

Synergistic Enhancement in Tensile Strength and Ductility of ABS by Using Recycled PETG Plastic

Bo Li, Xinlan Zhang, Qin Zhang, Feng Chen, Qiang Fu

Department of Polymer Science and Materials, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China

Received 8 June 2008; accepted 4 January 2009

DOI 10.1002/app.30002

Published online 2 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Acrylonitrile-butadiene-styrene (ABS)/poly(ethylene glycol-*co*-cyclohexane-1,4-dimethanol terephthalate) (PETG) blends with various ratios at three different processing temperatures were prepared. A significant synergistic enhancement in tensile strength and ductility for a wide range of compositions was achieved. Phase morphology with droplets, fibrils, and co-continuity was obtained, depending on the composition and processing temperature. Changes of the phase domain sizes and the composition range of co-continuity were found with the change of processing temperature and could be explained by temperature-induced coalescence effects. The synergism and

toughening mechanism were discussed based on the temperature-morphology-property relationships. Since the PETG used is a recycled plastic from the waste films and plates, our work provides a new and inexpensive means for the modification of ABS with high mechanical properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1207–1215, 2009

Key words: acrylonitrile-butadiene-styrene (ABS); poly(ethylene glycol-*co*-cyclohexane-1,4-dimethanol terephthalate) (PETG); mechanical properties; phase morphology; mixing temperature

INTRODUCTION

The improvements of tensile strength and ductility for polymer blends have attracted much attention both in academic study and industrial application. Adding rubbers or the second components containing rubbers to improve the toughness of blends is the most frequent way. Unfortunately, rubber toughening often causes a noticeable reduction in modulus and tensile strength. Consequently, due to the above consideration, another approach to obtain blends combining both high impact resistance and stiffness has been proposed: that is, so-called rigid-rigid polymer toughening in which a ductile polymer is toughened by using rigid organic particles instead of rubber. In this way, a synergistic enhancement in tensile strength, ductility, and impact resistance has been achieved.^{1–7} The “cold drawing mechanism” is considered to explain the improved ductility in the blends in which the impact energy is absorbed by a large plastic deformation of the brittle particles dispersed in a ductile matrix.^{1,5–7}

Acrylonitrile-butadiene-styrene copolymer (ABS) is an amorphous styrene-acrylonitrile thermoplastic copolymer (SAN) with a grafted polybutadiene (PBD) rubbery phase. Due to its chemically bonded rubbery phase, it is a tough polymer that has high impact resistance. However, its chemical resistance and heat stability are poor. Poly(ethylene terephthalate) (PET) is an oil-resistant, polar semicrystalline polyester. Blends of ABS and PET can achieve a wide range of properties. An improved tensile strength and heat deflection temperature of ABS by adding PET was reported, but a decrease in impact property was noted.⁸ A simultaneous increase of tensile strength and toughness in ABS/PET blends was achieved by Cook and coworkers, and this was ascribed as due to a considerable plastic deformation in both domains.⁹ The effect of processing temperature on the mechanical properties as well as the phase morphology was also investigated, and it was concluded that the degradation of PET would result in a dramatic loss in mechanical properties and change in phase morphology.¹⁰

Poly(ethylene glycol-*co*-cyclohexane-1,4-dimethanol terephthalate) plastic (PETG) is an amorphous thermoplastic copolyester. PETG does not have crystallization behavior if cyclohexanedimethanol (CHDM) reaches a certain content. Similar to PET, the copolymer PETG also has very low notched impact strength and can be treated as a rigid brittle polymer. In this article, PETG recycled from the waste films and

Correspondence to: F. Chen (chenfeng_china@hotmail.com) or Q. Fu (qiangfu@scu.edu.cn).

Contract grant sponsor: National Natural Science Foundation; contract grant number: 50533050.

Contract grant sponsor: Minister of Science and Technology of China; contract grant number: 2007BAE10B00.

Journal of Applied Polymer Science, Vol. 113, 1207–1215 (2009)
© 2009 Wiley Periodicals, Inc.

plates was used to modify ABS. Our attention will focus on the property-morphology-processing temperature relationships of ABS/PETG blends. It is expected that an ABS/PETG blend with good properties can replace the more expensive ABS/PET blends or ABS/PC blends used in automotives. The use of recycled PETG also significantly reduces the pressure of environmental pollution.

EXPERIMENTAL

Materials and sample preparation

Both ABS and PETG are commercially available. ABS (745N, Kumho, Petrochemical Co., Ltd., Seoul, Korea) is a copolymer of acrylonitrile (20%), butadiene (19%), and styrene (61%). PETG (0725, Shengxin Co., Ltd., Manyang, China; MFI = 41.76 g/10 min; 220°C, 10 kg) was recycled from waste film through several procedures such as breaking up, washing, and heating at T_g of PETG (at about 80°C) to shrink to particles with a diameter of 2–3 mm. Therefore it was not necessary to pelletize the recycled before using. It has an intrinsic viscosity of 0.58 g/dL according to the supplier, whereas the fresh PETG usually has an intrinsic viscosity of about 0.7 g/dL. The recycled PETG and ABS were dried at 100°C for 4 h to minimize the hydrolysis during processing. The melt blending of ABS/PETG blends with various compositions were conducted in a two-screw extruder with three ranges of barrel temperatures, 120–180, 120–220, and 120–240°C, respectively, to investigate the effect of processing temperature on the phase morphology and mechanical properties of the blends. The blends were then injection-molded in PS40E5ASE (Japan), also with three ranges of barrel temperatures 160–180, 160–220, and 160–240°C, accordingly, to obtain standard specimen for mechanical properties tests.

