

Influences of Hyperbranched Polyethylenimine on the Reactive Compatibilization of Polycarbonate/Polyamide Blends^{*}

Ming-ji Wang^{a, b}, Guang-cui Yuan^{a**} and Charles C. Han^{a**}

^a State Key Laboratory of Polymer Physics & Chemistry, Joint Laboratory of Polymer Science & Materials, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b Institute of Phenolic Resin, Jinan Shengquan Group Co., Ltd., Ji'nan 250204, China

Abstract The influences of hyperbranched polyethylenimine (hPEI), which possesses many reactive amino end-groups, on the blending properties of bisphenol-A polycarbonate (PC) and amorphous polyamide (aPA) were systematically investigated. Scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) were used to observe the effect of hPEI on morphologies of PC and aPA phases in bulk blends. While the interfacial fracture toughness between planar PC and aPA layers with and without hPEI was studied by using augmented double cantilever beam (ADCB) method. Results show that the compatibility in PC/aPA blends can be significantly improved by adding a small amount of hPEI, mainly due to the interchange reactions between the polymers leading to the formation of block copolymers, cross-linked polymers and molecules with other constitutions. The augmented double cantilever beam experiments showed that the reactive process drastically reinforced the interfacial adhesion between planar layers of PC and aPA. However, degradation takes place during annealing at 180 °C, which was responsible for the production of small molar mass species of PC.

Keywords: Polyamide; Polycarbonate; Polyethylenimine; Blend; Reactive compatibilization.

INTRODUCTION

Polyamide (PA) and bisphenol-A polycarbonate (PC) are important commercial polymers, each of them provides outstanding performances in a variety of applications. However, PA (for example, PA6) suffers from its considerable hygroscopicity while PC is insensitive to moisture and dimensionally very stable. On the other hand, PA6 is strongly resistant to most solvents while PC is not. For some important applications, *i.e.* automotive parts, it is important to enhance chemical resistance of the resins to aggressive solvent, for example, acetone, aromatic solvents, gasoline, and the like, in combination with excellent levels of other necessary properties, by use of certain novel blends or double layered structures of PC with polyamide. Therefore, extensive studies on blends of PA6 and PC have been conducted to obtain an excellent material which is resistant to organic solvents, insensitive to moisture, and durable under various weathering conditions^[1–5]. A major problem in blending PC and PA is their thermodynamically immiscibility over the whole range of composition. Compatibility was obtained after long time melt mixing through chemical reaction between PC and PA, giving rise to PC-PA block copolymers which act as compatibilizers^[6]. Another effective way to improve the interfacial adhesion between the phase components of PC/PA blends is by adding a third component as compatibilizer which will physically improve the compatibility of blending components or chemically react with both blending components^[5, 7–11].

^{*} This work was financially supported by the National Natural Science Foundation of China (No. 21004069).

^{**} Corresponding authors: Guang-cui Yuan (袁光萃), E-mail: gcyuan@iccas.ac.cn
Charles C. Han (韩志超), E-mail: c.c.han@iccas.ac.cn

Received August 15, 2014; Accepted September 12, 2014

doi: 10.1007/s10118-014-1475-0

For example, poly(propylene oxide) can increase the mobilities of PA6 and PC molecules due to the plasticizing effects and consequently increases the probability of the reaction between the $-\text{NH}_2$ and $-\text{O}-\text{CO}-\text{O}-$ groups of PA6 and PC, respectively^[10, 11]; epoxy resin was considered as an effective compatibilizer in PC/PA6 blends for the high chemical reactivity between the epoxide groups and the phenolic hydroxyl end groups of PC or the amide groups of PA6^[5].

Hyperbranched polymers are known to have special properties defined by their three dimensional structure and the large number of functional groups. The viscosity of a hyperbranched resin is lower than that of a linear resin with the same functionality and molecular weight. Therefore, hyperbranched polymers can be used as polymer rheology control agent as well as multifunctional macromolecules^[12]. In recent years, some hyperbranched polymers have been studied intensively in blends for various purposes. Massa *et al.*^[13] have found that, when PC was blended with hyperbranched polyesters, partial miscibility was observed due to strong hydrogen bonding and the blends exhibited an increase in the tensile and compression modulus. Voit *et al.*^[14] also showed that the blends of hyperbranched poly(ether amide) and PA6 exhibited a significant reduction in the melt viscosity without loss of mechanical properties as compared to pure PA6. Based on the investigation of the influence of hyperbranched polymers on the interfacial tension of polypropylene/PA6 blends, Månson *et al.*^[15] developed a model to relate the interfacial tension to the diffusivity and reactivity of the compatibilizer. Their model showed that the diffusivity and reactivity of a multifunctional hyperbranched polymer are higher than those of a linear polymer. Therefore, reactive hyperbranched polymers have strong potential as compatibilizers in diffusivity-dependent processes such as film co-extrusion and fusion bonding.

