Reactive blends of poly(butylene terephthalate)/polyamide-6 with ethylene glycidyl methacrylate

M. S. Han, B. H. Lim, H. C. Jung, J. C. Hyun, S. R. Kim and W. N. Kim*
Department of Chemical Engineering, Applied Rheology Center, Korea University, Anam-Dong, Seoul 136-701, Korea
Polymeric Materials Group, Samyang R & D Center, Samyang Corp., Taejeon 305-717, Korea
(Received September 10, 2001; final revision received October 26, 2001)

Abstract
Morphological, thermal, rheological, and mechanical properties of reactive compatibilized blends of poly(butylene terephthalate) (PBT) and Polyamide-6 (PA) containing EGMA copolymer were investigated using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), advanced rheometric expansion system (ARES), and universal testing machine (UTM). From the results of thermal analysis by DSC, the melting point of the 30/70 PBT-PA blend was broadened after EGMA was added in the blends, since the enthalpy of melting of the PBT-PA somewhat decreased with the increase of EGMA content. From this result, it is suggested that the EGMA affected to the crystallization behavior and crystallinity of the PBT-PA blends. From SEM micrographs of the 70/30, 50/50, and 30/70 PBT-PA blends, the droplet size of the 30/70 PBT-PA blend was about 0.8 μm which was smaller than that of the 50/50 and 70/30 PBT-PA blends. The complex viscosity of the 30/70 PBT-PA blend observed to be higher than that of the 50/50 and 70/30 PBT-PA blends. From the results of the morphology and rheological properties for the PBT-PA blends, it is suggested that the compatibility is increased in the 30/70 PBT-PA blend than the 50/50 and 70/30 PBT-PA blends. From the results of mechanical properties, it was found that the tensile strength of the 30/70 PBT-PA blend increased with the increase of EGMA up to 2 phr, while tensile strength of the blend in which EGMA content was higher than 2 phr decreased with the increase of EGMA content. From the results of morphological, thermal, rheological, and mechanical properties for the PBT-PA-EGMA blends, it is suggested that the EGMA could be used as a compatibilization role in the blends.

Keywords: reactive polymer blends, ethylene glycidyl methacrylate, reactive compatibilizer.

1. Introduction
Polymer blending is an effective way to obtain materials with specific properties. Most polymers are immiscible, therefore, blending usually lead to heterogeneous morphologies (Kim and Denn, 1992; Jung et al., 1998; Lee and Denn, 1999; Lee et al., 2001; Han et al., 2000, 2001). As a result, immiscible blends have quite lower mechanical properties than those of their components and the phase morphology is strongly dependents on the processing condition. Therefore, methods to improve adhesion between two immiscible blends, chemically and physically different, have been a subject of considerable research activities (Xanthos, 1988). One of the ways to enhance interaction between components is to use compatibilizers, either block or graft copolymers added separately or generated in situ by blending suitably functionalized polymer, it is supposed that the chemical reaction between blend components may cause interfacial tension to decrease or adhesion force of interface to increase. A variety of reactive copolymers have been identified as effective blend compatibilizers in earlier literatures (Xanthos, 1988, 1991; Dagli et al., 1994). Poly(butylene terephthalate) (PBT) and Polyamide-6 (PA) are both semicrystalline polymers with commercial significance (Chiou and Chang, 2000). Blends from them should be an ideal choice to create new and useful polymeric products possessing certain specific properties from base polymers (Huang and Chang, 1997a, 1997b). Pillon et al. (1984, 1987) have reported that the ester-amide interchange reaction was observed in the poly(ethylene terephthalate) (PET)-polyamide (PA-6,6) blends in the presence of p-toluensulfonic acid (TsOH), and an increase of crystallinity in the blends caused by enhanced nucleation of PA. Evstatiev et al. (1996) have studied the crystallinity and morphology of the PET-PA blends using by X-ray
scattering, scanning electronic microscopy (SEM), and differential scanning calorimetry (DSC). Recently, Li et al. (2000) and Xie et al. (2000) have studied the PBT-LCP and PBT-PA-66-LCP blends, and observed that the melting temperature of the PBT and PA-6,6 phase tends to decrease with increasing LCP addition and mechanical properties of this blend were improved by LCP presence. Chang and coworkers used tetrafunctional epoxy and bisphenol-A type solid state epoxy resin as a reactive compatibilizer in PBT-PA6 and PBT-PA6,6 blends, respectively. From the Changs works, mechanical properties and processability of polyamide and polyester blends were improved by the reactive compatibilizer which could caused the reaction between the components.