Determination of relative viscosity of the PETG samples

All samples were randomly selected from the specimens after they were extruded and injection-molded. They were then ground in a knife-mill and dried under vacuum at 100°C for 4 h prior to relative viscosity measurements. Relative viscosity was measured in triplicate at 25°C using a 50/50 (w/w) phenol/1,1,2,2-tetrachloroethane solvent mixture, according to ASTM D 4603-03, in an Ubbelohde viscosimeter.

Mechanical tests

Notched Izod impact strength was used to evaluate the toughness of samples. The notched specimens were tested with a VJ-40 impact test machine at room

temperature, according to ISO 80-1992 standards. Each impact test was repeated at least five times, and the results were averaged and reported by statistical error bar. The dumbbell-shaped specimens were tested on an AG-10TA tensile testing machine at room

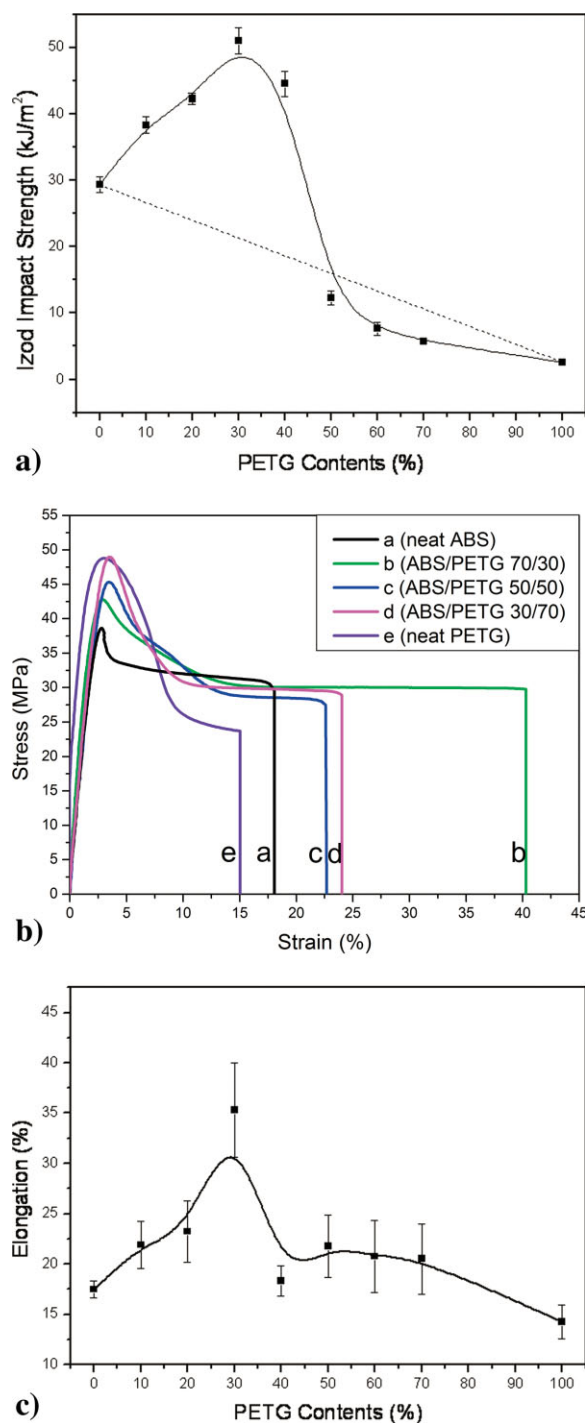


Figure 1 Mechanical properties of ABS/PETG blends as a function of PETG contents at 220°C. (a) Izod impact strength; (b) Stress-strain curves; a, neat ABS; b, ABS/PETG 70/30; c, ABS/PETG 50/50; d, ABS/PETG 30/70; e, neat PETG; (c) Elongation at break. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