In recent years, amorphous polyamide (aPA), which is transparent and has relatively high glass transition and thermal decomposition temperatures, has attracted more and more attentions from researchers. Thermoplastic blends comprising PC resin and aPA exhibit excellent physical properties^[16]. In our previous work, we have investigated the interchange reaction process at the interfaces between PC and an amorphous PA (aPA) in blends and bilayer samples^[17]. It has been found that, aminolysis was the main process at 160–180 °C with the random attack of amino terminal groups of aPA on the inner carbonate groups of PC, thus the simultaneously scission of PC chains and formation of PC-aPA copolymer chains during the reaction process can improve the compatibility between PC phase and aPA phase. Since the number of carbonate groups of PC which takes part in the reactions could be treated as infinite while the end reactive group of aPA was quite limited compared with the carbonate groups, the reaction kinetics was controlled by the diffusion of aPA to the interface and it followed a first-order diffusion controlled mechanism in the reaction process. The main purpose of this work is to investigate the influence of hyperbranched polyethylenimine (hPEI) on the blending properties of PC and aPA. Since the viscosity of blends can be affected through the addition of a diluent and the multifunctional reactive diluent can increase the efficiency of the reaction, the addition of hPEI was expected to improve the adhesion between two phases. On the other hand, the *in situ* reactive compatibilization is important in multilayer packaging film and multilayer coextruded tubing applications, therefore, the development of interfacial fracture toughness of multilayer specimens as a function of reaction time was also considered in the present work.

EXPERIMENTAL

Materials

Two PC samples with different molecular mass were used in this study and represented by PC1 and PC2 as shown in the following analysis. The PC1 was synthesized in our lab^[17] and the PC2 was purchased from Sigma-Aldrich. The number-averaged molar mass (M_n) and the polydispersity determined by gel permeation chromatography (GPC, Waters 1515) (comparing with polystyrene standard) with tetrahydrofuran as the solvent were 1.8×10^4 g/mol and 1.9 for PC1, and 3.8×10^4 g/mol and 2.0 for PC2.

The aPA was synthesized in our lab^[17]. The number-averaged molar mass and the polydispersity of the aPA used in this study were determined by GPC (comparing with polystyrene standard) with *N,N*-dimethylformamide as the solvent were 1.5×10^4 g/mol and 2.0, respectively.

The hPEI was purchased from Sigma-Aldrich as a liquid with purity > 99%. The $M_n = 1.0 \times 10^4$ g/mol,

probably determined by viscosimeter method, was provided by the manufacturer. The hPEI contains the primary, secondary, and tertiary amine groups in a 1:1.07:0.77 ratio.

Blend Preparation

The homopolymers were dried for 24 h at 75 °C under vacuum before use. Blend samples were mixed in a Haake miniCTW laboratory mixer with a rotor speed of 100 r/min at 240 °C for 3 min followed by melt compression at 240 °C and air cooling. The blended specimens with thickness about 1 mm were obtained. The specimens were annealed under vacuum at 180 °C for different time before measurements. The annealed specimens were fractured at room temperature. The fracture surfaces were coated with platinum in a vacuum chamber for SEM (JEOL JSM 6700F) observation. The SEM was operated at voltage of 5 kV. A selective solvent (dichloromethane) was used to remove the PC-rich phase in blend samples, and SEM was also used to investigate the topography of the exposed PA-rich phase.

Thermal Property Measurements

The glass transition temperatures (T_g s) of samples with various components were measured by differential scanning calorimetry (DSC, Mettler Toledo DSC822e). The samples, about 5 mg by weight, were cut from the extrusion-molded pieces and underwent the following thermal cycle: heating at 20 K/min from 20 to 250 °C, annealing for 5 min at 250 °C, cooling at 10 K/min to 40 °C, reheating at 10 K/min. The T_g was recorded in the second heating run as the temperature corresponding to the midpoint of the specific heat change.

Fracture Toughness Measurements

The augmented double cantilever beam (ADCB) method was used to estimate the fracture toughness, G_c , of samples with different annealing time^[18, 19]. The samples for ADCB have forms shown in Figs. 1(a) and 1(b). Bilayer samples shown in Fig. 1(a) were prepared to investigate the annealing time dependence of interfacial fracture toughness without adding hPEI. The PC and aPA layer with a thickness of 1 mm were first prepared on a hot press heated at 240 °C respectively. The mounted bilayer specimens were annealed under vacuum at 180 °C for different time before ADCB measurements. Samples shown in Fig. 1(b) were prepared to investigate the effects of hPEI on the development of interfacial fracture toughness as a function of annealing time. The PC/hPEI (100:1, $W:W$) and aPA/hPEI (100:1, $W:W$) blend films with a thickness of 1 μ m were prepared in advance by solution casting method from chloroform and 1,1,1,3,3,3-hexafluoro-2-propanol solutions with concentrations of 10 mg/mL, respectively. The films of PC/hPEI and aPA/hPEI blends were dried at 75 °C under vacuum and then mounted on top of the PC and aPA substrates respectively. The thick homopolymer substrates (thickness of 1 mm) with thin blend films mounted on top were heated at 240 °C for 5 min to insure that the blended tops were sufficiently bonded with the homopolymer plates. Samples shown in Fig. 1(b) were annealed at 180 °C for different time before the ADCB measurement at room temperature.

