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Toughening of PBT/PC blends with epoxy functionalized core-shell modifiers

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Abstract: Core-shell modifiers of MB-g-GMA have been synthesized by emulsion polymerization technique. For these modifiers, the core is made up of the cross-linked poly(butadiene) and the shell is methyl methacrylate (MMA) and glycidyl methacrylate (GMA) copolymer. These modifiers were used to toughen poly(butylene terephthalate) (PBT)/bisphenol A polycarbonate (PC) blends. The mechanical properties showed that the addition of 15% MB-g-GMA had a very good influence on the notched Izod impact strength and elongation at break of the PBT/PC blends. DMA results showed PBT was partially miscible with PC and the addition of MB-g-GMA further improved the miscibility of PBT and PC. DSC tests further testified the introduction of MB-g-GMA improved miscibility between PBT and PC. Scanning electron microscopy (SEM) displayed a very good dispersion of MB-g-GMA particles in PBT/PC blend. Transmission electron microscopy (TEM) proved MB-g-GMA particles were enveloped by a thin layer of PC, PBT and PC showed co-continuous structure or dispersed phase which depended on the content of MB-g-GMA. SEM results showed shear yielding of the matrix and cavitation of rubber particles were the major toughening mechanisms.

Introduction

PBT and PC are important commercial engineering polymers and each of them provides superior performance in a variety of applications. PBT is a semicrystalline polymer with good chemical resistance, electric insulation, and processability, and it finds wide applications in the automotive and electronic industries. PC is an amorphous polymer. It has several distinct properties such as dimensional stability, transparency, flame resistance, high impact strength, and a very wide range of service temperature. However, PC has some shortcomings, such as poor solvent resistance, low fatigue strength, and high melt viscosity. In general, it is believed that the PBT/PC blend can inherit its chemical resistance from PBT and its toughness from PC. Since PBT and PC are partially miscible polymers [1], simple melt blending of PBT and PC most probably produce a phase-separated PBT/PC mixture and usually cannot obtain satisfactory properties [2–5]. In order to improve the miscibility of polymer blends and increase interfacial strengths, the common way is based on the formation of a block or grafted copolymer A–B at the interface between the blend phases during melt mixing. The A–B copolymers can increase interfacial strengths and reduce the droplet coalescence rates through steric repulsion [6–8]. It is well known that the proper ester-exchange production could help to improve the miscibility between PBT and PC, but excessive ester-exchange reaction may lead to materials with poor mechanical properties such as reduced impact strength. In some cases, it is possible to add a third polymer into the blend, which is miscible with one of the blend component and reactive with the other blend component [9-11]. Fortunately, the inherent chemical functionality of PBT makes it possible to be modified properly by this way.

Numerous articles have described the approaches how to improve the toughness of PBT/PC blends. Bai et al. [12] reported that a combination use of PTW and POE lead to remarkable increase in the impact strength. Wang et al. [13] introduced ethylene-co-glycidyl methacrylate (E-GMA) elastomer into the PBT phase of a PBT/PC blend via sequential blending and the addition of short glass fibers were used to compensate for the yield strength and modulus loss due to the elastomer addition. The mechanical testing results showed that the blends have significantly improved impact strength. Wu et al. [14] studied the effect of the interfacial adhesion strength on the properties of the PBT/PC blends by incorporating different amounts of the PBT-PC copolyester into the PBT/PC blends and it was revealed that the PBT-PC copolyester could improve the compatibility between the PBT and PC, however, the impact toughness of the PBT/PC blends was low.

In the present paper, reactive monomer of GMA was induced to the shell of MB impact modifier via emulsion polymerization method. On the one hand, PMMA composite in MB-g-GMA shows good miscibility property with PC phase, on the other hand, the compatibilization reaction happened between the epoxy groups of GMA and the carboxyl or hydroxyl end groups of the PBT during melt processing which can improve the interfacial strength. This way is believed to be more effective to toughen PBT/PC blends and the super-toughness blend can be obtained. In this study, the mechanical properties were studied. DMA and DSC were used to study the miscibility of the toughened PBT/PC blends. SEM and TEM were used to explore the morphological properties of the PBT/PC blends, and the toughening mechanisms were then proposed.

