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Mechanical properties and reactions of PBT/PTW blends

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Abstract The new rubbery poly(ethylene-butylacrylate-glycidyl methacrylate) (PTW) containing epoxy groups was used as a toughener for poly(butylene terephthalate) (PBT). The morphology and mechanical property of the PBT/PTW blend was studied. The reactions between PBT and PTW resulted in improvement of toughness, and were affected by the content of PTW. The reaction during the blending process was followed using an internal mixer. The simulated interfacial reaction between PBT and PTW was studied using the ARES rheometer. The complex viscosity curve could be divided into three stages to characterize the interfacial reactions between PBT and PTW at different temperatures. The temperature strongly affected the rates of the interfacial reaction and diffusion. The reaction of the mixture of PBT and PTW in the internal mixer was much faster than that at the simulated interfacial region. Finally, the differences between the simulated interfacial reaction and the reaction during the real processing were discussed.

Introduction

Poly(butylene terephthalate) (PBT) is a commercial engineering plastic with typical semi-crystalline. Due to its unique property, such as mechanical strength, chemical resistance, high melting temperature, and dimensional stability, PBT is a material of interest for numerous applications. Like other semi-crystalline polymer, however, PBT does not show sufficient toughness, in particular, high notched impact strength [1, 2]. In order to improve its fracture toughness, PBT was usually blended with rubbery polymer [1, 2], but such blend, being comprised of only two ingredients, resulted generally in poor mechanical properties, because of the weak interfacial miscibility. Therefore, the selection of an appropriate compatilizer was an important route to increase the interfacial miscibility and to improve the performance of PBT blend.

According to the action mechanism, various compatilizers could be divided into two types: physical compatilizers and chemical compatilizers. Compared to the physical compatilizers, the chemical compatilizers need not be to carefully optimize to the molecular structure, and the morphology of the blend prepared by using chemical compatilizer should be easily predictable and more stable than that prepared by using physical compatilizer. The hydroxyl and carboxyl end-groups of PBT could provide the possibility of reaction with some chemical compatilizers. The epoxy group, which could in situ react with these end-groups of the PBT, was widely used to improve the properties. Some articles described that GMA (glycidyl methacrylate) grafted with other polymer was used to heighten the toughness of PBT, for example EPDM-*g*-GMA [3, 4], EGMA [5], ABS-GMA [6], E-MA-GMA [7] and PS-*g*-GMA [8, 9]. MAh (Maleic anhydride) grafted with elastomer, which could react with the hydroxyl group, was also used to toughen PBT, such as EPR-*g*-MAh [10], POE-*g*-MAh [11, 12] and EVA-*g*-MAh [13]. The epoxy functional group appeared to be more effective for PBT modification than anhydride functional groups.

In addition, some reports [14–18] devoted themselves to study the interfacial reaction of several polymer blends theoretically and experimentally, but the interfacial reaction of PBT/PTW system was not published so far.

Poly(ethylene-butylacrylate-glycidyl methacrylate) (PTW) is a new copolymer containing epoxy groups (glycidyl

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groups), which could react preferentially with carboxyl and with hydroxyl groups. The butylacrylate segments could provide very good low temperature properties. PTW could also be an attractive modifier for impact resistance because of its capability of reactive processing and rubber toughening. In the present paper, PTW was introduced into the PBT. The morphology and mechanical properties of the blend would be investigated. To study the nature of compatibility, the rheological properties of the blend were also measured.

Experiment

Materials

The poly(butylenes terephthalate) (PBT) containing terminal carboxyl and hydroxy groups with the melt point of ca 222 °C determined by DSC, a natural grade product supplied from Nantong Synthetic Materials Co. Ltd., China. Poly(ethylene-butylacrylate-glycidyl methacrylate) (PTW) containing epoxy groups with the melt point of ca 75 °C determined by DSC, available from DuPont .Co. Ltd.