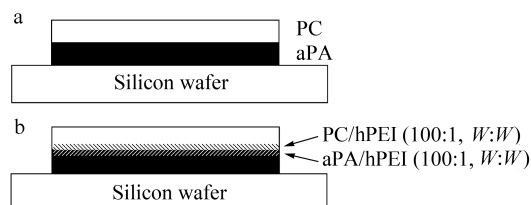


Fig. 1 Sample forms for ADCB method: (a) without hPEI and (b) with PEI at the interface

The operation steps of fracture toughness measurements were described by Ougizawa *et al.*^[19]. Samples were cut out to have a dimension of 50 mm (length) $\times$ 10 mm (width). A razor blade of thickness b was inserted at the interface between PC and aPA. Then the blade was gradually pushed into the specimen along the interface until it reached 10 mm from the sample edge. Here, the upper PC layer was deformed by the insertion of the razor blade. After 24 h, a yield crack length, a , between the edge of the blade and the crack tip was measured, and the blade was pushed in again by 5 mm. This procedure was repeated three times and the obtained crack

length was averaged. The fracture toughness, G_c , was then calculated by the following equation^[18, 19]:

$$G_c = \frac{3Ed^3b^2}{8a^4[1 + (0.64d/a)]^4}$$

where the E is the Young's modulus of PC (2.4 GPa) and d is the thickness of the upper PC layer.

RESULTS AND DISCUSSION

Morphologies

The morphology of polymer blends after mixing is controlled by many factors such as composition, viscosity ratio and elasticity ratio between the components, interfacial tension, and processing conditions^[20]. It is worth mention that PC and aPA are substantially immiscible^[17]. Figure 2 shows SEM images of fracture surface of

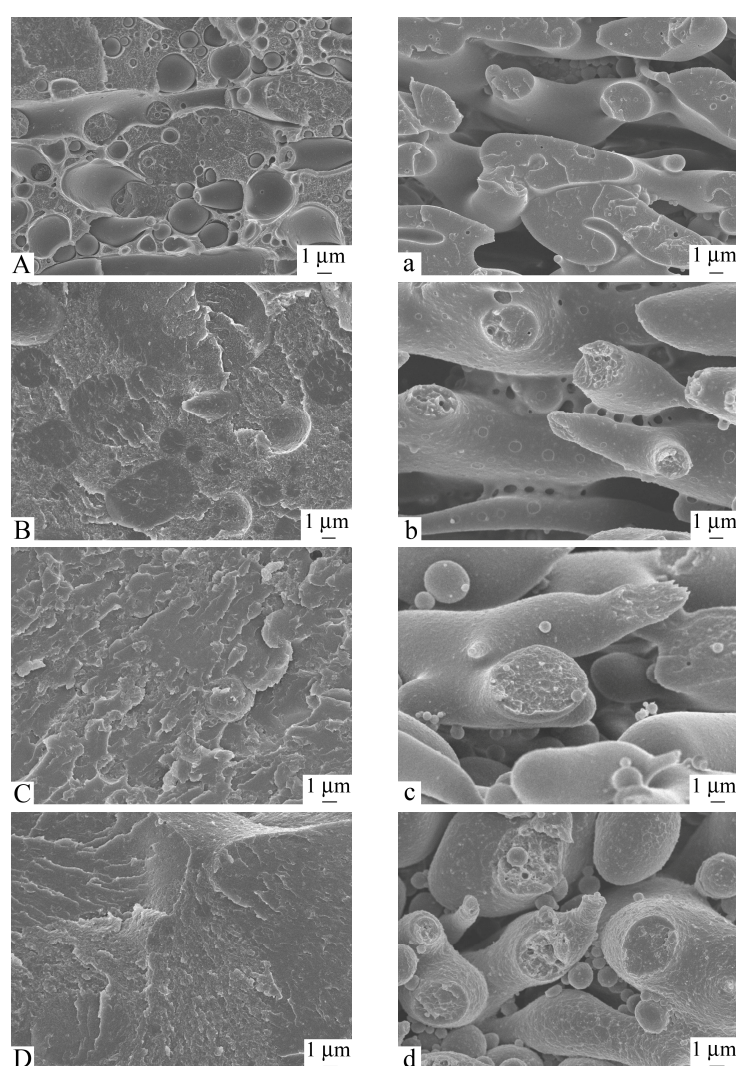
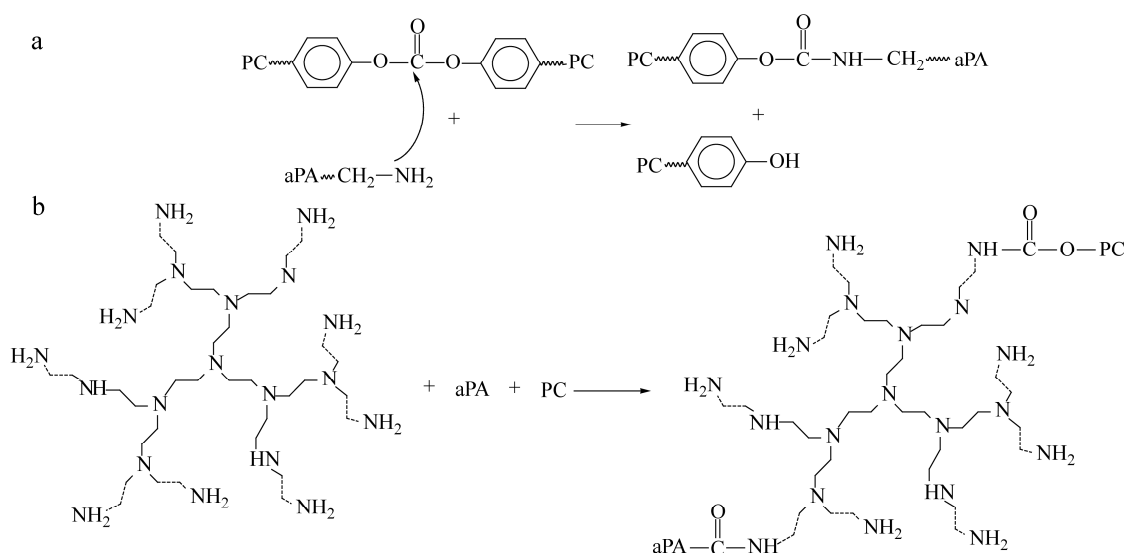