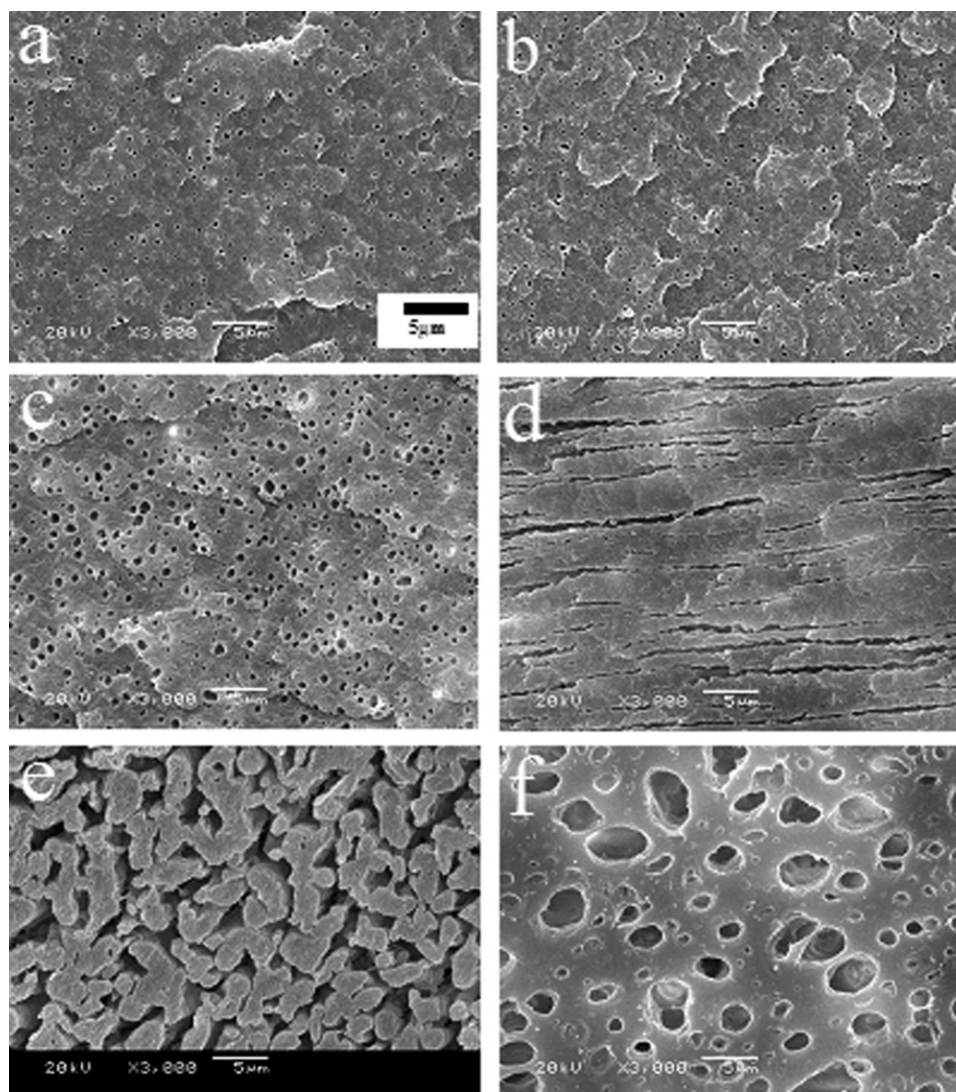


Figure 2 SEM images of ABS/PETG blends prepared at 220°C. The contents of PETG are (a), (b) 10%; (c), (d) 30%; (e) 50%; (f) 70%. (a), (c), (e), (f) cryo-fracture surface vertical to the injection direction; (b), (d) cryo-fracture surface along the injection direction. In (a)–(e), PETG was selectively etched with NaOH/ethanol, whereas in (f) ABS is selectively etched by acetone.

temperature. Test speed was kept at 50 mm/min, according to ISO 5893-2002 standards. Again at least five specimens were used, and the results were averaged and reported by statistical error bar.

Scanning electron microscopy experiments

The phase morphology of the prepared blends was studied by preferential etching of PETG phase in a 10 wt % solution of NaOH in ethanol for 72 h, or preferential etching of ABS by acetone. The samples were cryogenically fractured in the direction perpendicular or parallel to flow direction in liquid nitrogen before etching. The fractured samples were observed in a JEOL JSM-5900LV SEM instrument, using an acceleration voltage of 20 kV. All images were taken from the core layer of the samples.

Rheological characterization

Rheological properties were measured using a Shimadzu CFT-500D capillary rheometer. The length and diameter of the capillary die were 10 and 1 mm (L/D ratio = 10), respectively. End corrections were not applied; hence the viscosity values obtained are apparent viscosities. Measurements were carried out at 180, 220, and 240°C over a range of shear rates from 10 to 1000 s^{-1} .

RESULTS AND DISCUSSION

Mechanical properties

Figure 1(a) shows the mechanical properties of ABS/PETG blends prepared at 220°C. ABS copolymer is a very ductile material with impact strength of 30 kJ/m^2 ,

whereas PETG does not behave as a tough polymer, with impact strength of only 5 kJ/m^2 . By adding brittle PETG into ductile ABS, one observes an interesting increase of the Izod impact strength of ABS from 30 to 50 kJ/m^2 as PETG content increases from 0 to 40 wt %. A sharp decrease of the impact strength is observed as the PETG content is above 50 wt %, and this is related to the change of phase morphology from PETG droplet to PETG continuous structure (see below). The typical stress–strain curves of ABS/PETG blends are shown in Figure 1(b), including pure samples for comparison. An increase of tensile strength of the blends was observed as PETG content increased. On the other hand, as for the ultimate elongation, it was no more than 17% for the pure ABS and PETG samples. As for the ABS/PETG 70/30 sample, however, an obvious increase in elongation was seen. Thus a large improvement in tensile toughness is expected, which could be measured by integrated area under stress–strain curves, compared with the pure samples. In the present work, the tensile toughness of the blends increased only in a range of composition between 10 and 30 wt % of PETG contents. The ductility increased from about 16% for the pure samples to about 35% for the ABS/PETG (70/30) sample, and 100–150% enhancement was achieved. The elongation of the blends as a function of the composition is shown in Figure 1(c). Thus it can be concluded that by adding PETG to ABS, not only impact resistance and ductility but also enhancement of tensile strength can be achieved. The notched Izod impact strength of commercially available ABS/PET and PC/ABS was about 20 and 60 kJ/m^2 , respectively. In our work, the best impact strength of ABS/PETG blends was about 57 kJ/m^2 , which is much higher than that of ABS/PET blends and close to that of PC/ABS blends. Even more, the recycled PETG can also reduce the cost ABS/PETG blends. The ABS/PETG blends prepared in our experiments can be used to replace the more expensive ABS/PET blends or ABS/PC blends used in automobiles.

