Effect of Blending Sequence on the Impact Strength of PET/PC Blends

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Keywords: Impact Strength, Blending Sequence Effect, PET/PC Blends, Toughening, SEM, TEM

ABSTRACT

The impact behavior of PET/PC/E-GMA-MA blends at different temperatures was studied. The relationships between the processing conditions, morphology and mechanical properties were discussed. It was revealed that the toughening effect due to the E-GMA-MA copolymer appears at just above its glass transition temperature, and the blending sequence has a strong influence on the morphology and impact toughness of the blends. The brittle-ductile transition of the blends made under optimum processing conditions takes place at a relatively low temperature and with a low elastomer content. The major toughening mechanisms were identified to be massive cavitation plus matrix shear yielding. Both SEM and TEM were employed to study the morphology and toughening mechanisms.

INTRODUCTION

PET and PC have been known as engineering plastics with many desired engineering properties. PET has excellent chemical resistance and a good electronic property, whereas amorphous PC possesses a high glass transition temperature, high impact toughness and good dimensional stability. Theoretically, blending of PET and PC will lead to a polymer alloy with the property combination of high impact toughness, good dimensional stability from PC and excellent solvent resistance and electronic properties from PET. Previous researches show that PET and PC are partially miscible polymers, and thus simple molten blending of PET and PC in a mixer will only produce a phase-separated PET/PC mixture with a low mechanical strength. The key issues in PET and PC alloying are to improve the compatibility between PET and PC, and to toughen the PET/PC blend with a third rubbery component. Extensive research efforts over the past few decades have been devoted to the areas, such as miscibility of PET and PC, rubber toughening mechanisms and the effect of PET/PC molecular weight on the mechanical properties of PET/PC blends [1-10].

In the present work, we study the effect of processing conditions on the morphology and impact strength of PET/PC blends with different contents of copolymer elastomer, ethylene-glycidyl methacrylate-methacrylate (E-GMA-MA). The research was focused on the relationship between blending sequence and morphological structure, as well as the relationship between the microstructure and mechanical properties. Charpy impact tests were conducted in the temperature range from -80°C to 25°C. The morphology and fracture behavior of each PET/PC blend were studied using a transmission electron microscope (TEM) and a scanning electron microscope (SEM).

EXPERIMENTAL WORK

The PET/PC/IB blends employed in the present study were supplied by Sumitomo Chemical Ltd., Japan. Thirteen different PET/PC/IB blends were prepared with the addition of different contents of copolymer (0%, 2%, 5%, 10% and 15%) and three different blending sequences, namely, (PC/IB)/PET, (PET/IB)/PC and (PET/PC)/IB, where IB stands for the copolymer.

The morphology of the blends was studied using both SEM and TEM. The ultra-thin sections for TEM analysis were cut using a cryogenic Leica Ultracut R ultra-microtome. For improving contrast between different components, the TEM samples with a thickness of approximately 60 to 80 nm were stained with 2% OsO₄ water solution for a few days before prior to examination on a TEM, Phillips CM20.

Charpy impact tests were conducted with single edge notched specimens in the temperature range from -80°C to 25°C. The impact speed was 2.96 m/s. The dimensions of the specimens were 3.2 x 12.75 x 63.85 mm³. A sharp notch was introduced on one side of each specimen. During the tests, the specimens were kept cold in a liquid nitrogen/ethanol bath to the temperature required. The impact fracture energy was directly taken from the scale on the machine and analyzed using the essential work of fracture method [11].

RESULTS AND DISCUSSION

Effect of temperature and blending sequence

Fig. 1a-e illustrate the variation of impact fracture toughness with copolymer content at different temperatures for the PET/PC/IB blends prepared using different blending sequences. It was found that when the test temperatures were lower than the glass transition temperature (T_g) of the copolymer, i.e. -33°C, all the PET/PC/IB blends underwent brittle fracture. No blending sequence effect was sighted at -80°C and -60°C, refer to Fig. 1a-b

At -30°C, which is just above T_g of the copolymer, the toughening effect due to the copolymer was observed with the blends containing 15% copolymer. The impact toughness of all three PET/PC/IB-15% blends was indisputably higher than that of the PET/PC blend (Fig. 1c). At 10% copolymer loading level, only the (PC/IB-10%)/PET blend showed an increase in impact fracture toughness. No toughening effect due to the copolymer was found for other two blends.