Results and discussion

Mechanical properties

The notched Izod impact strength is one of the most important properties for PBT/PC rigid polymer blends because of their notch sensitivity. In the early studies, Chacko et al. [15] reported that the addition of 20% MBS as an impact modifier could lead to acceptable impact strength. Bai et al.[12] reported that a combination use of PTW and POE lead to remarkable increase in the impact strength and the impact strength is about 600 J/m. In this paper, we prepared MB-g-GMA (2 wt% GMA) to toughen PBT/PC blends. As shown in Fig. 1(a), the MB-g-GMA is a good modifier and improves the impact strength of PBT/PC blends tremendously. Brittle-ductile transition takes place when the content of MB-g-GMA is between 10-15 wt%. The impact strength is 940 J/m when the addition of MB-g-GMA is 15 wt%. The notch impact strength of PBT/PC blends reaches 1023 J/m when the content of MB-g-GMA is 20 wt% and shows super toughness.

It is reported that the tensile properties of polymer blends are very sensitive to the state of the interface [16, 17], that is, interfacial adhesion. The poor interface behaves as a flaw, and the failure initiates at the interface, which results in low elongation at break and tensile strength. In this study, the interface between PBT and PC is modified by the introduction of MB-g-GMA. Because of the good miscibility between

PC and MB and the epoxy groups of GMA can react with the end functional groups of PBT, the interface strength between PBT and PC phase is improved which is beneficial to the modification of interface.

