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Fibre formation based toughening in polycarbonate/polyethylene alloy compatibilized with diallyl bisphenol A ether grafted polyethylene

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The toughness of polycarbonate/polyethylene (PC/PE) alloy compatibilized with o, o′-diallyl bisphenol A ether (DBAE) grafted polyethylene (DBAEgPE) was significantly improved in comparison with that of the neat PC/PE alloy and the additivity value. Especially for the compatibilized alloy at 15 phr of PC concentration, the impact strength and the critical strain energy release rate (G_{1c}) reached 55.0 kJ/m^2 and 1.20 J/mm^2, respectively, compared to 19.0 kJ/m^2 and 0.18 J/mm^2 for the uncompatibilized alloy. Fibre formation and fracture of the dispersed PC phase were observed for the alloy with high energy absorbing capability through scanning electron microscope (SEM). Employing a structural diagram, fibre formation based toughening (FFBT) was put forward and it was attributed to the fibre formation and fracture which occurred under the influence of the external impact force and the pressure acting on the dispersed PC particles caused by the difference between thermal shrinkage of PC and PE from processing temperature to room temperature.

1. Introduction

Strength and toughness of polymers utilized as a class of structural materials, are two of the most important properties. A lot of studies have consequently been done to improve these two properties. Blending and alloying of structurally different polymers are well known techniques used for this purpose [1, 2]. The ways to enhance the toughness of polymers roughly include elastomer toughening and rigid filler toughening. The former has been used widely and the typical examples are HIPS (high impact polystyrene) and ABS (acrylonitrile-butadiene-styrene copolymer resin) [1]. The latter was only observed in few polymer blends, such as PC (polycarbonate)/AS (acrylonitrile-styrene copolymer) and PC/PMMA (poly(methyl methacrylate)) systems [3, 4]. Blending PC with polyethylene (PE) has been the subject of many studies on blending improvement of polymers. The previous work considered mainly inclusion of a small amount of PE into PC to improve processability, moisture resistance and stress crack resistance of PC [5, 6]. Recently, much attention was paid to PE matrix/PC minor phase blend for the purpose of increasing the mechanical properties and heat resistance of PE [7, 8]. This can lead to a kind of novel engineering plastics, in particular, polyolefin based engineering plastics. However, a problem which must be faced is how to improve the compatibility between PC and PE since these two polymers are extremely immiscible and incompatible. The authors have synthesized a new graft copolymer, diallyl bisphenol A ether grafted polyethylene (DBAEgPE), as a compatibilizer in this blending system. It was found that DBAEgPE had significant compatibilizing effects on the PC/PE blend, and remarkably improved the mechanical properties and heat resistance [9–11]. Especially an amazing high energy absorbing capability was observed in the blend with an appropriate ratio of PC, PE and DBAEgPE. Based on morphology observation of the blends by scanning electron microscopy (SEM) combined with a diagrammatic sketch, fibre formation based toughening (FFBT) mechanism was put forward to analyse the high energy absorbing capability of the blend.

2. Experimental

The polymers used in this study included polyethylene (PE), polycarbonate (PC) and diallyl bisphenol A ether grafted polyethylene (DBAEgPE). The polyethylene is a commercial grade, 5000S obtained from Yangzi Petroleum Chemical Co., China, whose melt flow index is 0.98 g/10 min at 190°C, using a force of 49N. The polycarbonate is K1300, a commercial product of Teijin Chemical Ltd., Japan, and its number average molecular weight is approximately 2.8–3.5 × 10^4. DBAEgPE prepared in our laboratory was a graft copolymer of diallyl bisphenol A ether and low density polyethylene and has been reported elsewhere [9], its melt flow index is 0.82 g/10 min and the content of diallyl bisphenol A ether grafted in the macromolecular chains of polyethylene is about 2.5% by weight.

