Reactive compatibilization of polymer blends of poly(butylene terephthalate) (PBT) and polyamide-6,6 (PA66): 1. Rheological and thermal properties

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Epoxy resin (EEW = 2060) has been demonstrated to be an efficient reactive compatibilizer for the incompatible polymer blends of polyamide-6,6 (PA66) and poly(butylene terephthalate) (PBT). Processability improvement has been achieved by reducing die swell and melt fracture during blending extrusion. Reactions involved in this three-component system are very complex but only the coupling reactions between epoxy and PBT and PA66 endgroups are considered essential. This epoxy resin is more compatible with PBT than with PA66 but the reactivity of the former is slower than that of the latter. Additionally, PBT has a lower melting temperature than that of PA66; this epoxy resin therefore has the first chance to react with PBT, then with PA66, at the interface. Certain mixed copolymers, epoxy-co-PBT-co-PA66, are expected to be formed and to anchor at the interface. These mixed copolymers are believed to be the major contributor in improving the compatibility of incompatible PA66/PBT blends. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The utilization of polymer blends is an increasingly important segment of the plastics industry. Poly(butylene terephthalate) (PBT) and polyamide-6,6 (PA66) are both semicrystalline polymers with commercial significance. PBT and PA6 should be an ideal blending pair chosen to create a new material possessing certain unique properties from both blend constituents. However, no commercial polymer blend product based on polyesters (including PBT) and polyamide (including PA66) has been known until recently. Even fundamental studies of the blends of these two important classes of thermoplastics are relatively scarce. Incompatibility of blends between these polymers is probably the reason why this seemingly ideal blend pair has not drawn the attention it should.

Utracki et al.1 studied the melt rheology of poly(ethylene terephthalate) (PET)/PA66 blends and reported a considerable degree of compatibility. Kamal et al.2 investigated the solid-state properties of PET/PA66 blends and found that the blends are brittle in tensile and impact testing conditions even though the individual polymers show ductile failure. The brittleness is attributed to poor interphase adhesion of the incompatible PET/PA66 system. Blending PET and PA in the melt process produces a polyester–polyamide copolymer through ester–amide interchange reaction of the PET/PA66 blends characterized by both 1H and 13C n.m.r. Nadkarni et al.7 studied the thermal and crystallization behaviour of blends of thermoplastic polyesters (including PET and PBT) and amorphous polyamide. Watanabe8 reported that straight blends of PBT and polyamide-6 (PA6) were incompatible. Wakita9 studied the melt elasticity of incompatible PBT/PA66 blends and reported that the extrudate swell of the blend varies with viscosity ratio and blend composition. The extrudate swell is caused by shape recovery of the dispersed particles. Evstatiev and Fakirov10 studied the effect of thermal prehistory on the crystallinity, compatibility and mechanical properties of the blends between polyesters (including PET and PBT) and PA6. Some indirect evidence showed the occurrence of the interchange reaction, and the ester–amide copolymer formed improved the compatibility of the blends.

In our previous reports11,12, we demonstrated that solid epoxy resin (bisphenol-A type) is an excellent reactive compatibilizer for blends of polycarbonate (PC)/PA6
and liquid crystalline polymer (LCP)/PET. This intermediate molecular weight epoxy resin (EEW = 2060) contains two epoxide terminal groups that can react with the carboxyl (PA6, LCP and PET) and amine (PA) endgroups in the melt state. The resultant block copolymers are able effectively to compatibilize the PC/PA613 and LCP/PET14 blends. In this study, we again use the same epoxy resin to compatibilize PBT/PA66 blends.

EXPERIMENTAL
Polyamide-6,6, Zytl 101L, was purchased from Du Pont. PBT, D-201, is the natural grade product from Shinkong Synthetic Fibers Corp. of Taiwan. Solid-state epoxy resin, NPES-909, has an epoxide equivalent weight of 2060 g eq−1 and was obtained from Nan Ya Plastics Corp. of Taiwan.

