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Reactive compatibilization of polyamide-12/poly(butylene terephthalate) blends with hyperbranched PEI-*g*-PA12: Morphology and thermal properties

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ABSTRACT

Thermal and morphology properties of polyamide-12 (PA12)/poly(butylene terephthalate) (PBT) blends with hyperbranched poly(ethyleneimine)-*g*-polyamide-12 (PEI-*g*-PA12) as reactive compatibilizer were studied by a combination of Optical Microscopy, DSC and ^{13}C NMR. This compatibilizer was synthesized by simple amidation reactions. The addition of PEI-*g*-PA12 greatly modified the morphology of PA12/PBT blends, which were originally an incompatible polymer pair. At the beginning of the addition of compatibilizers, the sizes of PA12 and PBT rich phases decreased and the blends dispersed better. Then the phase structures became more diffused with time. At last, bi-phase morphology disappeared totally and one homogeneous structure was obtained at 260 °C. The higher the PEI-*g*-PA12 compatibilizer content was, the faster the morphology changed. Our DSC measurements provided a consistent picture of the crystallization behavior of PA12 and PBT components. The comparison of ^{13}C NMR spectrums between PA12/PBT and PA12/PBT/PEI-*g*-PA12 undergoing the same thermal treatment indicated that compatibilization was originated from the formation of hyperbranched PBT-*co*-PEI-*co*-PA12 copolymers.

1. Introduction

Polymer blends or alloys are economically and sometimes technically necessary materials for various applications [1–7]. The morphology of polymer blends is a key factor that determines their properties. So the phase behavior of polymer blends has been the focus of both theoretical and experimental research in the field [8,9]. Because of the high enthalpy of mixing, most binary polymer blends are immiscible, which leads to a multiphase morphology and poor mechanical properties. Therefore numerous works have been done in order to understand the physical mechanism of using block or graft copolymers as compatibilizers in polymer blends, which can reduce interfacial tension, increase interfacial strength and improve morphological stability [10–12].

Normally, there are two categories of compatibilizers, namely, non-reactive and reactive type. The non-reactive compatibilizers mainly include block and graft copolymers which are miscible with two or all of the blend components thermodynamically. There are only physical interactions between compatibilizers and blend components. Theoretically, premade non-reactive compatibilizers prefer to span the interface, so they can stabilize and maintain phase-separated fine structures of polymer blends effectively [13,14]. However, experimentally, high viscosity in polymer melt system may prevent the non-reactive compatibilizers from dispersing completely, and they may form micelles or a separated phase, instead of residing at the interface of the phase-separated structures [12]. On the other hand, reactive type compatibilizers are normally in-situ formed at the phase interface during the reactive processing among the constituents of blends. So they can avoid forming compatibilizer micelles, and be more effective than non-reactive ones [15]. In most cases, the formation of reactive compatibilizers is controlled by diffusion and reaction of polymers to the interface [16–18].

Polyamides and polyesters are semi-crystalline plastics which have versatile industrial applications. They possess favorable properties, i.e., good thermal and chemical resistance, high strength and excellent barrier property. Unfortunately, they lack inter-phase adhesion and are known as incompatible polymer blends. Their binary blends do not present excellent properties at all [19–21]. Therefore, many research works have been carried out in order to find a useful and convenient compatibilizer to improve their compatibility. Huang and Chang [22–24] not only researched the

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rheological and thermal properties of poly(butylene terephthalate) (PBT)/polyamide (PA) blends with epoxy resin, but also investigated their morphology and mechanical properties. Shafi [25] studied the potential of phenoxy resins as compatibilizers in polyamide-6 (PA6) and PBT blends. Kalfoglou [26] successfully applied an acrylic-modified polyolefin type ionomer to poly(ethylene terephthalate) (PET)/polyamide-6 (PA6) blends, and good tensile and impact properties were obtained. In addition, morphologies and properties of PBT/PA6/EVA-*g*-MAH ternary blends were also investigated [27]. However, most of the strategies are based on single grafted copolymers with epoxy or maleic anhydride functional groups, which are not easily dispersed in high viscosity polymer melts. Little work has used hyperbranched or dendritic polymers as a compatibilizer to improve the phase structures and stability of blends.

Hyperbranched and dendritic polymers have special three-dimensional structures which endue them with low melt viscosities, lots of functional end-groups and globular shapes. Since they were described by Flory a half century ago [28], hyperbranched and dendritic polymers have attracted a great deal of attention. In recent years, some hyperbranched polymers have been studied intensively in blends for different purposes. Kim et al. [29] found that hyperbranched polyphenylene could reduce the viscosity and improve the thermal stability of the blends with polystyrene. Voit and his co-workers [30] studied the influence of the hyperbranched poly(ester-amide)s on the rheological behavior of their blends with PA6. Månson [31] reported that PP-HBP (hyperbranched polyester) effectively compatibilized polypropylene (PP)/polyamide-6 (PA6) blends by decreasing the interfacial tension.