With further increasing temperature to 0°C, the toughening effect due to the copolymer became substantial at 10 and 15% copolymer contents. The impact toughness of the blends having 15% copolymer was approximately two twice that of the PET/PC blend. The blending sequence effect was, however, not evident, refer to Fig. 1d.

Fig. 1. Variation of impact toughness vs. Copolymer content for the PET/PC/IB blends made using different blending sequence at (a) -80°C; (b) -60°C; (c) -30°C; (d) 0°C and (e) 25°C.

At 25°C, the toughening effect due to the copolymer was significant for the blends containing 15% copolymer. The fracture was completely ductile and the brittle-ductile (B-D) transition was observed. At 10% copolymer content, a remarkable blending sequence effect was found. The (PC/IB)/PET blends showed much higher impact strength than the other two blends, as demonstrated in Fig. 1e. At 5% copolymer level, the impact fracture toughness of the (PC/IB-5%)/PET blend was also higher than those of (PET/IB-5%)/PC and (PET/PC/IB-5%) blends.

Based on the above discussion, we may summarize that the E-GMA-MA copolymer had no toughening effect at testing temperatures below its T_g , regardless of blending sequences used. The toughening effect appeared at testing temperatures higher than T_g of the copolymer, but only those blends having 15% copolymer showed some increase in impact toughness at -30°C and 0°C. At 25°C, the toughening effect due to the copolymer was unambiguous and blending sequence effect was significant. The results suggest that the (PC/IB)/PET blends were superior to the other two blends and higher impact toughness at relatively low copolymer contents (i.e. 5% and 10%) was obtained. For the (PET/IB)/PC and (PET/PC/IB) blends to achieve the same high impact toughness, more than 10% copolymer must be added. Since the yield strength and Young's modulus of the blends decreases considerably with copolymer content, the overall mechanical properties of the blends having higher copolymer content are anticipated to be poorer.

Fig. 1. (Continue)

Morphology and toughening mechanisms study

Morphology study

Fig. 2 is a TEM micrograph of the (PET/IB-10%)/PC blend stained with OsO_4 . The continuous phase in gray color is the PET phase and the black dispersing particles are the PC domains. The copolymer particles are in white color because it cannot be stained by OsO_4 . The majority of the white particles have a size of 1 to 2 μm . It is very interesting to find that although the (PET/IB)/PC blend was made by blending the copolymer with PET first and followed by mixing of the (PET/IB) pre-blend with PC, all the white copolymer particles were exclusively located within the PC domains. This result implies that during the mixing of the (PET/IB) pre-blend with PC, immigration of the copolymer from the PET phase to the PC phase occurred.

Quite distinct to the microstructure found in Fig. 2, the microstructure of the (PC/IB-10%)/PET shown in Fig. 3 has following characteristics: (a) the PC domains are much smaller. The finer dispersion of the PC may suggest that pre-mixing PC with the copolymer might have improved the miscibility between PET and PC. (b) The copolymer particles have two size distributions. One is about $0.2\ \mu\text{m}$ and another is approximately $2\ \mu\text{m}$. (c) All the copolymer particles are in the PC phase. The large size particles are wrapped by a thin layer of black PC, having a core-shell structure

Fig. 4 is a TEM micrograph of the (PET/PC/IB-10%) specimen. Surprisingly, there are only two phases clearly seen, i.e. the white copolymer particles and the dark gray matrix. the PET/PC system is widely known to be a partially miscible system, and the PET/PC blends would have a distinct two-phase structure without catalyst-enhanced transesterification between PET and PC. In the present study, no extra effort was made to enhance the transesterification. It was, therefore, anticipated that the blend had a three-phase structure, i.e. PET-PC-IB structure. Further investigations using thermal analytical techniques may provide useful information to better understand the phenomenon.