Melt blending with desirable composition was carried out on a 30 mm twin-screw co-rotating extruder. The extruded pellets were dried in an oven at 100°C for at least 24 h and then injection moulded into standard 1/8 inch (~3 mm) thick ASTM specimens using an Arburg 3 oz (85 g) injection moulding machine. The detailed processing conditions for extrusion and injection moulding are listed in Table 1. The torque vs time relation was obtained in a Brabender Plastic-Corder 651 at 275°C and 50 rpm. Capillary rheological measurements of the blends and matrices were carried out at 275°C using a capillary rheometer (L/D = 40, orifice radius = 0.02 inch (0.5 mm), orifice length = 0.8 inch (20 mm)) from Kayeness Co Model Galaxy X. Die swell was determined by quenching the extrudate immediately on coming out of the extruder die with ice-water and measuring its diameter relative to the diameter of the die.

Thermal properties based on second scan were investigated by differential scanning calorimetry (d.s.c.) from 30 to 300°C at a heating rate of 10°C min−1 on a d.s.c. instrument model SSC-5000 from Seiko Co. of Japan. The sample was heated from 30 to 300°C (30°C min) and then cooled to 30°C (30°C min−1) prior to the second scan.

RESULTS AND DISCUSSION
Effect of compatibilizer on processability and melt properties

Incompatible polymer blends normally show highly elastic behaviour that often causes serious problems such as extrudate swell and melt fracture during extrusion. In general, such processability problems can be reduced or completely eliminated after compatibilization, depending on the composition and the amount of compatibilizer employed. The effect of compatibilizer on die swelling is illustrated in Figure 1, which shows that the greatest extrudate swell occurs, with or without presence of 3 phr compatibilizer, when the component ratio of PA66 and PBT is close to unity. This result is similar to that of an earlier report by Wakita. The extrudate swell is caused by the shape recovery of the dispersed particles. The blends with higher elasticity correspond to blends with higher extrudate swell. Figure 2 demonstrates that an increase of compatibilizer in PA66/PBT = 50/50 blends reduces die swell.

Figure 3 illustrates extruder power output vs composition of uncompatibilized PA66/PBT blends under identical extrusion conditions. The PA66/PBT = 50/50 blend shows the lowest power output, an indication of the lowest viscosity of a co-continuous blend. Figure 4 shows that a greater quantity of compatibilizer results in slightly higher extruder power output, as would be expected.

The torque vs time curves for the pure components and mixtures under identical conditions (275°C, 50 rpm) are shown in Figure 5. The viscosity order for the pure components is: PA66 > PBT > epoxy. The torque of the PA66/epoxy = 50/50 mixture (Curve D, Figure 5) increases gradually from the beginning up to 500 s but increases more rapidly after 500 s. This is probably due to the formation of the branched or lightly crosslinked epoxy-co-PA66 copolymers because each of the PA66–amine endgroups is difunctional, being capable of reacting with
two epoxides. The torque values of the PBT/epoxy = 50/50 mixture (Curve E, Figure 5) are fairly constant, after the initial rise, at 400 s. Since both PBT and epoxy endgroups are monofunctional, formation of only linear chain epoxy-co-PBT block copolymer is expected. The torque of the PA66/PBT = 50/50 mixture (Curve F, Figure 5) is lower than that of its respective pure components; this phenomenon is not unusual for an incompatible binary blend. The occurrence of potential condensation reaction between the amine and carboxyl endgroups is unlikely or insignificantly based on the observed lower viscosity. The torque of the compatibilized mixture, PA66/PBT/epoxy = 35/35/30, increases gradually up to 600 s and maintains an almost constant torque value thereafter. The reactions involved in this three-component system are more complicated, and further discussion will be given later.