In our previous work, Haeger and his co-workers (Degussa AG) synthesized star-branched polyamide-12 (PA12) grafted onto poly(ethylene imine) (PEI) core molecule in two ways [32–35]. They had characterized PEI-*g*-PA12 by DSC, GPC, and DMTA. According to the knowledge about compatibilization, we realize that PEI-*g*-PA12 can, for several reasons, be a potential compatibilizer for PA12/PBT blends. On the one hand, the PA12 segments in PEI-*g*-PA12 are miscible with polyamide; on the other hand, hyperbranched PEI has many amine end-groups which can potentially react with carboxylic end-groups in the blends. Taking into account of their high reactivity and low viscosity, their compatibilization must be more efficient than that of conventional linear ones. Potentially, these hyperbranched PEI-*g*-PA12 can carry more functional groups and migrate faster in the system than a linear chain with the same molecular weight, and compatibilize the blends better. In addition, the morphology of the blends can be controlled through the reaction rate.

2. Experimental section

2.1. Materials

Hyperbranched poly(ethylene imine) (PEI, Mw = 750,000 g/mol), polyamide-12 (PA12) (Vestamid L1600 9.004) and poly(butylene terephthalate) (PBT) (Vestodur 3000) were kindly provided by Degussa (AG). PEI was lyophilized before use. PA12 and PBT were dried at 100 °C for 72 h in a vacuum oven before use. The basic properties of materials were introduced in Supporting Information Table S1. All solvents and reagents used were purchased from Beijing Chemical Company. Deuterated trifluoroacetic acid (d-TFA 99.9%) was obtained from Cambridge Isotope Laboratories, Incorporation.

2.2. Synthesis of PEI-*g*-PA12

The synthesis of PEI-*g*-PA12 is shown in Scheme 1. PEI and PA12 were added into a reaction flask, and stirred for 4 h at 240 °C under nitrogen flow. The melted product was obtained and then precipitated by pouring it into distilled water. After filtration, the resulting product was washed with distilled water repeatedly. At last, hyperbranched PEI-*g*-PA12 was vacuum-dried at 40 °C for 96 h. And it was characterized by hydrogen nuclear magnetic resonance (^{1}H NMR) and the spectrum is shown in Fig. S1.

2.3. Blend preparation

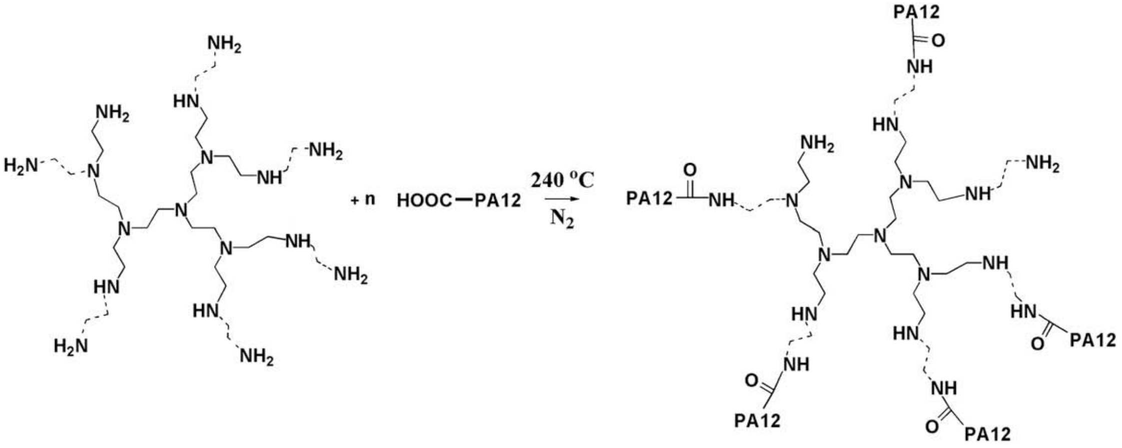
Solution blending was carried out at room temperature. PA12, PBT and PEI-*g*-PA12 were dissolved in trifluoroacetic acid together with stirring for 24 h, and the concentration was 5 wt%. After complete mixing, the solution of blends was slowly precipitated in a large amount of distilled water. The blends were obtained after water-washed several times and dried under vacuum at 40 °C for 96 h. In our study, the mass ratio between PA12 and PBT was fixed at 50:50, and the relative weight percentages of PEI-*g*-PA12 were 0%, 2.2%, 5.4%, and 10.5%, respectively.