Preparation

The PBT and PTW pellets were dried in vacuum oven at 80 °C and room temperature for 12 h before use. The blends were with different ratio of PBT to PTW (100/0, 97.5/2.5, 95/5, 92.5/7.5, 90/10, 85/15, 80/20, 75/25, 70/30, by weight) were prepared in a twin-screw extruder at 260 °C and under 120 rpm. All extrudates were cooled by water immediately, and a pelletizer was used to cut the extrudates for obtaining the blend pellets. These pellets were dried at 80 °C for over 10 h and molded at 260 °C by using a TTI-80 plastic injection machine (Dong Hua Machinery LTD., Dongguang, China). The test specimens were prepared in accordance to the ASTM standard.

Determination of mechanical properties

The tensile and flexure properties were measured with a CMT 4204 universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, China) at a crosshead speed of 2 mm/min. The tensile samples were prepared and tested according to ASTM D638, type I specification. An extensometer with the gauge length of 50 mm was used for modulus measurement. Test of flexural specimens was conducted using a universal testing machine and the three-point loading mode. The ASTM D 790 standard was followed; an 80 mm support span and a 2 mm/min crosshead speed were used. Notched impact strength was tested with an XJU-22 Cantilever Beam impact machine (Chengde testing machine Co. Ltd., Chengde, China) in accordance with ASTM D256. For all the mechanical property determination, five samples were tested at least and at standard condition. The resulted data were then averaged.

Morphology analysis

In order to estimate the particle size of the PTW phase dispersed in the PBT matrix and the morphology of the blend, the surface of fractured specimen prepared by freezing in liquid nitrogen was observed with a scanning electron microscope (SEM) (JSM-6360LV, JEOL, Japan) after it was etched with hot xylene at first and then gold-sputtered. The apparent diameter of the dispersed PTW phase was measured with a ruler on the amplificatory SEM photograph. All the dispersed particles on the photograph of specimen surface were determined to calculate the number average diameter.

Determination of the viscosity during blending processing

In order to affirm the reactions between PBT and PTW during melt processing macroscopically, an internal mixer (HAAKE Minilab, Thermo Electron Corporation) with the rheological capacity and the speed of 50 rpm at 240 °C was used. Before mixing, all pellets were dried as mentioned above. The viscosity/time curves (η) of PBT/PTW blends with varied component ratios (100/0, 95/5, 90/10, 85/15, 80/20, 0/100, by weight) were measured.

Determination of the complex viscosity

In order to affirm the intrinsic reaction in the interfacial region between PBT and PTW, a simulated process was carried out. Three plates, two made of PBT and one of PTW, were prepared by compression molding using smooth and clean stainless steel tool at 260 °C and 150 °C, respectively. Before molding, all the materials were dried as mentioned above. The thickness of the plates was 4 mm for PBT and 8 mm for PTW. After molding, the plates were cut carefully with a blade to form discs with a diameter of 25 mm. Each disc was washed by acetone in an ultrasonic basin and dried in a vacuum oven at room temperature. Thereafter, one disc of PTW and two discs of PBT were placed into the ARES rheometer (Advanced

Rheometrics Expansion System, TA Instrument). The disc of PTW was placed in the middle and the discs of PBT were placed on the top and bottom of the rheometer. As soon as the three discs were put into the ARES rheometer at four different temperatures (240, 245, 250, 255 °C, respectively) under nitrogen environment, the variation of complex viscosity (η^*) with time was monitored. The time zero was defined as the starting point when the heating chamber of the rheometer was closed. The strain amplitude (γ_0) and the angular frequency (ω) were 0.01 and 0.5rad/s, i.e. in the region of the measurement accuracy and would not impair the interface of the blend.

Result and discussion

Morphology

Figure 1(a–e) shows the morphologies of the blends with varied PBT/PTW ratios (97.5/2.5, 95/5, 90/10, 80/20 and 70/30). All the samples in Fig. 1(a–e) had been etched with xylene for 48 h at its boiling point and the holes left on the surface of the PBT matrix represented the phase of dispersed PTW pallets. The average diameters of PTW pallets in the blends are listed in the Table 1. The dispersed fine domains with irregular shape are observed in Fig. 1. It is clear that the average diameters of these particles increase and the distance between the PTW domains decease with increasing content of PTW. Compared to some unreactive systems [7, 8, 10–12], the diameters of the pallets in Fig. 1 are much smaller.