Prior to the blending experiment, the mixture of PC, PE and DBAEgPE was dried for 10 hours at 90 °C in the vacuum oven, then compounded in a co-rotating twin-screw extruder. The processing conditions were: temperature: 190 °C, 250 °C, 260 °C, 250 °C from hopper to die respectively; screw rotation: 100 rpm. The blends were extruded through a round die and pelletized, then subsequently injection molded into rectanglar strips of 120 mm × 60 mm × 10 mm on a reciprocating screw injection molding machine. The injection molding parameters were: temperatures for the different zones: 220 °C, 250 °C, 260 °C and 245 °C from feed zone to nozzle; injection pressure: 75 MPa; holding pressure: 55 MPa, injection time: 3 s; holding time: 12 s; cooling time: 40 s. The mold temperature was kept at 60 °C throughout the injection process and the hopper was heated to 100 °C by hot air to protect the materials from absorbing moisture during injection.

The rectanglar strips were used for a notched impact test and critical strain energy release rate (G_{1c}) test. The notched impact test was carried out by the use of an impact tester with an unsupported span of 40 mm. The dimension of the specimens machined from the injected rectanglar strips was 60 mm × 10 mm × 4 mm and the notch depth was one third of the specimen 4 mm thickness. The detailed experimental procedure used was ASTM D-638.

G_{1c} testing was conducted by Single Edge Notched Bending Test (SENB) according to ASTM D5045-93. The specimens were also machined from the injected rectanglar strips, and its dimension was 60 mm × 10 mm × 4 mm. A prefabricated V-shaped crack was made on the specimens by the use of a milling machine and the length of the crack was 5 mm. The specimen configuration is shown in Fig. 1. The stress ∼ strain curve of the specimen was obtained on an Instron testing machine at a cross-head rate of 10 mm/min and at a temperature of 20 °C. The G_{1c} value was calculated according to ASTM D5045-93.

A Hitachi SEM scanning electron microscopy (SEM) was used to explore the differences in morphological structures of the fracture surfaces. The surfaces for observation were prepared by two methods. One was obtained from the specimens directly impacted and fractured by an impact tester at room temperature, the other was made through fracturing the specimen after being frozen in liquid nitrogen for 60 minutes. Prior to observation all the surfaces were coated with a layer of gold and palladium in a vacuum chamber to make them conductive. The accelerating voltage of SEM was 20 KV.

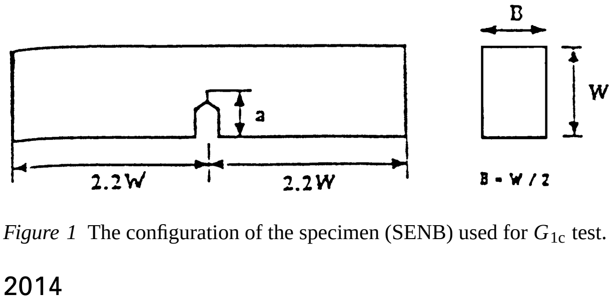

Figure 1 The configuration of the specimen (SENB) used for G_{1c} test.

3. Results and discussions

Polyethylene is a typical non-polar semi-crystalline polymer with a solubility parameter of $5.8 \times 10^3\ (\mathrm{kJ/m^3})^{1/2}$, while polycarbonate is a polar amorphous polymer with a solubility parameter of $14.5 \times 10^3\ (\mathrm{kJ/m^3})^{1/2}$ [12]. Therefore polycarbonate/polyethylene alloys are extremely immiscible from the thermodynamic standpoint. In general, it is of importance to know which component is the dispersed phase in an immiscible blend with an appropriate composition. For polycarbonate/polyethylene alloy in this study, the point of co-continuous phases was found at 45% by weight of PC. Hence, in the present work, the PC concentrations used in PC/PE alloys were less than 45 wt% to make sure that the polycarbonate was in the discrete phase.

3.1. Energy absorption properties of PC/PE alloy

Notched impact strength as a function of PC/PE alloy composition was shown in Table I. It can be seen that impact strength of PC/PE alloy without compatibilizer slowly increased with the PC concentration from 0 to 35 wt% based on the alloy, but it was still less than the value calculated from the additivity rule. When the PC/PE alloy contained 5 phr (total of PC and PE as 100 phr) by weight of diallyl bisphenol A ether grafted low density polyethylene (DBAEgPE) as a compatibilizer, the absorbing energy capability was increased rapidly for the blends with PC concentrations less than 15 wt%, and then decreased slightly above 15 wt% of PC, but the value was still much higher than that obtained from the additivity rule. Besides, a maximum notched impact strength was observed in the compatibilized 15/85 PC/PE alloy, whose impact strength reached 55.0 KJ/m^2, far exceeding the value, 19.5 KJ/m^2, obtained from the additivity rule at the same PC/PE composition, and the values, 45 kJ/m^2 and 15 kJ/m^2, for pure PC and PE, respectively.