2.4. NMR spectrometry

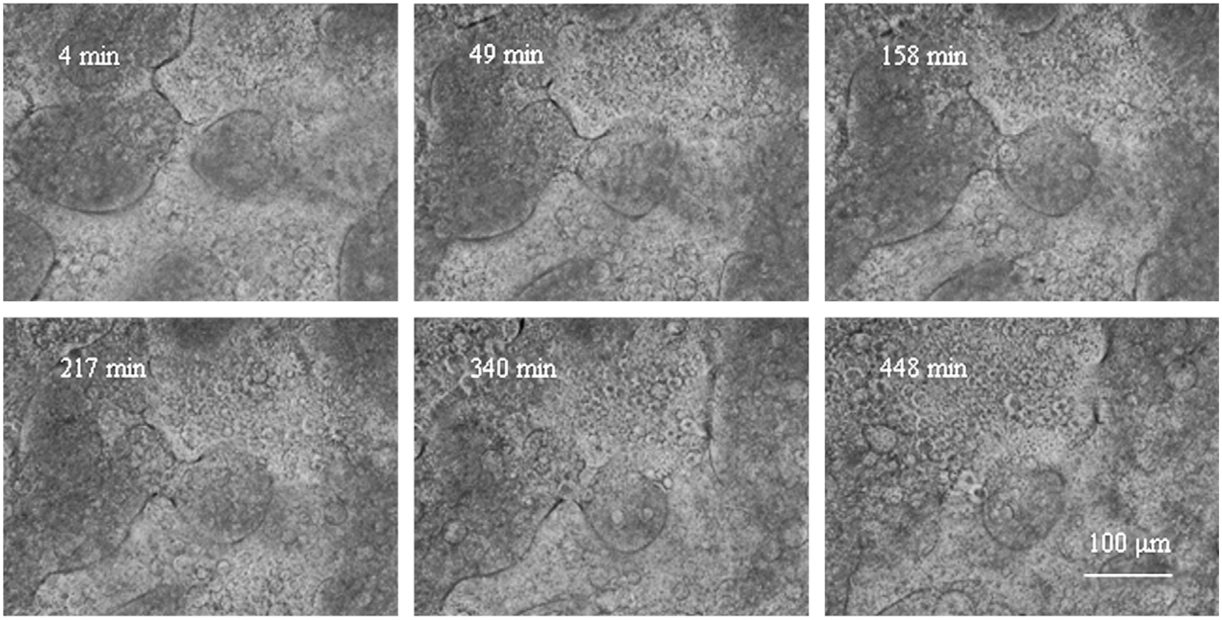
The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) was performed on a Bruker DRX-400 spectrometer at room temperature, using deuterated trifluoroacetic acid as the solvent.

2.5. Optical microscopy

The morphological observations were carried out using a phase-contrast Olympus (BX51) optical microscopy (PCOM) and an



Scheme 1. The synthesis route of PEI-*g*-PA12.