Fig. 2 SEM images of fracture surface of binary blends and ternary blends: (A) 50/50 PC1/aPA blend before annealing, (B) 50/50 PC1/aPA blend after annealing at 180 °C for 600 min, (C) 50/50/1 PC1/aPA/hPEI blend before annealing and (D) 50/50/1 PC1/aPA/hPEI blend after annealing at 180 °C for 600 min. The SEM images on right were the corresponding morphology of samples on left with the PC-rich phase being extracted by dichloromethane.

PC/aPA binary blends and PC/aPA/hPEI ternary blends. As shown in Fig. 2(A), the morphology of 50/50 PC/aPA blend, prepared in a mini extruder, was characterized by the presence of two well-segregated homophases of PC and aPA. The PC and aPA phases could be easily distinguished from the surface characteristics: the aPA fracture surface is very smooth compared to PC that breaks into a rough surface. Normally, the reactive compatibilization could be negligible after a short period mixing process^[3, 10]. In our studies, the adhesion between two phases was too poor to protect the interface from detaching before annealing process proceeded, which indicated chemical reactions are generally negligible during the melt blending procedure. The sample was annealed at 180 °C for 600 min after blending. Partial interaction was observed, with the PC phase more or less strongly bonded to the aPA phase (Fig. 2B). It seemed that there was no significant change in the co-continuous morphology, because the surface tension of both phases kept the polymer domains separated and impeded coalescence. The interactions were concentrated at the interface between the homopolymers, and the interfacial adhesion had been strengthened by chemical reaction enough to inhibit the generation of interfacial gap during fracture processing. The interfacial roughness can be the indicator of the interfacial tension which can be affected by the quantity of copolymers locate at the interface in some degree^[21–24]. The roughness of the interface can always reflect the interfacial tension which affected by the density of the copolymers in the interphase^[21, 22, 24, 25]. So the rougher interface shown in Fig. 2(b) for annealed blend sample as compared to that shown in Fig. 2(a) for unannealed sample, gave a further indication about the formation of adhesion promoting copolymers during a long time annealing.

As mentioned in our previous study^[17], the main reaction process between PC and aPA was an inner-outer reaction, where the amino terminals in aPA chains randomly reacted with the carbonate groups at the main chain of PC. The extent of reaction was controlled by the diffusion of aPA, specifically, the number of amino end-groups at the interface. The hPEI which possesses many amino end-groups can react with carbonate groups of PC and also with amide groups of aPA^[26]. The potential main reaction process in binary blend and ternary blends are shown in Scheme 1. Taking into account of the low viscosity of hPEI as a rheological control agent^[26], a small amount of hPEI were considered as an effective compatibilizer in blends. Figures 2(c) and 2(d) showed the fracture morphologies of PC/aPA/hPEI (50/50/1) ternary blends before and after annealing at 180 °C for 600 min, and the partial interaction between the polymers were observed; it did not present the well-separation of phases. This phenomenon indicated that the hPEI significantly decreased the interfacial tension.