Change of phase morphology as a function of composition

In the previous work of Cook,⁹ toughening and synergistic effects were found in ABS/PET blends. The notched Izod impact energy exhibited a maximum at 50 wt % PET. At that composition, the phase morphology of the blends was a co-continuous structure. In our experimental results, blends ratios had a great effect on the mechanical properties, as reported in the previous section of this article. Therefore, an SEM experiment was carried out to understand the phase morphology of ABS/PETG blends.

Figure 2 shows the phase morphology of the samples after selectively etching PETG or ABS phase domain. All these samples shown in Figure 3 were prepared at 220°C . Vertical to the flow direction, droplet morphology was observed, and the domain size increased as the PETG content increased from 10 to 30 wt %. However, along the flow direction, the phase structure of PETG changed from droplets to fibers. A co-continuous phase structure was found for the blend containing 50 wt % PETG. By careful examination, it was found that it is not a fully co-continuous structure, since the ABS phase continuity was not very high. As the PETG content reached 70 wt %, phase reversion occurred as ABS was dispersed in the PETG matrix. The change of phase morphology can be used to explain why a ductile–brittle transition is found between the 40 and 70 wt % PETG blends.

In the ABS/PETG 70/30 sample, which shows particularly high toughness and elongation, its fiber-like structure was further confirmed by etching SAN phase; morphology is shown in Figure 3. Many PETG fibers are found for this blend by etching. The average diameter of the PETG fibers is about $1\text{--}2 \mu\text{m}$, and the length of the most PETG fibers is

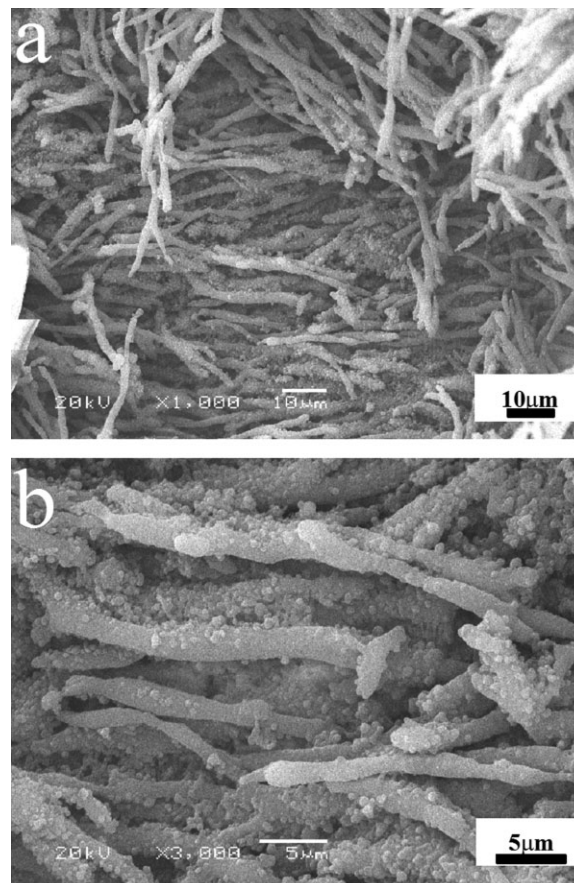


Figure 3 SEM micrograph of 30% PETG blends by etching SAN phase with acetone.

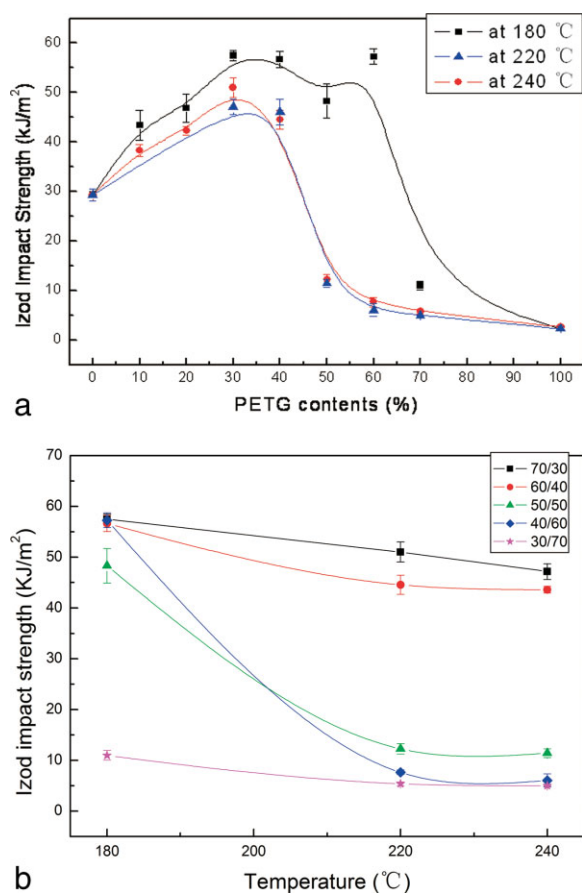


Figure 4 The effects of temperature on the Izod impact strength of ABS/PETG blends with various blend ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

longer than 30 μm . In the micrograph, the white small particles left on the fiber's surface may be the polybutadiene (PBD) particles, which could not be dissolved by acetone. The fact that PETG fibers are not always found oriented along the flow direction may be due to the effect of ultrasonic wave during etching.