Table 1 The diameters of PTW in the PBT/PTW blend

PTW content (wt%)	2.5	5	10	20	30
Particle diameters (μm)	0.23	0.30	0.34	0.37	0.58

Mechanical property

In Fig. 2, the tensile strength and flexure strength of PBT/PTW blends with varied PTW content are presented. Apparently, both the tensile strength and flexure strength of these blends decrease with increasing PTW content. The tensile modulus and flexure modulus as the function of PTW weight fraction are given in Fig. 3. In this figure, it is

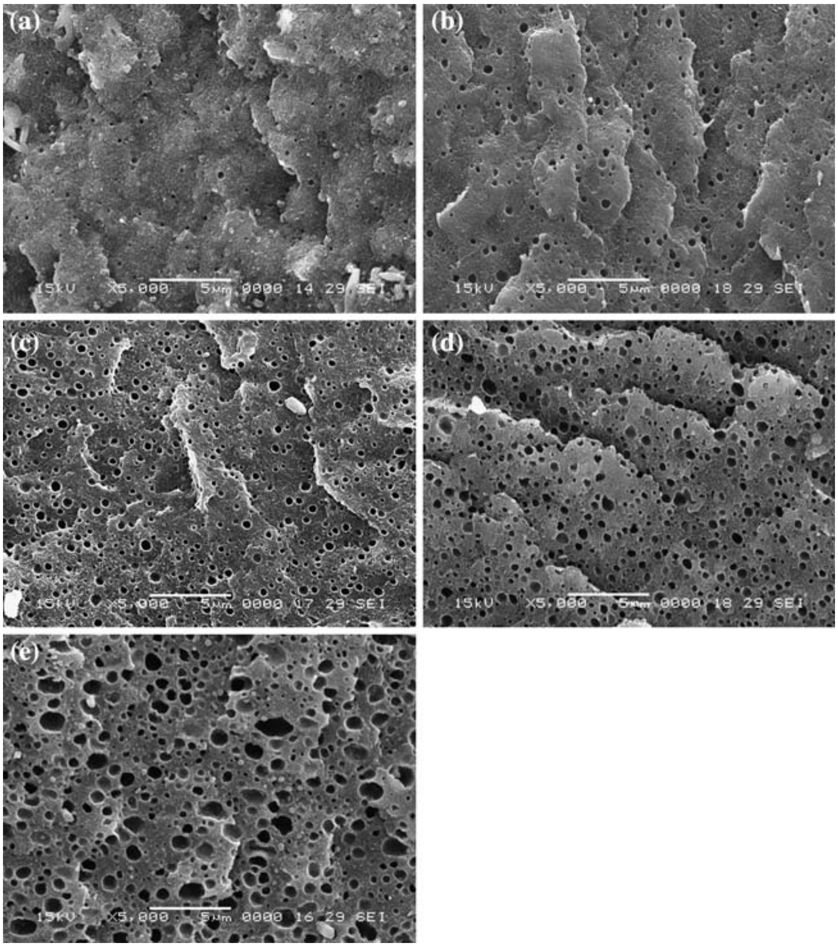


Fig. 1 Morphology of PBT/PTW blend, (**a**) 2.5 wt% PTW, (**b**) 5 wt% PTW, (**c**) 10 wt% PTW, (**d**) 20 wt% PTW, (**e**) 30 wt% PTW