Scheme 1 The reactions in the blends: (a) the aPA-co-PC formation reaction by the aminolysis of PC with active amino terminals of aPA and (b) the aPA-co-hPEI-PC formation reactions by the aminolysis of aPA and PC with active amino terminals of hPEI

After the PC-rich phase was etched, the cross section of the aPA-rich phase in Fig. 2(c) is rougher than that in Fig. 2(a), indicating that some PC were presented in the aPA-rich phase with the existence of hPEI. It could also be told from the severe roughness in Fig. 2(d) that the reaction compatibilization was greatly promoted by the small amount of hPEI.

Thermal Properties

The hPEI has different miscibility and reactivity with PC and aPA at a given annealing temperature. The annealing temperature 180 °C was chosen to avoid the thermal self-degradation of homopolymers and copolymers at higher temperatures^[1, 11, 27]. It is known that the shift in T_g provides a direct evidence of polymer miscibility^[28]. In order to investigate the effect of hPEI on the miscibility and reactivity of PC and aPA, a series of DSC measurements were performed, and typical thermograms are shown in Fig. 3. As the T_g of pure PC and aPA is 145.0 °C and 147.2 °C, respectively, owing to sensitivity, DSC could not distinguish the two T_g s of the separated homophase in PC1/aPA (50/50) blend (Fig. 3a). Even after the binary blend has been annealed at 180 °C for 600 min, no change in T_g was observed due to the limited extent of interfacial reaction. The small amount of hPEI in aPA/hPEI (100:1) blend did not change the T_g of aPA (Fig. 3b). This phenomenon suggested that the compatibility of hPEI in aPA and/or the aminolysis of aPA at 180 °C for 600 min might not be large enough to justify an observable T_g reduction, except that the T_g peak may be slightly broadened.

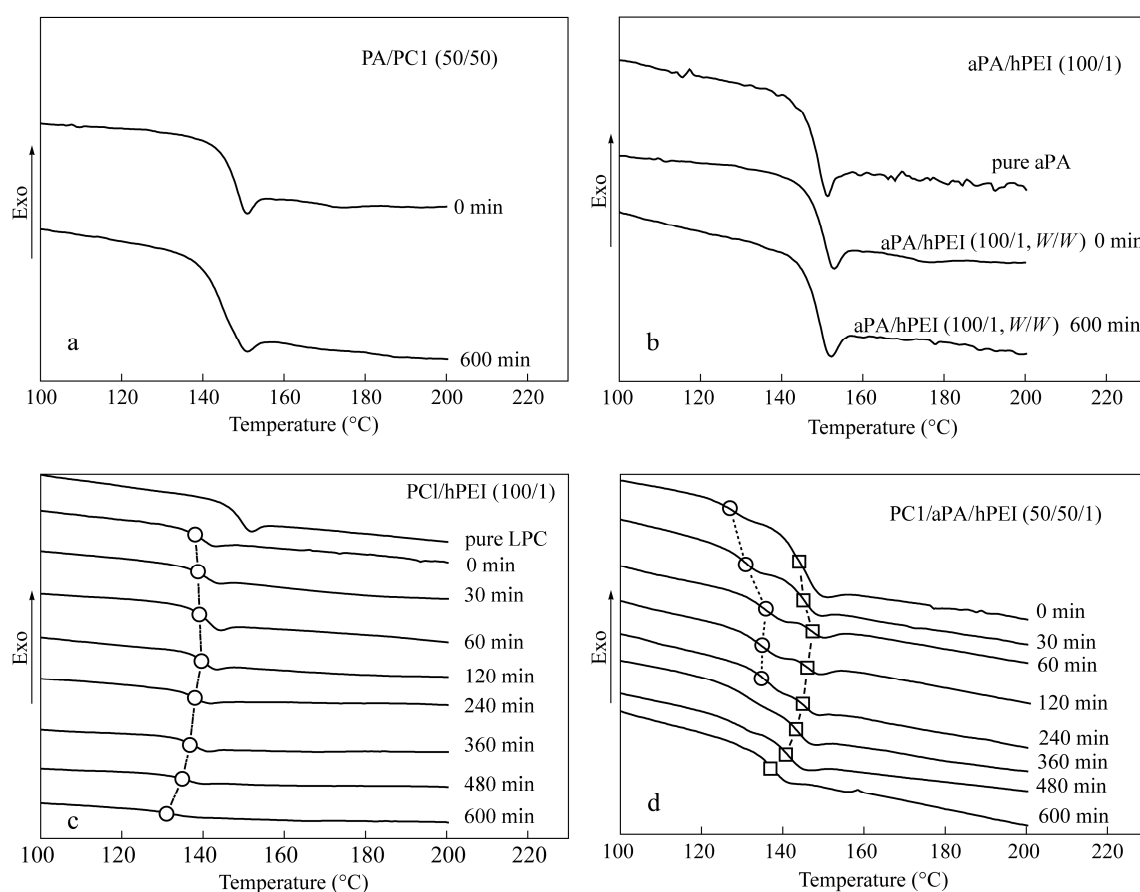


Fig. 3 Glass transitions of systems with different compositions as a function of annealing time