Interfacial action between the matrix and the dispersed phase in the polymer alloy could be characterized by the use of the critical strain energy release rate (G_{1c}). G_{1c} value indicates the absorbing energy used to form new surface during the specimen fracturing. The

TABLE I Relationship between notch impact strength of PC/PE alloy and PC content

PC content (phr)	Notch impact strength (kJ/m^2) a*	b*	c*
5	15.4	23.6	16.5
10	17.2	32.5	18.0
15	19.0	55.0	19.5
25	20.5	43.8	22.5
35	23.7	38.6	25.5

∗: (a) neat PC/PE alloy.

(b) PC/PE alloy compatibilized with 5 phr DBAEgPE (total PC and PE looked as 100 phr).

(c) according to addition law, $P = P_1\phi_1 + P_2\phi_2$, where P is the impact strength of PC/PE alloy, P_1, P_2 are 45 kJ/m^2, 15 kJ/m^2, the impact strength of neat PC, PE components, respectively, ϕ_1, ϕ_2 are the mass concentration of PC, PE in the alloy, respectively.

TABLE II Critical stran energy release rate (G_{1c}) of PC/PE alloy*

PC content (phr)	G_{1c} (J/mm^2)		
	PC/PE	PC/PE/DBAEgPE*	Additivity value**
5	0.15	0.32	0.25
15	0.18	1.20	0.34
35	0.26	0.82	0.51

*: DBAEgPE concentration is constantly 5 phr (total PC and PE looked as 100 phr).

**: G_{1c} of pure PC and PE is 1.06 and 0.21, respectively.

greater the G_{1c} is, the stronger the interaction between the matrix and the dispersed phase.

The G_{1c} values of the neat PC/PE alloys and the compatibilized ones with 5 phr by weight of DBAEgPE are given in Table II. The trend of G_{1c} as a function of PC content was the same as that of the notched impact strength shown in Table I. A maximum G_{1c} value, 1.20 J/mm^2, was also observed at 15 phr by weight of PC, much higher than that of neat alloy at the same PC content, and that of pure PC, PE component.

Normally, if a polymer pair is incompatible, the absorbing energy capability is poorer than that of each component in the alloy, even if the polymer is thermodynamically miscible, the capability of absorbing energy is only the value calculated in terms of the additivity rule. The above results displayed a noticeable toughening phenomenon where the toughness of the compatibilized PC/PE alloys in the presence of DBAEgPE was significantly improved in comparison with the neat PC/PE alloy and the additivity value. Especially, when the alloy contained 5 phr DBAEgPE as a compatibilizer, the notched impact strength and G1c value exceeded those of PC and PE.

3.2. Morphology of PC/PE alloy observed through SEM

The scanning electron microscopic photographs of the neat PC/PE alloy fractured in liquid nitrogen are shown in Fig. 2. The photographs show a spherical dispersion of PC phase in the PE matrix, and a smooth interface between PC and PE was observed. This confirms that PC and PE are extremely incompatible. Besides, increasing PC content, the size of PC particle increased, which indicates that the coalescence of PC particles got more dramatic in the course of processing at high PC concentrations.

Fig. 3 shows the morphology of the fracture surfaces of the PC/PE compatibilized with 5 phr of DBAEgDE, in which Fig. 3a, b and c were the morphology of the alloys fractured in liquid nitrogen, and Fig. 3a′, b′ and c′ were the corresponding ones alloys fractured by an