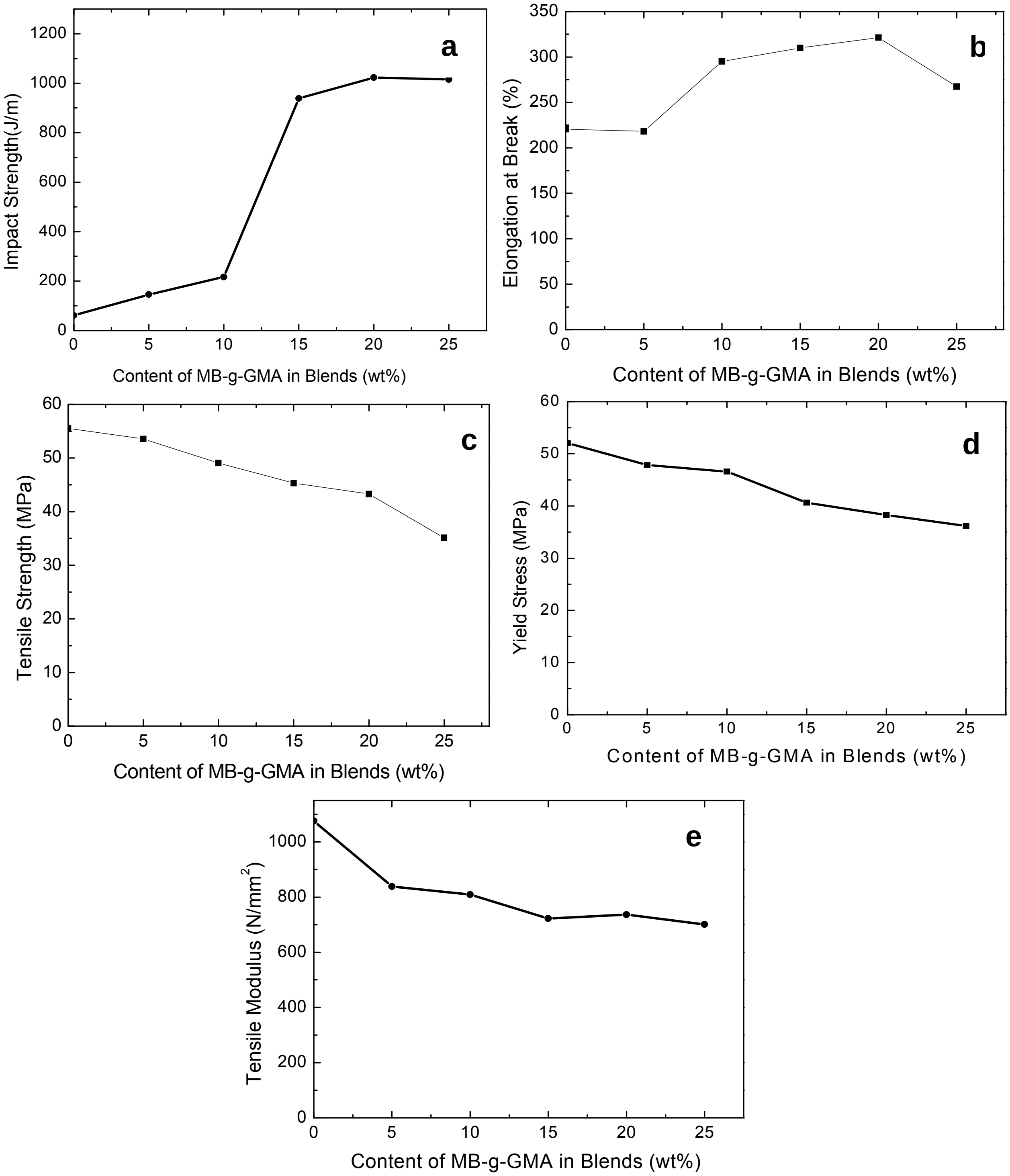


Fig. 1. Mechanical properties of PBT/PC/MB-g-GMA (50-*x*/2)/(50-*x*/2)/*x* blends with different MB-g-GMA contents: (a) notched impact strength, (b) elongation at break, (c) tensile strength, (d) yield stress, (e) tensile modulus. (*x* indicates the weight percent of MB-g-GMA in the blends).

Fig. 1(b) displays the elongation at break of the PBT/PC/MB-g-GMA blends. It can be seen that the elongation at break of the PBT/PC/MB-g-GMA blends is higher than PBT/PC blend and all the blends show excellent tensile property. Fig. 1(c), (d), (e) display that the tensile strength, yield stress and tensile modulus of the PBT/PC/MB-g-GMA blends decrease slightly with the increase of the MB-g-GMA content. This can contribute to the low stiffness of the MB-g-GMA.

DMA and DSC analysis

The miscibility property of PBT, PC and its blends was studied by DMA. As can be seen from Fig. 2(a), the peak at 54 ^{o}C is the T_g of pure PBT amorphous phase, and the pure PC exhibits a T_g peak at 157 ^{o}C. For the PBT/PC blend, the peak at 62 ^{o}C displays the T_g peak of PBT which shifts to the high temperature and the T_g peak appeared at 153 ^{o}C shows the T_g peak of PC which shifts to the low temperature. The T_g peaks of PBT and PC approach to each other shows that PBT and PC are partially miscible. Fig.2(b) is the DMA curves of PBT/PC/MB-g-GMA blends. It shows that the T_g of PBT and PC access to one another with the increase of MB-g-GMA content. This may contribute to the good miscibility between PC and MB and the reaction between the epoxy group of GMA in MB-g-GMA and the carboxyl or hydroxyl end groups of the PBT during melt processing, leading to the improved miscibility of PBT and PC. Fig. 3 is the elastic dynamic modulus curves of PBT/PC/MB-g-GMA blends. It can be seen that the T_g correspond to that of Fig. 2(b). Additionally, it can be found that E' decreases with the increase in the MB-g-GMA content.