Figure 6 gives the apparent viscosity vs shear rate plots for PA66, PBT, PA66/PBT = 50/50 and PA66/PBT/epoxy = 50/50/3. The uncompatibilized blend also shows lower viscosity than both of the pure components, and this result is consistent with the earlier torque vs time and extruder power output data. The compatibilized blend has substantially higher viscosity than the corresponding uncompatibilized blend because of the anticipated covalent reactions. Figure 7 shows that a greater quantity of compatibilizer results in higher viscosity for the selected
PA66/PBT/epoxy = 30/70/x blends. A similar trend has also been observed on blends with different PA66/PBT ratios (data not shown).

**Differential scanning calorimetry (d.s.c.)**

Figure 8 shows the second d.s.c. scans of PA66, PBT and uncompatibilized blends of various compositions. Both PA66 and PBT base polymers possess a minor endotherm in front of the major endotherm. The melt temperatures, heats of fusion and peak widths of the uncompatibilized blends of PA66 and PBT are essentially unchanged from those of their respective pure components. This is indicative of little interaction of these incompatible blends. The glass transition temperatures of PA66 and PBT cannot be identified from these thermograms. No crystallization-related exothermic peak up to 200°C can be found for the base polymers and blends from these quenched samples (second scans). PA66 and PBT are both highly crystalline polymers that can crystallize rapidly, even under a quenched condition.

A small exotherm can be seen between the two endotherms for PBT, in base polymer and blends. The same result has also been observed by Nadkarni et al. PBT is one of the fastest crystallizing polymers and the crystallization kinetics have only been partially investigated. PBT has two crystalline structures, \( \alpha \) and \( \beta \) forms, which can undergo a reversible transformation at a low level of applied stress. The appearance of two endotherms can be interpreted reasonably as the result of the sequential melting of the two different crystalline structures, but this is certainly unable to explain the appearance of the exotherm between the two endotherms. The nature of the fast crystallization rate for PBT could result in a small fraction of less perfect crystallites. The first endotherm could be attributed to the partial melting of these less perfect crystallites at a temperature slightly lower than that of normal crystallites. The partially melted PBT crystallites are able to recrystallize immediately to form the better oriented crystallites and release the heat of crystallization. A further temperature increase causes melting of the original and recrystallized crystallites to form the second and larger endotherm. If the above assumption is correct, the heat release of the exotherm should be less than, or at most equal to, the melting heat of the first endotherm, depending on how close the exotherm is to the second endotherm. Such an assumption can reasonably explain the observed phenomenon for pure PBT and those uncompatibilized PA/PBT blends as shown in Figure 8 but fails to explain the phenomenon observed for the compatibilized blends.

The d.s.c. second scans of uncompatibilized and compatibilized PA66/PBT = 30/70 blends are given in Figure 9. The endotherm of PA66 has been broadened after compatibilization and the minor endotherm disappears. The PBT minor endotherm in the uncompatibilized blend disappears after compatibilization while the initial temperature of the exothermic peak is at a slightly lower temperature (about 4°C lower). If the exotherm has strictly come from the recrystallization of the partially melted crystallites, it should never appear as an exotherm. It is therefore most likely that the crystallization of amorphous PBT molecules closely tied up to the crystallites is responsible for the occurrence of this exotherm. The presence of compatibilizer in the blends tends to interfere with PBT crystallization (especially at the interface) and causes a greater fraction of amorphous PBT. Those still tightly linked amorphous PBT segments or molecules are difficult to crystallize at low temperatures and require a substantially higher temperature (near \( T_m \)) to crystallize. This is probably the reason why an exotherm appears only for the compatibilized blends, as shown in Figure 9. However, the absence of the first endotherm does not necessarily mean that the melting of the less perfect crystallites does not occur. It may take place but is completely offset by the larger exothermic peak.
Mechanism of in situ reactive compatibilization

In any reactive compatibilization system, the types of chemical reaction, the extent of each reaction, where the reaction occurs, the final locations of the reacted products and the resultant compatibility improvement are very complex, but important in order to design an optimized reactive compatibilization system. Several variables need to be considered such as reactivity, composition, processing condition, blending sequence, component mutual compatibility and melting temperature (if it is a crystalline polymer).