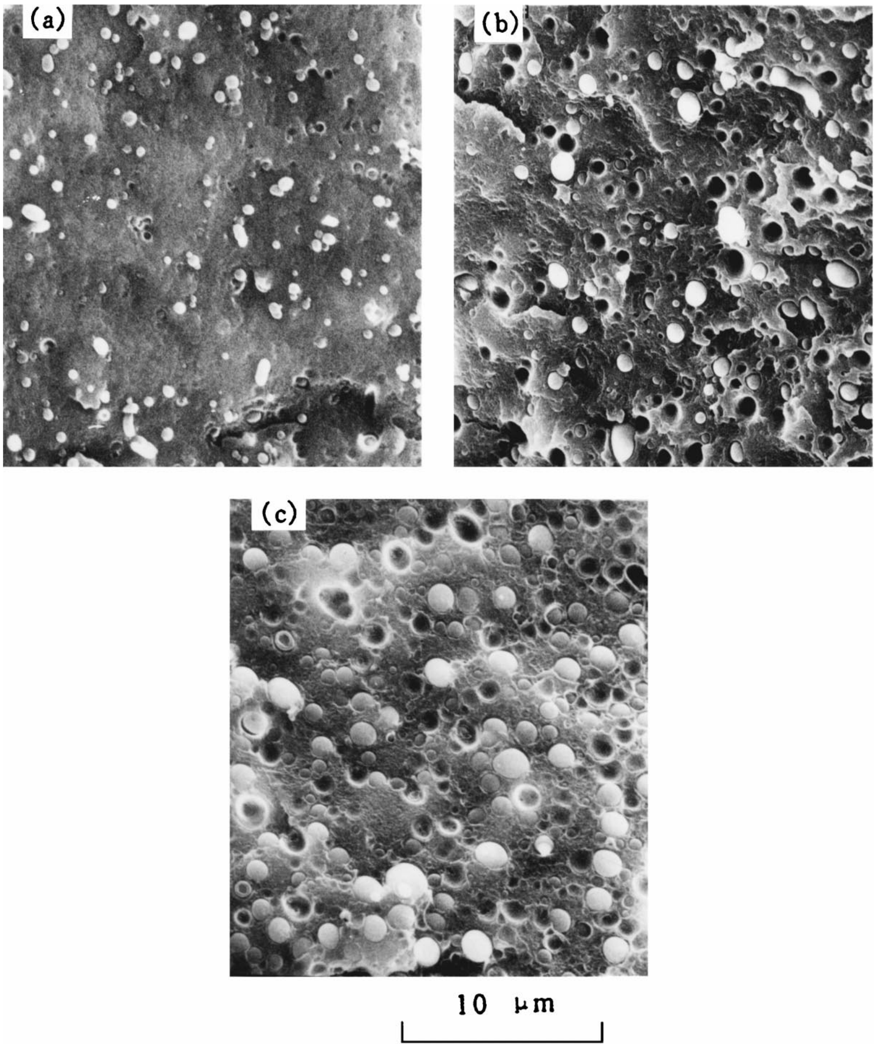

Figure 2 Scanning electron micrograph of the fracture surface of the frozen neat PC/PE alloy. PC content is (a) 5 phr, (b) 15 phr, (c) 35 phr.