a PA12/PBT/PEI-g-PA12=50/50/0

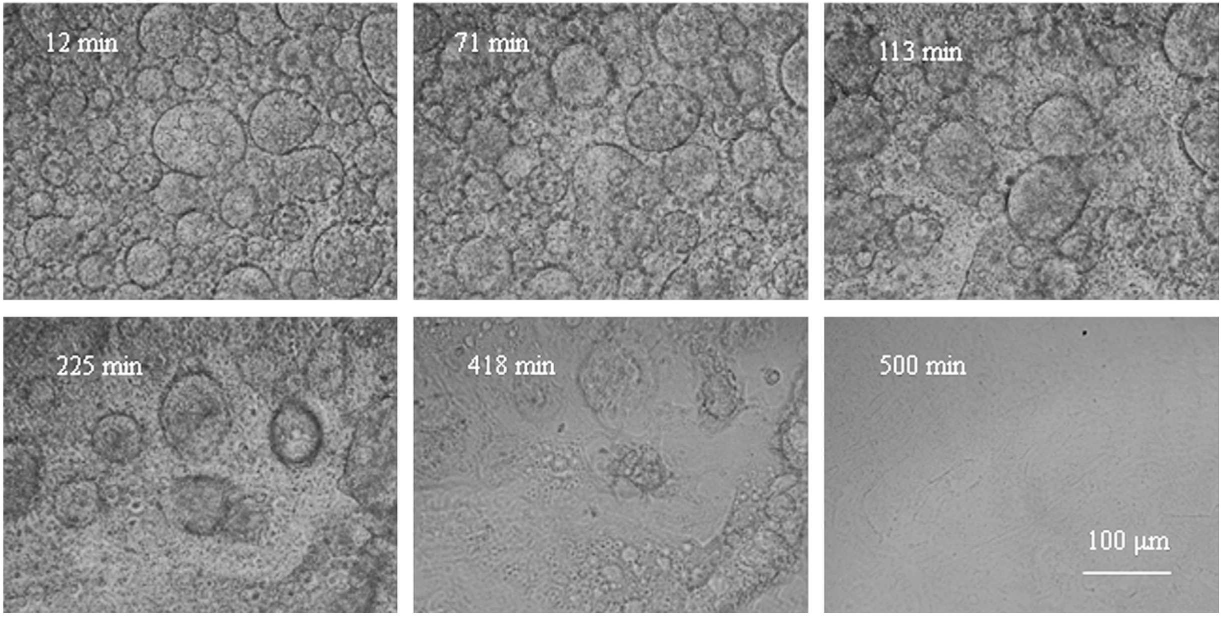

b PA12/PBT/PEI-g-PA12=50/50/2.2

Fig. 1. The phase-contrast optical micrographs at 260 °C for different time of phase separation. The composition of PA12/PBT/PEI-g-PA12: (a) 50/50/0, (b) 50/50/2.2, (c) 50/50/5.4, (d) 50/50/10.5. The inset bar is 100 μm.

Olympus (C-5050ZOOM) camera. A Linkam LTS350 hot stage was used to control the experimental temperature. All the experiments of PCOM were operated under the protection of N_2 stream. The blends were sandwiched between two clean glass slides and prepared by hot-press at 280 °C for 10 s. The thickness of samples was 50–100 μm. All the samples were melted at 280 °C for 10 min to eliminate thermal history before they were quenched to 260 °C for phase separation. The heating and cooling rates were fixed at 30 °C/min.

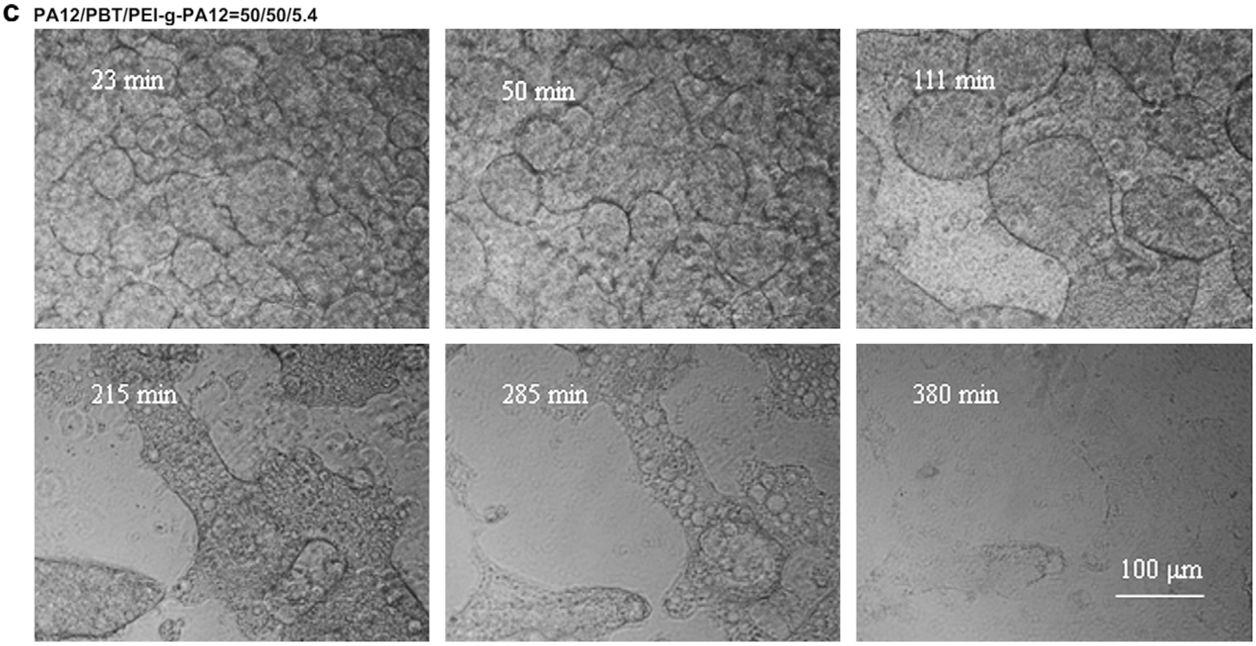
2.6. DSC analysis

Thermal properties of all the samples were recorded by a differential scanning calorimetry (DSC) instrument TA 2910 at a heating/cooling rate of 10 °C/min. Normally the mass of samples was about 5 mg. At first, the blends were heated from ambient temperature to 280 °C, and kept at this temperature for 10 min to eliminate thermal history. Then the blends were quenched directly to 260 °C for different time to phase separation. After that, the samples were cooled to −30 °C and then heated to 300 °C to record the influence of phase separation time on their crystallization and melting behaviors.

