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TOUGHENING OF POLYCARBONATE WITH PBA-PMMA CORE-SHELL PARTICLES*

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Abstract The miscibility, mechanical properties, morphology and toughening mechanism of PC/PBA-PMMA blends were investigated. The dynamic mechanical results show that PC/PBA-PMMA blend has good miscibility and strong interfacial adhesion. The Izod impact strength of blend PC/PBA-PMMA with 4% (volume fraction) PBA-PMMA core-shell modifier is 16 times higher than that of pure PC. The core-shell volume fraction and thickness of the PMMA shell have effect on the toughness of PC/PBA-PMMA blends. As PMMA volume fraction increases, the toughness of PC/PBA-PMMA blend increases, and reaches a maximum value at 30% volume fraction of PMMA or so. The tensile properties of PC/PBA-PMMA blend with a minimum amount of PBA-PMMA modifier show that brittle-tough transition has no significant variance in comparison with that of pure PC. The scanning electron microscopic (SEM) observation indicates that the toughening mechanism of the blend with the pseudo-ductile matrix modified by small core-shell latex polymer particles is the synergetic effect of cavitation and shear yielding of the matrix.

Keywords: Toughening; PC/PBA-PMMA blends; Core-shell particle.

INTRODUCTION

Bisphenol A polycarbonate (PC) is an important and extensively used engineering polymer because of its excellent balance of properties including optical clarity, high heat deformation temperature, toughness and electrical properties^[1]. However, the toughness noted for it is not retained in thick molded sections, with sharp notches, at low temperatures after physical aging. In addition, it has poor radiation, solvent and hydrolysis resistance. A number of approaches have been used to improve these end — use properties^[2–5].

It is generally known that the effectiveness of toughening plastics with rubber depends on the morphology of the rubber/plastics blends, such as the shape of the dispersed phase, its size and distribution, and the degree and the nature of the adhesion between the two phases. The use of core-shell latex polymer particles as tougheners is an excellent methods for better controlling of the toughener's particle size and dispersion in the matrix, while the introduction of core-shell latex polymer into a matrix can not only provide effective toughening but also obtain other desirable mechanical properties of the matrix to meet the consumer's need. These advantages are resulted from the specific structure of the core-shell latex polymer, because the core size and shape and the thickness of the shell are controllable in the synthesis of core-shell latex. At the same time, the core is "locked in" by slight crosslinking and grafting with its shell so that its morphology and size during the mechanical blending of core-shell latex polymer with its matrix (PC) and subsequent molding of the blends could be maintained. Grafting at interface is required for the purpose of stress transfer at the interface of core and shell, and is commonly

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referred to as graftlinking. Crosslinking is necessary in order to prevent the loss of particle integrity during blending the core-shell latex polymer with its matrix (PC) at 243–246°C. On the other hand, the adhesion between core-shell latex polymer phase and the polymer matrix phase depends strongly on the degree of miscibility^[6–8]. However, complete miscibility is not always necessary for blends used in different applications. In some cases, partial miscibility of the components is favorable to obtain blends with desired properties (e.g. Impact modifier blend).

This work deals with the blend of PC and PBA-PMMA core-shell latex polymer. PC is compatible with PMMA and immiscible with PBA in the core-shell latex, moreover, PBA is “locked in” by slight crosslinking and grafting with PMMA, the core-shell latex is expected to be a good toughener for PC.

EXPERIMENTAL

Materials and Specimen Preparation

Butylacrylate was available from the First Chemical Plant of Shanghai, China. Methyl methacrylate was obtained from the Baitong Chemical Plant, China. Both monomers were of chemical pure reagents. PC (bisphenol A type) was a commercial product. PBA-PMMA core-shell latex was synthesized by emulsion polymerization in our laboratory.

Blends of PC and PBA-PMMA

To avoid the hydrolysis of PC, the material was dried at 100°C for 12 h in a vacuum oven to remove adsorbed water before the melt processing. The PC/PBA-PMMA blends with different PC contents were mixed in a Brabender-like plastograph (Rheocoder XSS-300, made in Shanghai, China) at 245°C for 5 min at a roller speed of 40 r/min.

Notched Impact tests

The notched Izod impact strengths of PC/PBA-PMMA blends were measured on an Izod impact tester (XJU-22 made in Chengde, China) at 9°C. The specimens for impact testing were obtained by compression-molding the PC/PMMA blends at 250°C, then they were cut into rectangular shape which were sharply notched with a sharp razor blade. The size of the rectangular specimens was $63.3 \times 12.7 \times 3.2$ mm. The radius of the notch was 0.025 mm.