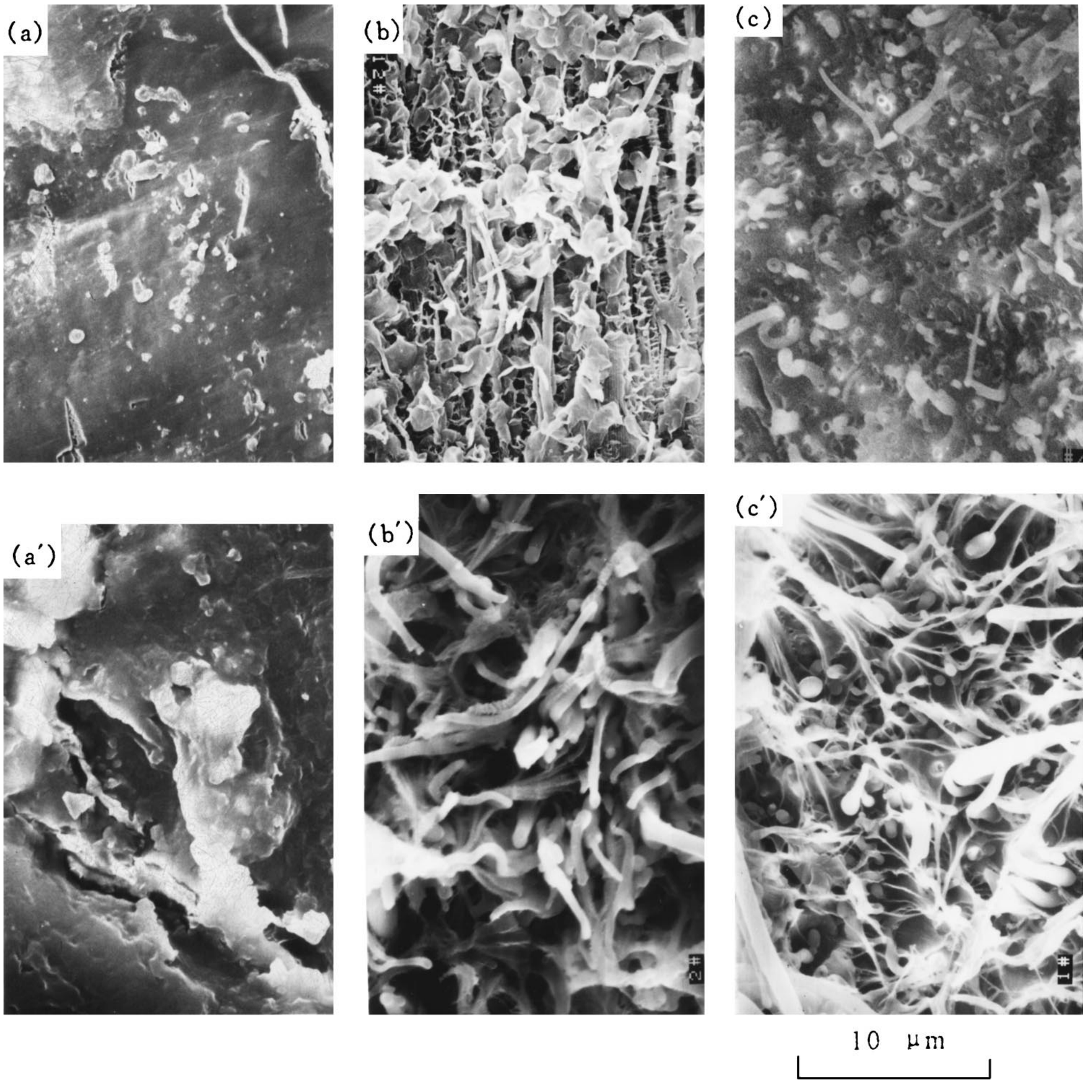

Figure 3 Scanning electron micrograph of the fracture surface of the PC/PE alloy compatibilized with 5 phr DBAEgPE. (a), (b) and (c): the surfaces obtained from fracturing in liquid nitrogen; (a′), (b′) and (c′): the surfaces obtained from impact fracturing at room temperature; The PC content is (a) and (a′) 5 phr, (b) and (b′) 15 phr, (c) and (c′) 35.

impact tester at room temperature. It can be seen that the 5 phr DBAEgPE made the morphology undergo a considerable change and the phase interface appears to be dim except that some indistinct fibre structures can be seen in Fig. 3b and c. This indicates that the compatibilizer, DBAEgPE, caused efficient compatibilization in PC/PE alloy. Moreover, when Fig. 3a, b and c are compared with Fig. 3a′, b′ and c′, respectively, the results showed that when the alloy contained 5 phr PC (Fig. 3a and a′), no obvious difference can be observed, but for the alloys containing 15 phr and 35 phr PC (Fig. 3b′ and c′) fractured at room temperature, a large number of fibres were formed and these fibres were plastically deformed, especially, the alloy with 15 phr PC was more significant.

From this, it is suggested that the fibre formation and plastic deformation are related to the toughening phenomenon in the PC/PE alloy compatibilized with 5 phr DBAEgPE.