3. Results and discussion

3.1. Morphology of blends

Both theoretical and experimental works have concluded that there are many variables controlling the morphology of blends,


c PA12/PBT/PEI-g-PA12=50/50/5.4

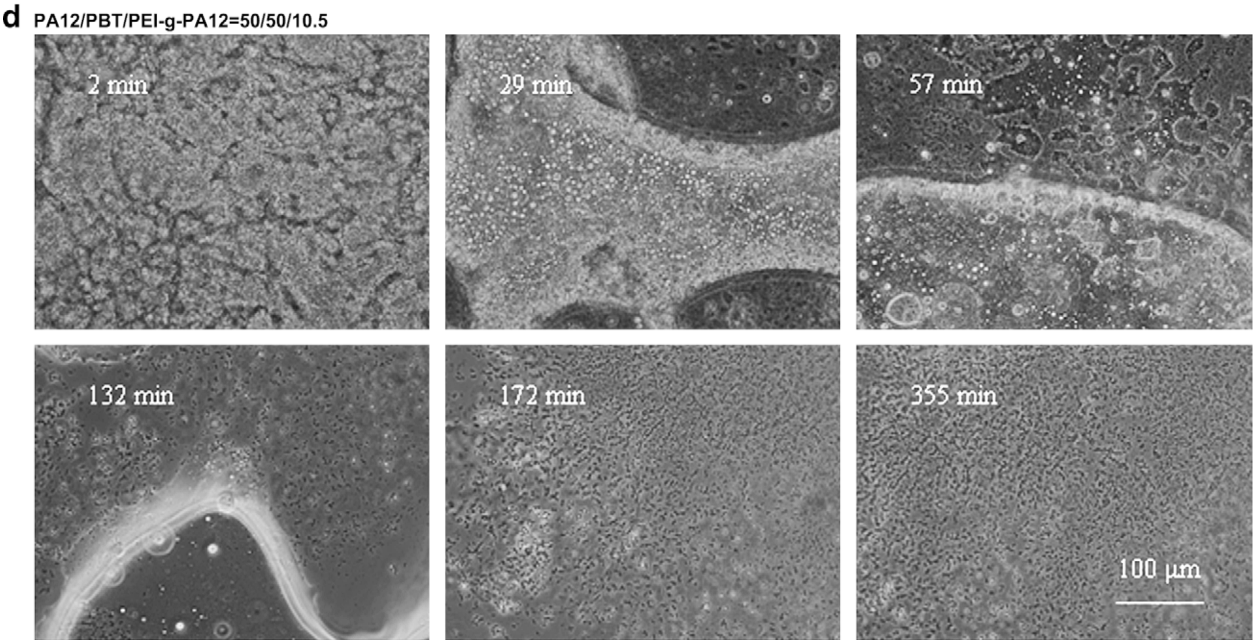

d PA12/PBT/PEI-g-PA12=50/50/10.5

Fig. 1. (*continued*).

including viscosity, elasticity, interfacial tension, and thermal history [36]. PA12/PBT blends are known as immiscible blends. Mixing them together can lead to a bi-phase morphology. As shown in Fig. 1(a), the size of phase domains is several hundreds of micrometers and is broadly dispersed. As the time of phase separation at 260 °C is prolonged, the morphology of sample does not change significantly because the sample is already at the very late stage of phase separation. It can be observed that the domain break-up through hydrodynamic flow is over and the coalescence through collision–coalescence is slow due to the high viscosity. However, after about 400 min, a little hazy interface is observed. Samperi [37] has reported that the ester–amide exchange reaction occurred when PA6/PBT blends were heated at 280 °C for 30 min. In our system, both amino and carboxyl groups co-exist, so it is possible that acidolysis, aminolysis ester–amide exchange reactions happen to form new copolymers under a proper temperature and time. The new copolymers which mainly formed at the domain interface may become the compatibilizer. So the morphology of blends changes a little. However, this influence on morphology by reaction resultant copolymers just occurs to a minor extent because of the low reactivity between PA12 and PBT. This effect may be ignored if the time of isothermal treatment is shorter than 400 min.