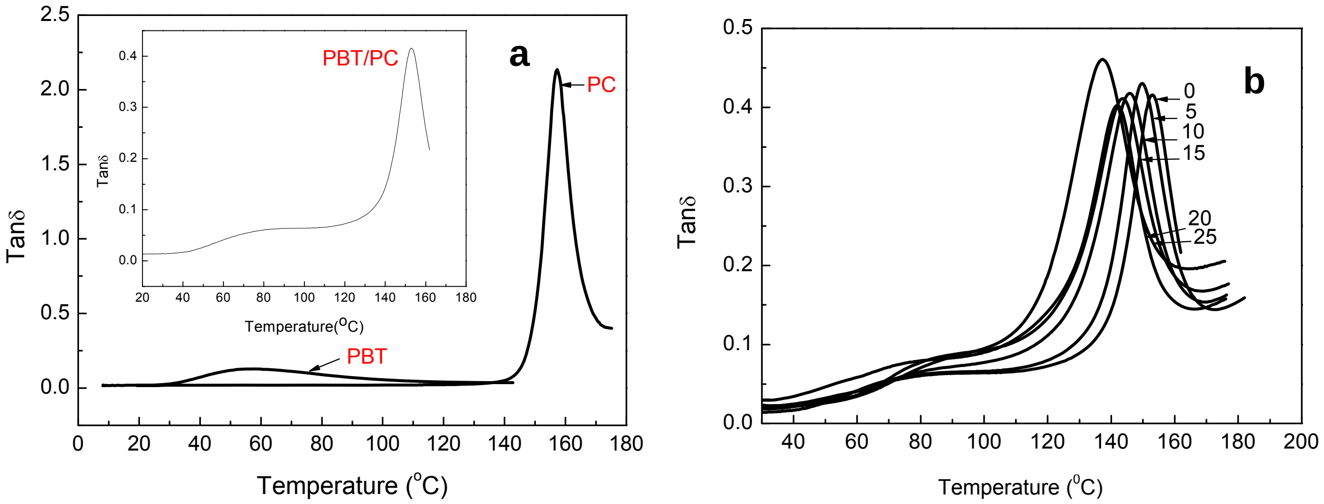


Fig. 2. DMA curves of PBT, PC and PBT/PC blends (0, 5, 10, 15, 20, 25 indicate the content of the MB-g-GMA in PBT/PC blends).

DSC was used to study the melting behaviours of PBT/PC blends. As can be seen in Fig. 4, PBT phase exhibits one main melting peak at higher temperature together with a small melting peak at lower temperature that could be attributed to secondary infilling crystallization [18-21]. The first small peak could be attributed to the partial melting of a small fraction of less perfect crystals. The second large peak could be attributed to the melting of original and recrystallized crystallites. The curves in Fig.4 demonstrate that the melting peak of PBT shifts to lower temperature with the increase of MB-g-GMA content in PBT/PC/MB-g-GMA blend. The shift of PBT melting peak to lower temperature is believed to originate from the formation of PBT-g-MB grafted copolymer which hinders the process of crystallization. Therefore, the miscibility between PBT and PC was further improved according to the T_m depression criterion [22].

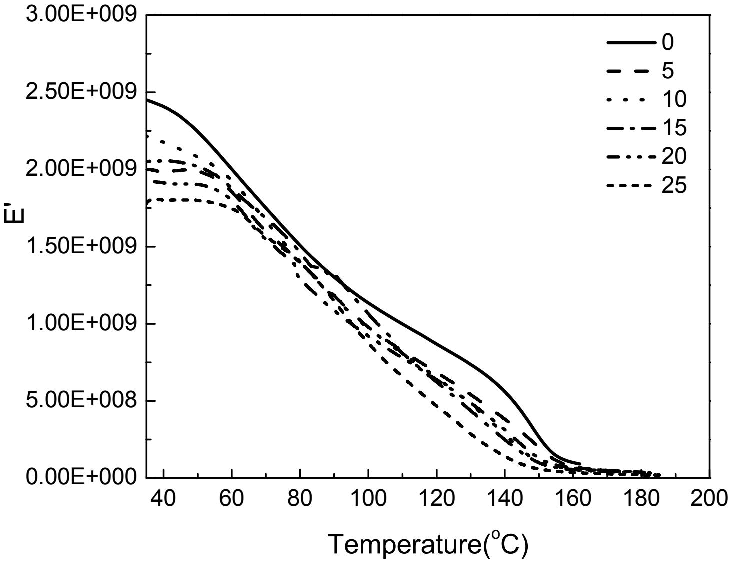


Fig. 3. Elastic dynamic modulus curves of PBT/PC/MB-g-GMA blends (0, 5, 10, 15, 20, 25 indicate the content of the MB-g-GMA in PBT/PC blends).