Morphological Observation

The morphology of each PC/PBA-PMMA blends was characterized with a scanning electron microscope (SEM) (model JXA-840, Japan). The test specimens were first cold-fractured in liquid nitrogen, then coated with a thin layer of gold-palladium alloy to avoid charging under the electron beam.

Mechanical Properties

The dynamic mechanical behavior of blends was tested with a DDU-11 dynamic viscoelastic tester with a heating rate of 2 K/min, and a frequency of 3.5 Hz, the peak of $T\text{-tan}\delta$ was taken as T_g .

RESULTS AND DISCUSSION

The dynamic mechanical properties of PC/PBA-PMMA blends were demonstrated in Fig. 1 for the storage modulus as a function of temperature. In Fig. 1, the storage modulus decreases sharply at around 150°C for the polycarbonate component, at around 120°C for the PMMA component, and around –40°C for the PBA component, and at between –40°C and 150°C for the blends. At low temperatures, the differences in the storage modulus could be observed. The results for the temperature dependence of the storage indicate that PBA-PMMA core-shell component has two transition temperatures, i.e. one near –40°C and the other near 125°C. In addition, PC has one transition at around 156°C. These transitions, supplemented with the literature information, are assigned to the glass transition of PBA phase, PMMA phase, and PC phase, in the order of decreasing temperature. For the blend of PC/PAB-PMMA in the ratio 90/10 there were two transition temperatures, one at –40°C, the other at 160°C, the latter is lower than the glass transition temperature of pure PC (165°C), indicating

the miscibility between PMMA and PC. With the increase of PBA-PMMA content in the blends, the two transition temperatures do not alter, which means the miscibility of PC and PMMA is finite. There are two phases, one is the PC phase and the other is the PMMA phase in the blends with higher content of PBA-PMMA. In a PC/PBA-PMMA blend with the ratio of 70/30, three transition temperatures corresponding to PBA, PMMA and PC phases are observed.

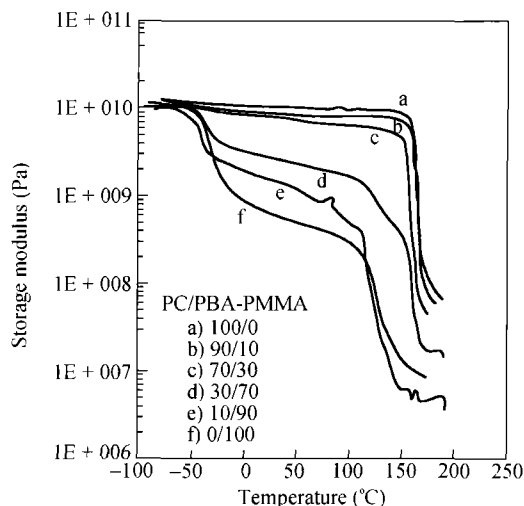


Fig. 1 Dynamic mechanical spectrum of PC/PBA-PMMA blends

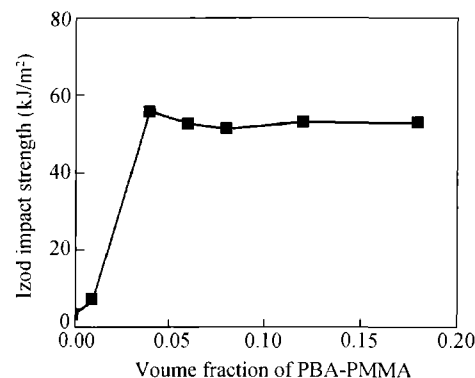


Fig. 2 Variation of notched Izod impact strengths versus volume fraction of PBA-PMMA in PC/PBA-PMMA blends

Izod impact properties of a series of PC/PBA-PMMA blends containing 0 vol%–20 vol% PBA-PMMA were determined. Figure 2 shows the variation of notched Izod impact strengths for specimens with increasing the core-shell polymers at 25°C. The notched impact strength for pure PC is 3.4 kJ/m, when the volume fraction of PBA-PMMA is lower than 4% in the blends, the notched impact strength of the blends does not change so much as compared with that of pure PC. But when the volume fraction of PBA-PMMA core-shell latex polymer is 4%, the notched impact strength of the blend is greatly improved, and increases to about 17 times that of pure PC. In addition, the blends turn from brittle to tough. The notched impact strength of the blend does not change very much, when the volume fraction of the PBA-PMMA core-shell latex polymer is higher than 4% in the blends, indicating that PBA-PMMA core-shell latex polymer is a very effective modifier.

The yielding strength and tensile properties of PC and PC/PBA-PMMA core-shell latex polymer blends are shown in Table 1. The tensile test results show that the tensile properties of the PC/PBA-PMMA core-shell latex polymer blend with the minimum amount of PBA-PMMA modifier at which the brittle-tough transition occurs show no significant variance compared with that of pure PC.