In the present work, ethylene glycidyl methacrylate (EGMA) copolymer with GMA content 1% has been used to compatibilize the blends of PBT and PA. The epoxy groups in EGMA can react with hydroxyl group of PBT and amine group of PA, and make it possible to form PBT-co-EGMA-co-PA copolymer which can act as an compatibilizer for the PBT-PA blends. Also, we demonstrate the effectiveness of EGMA as a reactive compatibilizer for the PBT-PA blends using morphological, thermal, rheological, and mechanical methods.

2. Experimental

2.1. Polymers

The polymers used in this study were obtained from commercial sources. The poly(butylenes terephthalate) (PBT), TRIBIT-1500, was provided by Sum Yang Co. The polyamide-6 (PA), 1021-BRT, was provided by Rhodia Co. The reactive compatibilizer, ethylene glycidyl methacrylate (EGMA) with GMA content 1% was obtained Elf-Atochem Co. The chemical structure and characteristics of the PBT, PA, and EGMA are shown in Fig. 1 and Table 1, respectively.

2.2. Blend preparation

Blends of PBT and PA were prepared in 70/30, 50/50, and 30/70 PBT-PA weight concentration using a 42 mm diameter twins screw extruder, with a 3:1 length to diameter screw. The time of mixing was defined by the attainment of constant torque, and this occurred generally in about 6 min. Concentration of EGMA copolymer, ranging from 0 to 20 wt% (phr) with respect to the whole weight fraction of PBT-PA blends were used.

The polymer samples were dried under vacuum (< 1 mmHg) at 100°C for 24 hours. The temperature of the extruder was set at 220 and 240°C in feeding zone and barrel zones, respectively. Samples were compression molded using a hot press at 240°C and 40 psi for 5 min.

2.3. Differential scanning calorimetry

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer DSC, Model DSC-7. Temperature calibration was performed using indium (Tm = 156.60°C, ΔHf = 28.5 J/g). Blend samples were heated in a nitrogen atmosphere from 50 to 260°C at a heating rate of 20 K/min and then quenching to 50°C for the second scan.

2.4. Scanning electron microscopy

The morphology of the cross-section of the extrudate prepared by cryogenic fracturing was examined by Hitachi field emission scanning electron microscopy (Model S-4300) at 20 kV accelerating voltage after gold sputter coating (500 Å).

2.5. Rheology

Dynamic measurements were carried out on advanced rheometric expansion system (ARES) in oscillatory shear at 5% strain in the parallel-plate arrangement with 25 mm plate. The sample used in this study was fabricated in a
disk with 2 mm in thickness. The frequency sweeps from 0.01 to 100 rad/sec were carried out at 240°C. For all measurement, it has been verified that the behavior of the sample was linear viscoelastic.

Extrudate swell was determined by quenching the extrudate immediately on coming out the extruder die with ice-water and measuring its diameter relative to the diameter of the die. Also, the torque change with mixing time was obtained in a Haake Rheomix 600P at 240°C and 50 rpm.

2.6. Mechanical property

Tensile test was carried out at ambient conditions using an Instron universal testing machine (Model 4467) according to ASTM-D 638. In tensile test, a cross head speed was 1.2 mm/min.

3. Results and discussion

3.1. Morphology

The morphology of the PBT-PA blends was studied using scanning electron microscopy. Figs. 2-4 show micrographs of the cryogenically fractured cross-section surfaces for the 70/30, 50/50, and 30/70 PBT-PA blends, respectively. In Fig. 2(a), the average radius of the PA droplet for the 70/30 PBT-PA blend is about 2-3 \( \mu \)m. When the 2.5 and 10 phr EGMA added to the 70/30 PBT-PA blend, the droplet size decreases in the PBT matrix. While the EGMA con-
tent was higher than 10 phr, the dispersed droplet could be found in the 70/30 PBT-PA blend. This phenomenon may be due to segregation and formation of unreacted EGMA copolymer as a third phase in the 70/30 PBT-PA blend. In Fig. 3(a), the average radius of the droplet for the 50/50 PBT-PA blend is about 6-7 µm. This morphology may be due to poor adhesion between the PBT and PA. In Fig. 3(b)-(c), when the 2.5 and 10 phr EGMA added to the 50/50 PA-PBT blend, the droplet size of the 50/50 PA-PBT blend decreases in the matrix as shown in Fig. 2(b)-(c). In Fig. 4(a)-(c) show the morphology of the 30/70 PBT-PA blend with 0.0, 2.5, and 10 phr EGMA, respectively. In Fig. 4(a), the droplets of the 30/70 PBT-PA blend are very uniform and average radius size is about 0.8 µm. It was reported previously that the PBT-PA has ester-amide interchange reaction without EGMA in PBT-PA blends using by the melt rheology, nuclear magnetic resonance spectroscopy, and differential scanning calorimetry, respectively (Utracki, 1982; Pillon and Utracki, 1984; Pillon et al., 1987). Therefore, it is suggest that finer morphology of the 30/70 PBT-PA blend compared with 70/30 and 50/50 PBT-PA blend without EGMA may come from ester-amide interchange reaction between PBT and PA. Also, from the Figures 2 and 4, we can deduce that the ester-amide interchange reaction may be easily happened when the PA content is higher than that of PBT in the PBT-PA blends. As will be discussed rheology section, it is suggested that this finer morphology of the 30/70 PBT-PA blend compared with 70/30 and 50/50 PBT-PA blend without EGMA may affect to the rheological behavior of the blends.