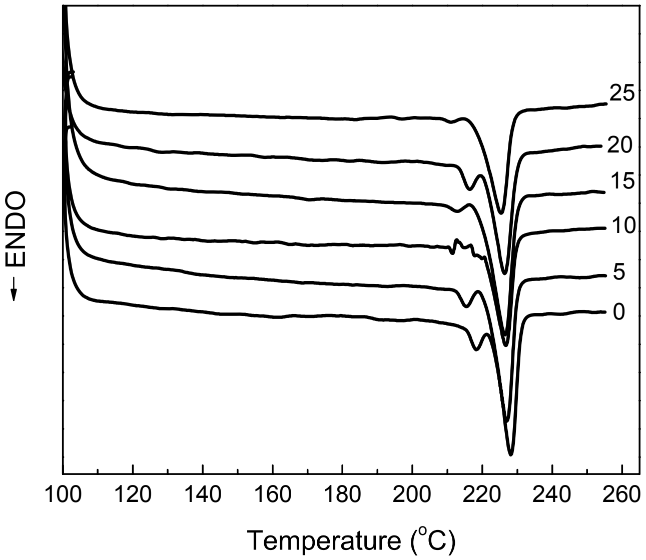
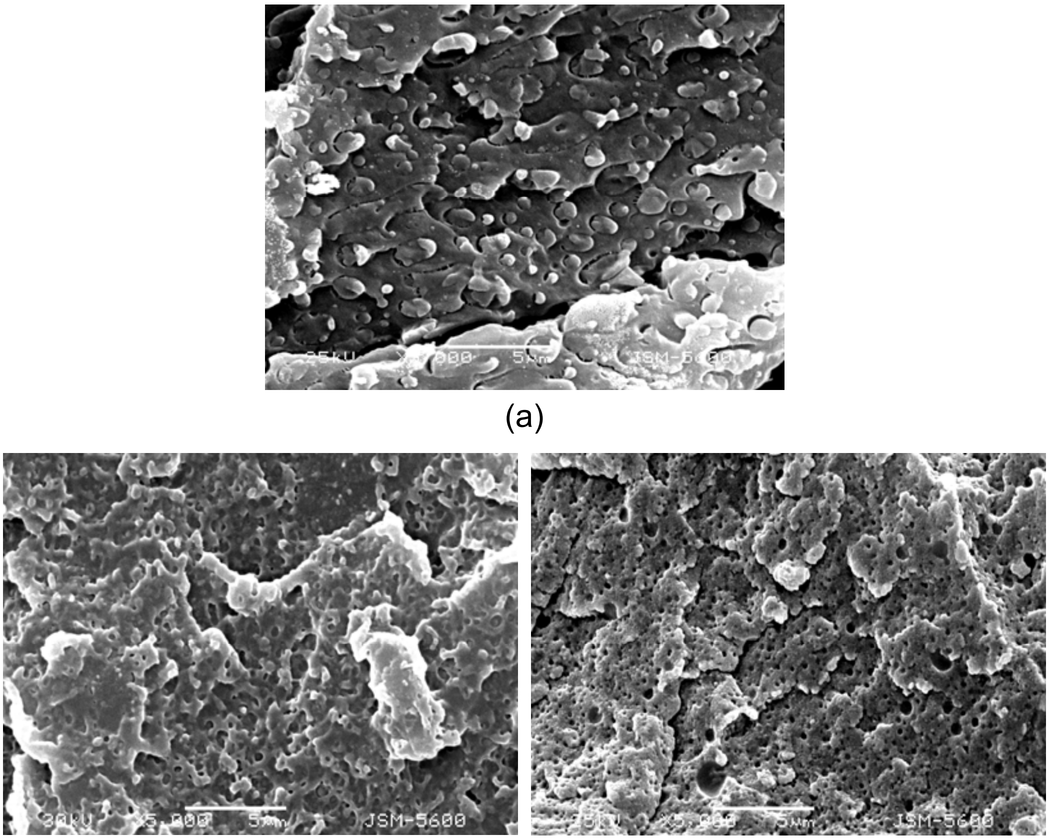


Fig. 4. The melting behavior of PBT/PC/MB-g-GMA blends with different MB-g-GMA contents. (0, 5, 10, 15, 20, 25 indicate the content of the MB-g-GMA in PBT/PC blends).

Morphological properties

SEM was used to investigate the morphology of the blends. The morphology of the PBT/PC blend is displayed in Fig. 5(a). It can be seen that when PBT is mixed with PC, PC disperses into PBT-rich matrix. The average particle size of PC domains is

0.8−1 μm, so it indicates that PBT and PC are partially miscible. Fig. 5(b) and (c) display the SEM micrograph of the PBT/PC blends with 10 and 20 wt% MB-g-GMA separately. It can be seen that MB-g-GMA particles disperse in the matrix uniformly. The addition of MB-g-GMA particles gives rise to a finer interfacial adhesion between PBT and PC. Fig. 5(b) and (c) show only two phases: modifier particles and a seemingly homogeneous matrix. So we can conclude that the miscibility between PBT and PC is improved by MB-g-GMA.