However, when hyperbranched PEI-g-PA12 is added to PA12/PBT blends, not only the structure of the ternary blends but also the kinetic process of phase separation has changed completely. As presented in Fig. 1(b)–(d), at the initial stage of observation at 260 °C (∼20 min), the phases disperse better and the phase sizes decrease to 10–100 μm with the increase of PEI-g-PA12. When the

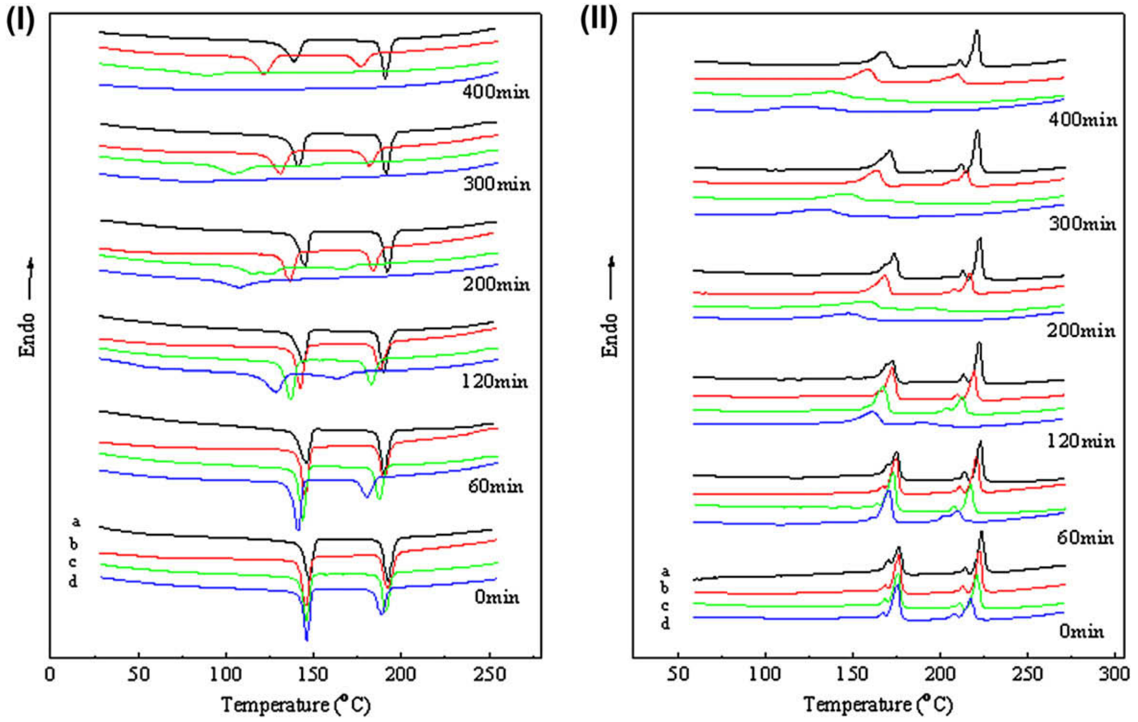


Fig. 2. DSC thermograms of ternary blends of PA12/PBT/PEI-*g*-PA12 (%): (I) cooling, (II) heating. The inset text shows the isothermal time at 260 °C. In each group (the same time), from the top to bottom is: (a) 50/50/0, (b) 50/50/2.2%, (c) 50/50/5.4%, (d) 50/50/10.5%.

time of isothermal treatment increases, some phases coalescent and grow. At the same time, dispersed phase area decreases. Finally a homogeneous morphology is observed in all of the three samples with different amounts of PEI-*g*-PA12. By the comparison of different contents of PEI-*g*-PA12 (2.2 wt%, 5.4 wt% and 10.5 wt%), we find that this kind of morphology changes from heterogeneous to homogeneous becomes more rapid with the increase of PEI-*g*-PA12. The unusual kinetic phase separation of ternary blends suggests that PEI-*g*-PA12 compatibilizers induce some kind of chemical reaction in the blends. As mentioned before, the formation of copolymers is controlled by both diffusion and reaction of polymer molecule to the interface in reactive blends. When the content of PEI-*g*-PA12 is higher, there is greater probability for compatibilizer to diffuse to and exist at the interface. Therefore, the rate of morphology change is controlled by the content of PEI-*g*-PA12 if the PEI-*g*-PA12 can further react with PBT. Meanwhile, a homogeneous morphology is observed, which shows that the chemical reaction happens not only at the interface but also inside the phase domain.

3.2. DSC measurements

In order to investigate the thermal effect of PEI-*g*-PA12 on phase separation, the same experimental condition with optical microscopy observation was used for the DSC tests. The time-resolved DSC thermograms are shown in Fig. 2. The double melting endotherm is seen from PA12 and PBT because of recrystallization, which is a common phenomenon for nylon and PBT. The serial traces on the bottom of Fig. 2 correspond to the temperature scanning of samples with different PEI-*g*-PA12 contents (0%, 2.2%, 5.4% and 10.5%), and they do not undergo isothermal treatment after eliminating thermal history at 280 °C. Both melting and crystallization temperature of PA12 and PBT hardly shift with the contents of PEI-*g*-PA12.