3.3. Fibre formation based toughening in compatibilized PC/PE alloy

On the basis of the alloy morphology observed by SEM, it can be concluded that the amazing toughening phenomenon was caused by a toughening mechanism, different from elastomer toughening and rigid filler toughening. Hereafter this novel toughening mechanism is referred to as fibre formation based toughening mechanism (FFBT). Its toughening process can be illustrated through the structural diagram shown in Fig. 4. As shown in Fig. 4a and a′, whether the alloys were compatibilized or not, the PE matrix embedded tightly the dispersed PC droplet [13]. This resulted from the thermal history of the alloy. When the alloy cooled from the processing temperature (260 °C) to room temperature, the PE shrank much more than the PC did since the coefficient of thermal expansion of the PE is greater than that of PC. Therefore, for PC matrix/PE dispersed phase alloy, there are voids between PE particles and the PC matrix which can be found in Fig. 5 where the composition of PC/PE is 65/35 by weight. For PC minor phase/PE matrix alloy shown in Fig. 3, PE and PC have tight interfacial contact. This led to a high pressure between PC and PE shown through the arrows inside the square in Fig. 4a and a′. In the course of the impact, force represented by the arrows outside the square applying to the alloy specimen, the matrix, PE, was deformed and subsequently transmitted a force

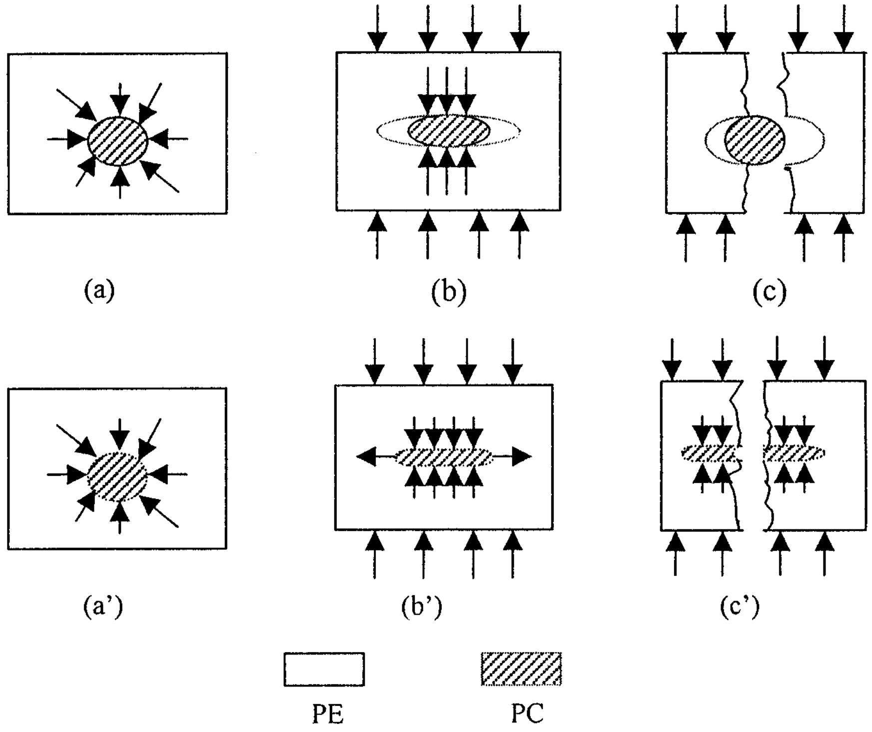

Figure 4 Diagram of the process of fibre formation based toughening. (a), (b) and (c) are uncompatibilized, (a′), (b′) and (c′) are compatibilized where a dotted line is used to indicate the compatibilizing effect of the interface, (a) and (a′) are the original specimens, (b) and (b′) are the specimens in the course of impacting by an external force, (c) and (c′) are the specimens broken by the impact force. The arrows outside the square present the external impact force, and the arrows inside the square present the compression from the matrix (and the interactions between the dispersed phase and the matrix in the compatibilized alloy).

Figure 5 Scanning electron micrograph of 65/35 by weight PC/PE alloy where PC is the matrix.