The effect of temperature on mechanical properties and phase morphology

In such binary blends, processing temperature plays an important role in the mechanical properties. Under the mixing temperature of 180°C, the Izod impact strength of the blends first increases via PETG contents from 0 to 60 wt %, then sharply drops, as shown in Figure 4(a). However, the Izod impact strength of blends prepared at 220 and 240°C increases only in the range of 0–40 wt % of PETG, as shown in Figure 4(a). The correlation between the processing temperature and Izod impact strength is clearly presented in Figure 4(b). In the compositions of ABS/PETG 70/30, 60/40, and 30/70, one observes a slight decrease of Izod impact strength when the

processing temperature increases from 180 to 240°C. However, in the compositions of ABS/PETG 50/50 and 40/60, dramatic decrease of Izod impact strength is found as the processing temperature increases. The change of impact strength as increase of processing temperature is due to a change of phase morphology and a possible degradation of PETG. To prove the possible degradation of PETG at a higher processing temperature, PETG was extruded at different temperatures and its relative viscosity η_r change was measured; the result is shown in Figure 5. The relative viscosity value decreases from 1.496 at 180°C to 1.402 at 240°C. Even the change of relative viscosity is not much, but it indicates a possible degradation of PETG when prepared at a higher processing temperature. However, the slight degradation did not play a major role, since the impact strength was greatly decreased as an increase of processing temperature was not found for all the compositions investigated. For example, in the ABS/PETG 30/70 blend, one observes almost constant impact strength as processing temperature changes. Thus a change of phase morphology as function of processing temperature should be considered with the change of impact strength. For example, the changes of phase morphology as a function of processing temperatures for ABS/PETG (70/30), (50/50), and (30/70) are shown in Figure 6. One observes an increased phase domain size as an increase of processing temperatures for all three blends. For the ABS/PETG (50/50) blend, the average diameters of the phase size were about 1 μm at 180°C and 2–3 μm at 240°C. For the ABS/PETG (30/70) blend, the average diameters of the phase size were about 0.5–1 μm at 180°C and 1–5 μm at 240°C.

Another interesting phenomenon is that the composition range of co-continuous microstructure also changed with temperature. The composition range

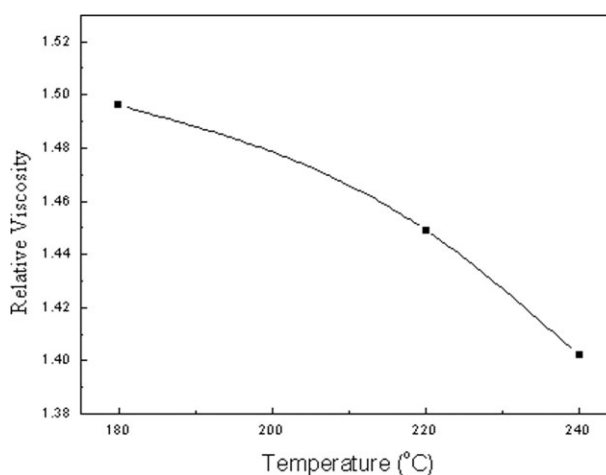


Figure 5 The relative viscosity of PETG samples prepared at different mixing temperatures.

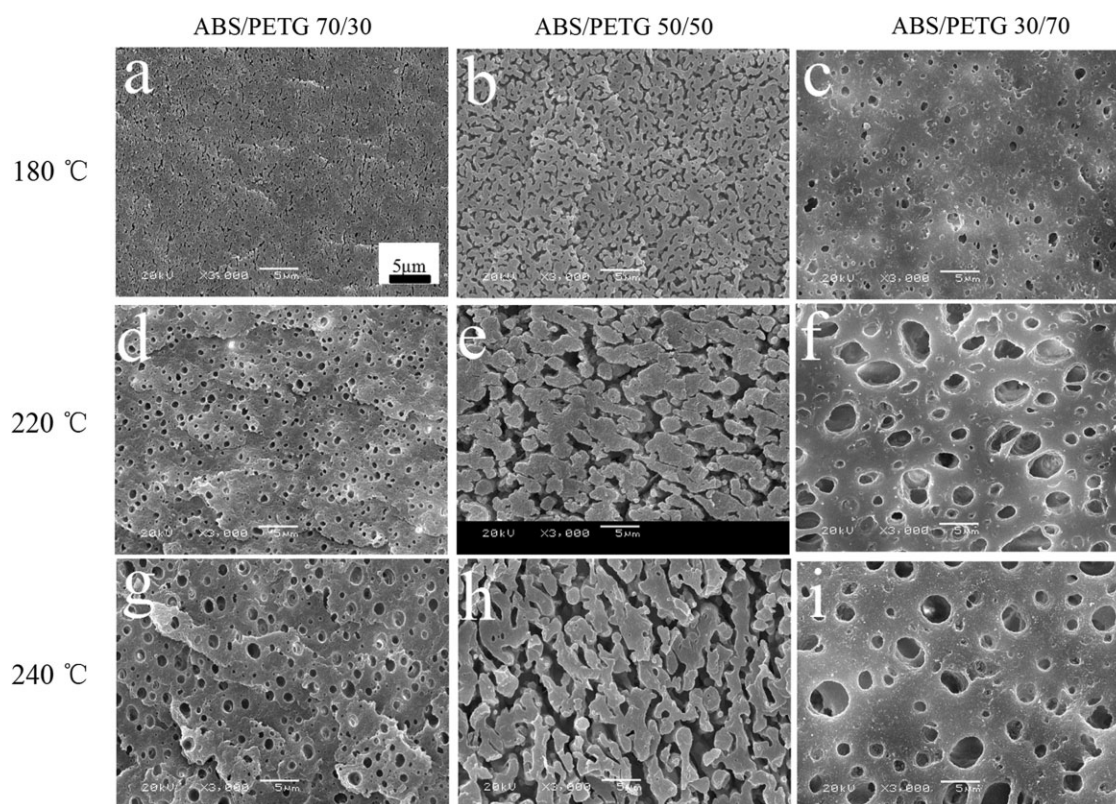


Figure 6 SEM images of ABS/PETG blends prepared at three different temperatures. The composition and processing temperatures of the blends are indicated in the figures. The PETG domains of (a), (b), (d), (e), (g), (h) samples were etched by NaOH/ethanol; ABS domains of (c), (f), (i) samples were etched by acetone.