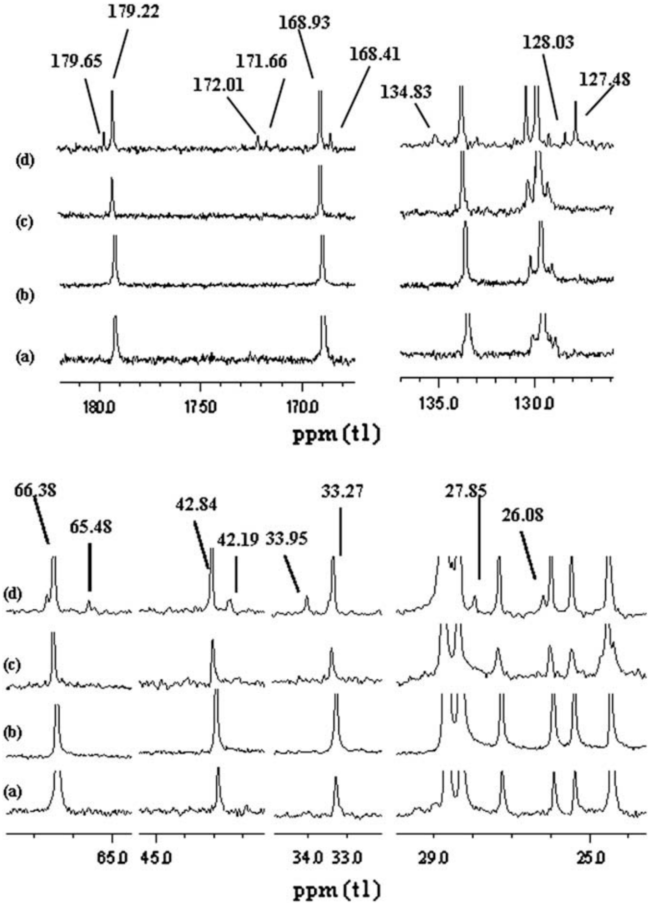
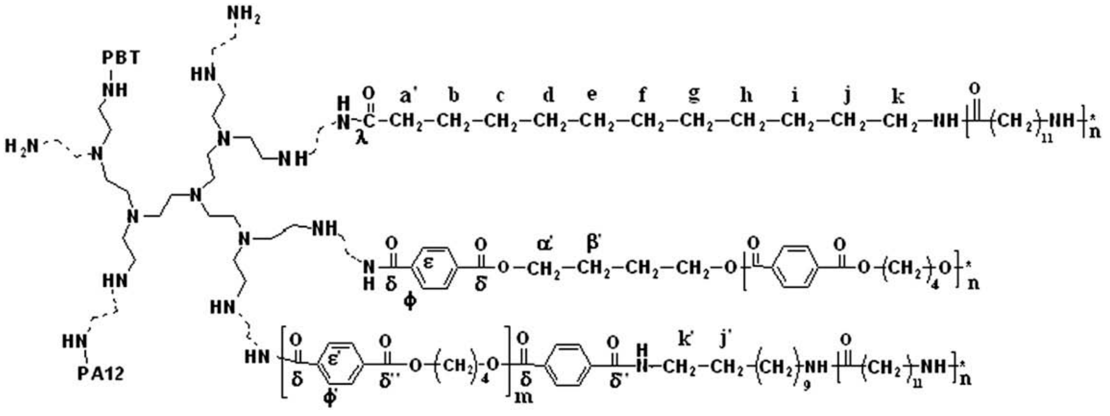


Fig. 3. ^{13}C NMR spectra of PA12/PBT/PEI-*g*-PA12 blends: (a) 50/50/0, 0 min at 260 °C; (b) 50/50/0, 400 min at 260 °C; (c) 50/50/5.4, 0 min at 260 °C; (d) 50/50/5.4, 400 min at 260 °C.



PBT-co-PEI-co-PA12

Scheme 2. The chemical structure of PBT-*co*-PEI-*co*-PA12.

For the PA12/PBT blends without any hyperbranched PEI-*g*-PA12, the isothermal annealing process at 260 °C has very small influence on their crystallization and melting behaviors. For example, the crystallization temperature of PA12 shifts from the original 147.36 °C to 138.79 °C when kept at 260 °C for 400 min. Accordingly, the heat of crystallization (ΔH_c) decreases from 21.04 J/g to 20.01 J/g. A few acidolysis, aminolysis or ester-amide exchange reactions between PA12 and PBT may lead to such difference, which is consistent with the morphological development as shown in Fig. 1.