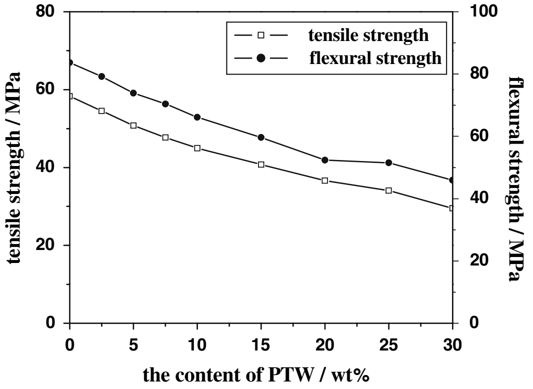


Fig. 2 The strength of PBT/PTW blends

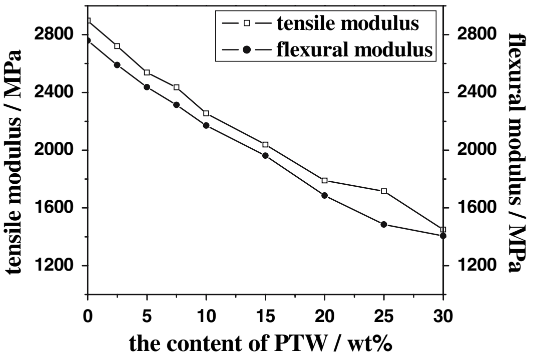


Fig. 3 The modulus of PBT/PTW blends

shown that the stiffness of the blend also tends to decrease with increasing PTW content. This should be the typical behavior of polymeric material toughened by rubber.

The variation of notched impact strength and elongation at break is shown in Fig. 4. When PTW content is low (less than 10 wt%), the notched impact strength of PBT/PTW blend increases slowly. As the PTW content grows over 10 wt%, however, the notched impact strength shows a sharp increase and the PBT/PTW blends become super tough. The notched impact strength increases from 38.5 J/m for pure PBT up to over 850 J/m for the blend containing 30 wt% PTW. The effect of PTW content on the elongation at break is more or less similar to its effect on the notched impact strength.

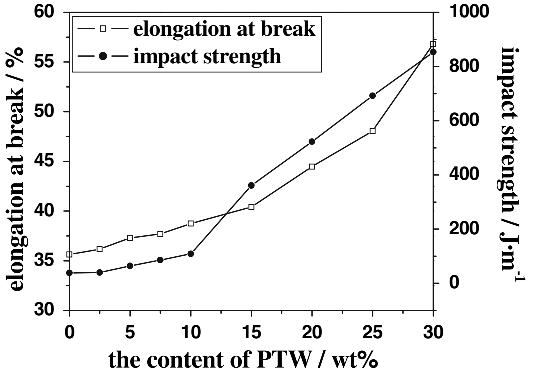


Fig. 4 The elongation at break and notched impact strength of PBT/PTW blends

Variation of the viscosity during processing in the internal mixer

In order to understand the reaction between PBT and PTW preliminary, rheological measurement was used to obtain qualitative information concerning the chemical reactivity during blend processing. Compared to pure polymer and the blend formed without any reaction, chemical reaction between reactive components would lead to increasing the blend viscosity. Figure 5 gives the relation of shear viscosity (η) to time for pure PBT, pure PTW and PBT/PTW blends tested at 240 °C. The η value of pure PBT or PTW is low and remains almost constant after several seconds. The fact that the η value of pure PBT decreases slightly might be attributed to its degradation. The η values of the PBT/PTW blends are significantly higher than that of pure PBT or PTW, increase with higher content of PTW. In Fig. 5, every curve for PBT/PTW blend could be divided into two stages, which should represent the reaction stage and the stage of reaction stop. The reaction stage shows the slope of the viscosity curve (dη/dt) due to the reaction between PBT and PTW, while the stage of reaction stop shows constant η value, meaning that the reaction is finished, but the curves of the blend containing lower weight percent of PTW in Fig. 5 drop after several minutes, which should be related to the degradation of PBT. Furthermore, the PTW content influences the reaction time dramatically.

