends broke in a ductile manner. At this concentration, the impact strength is up to 32.7 kJ/m². This blend composition displays very high impact strength and a ductile fracture mode, exhibiting extensive stress whitening. For the 100/30 PET/POE-g-MA blends, the impact resistance

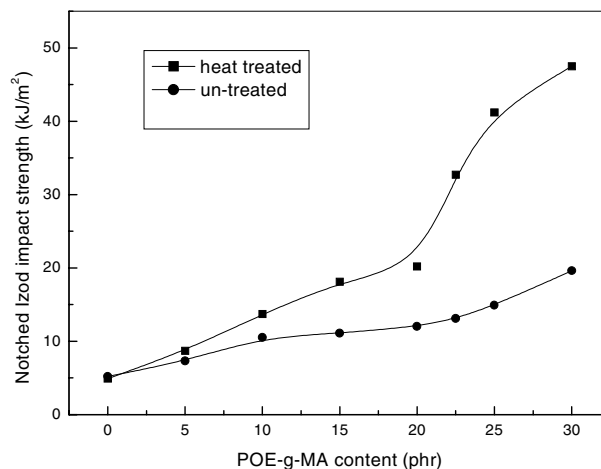


Figure 2 Effects of the heat treatment on notched Izod impact strength of PET/POE-g-MA blends.

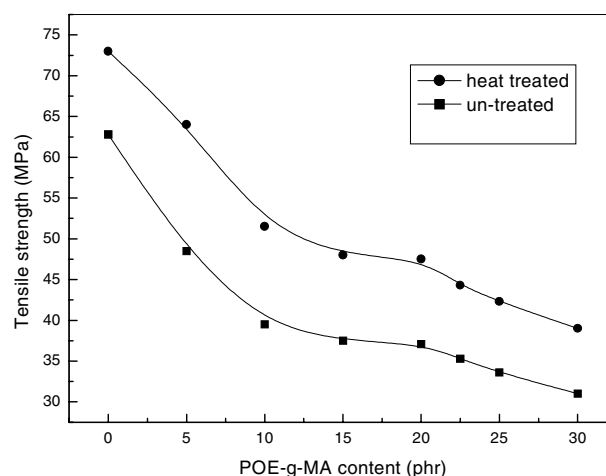


Figure 3 Effects of the heat treatment on tensile strength of PET/POE-g-MA blends.

increases approximately 9 times and 2.5 times with respect to that of pure PET and the same concentration un-annealed samples, respectively.

Fig. 3 demonstrates the tensile strength of the PET/POE-g-MA blends, annealed and un-annealed, respectively. The tensile strength is found to decrease with increasing dispersed phase concentration, but still remains high due to the semicrystalline nature of the PET matrix. This result is expected, since the dispersed phase (POE-g-MA) creates stress concentrations and forces the material to yield at small strain values. Moreover, as the decrement in tensile strength is monotonic, it is likely that a good dispersion of elastomeric particles in the matrix is obtained. However, after annealing at the 120 °C, the tensile strength of all dumbbell specimens would be improved too. The tensile strength for each group of samples increases about 10 MPa on average, and the biggest extent of increase is up to 32%.

In this study we have shown that the maleic anhydride grafting of POE has good compatibility with PET, and the use of POE-g-MA can improve notched Izod impact strength of PET/POE blends. In addition, the heat treatment can remarkably increase not only the tensile strength but also notched impact strength of PET/POE-g-MA blends. A maximum in the impact strength of the PET/POE-g-MA is observed when the modified

elastomer concentration in the blend is 30 phr in our experiment. At this concentration, the notched Izod impact strength increases approximately 9 times and 2.5 times compared to that of pure PET and same concentration un-annealed samples, respectively; thus the blend is identified as “super tough”.

Future studies may focus on the toughening mechanism of PET/POE-g-MA blends by heat-treating; also whether the similar phenomenon can be observed in other polar polymers and other elastomer systems should be studied.

References

1. W. HALE, L. A. PESSAN, H. KESKKULA and D. R. PAUL, *Polymer* **40** (1999) 4237.

2. H. KANAI, V. SULLIVAN and A. AUERBACH, *J. Appl. Polym. Sci.* **54** (1994) 527.
3. S. WU, *Polymer* **26** (1985) 1855.
4. M. PENCO, M. A. PASTORINO, E. OCHIELLO, F. GARBASSI, R. BRAQLIA and G. GIANNOTTA, *J. Appl. Polym. Sci.* **57** (1995) 329.
5. A. G. SIMANKE, G. B. GALLAND, R. S. MAULER, L. FREITAS, A. H. JOAO and R. QUIJADA, *Polymer* **40** (1999) 5489.
6. Q. F. LI, D. G. KIM, D. Z. WU, K. LU and R. G. JIN, *Polym. Eng. Sci.* **41** (2001) 2155.
7. Z. Z. YU, Y. C. OU and G. H. HU, *J. Appl. Polym. Sci.* **69** (1998) 1711.
8. H. W. TAI, R. G. JIN and L. C. ZHANG, *J. Hebei Univ. Tech.* **28** (1999) 29.

Received 24 July

and accepted 16 December 2003