In Fig. 4(b) and (c), which show the morphology of the 2.5 and 10 phr EGMA are added to the 30/70 PBT-PA blend, good adhesion between the continuous phase (PA) and dispersed phase (PBT) are observed. From Figs. 2-4, it is suggested that the EGMA acted as an effective compatibilizer in the PBT-PA blends.

3.2. Differential scanning calorimetry (DSC)

The effect of blend composition on the melt temperature \(T_m\) and crystallization temperature \(T_c\) of the PBT-PA blend is shown in Figs. 5 and 6. In Fig. 5, \(T_m\) of the PBT was founded at 223 °C, and the \(T_m\) of the PA was founded at about 212 and 223 °C, respectively. From Fig. 5, since the melt temperature of pure PBT is so close to the major melt temperature of pure PA (223 °C), the melt temperature of the PBT-PA blends tend to fuse together and could not be determined separately. In Fig. 5, double endotherms for

---

**Fig. 4.** SEM micrographs for the PBT-PA-EGMA blends prepared at 240°C: (a) 30/70/0.0; (b) 30/70/2.5; (c) 30/70/10.

**Fig. 5.** DSC heating thermograms of the PBT-PA blends.
Reactive blends of poly(butylene terephthalate)/polyamide-6 with ethylene glycidyl methacrylate

Korea-Australia Rheology Journal December 2001 Vol. 13, No. 4

173

the pure PA were observed, and the double endotherms were previously reported by Campoy et al. (1998). PA can exhibit different polymeric forms like the $\alpha$, $\gamma$, and $\gamma^*$ which represent the different crystalline structures (Campoy et al., 1998). Therefore, double melt for the PA in Fig. 5 may come from sequential melting of the two different crystalline structures ($\alpha$ and $\gamma^*$).

The crystallization temperatures of the pure PBT and PA are founded at 173 and 168°C in Fig. 6, respectively. In Fig. 6, it is observed that the $T_c$ of the PBT-PA blends are higher than those of the pure PBT and PA, and these crystallization behavior of the PBT-PA blends can be interpreted a mutual nucleating agent to enhance the crystallization on the other component (Chiou and Chang, 2000). From Fig. 6, double exotherm peaks are observed for the 70/30 and 50/50 PBT-PA blends, which suggested the lower and higher exotherm peaks are related to the PA and PBT crystallizations, respectively. Also, we can deduce that PBT and PA exotherm peaks were overlapped in the 30/70 PBT-PA blend, so single exotherm peak is observed in Fig. 6.

Fig. 7 shows the melting point of the 30/70 PBT-PA blend. In Fig. 7, the endotherm of the 30/70 PBT-PA blend was broadened after EGMA was added in the blends, since the enthalpy of melting of the PBT-PA somewhat decreases with the increase of EGMA content. This phenomenon may be explained by that the EGMA affects to the crystallization behavior and decreases crystallinity of the PBT-PA blends. From the thermal analysis results of the PBT-PA blends, it is suggested that the EGMA affected to the crystallization behavior of the PBT-PA blends. As will be discussed below, this result is interpreted with the results of rheological and mechanical properties.

3.3. Rheology

Figs. 8-10 show the complex viscosity of the 30/70 PBT-PA containing various EGMA content: (▲) 30/70 PBT-PA; (■) 30/70/2.5 PBT-PA-EGMA; (○) 30/70/10 PBT-PA-EGMA; (▼) 30/70/20 PBT-PA-EGMA; (◆) PA; (△) PBT.
From Figs. 2-4, the droplet size of the 30/70 PBT-PA blend is about 0.8 \( \mu \)m which is smaller than that of the 50/50 and 70/30 PBT-PA blends, which suggests that the increase of the compatibility in the 30/70 PBT-PA blend. Therefore, increase in the viscosities of 30/70 PBT-PA blend without EGMA in Fig. 8 is probably due to the ester-amide interchange reaction between PBT and PA.