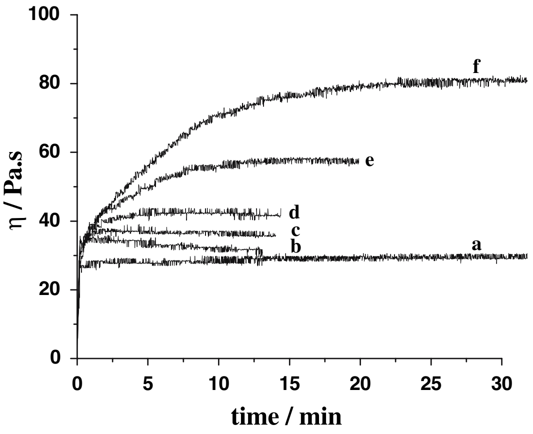


Fig. 5 The viscosity during PBT/PTW processing, (**a**) pure PTW, (**b**) pure PBT, (**c**) 5 wt% PTW, (**d**) 10 wt% PTW, (**e**) 15 wt% PTW, (**f**) 20 wt% PTW

The more the PTW content, the longer is the reaction period.

Variation of the complex viscosity

Figure 6 shows the relation of the complex viscosity (η^*) at 245 °C of PBT blended with unreactive silicone oil to time. The η^* value of this blend increases rapidly (less than 200s) and then reaches a steady value, does not change any more. Compared to the other study [19], much shorter time is needed to approach the steady value of this blend due to the small molecules and faster diffusion of silicone oil.

Figure 7 shows the variation of η^* values of the blend consisting of PBT and PTW at four different temperatures as reaction time goes on. It could be assumed that, for this blend, copolymers were formed at the PBT/PTW interface, which improved the interfacial bonding strength and increased the system's mean molecular weight. As the result, η^* value increased, accordingly. The rheological properties (η^*) should be related to the mean molecular weight, which was influenced by the amount of the in situ formed copolymers. In addition, a typical common character of the variation of η^* values could be found by analyzing the curves determined at 240, 245, 250, and 255 °C. Every one of these curves could be divided into three different stages. In the first stage, η^* value dramatically increases in initial short time. Following this stage, the curve of η^* value almost be kept as a horizontal line. At last, the curve of η^* value slowly increases again and reach a steady slope value. This phenomenon is quite different from non-reactive blends, where there is only an increase of η^*value in very short time before reaching a steady value.

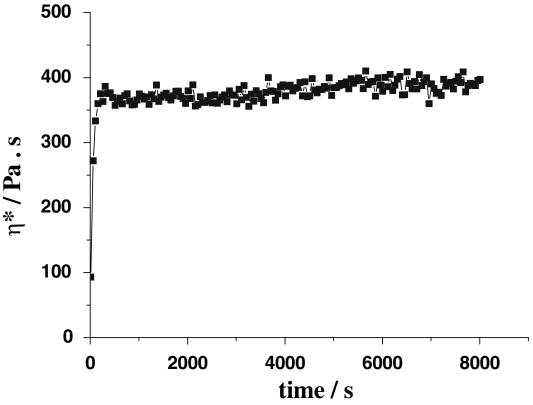


Fig. 6 The complex viscosity of PBT/ unreactive silicone oil blend at 245 °C

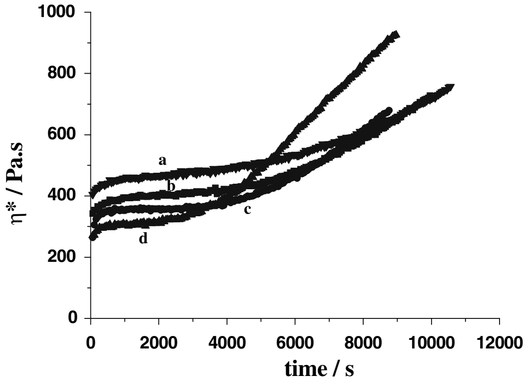


Fig. 7 The complex viscosity of PBT/PTW blend, (**a**) 240 °C, (**b**) 245 °C, (**c**) 250 °C, (**d**) 255 °C

Figure 7 shows also the dependence of the interfacial reaction on the temperature. The higher the temperature, the lower the η^* value is and the shorter time of the first and second stage goes on. Furthermore, the slope of η^* curve at the third stage also increases with increasing temperature.