The chemical reactions that may possibly be involved in this study are listed as follows.

A. Condensation reaction between amine and carboxyl endgroups (Scheme 1). This reaction is similar to the usual polycondensation of diamine and diacid by releasing a water molecule, which is a reversible type reaction. This reaction takes place at the interface and requires suitable conditions in order to release the water molecules. Under a typical melt blending condition, such a condensation reaction probably does not occur, or occurs insignificantly, on the basis of the observed viscosity.

B. Coupling reaction between amine and carboxyl with epoxide endgroups (Scheme 2). For diamine-terminated PA66, this reaction is similar to that of a typical bifunctional epoxy monomer cured by a diamine curing agent except that the molecular lengths of the epoxy monomer and the curing agent are significantly greater. Each amine endgroup is capable of reacting with two epoxides under suitable conditions to form a branched or even crosslinked network. To function as an efficient compatibilizer, excessive reaction to form the branched or crosslinked copolymer is undesirable. However, the chance of forming a noticeable amount of these branched and crosslinked copolymers is slim in the current blending system. For carboxyl-terminated PA66 (one end or both ends), the covalent bond reaction between the carboxylic acid endgroup and the epoxide has been well recognized.

C. Coupling reaction between carboxyl and hydroxyl with epoxide endgroups (Scheme 3). PBT endgroups are either aliphatic hydroxyl or carboxyl. The PBT employed in this study has an acid content of 14.6 meq kg⁻¹. That means that only approximately 10–15% of the PBT endgroups are in the carboxyl form. The reactivity of epoxide with carboxyl is substantially higher than that with aliphatic hydroxyl due to the acidity difference. Without the presence of a suitable catalyst, it is possible that only the carboxyl endgroups can actually react with the epoxide while the hydroxyl endgroups simply function as an inert chain-end during melt mixing. This is why the observed torque of the PBT/epoxy = 50/50 mixture stays at a constant level after the initial increase (Curve E, Figure 5), and only the linear chain block epoxy-b-PBT copolymers can be formed.

D. Ester-amide interchange reaction (Scheme 4). This ester–amide interchange reaction is derived from a similar reaction between PA66 and PET recorded by Pillon and Utracki. The ¹H n.m.r. spectrum of the melt-blended PA66/PET mixture with the presence of catalyst and at a higher temperature resulted in the appearance of a minor characteristic peak (δ = 8.199 ppm), corresponding to these ester–amide interchange reaction products. Figure 10 shows the ¹H n.m.r. spectrum of the melt-blended PA66/PB = 50/50 mixture without catalyst, in which the characteristic peak at around 8.3 ppm (in front of the X peak in our system, Figure 10) is absent. This result confirms the earlier report that the ester–amide interchange reaction does not take place to a detectable amount without the presence of a suitable catalyst.

E. Alcoholysis between hydroxyl and ester (Scheme 5). The interchange reaction in a phenoxy/PBT blend...
through alcoholysis of the hydroxyls of the phenoxy and the ester groups of the PBT has been investigated previously. Scheme 5 shows only the initial stage of the alcoholysis reaction. Since every repeated unit contains a hydroxyl (for phenoxy) or ester (for PBT) functional group, excessive interchange reaction could result in branched copolymers or even a crosslinked network. Since the rate of this alcoholysis is considerably lower than those coupling reactions mentioned above, only a small amount of the branched copolymers are expected during blending. This alcoholysis reaction does not consume any epoxide endgroup. The epoxide groups of the interchange products are still able to react with PA66 amine or carboxyl endgroups at the interface.