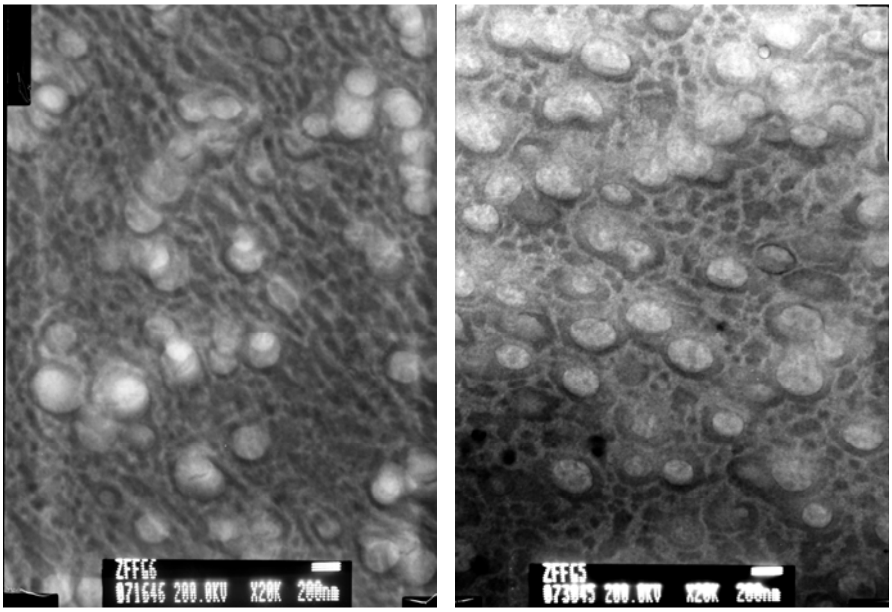


(a)

(b) (c)

Fig. 5. SEM micrographs of the cryo-fractured surface of the PBT/PC/MB-g-GMA blends (a) PBT/PC 50/50, (b) PBT/PC/MB-g-GMA 45/45/10, (c) PBT/PC/MB-g-GMA 40/40/20.

From SEM investigation to the morphology of PBT/PC/MB-g-GMA blend, we cannot identify the location of the MB-g-GMA phase in the blend. TEM investigation is a perfect way to supply us with the microstructure of the blends. Fig. 6 shows the micrographs of PBT/PC blends with 10 and 20 wt% MB-g-GMA. The white dispersing particles are enveloped by a thin layer of PC phase which shows black. Additionally, in Fig. 6(a), the PBT and PC display a co-continuous structure. However, PC shows dispersed phase in Fig. 6(b). This is because with the increase of MB-g-GMA content, it needs more PC to encapsulate the MB-g-GMA which leads to the decrease of PC content in the matrix. Different from Fig.5 (a), the PBT and PC domains seem much finer; the thickness of PC domain is about 0.1 μm, and the thickness of PBT domain is less than 0.1 μm. This is the reason why the PBT/PC/MB-g-GMA blends show a homogeneous matrix in Fig. 5(b) and (c).

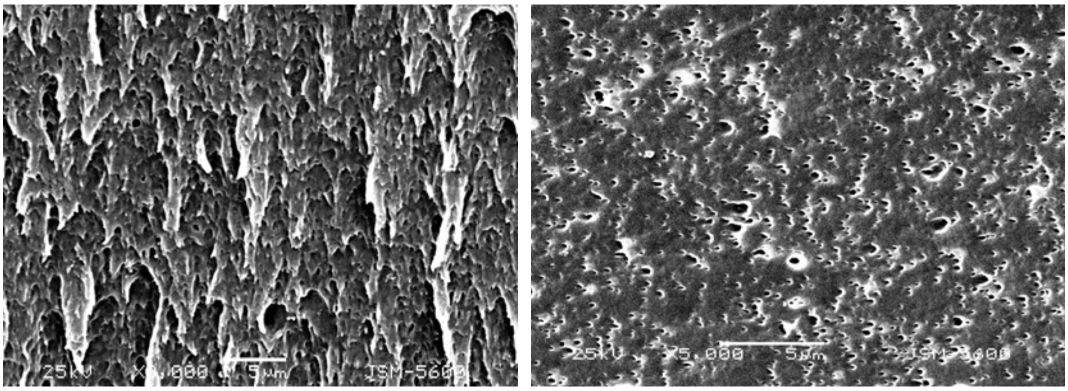


(a) (b)

Fig. 6. The TEM morphology of the PBT/PC/ MB-g-GMA blends.PBT/PC/MB-g-GMA 45/45/10 (b) PBT/PC/MB-g-GMA 40/40/20.