In Fig. 3(c), for the pure PC, the T_g decreases from 145.0 °C to 137.5 °C when 1% hPEI was presented, indicating the good miscibility of hPEI in PC and the aminolysis during blend preparation at high temperatures. It is likely that the miscibility is enhanced by the formation of inter-associated hydrogen bond between hPEI and

PC^[29, 30]. As indicated by the dash-line in Fig. 3(c), the T_g of PC/hPEI blend first increased slightly and then diminished continuously with increasing annealing time. The T_g for blend sample annealed for 120 min is 139.6 °C while for sample annealed for 600 min is 131.2 °C. The initial increment was attributed to one of the reaction products, the star-branched PC grafted onto hPEI core molecule. The subsequent reduction of T_g was attributed to another reaction products, the low molar mass PC species snipped from original PC chains, which would play the role of plasticizer.

Two T_g s were presented in PC1/aPA/hPEI (50/50/1) blend, clearly indicating the existence of two amorphous phases (Fig. 3d). Although the T_g of PC-rich phase and that of aPA-rich phase in the binary (50/50) blend was undistinguished (Fig. 3a), we knew from Fig. 3(c) that the T_g of PC could be reduced by the presence of hPEI and from Fig. 3(b) that T_g of aPA was almost unaffected by hPEI. Therefore, in Fig. 3(d), the first T_g (denoted by black circles) was contributed from the PC-rich phase, and the second T_g (denoted by blue squares) was contributed from the aPA-rich phase. With the increasing of annealing time, the tendency of both T_g s change in ternary blend is similar and more obvious as compared to the PC/hPEI blend. The synchronous increasing of both T_g s in the early stage of annealing (0–120 min) proved that both PC and aPA participated in the reaction. After long time annealing (> 360 min), the lower T_g became hard to define and finally two T_g s seemed to merge into one, indicating that an apparent homogeneous blend was obtained as a consequence of the interfacial action, from which the increasing copolymer mediates the compatibilization of two components. This phenomenon was consistent with morphology observation discussed above. The decreasing of the T_g of the final product was also attributed to the release of low molar mass species during aminolysis.

GPC can be used to examine the degree of the reactions in the PC/PA system as indicated by earlier works^[1, 2]. In order to find out if and to what extent degradation reactions occurred, as a function of annealing time, the PC components were extracted from the PC/aPA (50/50) and PC/aPA/hPEI (50/50/1) blends and their molecular weight distribution were analyzed by GPC. Two main features can be seen from the GPC results shown in Fig. 4: with the presence of hPEI, the whole curve moves toward higher elution volumes as a consequence of aminolysis due to the amino terminal groups of the aPA chains and hPEI; the degradation involves the highest molecular masses, causing the number-average molecular mass M_n significantly reduced. Besides that, the tails for the very low molecular mass fractions have become prominent.

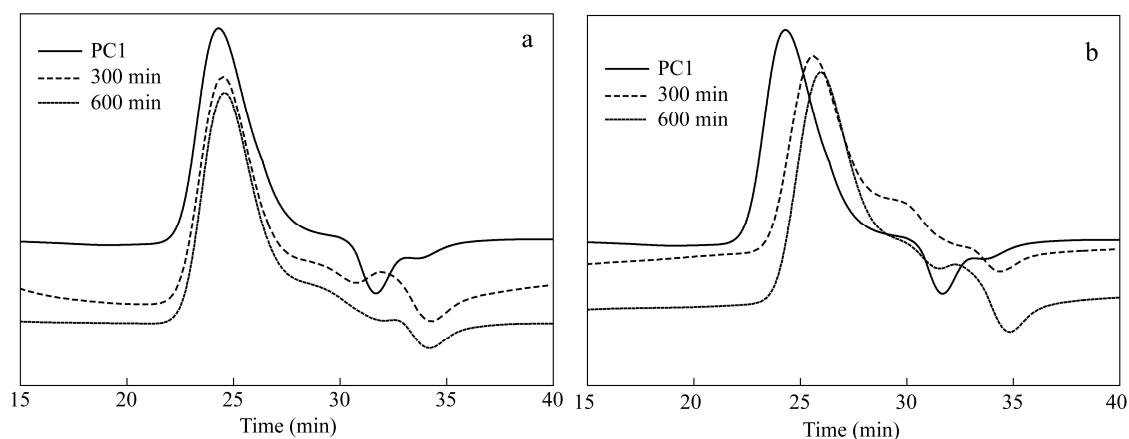


Fig. 4 GPC chromatograms of PC extracted from (a) 50/50 PC1/aPA blends and (b) 50/50/1 PC1/aPA/hPEI blends as a function of annealing time