Figure 10 \(^1\)H n.m.r. spectrum of uncompatibilized PA66/PBT = 50/50 blend

\[\text{PBT} \quad \text{Nylon 6,6}\]

\[\text{Ester-amide interchanged product}\]

Scheme 4

\[\text{Scheme 5}\]

\[\text{Figure 10} \quad ^1\text{H n.m.r. spectrum of uncompatibilized PA66/PBT = 50/50 blend}\]
On the basis of our viscosity data and the known relative reactivity of each reaction, only two coupling reactions (B and C, Schemes 2 and 3) are considered essential in this three-component blending system. Other reactions cannot be ruled out completely, but their potential influence on the resultant compatibility should be minimal and negligible. Ir. spectra have been tried to identify all the reactions without success, due to the low response from the anticipated reaction products.

This solid epoxy resin is an amorphous low molecular weight polymer with $T_g$ significantly lower than the $T_m$ of PBT and PA66. Epoxy resin is more compatible with PBT than with PA66 because it is miscible or nearly miscible with PBT. The solubility parameters of phenoxy resin (higher MW epoxy resin), PET and PA66 are 10.68 (20), 10.71 (21) and 13.59 (21) (cal cm$^{-3}$)$^{1/2}$ respectively. PBT has a lower melting temperature than that of PA66 (222 vs 260°C). Therefore the epoxy resin is expected to be dissolved or distributed in the PBT phase before or after melting of PA66 during a one-step three-component melt blending. This epoxy resin has the first opportunity to make contact and react with the PBT endgroups. However, only a fraction of the epoxy is consumed when it has the chance to make interfacial contact with the melted PA66 phase. Since the more reactive carboxyl endgroups comprise only 10–15% of the total PBT endgroups and the time interval between meltings of PBT and PA66 is very short in a typical melt blending, we can expect that a substantial fraction of the unreacted epoxy is left to react with the amine and/or carboxyl endgroups of the PA66. Reactivity of epoxide with amine is substantially greater than that with carboxyl. If the epoxy reactive compatibilizer employed is more compatible with PA66, while the PA66 has a lower melting temperature than PBT, the epoxy would have been consumed completely by reacting with amine (and/or carboxyl) endgroups before it has the opportunity to make contact and react with PBT during a typical melt blending. In such a case, the resultant EP-co-PA66 copolymers tend to reside in the PA66 phase rather than to anchor at the interface. In this situation, this epoxy resin would not be an effective reactive compatibilizer. Therefore, the epoxy resin employed in this study is an ideal reactive compatibilizer in the PA66/PBT blending system. This has been demonstrated in finer morphologies and significantly improved mechanical properties of the compatibilized blends that will be presented in the second part of this paper.

CONCLUSIONS

A readily available low-cost solid epoxy resin has been demonstrated to be an effective reactive compatibilizer for incompatible polymer blends of PA66 and PBT. In the presence of this reactive compatibilizer, the processability problems encountered for the incompatible PA66/PBT blends such as die swell and melt fracture have been substantially reduced or completely eliminated. Epoxy resin is more compatible with PBT than with PA66. PBT has a lower melting temperature than that of PA66. Epoxy resin thus tends to be dissolved in the PBT phase first, and it certainly has the first opportunity to react with PBT endgroups. However, the reaction rate of epoxy with PBT is lower than that with PA66. The reaction between the epoxy and the amine (and/or carboxyl) endgroups of PA66 can take place only at the interface. A certain fraction of the added epoxy resin has the chance to react with both PBT and PA66 simultaneously to form mixed epoxy-co-PBT-co-PA66 copolymers. Such mixed copolymer, possessing both long PBT and PA66 segments, is considered the most efficient compatibilizer for the PA66/PBT blend. The effective compatibilization of this in situ reactive system will be further demonstrated in terms of morphologies and mechanical properties in the second part of this paper.

The appearance of a small exotherm between two endotherms of PBT was thought to be the recrystallization of partially melting PBT crystalites. The first minor endotherm of PBT disappears but the exotherm remains in the compatibilized blends. This indicates that the exotherm has nothing to do with recrystallization of the partially melted PBT crystalites. This exotherm should be the result of the recrystallization of amorphous PBT tie-molecules between crystalites.

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