of co-continuity narrowed as processing temperature increased. For example, one observes a co-continuity for the blends from 40 to 60 wt % PETG content at processing temperature of 180°C, whereas only the blend containing 50 wt % PETG showed the co-continuity at a processing temperature of 240°C, as shown in Figure 7. A similar phenomenon was found in poly(ϵ -caprolactone)/polystyrene blends reported by Favis,¹¹ who demonstrated that temperature-induced coalescence effects during melt mixing had a major influence on the concentration range of dual-phase continuity and an order of magnitude effect on the co-continuous microstructure phase size. The coalescence mechanism contains four distinct stages: the collision between the two particles, the drainage of the matrix film separating the colliding particles, the rupture of the matrix film, and the final merging into a fully coalesced larger spherical particle.^{12,13} Favis¹¹ also concluded that the effect of temperature on the composition range of co-continuity and phase size would be ascribed to the incomplete merging of the dispersed phase during the coalescence phenomenon at low temperature. Therefore the observation that the phase domain sizes of the microstructure and the composition range of co-continuity vary with the temperature in ABS/PETG system can be explained by temperature-

induced coalescence effects. It is well known that the coalescence rate can be reduced when the matrix becomes highly viscous,^{14,15} and low dispersed phase viscosity benefits coalescence.^{12,15} Figure 8 shows that the viscosity of ABS varies much more with temperature than the viscosity of PETG at high shear rates. Because the shear rate during extruding and molding is about 100–1000 s⁻¹, we focused the discussion on this high shear rate area. The temperature effect of domain sizes for blends containing 30 wt % PETG is not as remarkable as that with 70 wt % PETG content. The effect of temperature on the viscosity of ABS is much greater than that for PETG. This effect leads to much more pronounced morphology effects for ABS in PETG than for PETG in ABS.

Lee and Han^{16,17} considered that the co-continuous morphology was always a transitory morphology state between two modes of dispersed morphology. They also showed that if a sufficient time was allowed for melt blending or proper processing condition such as temperature or shear rate was chosen, a co-continuous morphology would be transformed into a dispersed morphology. Lee and Han also concluded that there was a critical value of mechanical energy required to transform a co-continuous morphology into a dispersed one. We also

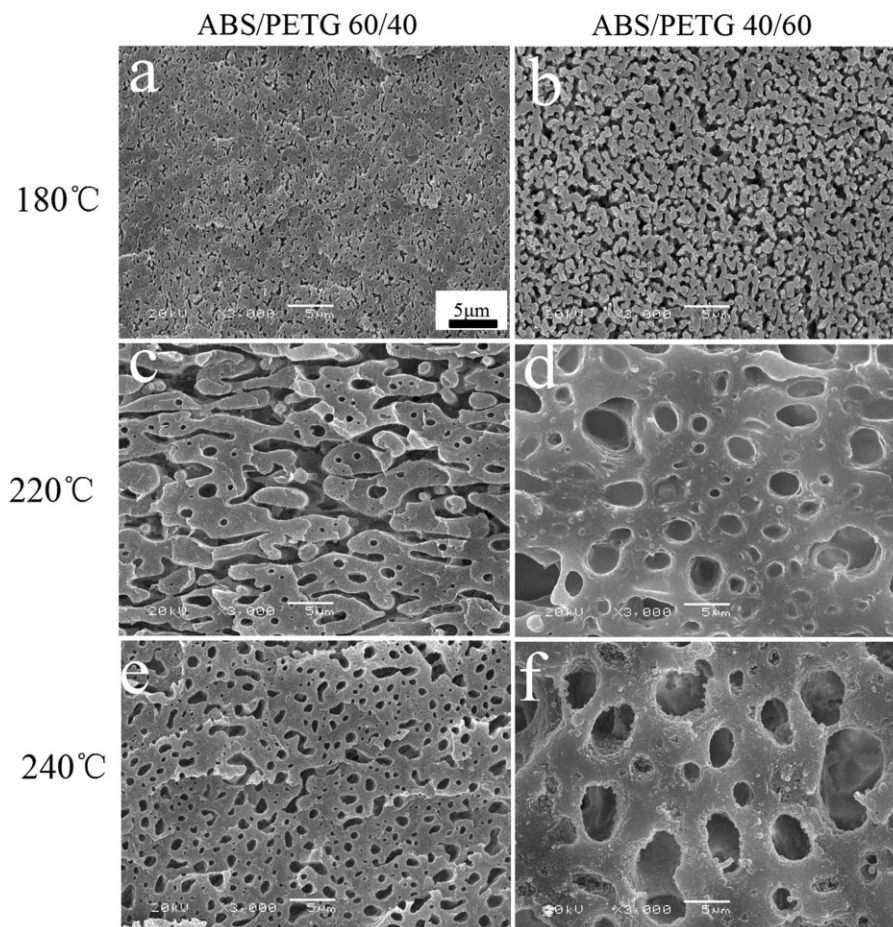


Figure 7 SEM images of ABS/PETG blends prepared at three different temperatures. The composition and processing temperatures of the blends are indicated. The PETG domains of (a), (c), (e) samples were etched by NaOH/ethanol; ABS domains of (b), (d), (f) samples were etched by acetone.

observed a transformation from a co-continuous to a dispersed morphology (see Fig. 7). For both blends containing 40 and 60 wt % PETG, a co-continuous morphology transformed to a dispersed one as the mixing temperature increased. This phenomenon further indicates that the co-continuous morphology is not stable if mixing temperature is increased.