Fig. 2. TEM photograph of a (PET/IB-10%)/PC blend. While copolymer particles are included in black PC phase.

Fig. 3. TEM photograph of a (PC/IB-10%)/PET blend. While copolymer particles are included in black PC phase. PC domains are smaller compared to Fig. 2.

Fig. 4. TEM photograph of a (PET/PC/IB-10%) blend. Only two phases are seen, i.e. white copolymer particles and gray matrix of PET/PC.

Toughening mechanisms

Among all the PET/PC/IB blends studied, the blends made by (PC/IB)/PET sequence showed higher impact toughness at a lower copolymer content. The fractographic study revealed that the major toughening mechanisms of the (PC/IB-10%)/PET blend are combined cavitation and matrix

shear deformation, see Fig. 5. For comparison, SEM micrographs of the (PET/IB-10%)/PC blend are shown in Fig. 6. The fracture surface is essentially featureless, except slight stress whitening taking place at the crack initiation area.

As discussed in previous section, a different blending sequence caused some changes in the microstructure of the PET/PC/IB blends. The large (PC/IB) domain structure in the (PC/IB)/PET blend consists of a core-shell structure with the elastomer as rubbery core and the thin PC layer as rigid shell. It has been widely reported in literature that some core-shell rubber particles can toughen brittle polymers more effectively than use of conventional rubber particles without a rigid polymer shell [12-15], because the rigid shell can provide efficient interfacial connections between the rubbery core and the matrix and transfer stresses effectively between the different phases. Therefore, we may tentatively attribute the high impact toughness of the (PC/IB-10%)/PET blend to the blending sequence used. With this blending sequence, the miscibility between PET and PC is enhanced to a certain degree so that PC can disperse in PET to a small size forming a core-shell structure with the copolymer as inclusions to . These *in situ* (PC/IB) core-shell particles may toughen the PET matrix more effectively.

Fig. 5. SEM photographs taken from a (PC/IB-10%)/PET blend. Large area plastic deformation (a) and massive cavitation (b) are clearly seen.

Fig. 6 SEM photographs taken from a (PET/IB-10%)/PC blend. Entire fracture surface is featureless (a). The enlargement (b) shows semi-brittle fracture occurred.

Concluding remarks

Impact tests of PET/PC blends at different temperatures revealed that the E-GMA-MA copolymer had no toughening effect when the testing temperature was lower than its glass transition temperature. At higher temperatures, impact strength increased with the copolymer content and the brittle-ductile transition was observed. The blending sequence showed a significant influence on the impact behavior of the PET/PC/IB blends. The blends made with

the (PC/IB)/PET blending sequence had a higher toughness at a lower copolymer content and the brittle-ductile transition appeared at lower temperatures.

Morphology study revealed that blends made by different blending sequences had different microstructure. The (PET/PC/IB) blends had an unexpected two-phase structure. The copolymer particles were found to be distributed in a seemingly homogeneous PET/PC matrix. In the processing of (PET/IB)/PC blends, copolymer migration from PET to PC was observed. It was noted that though the copolymer was mixed with PET first, the final (PET/IB)/PC blends showed that copolymer particles were exclusively located within the PC phase. The copolymer particles in the (PC/IB)/PET blends had two size distributions, i.e. at 0.2 μm and 2 μm . Moreover, a core-shell particle structure was found in the blends, which may be the origin of high fracture toughness found with the blends.

The toughening mechanisms were investigated using a SEM. The SEM analysis suggests that the major energy absorbing events during fracture of the toughened PET/PC/IB blends were combined cavitation and matrix shear deformation. Detailed toughening processes need more TEM work to confirm.

Acknowledgments

The authors wish to thank the Materials Characterization and Preparation Facility (MCPF) of the Hong Kong University of Science & Technology for placing their facilities at our disposal. Thanks are due to Sumitomo Chemical Co. Ltd. Japan for the supply of materials for testing. The authors wish to acknowledge the financial supports from the Hong Kong Research Grants Council (Project No. HKUST810/96E).

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