However, once PEI-*g*-PA12 was added into the blends, obvious changes in the thermal properties appeared. From Fig. 2, all of the endothermic and exothermic peaks gradually decrease and shift to lower temperature. At last, they disappear after the samples are kept for long enough time at 260 °C. Though the melting peaks of blends with 2.2 wt% PEI-*g*-PA12 did not completely disappear after 400 min at 260 °C as shown in Fig. 2(b), we have data (which are not shown here) to proof this tendency in our experiments when the samples undergo isothermal treatment at 260 °C for longer time. It is noticed that all the blends in our experiments are physically mixed. If there is just normal physical mixing or de-mixing happening in the isothermal treatment at 260 °C, then the crystallization and melting peaks of PA12 and PBT should not disappear completely. Therefore, the former suggestion of reaction compatibilization must have happened. Further, with the increase of PEI-*g*-PA12 amounts, the crystallization and melting peaks disappear in shorter annealing time. Meanwhile, we notice that the change of PBT peaks is more significant compared with PA12 after the same treatment. All these reflect the details of the reaction mechanism.

3.3. NMR analysis

All the former experimental results indicated that reaction compatibilization occurred in the isothermal process at 260 °C. However, we still did not know well the reaction mechanism and the chemical structure of corresponding products. So we characterized the chemical structure of blends by means of ^{13}C NMR which is much sensitive to the molecular sequence and can trace the reaction process. Two samples were chosen for our experiments, respectively, 50/50/0 and 50/50/5.4 (PA12/PBT/PEI-*g*-PA12). They were kept at 260 °C for 0 min and 400 min, and then were totally dissolved in d-CF_3COOH for ^{13}C NMR measurement. Their ^{13}C NMR spectra are shown in Fig. 3.

In contrast with spectrogram (a) in Fig. 3, there are no new peaks presented in spectrogram (b) when PA12/PBT (50/50) blends without PEI-*g*-PA12 are isothermally treated for 400 min at 260 °C, although there may be very little ester–amide exchange reactions happened in this process. When 5.4% PEI-*g*-PA12 is added to the blends, almost the same spectrogram with (a) and (b) is obtained at the beginning of isothermal treatment at 260 °C for 0 min as presented in Fig. 3(c). However, when blends (50/50/5.4) are annealed at 260 °C for 400 min, some new signals appear in Fig. 3(d). By the analysis of the ^{13}C NMR spectra, it is ascertained that the ternary copolymers (shown in Scheme 2) are formed in the melt-mixing process, which is the reason for compatibilization. And the carbon signal assignments of copolymer sequences are shown in Table 1.

Comparing spectrum (c) with (a), we find that the signals of PEI molecular unexpectedly do not appear in the spectra of 50/50/5.4 sample. Due to special three-dimensional structure of hyperbranched polymer, the PEI segments probably shrink and are packed inside the PA12 and PBT segments. So there is no clear carbonyl resonances signal of PEI showed up in ^{13}C NMR measurement. As a conclusion, the formation of hyperbranched copolymer is the essential reason for the change in morphological and thermal properties in PA12/PBT/PEI-*g*-PA12 blends. This special reaction compatibilization can be used for controlling interface modification as well as to a certain extent to control the homogenization of blends if necessary. We all know that there are many different reaction routes in such a complicated system of polyamide and polyester blends, such as ester–amide exchange, acidolysis, aminolysis,

Table 1
The carbon signal assignments of copolymer sequences.

	PA12								PBT					
	λ	*a*	*b*	*c*	*d–h*	*i*	*j*	*k*	*δ*	*δ*′(*δ*″)	*ε*	*ϕ*	*α*	*β*
PA12	179.22	33.27	24.40	27.20	28.25–28.68	25.40	28.68	42.85						
PBT									168.93	168.93	133.50	129.53	66.38	25.95
PBT-*co*-PEI-co-PA12	179.65	33.95	24.40	27.20	28.25–28.68	25.40	27.85	42.19	172.01 171.66	168.41	134.83	128.03 127.48	65.48	26.08

alcoholysis, etc. [37–39]. So future investigation is needed to make clear what exactly have happened in the complex melt state.

4. Conclusion

The results presented in this paper demonstrate that hyperbranched PEI-*g*-PA12 can effectively compatibilize PA12/PBT blends and decrease the dispersed phase size. The change from heterogeneous to homogeneous in PA12/PBT blends becomes more rapid with the increase of PEI-*g*-PA12 content. Both melting and crystallization peaks of PA12 and PBT disappear in shorter annealing time at 260 °C with the increase of PEI-*g*-PA12 contents. Based on the analysis of ^{13}C NMR spectra, we conclude that a ternary copolymer (PBT-*co*-PEI-*co*-PA12) is formed in the process of isothermal treatment at 260 °C for PA12/PBT blends with some hyperbranched PEI-*g*-PA12. Our work sheds some light on selecting or designing new kinds of compatibilizers for incompatible blend systems.

Acknowledgement

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2009.02.040.

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