Fracture Toughness Measurements

The addition of block or graft copolymers has been widely attempted to improve the adhesion between immiscible polymer pairs^[31]. For the interface where pre-made copolymers are present, two factors are believed to be important in contribution to the adhesion, the degrees of polymerization of the blocks N and the areal density of copolymer at the interface Σ ^[32, 33]. If Σ is very low, the interface fails without any significant amount

of plastic deformation at the crack tip at a level of stress below the crazing stress. As pointed out by Kramer *et al.*^[32, 33], the fracture mechanisms of planar interfaces changed when N went from below to above the average degree of polymerization between entanglements, N_e . If $N < N_e$, the chains are pulled out without any significant amount of plastic deformation; this is the case of the weakest interfaces. If $N > N_e$, G_c is proportional to $N^2 \Sigma$ or varies with $N^2 \Sigma^2$ for some times.

The fracture toughness, obtained from ADBC for planar layer samples with hPEI and without hPEI at the interface is shown in Fig. 5. For bilayer sample PC/aPA, G_c was increasing with reaction time (that is, the amount of copolymer formed). The development of reaction conversion with time, and its relationship with the development of interfacial roughness for the PC1/aPA bilayer sample annealed at 180 °C, have been revealed in our previous paper^[17]. One of the findouts was that, there was acceleration in reaction rate after reaction for about 150 min, which was seemingly in synchronous with an abrupt increase in root-mean-square roughness of the interface. This phenomenon indicated that, for reactive interface, G_c has to be related to the amount of copolymer formed at the interface because the reinforcement mechanism is believed to be caused by a “stitching” effect by the copolymers located at the interface^[19]. The addition of hPEI greatly promoted the formation of copolymers, as it could be seen in Fig. 5 that the G_c for samples with hPEI increased much faster with time. However, for sample with low molar mass PC (PC1/aPA/hPEI), there was an obvious and continuous weakening of G_c with the elongation of reaction time after 240 min, and this might be due to interfacial corrugation or the emulsification transition induced by the interfacial instability. Interfacial interchange reaction are easier to induce interfacial instability than end-coupling reaction, because copolymer was formed and polymer with low molecular weight was released as products of interchange reaction and both species could act as a compatibilizer. If the interfacial areal density of reaction product reached a certain value, the interfacial adhesion will be greatly reduced, leading to an interfacial instability^[34]. In fact, the average molar mass between entanglement in PC was determined as 2400, which is equivalent to 9.5 repeating units and abnormally small^[35], so it is reasonable that the G_c for samples with high molar mass PC (PC2/aPA/hPEI), was higher than that of PC1/aPA/hPEI and there was no decreasing of G_c within the experimental time range.

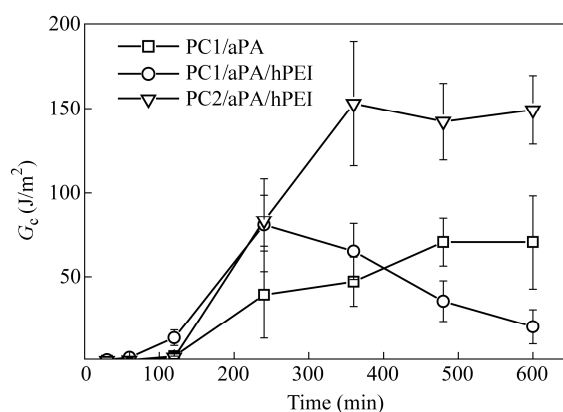


Fig. 5 Fracture energy, G_c , as a function annealing time in planar layer samples with and without hPEI at the interface

The error bars were obtained from at least three independent measurements.

CONCLUSIONS

As PC and aPA are immiscible polymer pairs, PC/aPA blends presented typical biphasic structure with poor adhesion. Interfacial compatibility between PC and aPA homophases was to some extent presented for long time annealing at 180 °C, due to the aminolysis between the amino terminal groups of aPA and the inner carbonate groups of PC. The influences of hyperbranched compatibilizers hPEI, which possess many reactive amino end-groups, on the fracture morphology and fracture toughness between PC and aPA were systematically

investigated. The presence of a small amount of hPEI can significantly increase the compatibility of blends, which was mainly due to the interchange reactions between the polymers giving rise to the formation of block copolymers, cross-linked polymers and polymers with other constituents. The ADBC method demonstrated that the reactive process drastically reinforced the interfacial adhesion between planar layers of PC and aPA. However, degradative phenomenon would take place during the annealing at 180 °C, which was responsible for the production of small molar mass species of PC, as shown by GPC, and probably for some copolymers between the two components. Therefore, if the miscibility between PC and aPA can be well controlled by adding hPEI as a compatibilizer, PC/aPA blends, bulk blends or multi-layered composites, which synergistically combine advantages of aPA and PC can be formed.