Table 1. Mechanical properties of PC and PC/PAB-PMMA blends

Properties	PC	PC/PBA-PMMA
Yield strength (MPa)	57.3	55.0
Extension at break (%)	103.5	107.5
Modulus (MPa)	984.5	980.7

The volume of PBA-*cs*-PMMA is 5%, and the volume of PMMA is 33% in PBA-PMMA core-shell particles

The pure PC and PC/PBA-PMMA blend samples were cryogenically fractured and examined using SEM. Figure 3(a) shows that there are only a few smooth lines and a large area of smooth fracture surface for pure PC, indicating the absence of a significant energy-absorption-related deformation process. Compared with the

featureless fracture surface of pure PC, the surface of the PC/PBA-PMMA (96/4) blend (Fig. 4b) is no longer smooth. It can clearly be seen that PBA-PMMA core-shell latex polymer particles with a diameter of 0.4–0.5 μm are dispersed finely and homogeneously in the PC matrix. This phenomenon implies that relatively small interfacial tension and good adhesion exist between the PBA-PMMA core-shell latex polymer phase and the PC matrix.

Further more, it is observable that in the boundaries between the PBA-PMMA core-shell latex polymer phase and the PC matrix, there are many cavities (Fig. 3b), which are beneficial to relieving triaxial tension. Upon fracture cavities may be formed first and then followed by enhanced shear yielding of the matrix. Therefore, when the PC/PBA-PMMA blends are subjected to an impact, the cavities and the following shear yielding of the matrix will relieve the plane strain constraint, dissipate the impact energy and reduce the notch and rate sensitivity of this material. This is believed to be the toughening mechanism for PC/PAB-PMMA core-shell latex polymer blends.

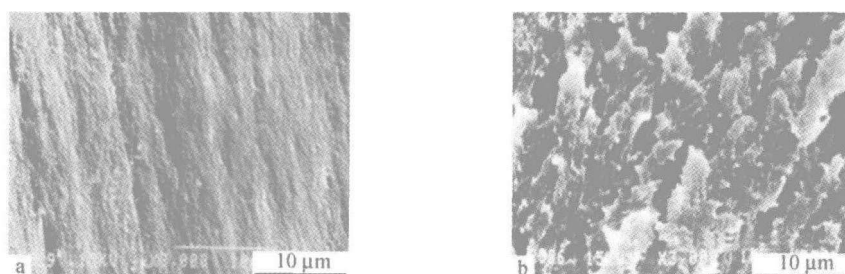


Fig. 3 SEM micrographs the fracture surface of PC (a) and PC/PBA-PMMA blend (b) $V_{\text{PBA-PMMA}} = 4\%$

CONCLUSIONS

PBA-PMMA core-shell latex polymer is used to toughen PC resin and a super-tough PC blend is obtained. The notched Izod impact strength of the blend is increased greatly when core-shell latex polymer content is only 4 vol%. The SEM image of PC/PBA-PMMA (96/4) blends shows that the core-shell latex polymer is evenly dispersed in PC matrix with a particle diameter size of 0.4–0.5 μm , indicating that there is good adhesion between PBA-PMMA core shell latex polymer phase and the PC matrix. The great increase in toughness of PC/PBA-PMMA blends may be due to the cavities existed at the boundaries of core-shell latex polymer and the following shear yielding of the matrix. The tensile properties of PC/PBA-PMMA core-shell latex polymer blends with a minimum amount of PBA-PMMA modifier at which brittle-tough transition occurs do not show significant variance compared with those of pure PC.

REFERENCES

- 1 Olabisi, O., Robeson, L. M. and Shaw, M. F., "Polymer-Polymer Miscibility", Academic Press, New York, 1979, p.25
- 2 Chun, J. H., Maeng, K. S. and Suh, K. S., J. Mater. Sci., 1991, 26: 5347
- 3 Fowler, M. E. and Keskkula, H., Paul, D. R., Polymer, 1987, 28: 1703
- 4 Lu, D., Dong, L., Feng, Z., Zhang, H., Wang, X. and Wang, L., Macromol. Chem. Phys., 1998, 199: 1709
- 5 Wang, X., Wang, Z., Jiang, W., Liu, C., Yang, H., Zhang, H. and Jiang, B., Polymer, 1997, 38: 6251
- 6 Wang, L., Zhang, H. and He, D., Polym. Mater. Sci. Eng., 1998, 14: 98
- 7 Lu, D., Dong L. and Feng, Z., J. Macromol. Sci. -Phys., 1998, B 37(5): 699
- 8 Lu, D., Dong, L. and Feng, Z., Macromol. Rapid. Commun., 1997, 18: 411