Toughening mechanism

According to the mechanical properties achieved in this work, synergism has been noted in both notched Izod impact strength and ductility, particularly for ABS-rich blends. Since droplets, fibrils, and co-continuity were observed, the toughening mechanism should be discussed separately, based on the phase morphology.

For blends containing 10 wt % PETG at 220°C, droplet/matrix phase morphology was confirmed by the images of the two directions [seen in Fig. 2(a,b)]. The synergism noted in impact resistance may be attributed to the mechanism that PETG particles serve as stress concentrators to trigger cavitation

mechanism, such as crazing and interfacial debonding. This mechanism might explain why the blend absorbs more impact energy than pure ABS sample.

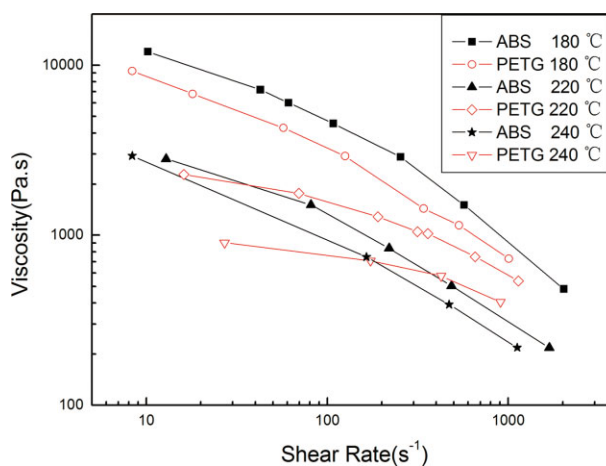


Figure 8 Viscosity as a function of shear rate of frequency for three temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

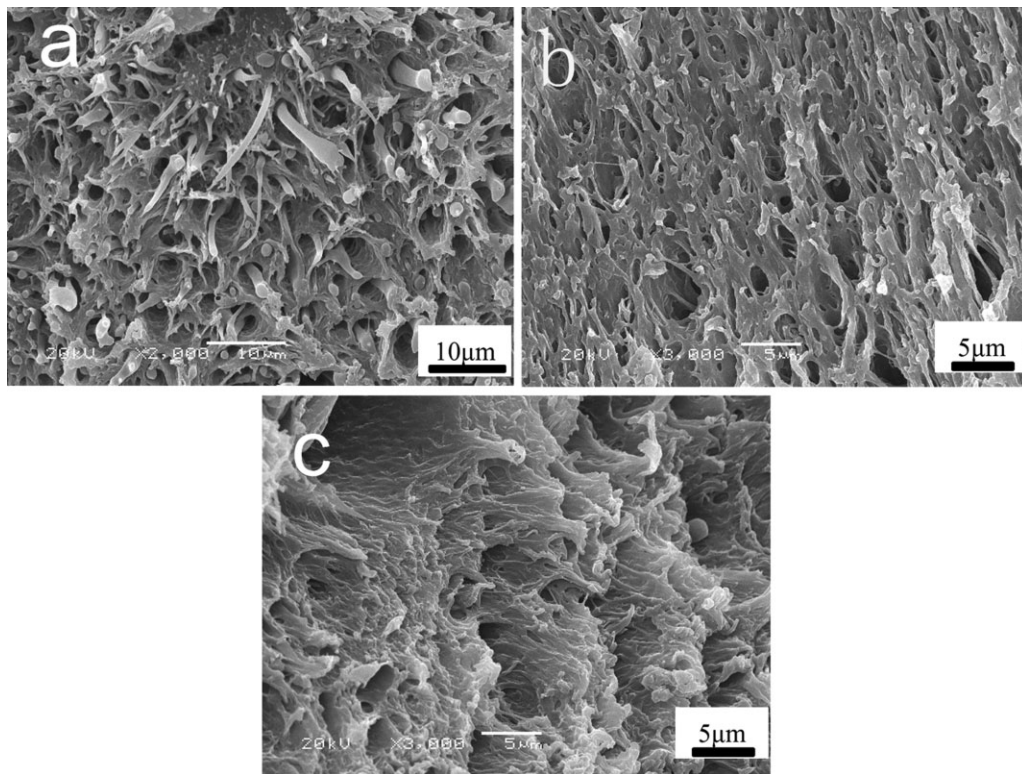


Figure 9 SEM micrographs of surfaces of Izod impact fracture. (a) 30% PETG blends at 220°C, (b) 60% PETG blends at 180°C, (c) 40% PETG blends at 220°C. The surfaces are perpendicular to the flow direction during molding.