Fracture mechanisms

The notched impact toughness of the PBT/PC blends is low. Failure mechanism studies disclose that the PBT is a strain rate sensitive polymer. It becomes more rigid at higher strain rate and imparts a high plastic constraint on the ductile PC domains. The high constraint will maintain plane-strain conditions at the crack-tip and promote brittle fracture for the blends, leading to low impact toughness. Deformed morphology of the fractured surface is shown in Fig. 7(a).



(a) (b)

Fig. 7. SEM micrographs of notched Izod fracture surface (a) and the deformation zone under the fracture surface (b) for PBT/PC/MB-g-GMA (40/40/20) blends.

It is not difficult to find that extensive plastic flow of the matrix happens. Evidently, the shear yielding is initiated by the stress concentrations associated with rubber particles. The introduction of MB-g-GMA releases the plastic constraint of PBT to PC and the stress field of PC matrix changes from plane-strain to plane stress. This change induces extensive plastic deformation of PC matrix. Then the plastic deformation takes place for PBT phase around PC due to the thin PBT domain, and extends to the whole matrix. It is clearly shown that shear yielding of the matrix is the major toughening mechanism in the MB-g-GMA modified PBT/PC blends. From Fig. 7(b) we can find, below the surfaces parallel to the notched Izod impact fracture surface, the small holes resulting from voiding of the rubber particles was observed. Since the samples were not etched and no matrix crazing happen in high strain rate, the shear yielding of PBT/PC matrix and cavitation of PB particles were the major toughening mechanisms.

Conclusions

GMA functionalized MB particles have been prepared by emulsion polymerization processes. The epoxy-functionalized MB particles were used as impact modifiers for toughening the PBT/PC blend.

Mechanical properties show that the introduction of MB-g-GMA modifiers improves the impact strength of PBT/PC blends tremendously. Brittle-ductile transition takes place when the content of MB-g-GMA is between 10 and 15 wt%. The impact strength is 940 J/m when the addition of MB-g-GMA is 15 wt%. The notch impact strength of PBT/PC blends reaches 1023 J/m when the content of MB-g-GMA is 20 wt% and shows supper toughness.

DMA and DSC tests prove PBT was partially miscible with PC and the addition of MB-g-GMA further improved the miscibility of PBT and PC.

SEM displayed a very good dispersion of MB-g-GMA particles in the PBT/PC blends. TEM proved MB-g-GMA particles were enveloped by a thin layer of PC. PBT, PC showed co-continuous structure or dispersed phase which depended on the content of MB-g-GMA.

Deformation results showed shear yielding of the matrix and cavitation of rubber particles were the major toughening mechanisms.

Experimental part

Materials

The PBT was S3120 purchased from Engineering Plastics Plant of Yihua Group Corp, China; The PC used was a commercial product of Bayer Plastics designated as Makrolon 2805.

The MB-g-GMA materials were synthesized by emulsion polymerization method in our lab. The MB-g-GMA is the typical core-shell polymer with a soft core of PB which is grafted by a ‘shell’ of MMA and GMA copolymer. The central nucleus of PB particle provides the soft phase that induces toughening. The shell PMMA allows isolation of particles from the emulsion by providing a hard coating that keeps the rubbery cores from adhering to one another during the drying process. The average particle sizes of MB-g-GMA were between 300-500 nm.