REFERENCES

- Gattiglia, E., Turturro, A., Lamantia, F.P. and Valenza, A., *J. Appl. Polym. Sci.*, 1992, 46: 1887
- Gattiglia, E., Turturro, A. and Pedemonte, E., *J. Appl. Polym. Sci.*, 1989, 38:1807
- Gattiglia, E., Turturro, A., Pedemonte, E. and Dondero, G., *J. Appl. Polym. Sci.*, 1990, 41: 1411
- Gattiglia, E., Mantia, F., Turturro, A. and Valenza, A., *Polym. Bull.*, 1989, 21: 47
- Wang, Q., Jiang, Y.G., Li, L.P., Wang, P., Yang, Q. and Li, G.X., *J. Macromol. Sci. B.*, 2012, 51: 96
- Montaudo, G., Puglisi, C. and Samperi, F., *J. Polym. Sci., Part A: Polym. Chem.*, 1994, 32: 15
- Montaudo, G., Puglisi, C., Samperi, F. and Lamantia, F.P., *J. Polym. Sci., Part A: Polym. Chem.*, 1996, 34: 1283
- Horiuchi, S., Matchariyakul, N., Yase, K., Kitano, T., Choi, H.K. and Lee, Y.M., *Polymer*, 1996, 37: 3065
- Horiuchi, S., Matchariyakul, N., Yase, K., Kitano, T., Choi, H.K. and Lee, Y.M., *Polymer*, 1997, 38: 6317
- Costa, D.A. and Oliveira, C.M.F., *J. Appl. Polym. Sci.*, 1998, 69: 857
- Costa, D.A. and Oliveira, C.M.F., *J. Appl. Polym. Sci.*, 2001, 81: 2556
- Kim, Y.H. and Webster, O.W., *Macromolecules*, 1992, 25: 5561
- Massa, D.J., Shriner, K.A., Turner, S.R. and Voit, B.I., *Macromolecules*, 1995, 28: 3214
- Huber, T., Pötschke, P., Pompe, G., Häßler, R., Voit, B., Grutke, S. and Gruber, F., *Macromol. Mater. Eng.*, 2000, 280–281: 33
- Jannerfeldt, G., Boogh, L. and Månson, J.A.E., *J. Polym. Sci., Part B: Polym. Phys.*, 1999, 37: 2069
- Clagett, D.C., Maresca, L.M. and Wascher, U.S., 1989, U.S. Pat., 4,798,874 A
- Wang, M.J., Yuan, G.C. and Han, C.C., *Polymer*, 2013, 54: 3612
- Kanninen, M.F., *Int. J. Fract.*, 1973, 9: 83
- Koriyama, H., Oyama, H.T., Ougizawa, T., Inoue, T., Weber, M. and Koch, E., *Polymer*, 1999, 40: 6381
- Majumdar, B., Keskkula, H. and Paul, D.R., *J. Appl. Polym. Sci.*, 1994, 54: 339
- Kim, B.J., Kang, H., Char, K., Katsov, K., Fredrickson, G.H. and Kramer, E.J., *Macromolecules*, 2005, 38: 6106
- Lyu, S.P., Cernohous, J.J., Bates, F.S. and Macosko, C.W., *Macromolecules*, 1999, 32:106
- Diaz, M.F., Barbosa, S.E. and Capiati, N.J., *Polymer*, 2007, 48: 1058
- Lee, J.S., Park, K.Y., Yoo, D.J. and Suh, K.D., *J. Polym. Sci., Part B: Polym. Phys.*, 2000, 38: 1396
- Lee, P.C., Kuo, W.F. and Chang, F.C., *Polymer*, 1994, 35: 5641
- Wang, P.L., Meng, K., Cheng, H., Hong, S., Hao, J.K., Han, C.C. and Haeger, H., *Polymer*, 2009, 50: 2154
- Flory, P.J., *J. Am. Chem. Soc.*, 1942, 64: 2205
- Olabisi, O., Robeson, L.M. and Shaw, M.T., *Polymer-Polymer Miscibility*, Academic Press New York, 1979
- Coleman, M.M. and Painter, P.C., *Prog. Polym. Sci.*, 1995, 20: 1
- He, Y., Zhu, B. and Inoue, Y., *Prog. Polym. Sci.*, 2004, 29: 1021
- Paul, D.R., *Polymer Blends*; Academic Press: New York, 1978
- Washiyama, J., Kramer, E.J., Creton, C.F. and Hui, C.Y., *Macromolecules*, 1994, 27: 2019
- Creton, C., Kramer, E.J., Hui, C.Y. and Brown, H.R., *Macromolecules*, 1992, 25: 3075
- Jiang, G.J., Wu, H. and Guo, S.Y., *Polym. Eng. Sci.*, 2010, 50: 2273
- Mercier, J.P., Aklonis, J.J., Litt, M. and Tobolsky, A.V., *J. Appl. Polym. Sci.* 1965, 9: 447