For blends containing 30% PETG at 220°C, the blend provides better mechanical properties compared with the blends of other compositions. Microfibrillar dispersed morphology was confirmed in such blend [shown in Figs. 2(d) and 3]. A few studies have reported on the toughening effect of fiber material on ductility. In our previous work on polypropylene/carbon nanotubes composites, the observed high ductility was discussed based on the increased mobility of carbon nanotubes as they were oriented along tensile deformation direction and the bridging effect of the oriented carbon nanotubes on the crack development during tensile failure.¹⁸ As shown in Figure 9, some evidence of a bridging effect was also found in our work. The photo was taken at the side surface of the sample after being stretched until breakup. The oriented PETG fibers should have enough mobility along the tensile direction. Therefore when stretching the sample, PETG fibers served as a bridge for connecting the cracks. As shown in Figure 10(a) of the Izod impact fracture surface, matrix distortion, interface debonding, and drawn-out fibers are found all over the image. Matrix distortion, interfacial debonding, and drawn-out fibers are believed to participate in energy dissipation, thus improving the ductility of the blends.

Figure 10(b,c) shows SEM micrographs of the Izod impact fracture surfaces for a blend containing 60 wt % PETG at 180°C and a blend containing 40 wt %

PETG at 220°C, respectively. A large amount of phase distortion and cavities can be found. For the blends that exhibit fully co-continuous morphology, it is easy to understand the toughening mechanism. The co-continuous blends such as ABS/PETG (60/40) (at 220°C) and (40/60) (at 180°C) have so much interface between the two phases that the interfacial debonding dissipated large amounts of energy. The cavities found on the surface of the blends and the distortion of ABS phase also absorbed much energy. Furthermore, the interpenetrating structure can

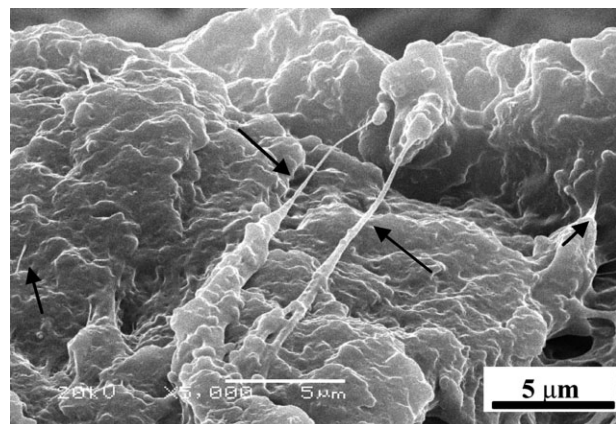


Figure 10 SEM micrographs of the side surface of the sample (30% PETG) pulled to fracture.

perfectly deliver the stress and absorb more impact energy.

CONCLUSIONS

Synergism for Izod impact resistance and tensile ductility was obtained in a wide composition range at three mixing temperatures. Significant improvement of Izod impact strength and tensile ductility was achieved for blends containing 30% PETG prepared at 220°C, which exhibited a microfibrillar structure. The ductility toughening mechanism of this microfibrillar structure was ascribed to the "bridge effect." Phase morphology with droplets, fibrils, and co-continuity were obtained, depending on the composition and processing temperature. The toughening mechanism for fully co-continuous blends might be due to energy dissipated through the debonding of the interface, the distortion of phases, and the cavitation mechanism, which also could play an important role in the toughening mechanism of the droplet/matrix morphology and microfibrillar morphology. The change of the phase domain sizes and the composition range of co-continuity were observed with the change of processing temperature and could be explained by temperature-induced coalescence effects.

References

1. Kurauchi, T.; Ohta, T. *J Mater Sci* 1984, 19, 1699.
2. Kyu, T.; Saldanha, J. M.; Kiesel, M. J. In *Two-Phase Polymer Systems*; Utracki, L. A., Ed. Hanser: Munich, 1991; p 259.
3. Murff, S. R.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1984, 29, 3281.
4. Lovinger, A. J.; Williams, M. L. *J Appl Polym Sci* 1980, 25, 1703.
5. Koo, K. K.; Inoue, T.; Miyasaka, T. *Polym Eng Sci* 1985, 25, 741.
6. Ruiz De Gauna, B. E.; Gaztelumendi, M.; Nazabal, J. *Eur Polym J* 1997, 33, 13.
7. Peng, J.; Wei, G. S.; Zhang, Y. D. *J Appl Polym Sci* 2003, 88, 2478.
8. Paul, S.; Kale, D. D. *J Appl Polym Sci* 2001, 80, 2593.
9. Cook, W. D.; Zhang, T.; Moad, G.; Deipen, G. V.; Cser, F.; Fox, B.; O Shea, M. *J Appl Polym Sci* 1996, 62, 1699.
10. Cook, W. D.; Moad, G.; Fox, B.; Deipen, G. V.; Zhang, T.; Cser, F.; McCarthy, L. *J Appl Polym Sci* 1996, 62, 1709.
11. Sarazin, P.; Favis, B. D. *Polymer* 2005, 46, 5966.
12. Chesters, A. K. *Trans Icheme* 1991, 69, 259.
13. Janssen, J. M. H.; Meijer, H. E. H. *Polym Eng Sci* 1995, 35, 1766.
14. Sundararaj, U.; Macosko, C. W. *Macromolecules* 1995, 28, 2647.
15. Fortelny, I.; Kovar, J. *Polym Compos* 1988, 9, 119.
16. Lee, J. K.; Han, C. D. *Polymer* 1999, 40, 6277.
17. Lee, J. K.; Han, C. D. *Polymer* 2000, 41, 1799.
18. Zhao, P.; Wang, K.; Yang, H.; Zhang, Q.; Du, R. N.; Fu, Q. *Polymer* 2007, 48, 5688.