to the PC particle. Because of the deformation of PE, there was a relative motion tendency in the interface between PC and PE. As a result of this, the PC particle received two forces and would, to some extent, deform, as shown in Fig. 4b and b′. However, the deformation of PC in the alloy without the compatibilizer should be distinctly different from that of PC in the alloy compatibilized with DBAEgPE. For the neat PC/PE alloy, because the adhesion between PC and PE was very poor, relative motion occurred at the interface. The PC particle consequently produced slight plastic deformation, even elasticity, and voids appeared at the end of the PC particle parallel to the direction of the deformation of PE. As to the compatibilized alloy, based on the fact that the compatibilizing effect of DBAEgPE on the PC/PE alloy was very effective, the interactions between PC and PE were so strong that the PC particle under the influence of the pressure exerted by the PE matrix was plastically deformed into fibre. PC fibre and PE matrix contacted tightly and there was no void at the end of the PC fibre in comparison with the uncompatibilized alloy. When the PE matrix was fractured during the impact, the dispersed PC showed different results for the compatibilized and noncompatibilized alloys, as shown in Fig. 4c and c′. The PC particle in the noncompatible one still kept its original shape (sphere) or showed a slight plastic deformation (ellipsoid), while in the compatible one, because the compatibilizer made PC fibre and PE matrix adhere firmly, the PC fibre was fractured together with the matrix. It is obvious that, in the compatibilized alloy, a great quantity of energy was dissipated when the PC particle was deformed into fibre and then the PC fibre was fractured. Therefore the compatibilized alloy had a remarkable energy absorbing capability resulting from the fibre formation based toughening (FFBT). The energy absorption in the FFBT can be expressed as follows:

$$E_{\mathrm{I}} = E_{\mathrm{ym}} + E_{\mathrm{yd}} + E_{\mathrm{bm}} + E_{\mathrm{bd}} + E_0 \qquad (1)$$

where E_{I} is the total energy absorption, E_{ym} is the energy absorption caused by ductile yield of the matrix, E_{yd} is the energy absorption of the dispersed particles deformed into fibres, E_{bm} is the fracture energy absorption of the matrix, E_{bd} is the fracture energy absorption of the fibres and E_0 is the energy absorbed through other ways. For the noncompatible system, E_{bd} equaled 0 and E_{yd} was also very low, so the alloy had comparatively small energy absorbing capability, whereas in the well-compatibilized alloy, E_{bd} and E_{yd} were very high, and the alloy showed significant fracture toughness. As discussed above, it can be concluded that the conditions for FFBT are the following: (i) prior to the alloy being impacted, in the dispersed phase there is a rather high pressure which is combined with the external impact force to make the particle deform, (ii) the matrix and dispersed phase should have high interfacial interaction, hence in the process of the impact force acting on the alloy, the particles can be considerably plastically deformed into fibres, and consequently the fibres are broken together with the matrix; (iii) if the original particles have the shape such as rodlike particles, it is of benefit to produce FFBT. Moreover, the concentration of the discrete phase in the alloy plays an important role in FFTB. In the alloy with a low concentration of the dispersed phase, the size of the particles is too small and the particles are mostly spheres, so the particles are difficult to deform, and even if some particles are deformed, the contribution of the energy absorption caused by particle deformation to total energy absorption is small. When the concentration of the dispersed phase is very high, even though the compatibilizer is added into the alloy, the domains of the dispersed phase are too large, which makes the particle also difficult to deform and fracture. Therefore, there is an optimal concentration of the dispersed phase to produce FFBT. In PC/PE alloy, the optimal concentration of PC is approximately 15 phr (total of PC and PE as 100 phr).

Fibre formation based toughening is a novel toughness mechanism in polymer alloys. It is theoretically and technologically important because it can offer the potential to develop a polymer alloy with high toughness. Further work will involve more evidence to confirm FFBT.

4. Conclusion

1. The toughness of the PC/PE alloy compatibilized with DBAEgDE was significantly improved compared to neat PC/PE alloy and the additivity average. Especially, for the compatibilized alloy at 15 phr of PC concentration, the impact strength and the G_{1c} value reached 55.0 kJ/m^2 and 1.20 J/mm^2, respectively, while 19.0 kJ/m^2 and 0.18 J/mm^2 for the uncompatibilized alloy.

2. SEM photographs of the alloy suggest that the fibre formation and plastic deformation of the fibre were connected with the amazing toughening phenomenon in the compatibilized PC/PE alloy.

3. Fibre formation based toughening (FFBT) mechanism was proposed to explain the toughening phenomenon. The high absorbing energy capability was attributed to the fibre forming and fracturing, which occurred under the influence of the external impact force, and the pressure acting on the dispersed PC particles caused by the difference between thermal shrinkage of PC and PE from processing temperature to room temperature.

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