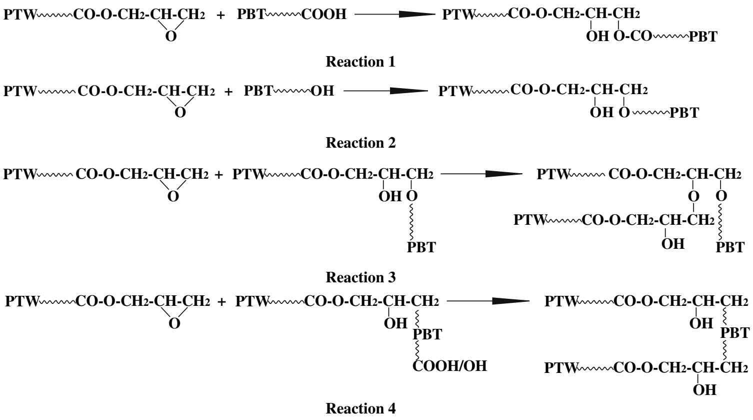
Reactions between PTW and PBT

The above results could be qualitatively explained by the reaction between PTW and PBT. For PBT/PTW blends in the present report, the processing conditions of each example were same. Therefore, the influence of the melt processing condition could be ignored. The reason why the blend exhibited such excellent toughness should be attributed to chemical reactions. The reactions between PTW and PBT were very complex and difficult to be clearly followed, but the dominant reactions took place between the GMA of PTW and the COOH– as well as OH– groups of PBT, which could be symbolically described in Scheme 1.

A few papers have reported on similar reactions involving the GMA functional groups, such as those related to the rubber-modified PBT and PET [6, 19–21]. In a recent publication, the reactions between GMA and the functional groups of PBT in Scheme 1 were confirmed [7].

In Scheme 1, the reaction 1 and 2 belong to the reactions between epoxy groups of PTW and carboxyl or hydroxyl end groups of PBT. The copolymers, formed at the interface between PTW and PBT by the reaction 1 and 2, acting as compatilizer, could promote the interfacial bonding strength and would be helpful for forming finely dispersed PTW phase in two ways. Firstly, the coalescence rate of disperse phase was reduced, due to steric repulsion. Secondly, the breakup rate of the dispersed phase was increased due to lowered interfacial tension. These factors resulted in fine distribution of the PTW phase and in better morphological behavior and mechanical properties of the PBT/PTW blends.

Scheme 1 Reactions during forming PBT/PTW blend



Reaction 3 and 4 in Scheme 1 represent the cross-linking reactions existing during processing the PBT/PTW blends. One start polymer of the reaction 3 involved the secondary hydroxyl groups along the molecular chains of the copolymer formed on the PBT/PTW interface during the reaction 1 and 2, and this reaction 3 could takes place in the disperse phase itself. The reaction 4 was based on the bifunctionality of the PBT matrix, as PBT contained two functional groups, which could react with the epoxy groups. Both cross-linking reactions should increase the viscosity of the blend and were unfavourable factors for dispersion of the PTW phase.

The four reactions represented in Scheme 1 resulted in the morphological behavior and the mechanical properties of PBT/PTW blends described above. The reaction 1 and 2 should contribute to better compatibility. Increasing the content of PTW, meaning less content of PBT with its reactive groups, could lead to more chances for cross-linking reaction during melt processing.

Due to the reaction 1 and 2, the toughness of the blend was improved very much. For the polymeric materials toughed with rubber, the craze and the shear zone are the main facts contributing to toughness, and both facts are influenced by the interface bonding strength, the diameter of the rubbery particles and the distance between the rubbery particles. For the blend of this report, the reaction 1 and 2 resulted in finely dispersed rubbery phase and much strong interfacial bonding strength, which could transfer the shear strength, bring to craze and shear zone in the blend. Additionally, the average distance between dispersed rubbery particles also dramatically influenced the toughness [5, 22]. At low PTW content, the average distance between the PTW particles was too long to form continuous craze and shear zone that resulted in slow increase of toughness. With increasing PTW content, the average diameter of the rubbery particles increased, which was disadvantageous to the toughness, but the average distance between the rubbery particles became shorter. According to the experimental results, the latter should be the major factor for forming continuous craze under fracture. Therefore, the blend with increasing rubbery PTW content became super tough, but there was a critical concentration for satisfactory toughness. In this study, the critical concentration of the PTW was 10 wt%, similar to those published by other articles [5, 11, 12].