Preparation of MB-g-GMA

MB-g-GMA was achieved by emulsion polymerization method. In the preparation process, a PB polymer was synthesized first and then MMA and GMA were polymerized on PB particles. PB latex used in this study was supplied by Jilin chemical industry group synthetic resin factory. The recipe for the preparation of MB-g-GMA is given in Table1. An oil-soluble initiator, cumene hydro-peroxide (CHP) was used in combination with a redox system. The redox initiator system, CHP, sodium pyrophosphate (SPP), dextrose (DX) and iron (II) sulfate ($FeSO_4$) was used without further purification. The emulsion polymerization was performed in a 3L glass reactor under nitrogen at 63 ^{o}C, and the reaction took place in an alkaline condition at PH 10. First, the water, PB, Initiator and KOH were added to the glass reactor and stirred 5 min under nitrogen, then the mixture of MMA and GMA was added in a continuous feeding way to the glass reactor. When the reaction was finished, the polymers were isolated from the emulsion by coagulation and dried in a vacuum oven at 60 ^{o}C for 24 h before being used. In the preparation of MB-g-GMA, the content of GMA was 2 wt% in MB-g-GMA.

Tab. 1. The Recipe of MB-g-GMA.

Ingredients	Content (g)
Water	1500
MMA	228
GMA	12
PB	360
CHP	2.6
SPP	2.4
DX	3.6
$FeSO_4$	0.06
KOH	0.6

Reactive blending and molding procedures

The PBT and PC pellets were dried in an oven at 80 ^{o}C for 12 h at least prior to blending. The PBT/PC 50/50 (wt/wt) blend was selected as the matrix of composites. The contents of MB-g-GMA in PBT/PC blends were fixed at 0, 5, 10, 15, 20 and 25 wt% respectively. The blending was carried out in a twin-screw extruder. The temperature along the extruder were 220, 230, 240, 240, 240, 240, 240, 220 ^{o}C and the rotation speed of the screw was 60 rpm. The melt stripes of blends were cooled in a water bath and then pelletized.

The extruded blends pellets were dried in a vacuum oven at 80 ^{o}C for 12 h then injection molded to prepare Izod impact specimens and tensile specimens.

Mechanical measurements

The notched Izod impact behaviour of the blends was determined using a XJU-22 apparatus at 23 ^{o}C according to ASTM D256. The samples with dimensions 63.5×12.7×6.35 mm^3 were obtained from injection molded specimens. The notch was milled in mill having a depth of 2.54 mm, an angle of 45^{o} and a notch radius of 0.25 mm. The uniaxial tensile behavior was carried out using an AGS-H tensile tester at 23 ^{o}C according to the ASTM D638, and the cross-head speed was 50 mm/min. For both mechanical tests at least five samples were tested and the average values reported. The samples were dried overnight at 23 ^{o}C prior to testing until the measurements were performed.

DMA and DSC analysis

The extruded polymer blends were compression molded in order to obtain bars that were suitable for DMA measurements. The polymer blends were melted at 240 ^{o}C for 5 min, then a slight pressure was applied. The melted samples were cooled under pressure, then solid bars were obtained. These bars were sized 30×10×1 mm^{3}. The apparatus used was the Diamond PE-115 from PE company of America. The DMA measurements were performed over a temperature range from 30 ^{o}C to 160 ^{o}C at a constant heating rate of 5 ^{o}C /min, and at a frequency of 10 HZ.

DSC measurements were conducted using a Perkin-Elmer DSC-7 from Perkin-Elmer company of America to study the melting behaviour of PBT/PC/MB-g-GMA blends. The samples were taken from the injection molded specimens and had a normal weight of about 10 mg. The samples were first heated from 0 up to 260 ^{o}C at 10 ^{o}C /min and maintained 10 min to remove thermal history, then cooled to 0 ^{o}C at 10 ^{o}C /min and then heated to 260 ^{o}C at 10 ^{o}C /min to obtain the melting temperature (T_m). The whole experiment was carried out under nitrogen atmosphere.

Morphological observation

The morphology of the blends was investigated using both SEM and TEM. The morphologies of the fractured surfaces of the blends were observed by SEM (model Japan JSM-5600). The samples were fractured in liquid nitrogen. The fracture surfaces were perpendicular to the mold filling direction (MFD) of the injection-molded bars and sputter coated with gold for SEM observation. Ultra-thin sections for TEM analysis were cut using a Leica ultra cutter at -100 ^{o}C to avoid the deformation of MB-g-GMA particles. The thin sections were then mounted on copper grids and, for improved contrast the specimens were exposed to RuO_4 vapor for approximately 30 min. The TEM study was carried out in a JEM-2000 EX.

Acknowledgements

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