The character of the viscosity of the blend during processing was differently influenced by the two type reactions taking place during blending. When the PTW content was low, reaction 1 and 2 was dominant, and the viscosity was not high. Adding more PTW, the η value increased more dramatically and the reaction finished quickly (compare the viscosity curve of 5% PTW to that of 10% PTW in Fig. 5). Otherwise, when the content of PTW was high, the cross-linking reaction 3 and 4 took place, except the compatibility reaction 1 and 2. Due to the second hydroxyl groups with weaker reactivity, the process needed more time and finished much later (see the viscosity curves of 15% and 20% PTW in Fig. 5).

As explained above, the interfacial reaction was divided into three different stages. The three stages could be tentatively represented as reaction-controlled stage, diffusion stage and diffusion-controlled stage.

During the reaction-controlled stage, the interface bonding strength increased due to the easy contact and the reaction (mainly the reaction 1 and 2 in Scheme 1) of the reactants PBT and PTW at their interface. The η^* value increased rapidly.

During the diffusion stage, the η^* value increased only a little. Most reactive groups at the interfaces might have been exhausted. A few reactive groups near the interfaces might react in accordance to the reaction 3 and 4 in Scheme 1, but such reactions did not contribute to any detectable reological properties. In this period, the molecules with reactive groups diffused from the bulk of the reactants into the interfacial region due to the concentration gradients, but these reactants could not contact and react easy with each other. Therefore, the variation of η^* value was hardly detected.

During the diffusion-controlled stage, the reactive molecular chains penetrated more and more from the polymer bulk into the interfacial region being composed of the grafted copolymers in the first stage, and the reactive groups contacted with each other, the reaction 1, 2, 3, and 4 took place again. The reactions were controlled by diffusion and kept steady at a given temperature. The reaction rate was dependent on the penetrating rate of the reactants from the bulk into the interfacial regions. The temperature influenced the reaction rate and the movement of the molecules.

There were many differences between the reactions during real processing and the simulated interfacial reaction. During the real processing, the particles of the dispersed polymer were broken up and coalesced by the disturbance of the screws. New interfaces appeared and disappeared again and again. When new interfaces appeared, the reactive polymers could contact each other, and the reactions could take place to form new copolymers. For the simulated interfacial reaction, the reactants were almost immobile. The reaction took place only at the interface of the two plates. When the reactants at the interface were exhausted and form the interfacial region composed of new copolymers, there was only one possibility, i.e., diffusion through the copolymer region and then the three stages of the interfacial reaction could be explained.

Conclusion

The multifunctional PTW with epoxy groups was an efficient reactive rubbery toughener for PBT. The viscosity measurements could give the indirect evidence that the reactions between PBT and PTW were effective to reduce and stabilize the size of the dispersed PTW domains and to enhance the toughness of PBT/PTW blends greatly. There was a critical PTW content of ca 10 wt% in respect to satisfactory toughness. If the PTW content was lower than the critical percent, the toughness increased insufficient, but, when the content was higher, the toughness showed distinct improvement, while the tensile and flexure strength of the PBT/PTW blend decreased.

The η value of the PBT/PTW blends during processing were significantly higher than that of pure PBT and PTW, increased with increasing content of PTW, and its variation curve could be divided into two stages. The curve of the variation of η^* value could be divided into three stages and the η^* value was influenced also by temperature.

The improvement of toughness and the variation of viscosity during processing should be attributed to the reactions between PBT and PTW.

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