For the 70/30, 50/50, and 30/70 PBT-PA blends, in Figs. 8-10, complex viscosity of the blends increases with the increase of EGMA content at the low frequencies and decreases at the high frequencies. The effect of the compatibilizer on the viscosity of the blends is very complicated in reactive blend system because there are several variables such as composition, viscosity ratio, functionality, compatibilizer quantity and plasticization. Molecular weight increases through in situ reaction are mainly responsible for such viscosity increase after compatibilization (Chiou and Chang, 2000). Thus, increase complex viscosity at the low frequencies for the PBT-PA blends with EGMA content can be interpreted that the EGMA is effective as a compatibilizer. In addition, decrease of complex viscosity with the increase of EGMA content at the high frequencies for the PBT-PA blends might be explained by that the dispersed domains in the PBT-PA blends containing the higher amount of PBT-g-PA copolymer, which is presented in interface of PBT-PA blends compatibilized with EGMA, are more easily deformed by an oscillation flow (Jeon and Kim, 1998). Also, similar rheological behaviors in reactive blends were earlier reported by Chang et al. (1991) and Bousmina et al. (1995).

Extrudate swell and melt fracture during extrusion could cause the serious problem in incompatible polymer blend because it has a high elasticity. In general, such processability problems can be reduced or completely eliminated after compatibilization, depending on the composition and the amount of compatibilizer employed (Wakita, 1993). Fig. 11 shows the effect of EGMA as a compatibilizer on the extrudate swell for the PBT-PA blends. In Fig. 11, extrudate swell ratio of the pure PBT, PA, and PBT-PA blends with 10 phr EGMA is about 1.5. When the compatibilizer was added to the PBT-PA blends, the extrudate swell ratio of the compatibilized PBT-PA blends was sharply reduced in all the blends compositions. From Fig. 11, it is suggested that EGMA may have a compatibility with pure components, therefore, the extrudate swell ratio of the compatibilized PBT-PA blends was similar to that of pure components. This result is similar to that of an earlier reported by Huang and Chang (1997a).

The torque change curves with time for the pure components and blends under experimental condition (240°C, 50 rpm) are shown in Fig. 12. From the torque curves vs mixing time for the PBT, PA, PBT-EGMA, PA-EGMA, and PBT-PA-EGMA blends, the torque curves generally show an apparent maximum during the initial loading of
Reactive blends of poly(butylene terephthalate)/polyamide-6 with ethylene glycidyl methacrylate

Korea-Australia Rheology Journal December 2001 Vol. 13, No. 4

175

the pellets, and they then gradually approach a steady-state value. From Fig. 12(a) and (b), the steady torque value of the PA with EGMA 10 phr blend is larger than that of the pure PA. This is probably due to the reaction between the PA and EGMA and formation of the PA-co-EGMA copolymer. Whereas the steady torque value of the PBT with EGMA 10 phr blend is slightly increased when it compared to the values of the pure PBT in Fig. 12(e) and (f). In generally, it is known that the reactivity of epoxide group with hydroxyl group of PBT is substantially greater than that with amine of PA (Orr et al., 2001). According to the results of Orr et al. (2001), we can predict that the value of torque for the pure PBT with EGMA is greater than that of PA with EGMA in Fig. 12. However, as shown in Fig. 1, PA have more reactive site (difunctional amine and one carboxyl end-group), which can caused the reaction with epoxide in EGMA, than that of PBT (one carboxyl and one hydroxyl end-group). Also, weight average molecular weight for the PA is much smaller than that of PBT in this study. Since the numbers of reactive site per unit mass for the PA are larger than that of PBT, it is suggested that the reaction between PA and EGMA is more easily happened than the reaction between PBT and EGMA in this study. These difference of number of the reactive site for the PA-EGMA and PBT-EGMA blends may affected to the torque change with mixing time as shown in Fig. 12. In Fig. 12(c) and (d), the torque value of the 50/50/10 PBT-PA-EGMA blend is significantly higher than that of 50/50 PBT-PA blend. These results give indirect evidence that the reaction between PA and PBT with EGMA.

3.4. Mechanical property

The material mechanical properties can roughly be classified into two categories: strength and toughness. Tensile strength and flexural modulus can be considered the material strength, while tensile elongation and Izod impact energy are the material toughness (Huang and Chang, 1997b; Chiou and Chang, 2000). To investigate of improvement of mechanical properties for the PBT-PA-EGMA blends, we measured tensile strength and tensile elongation using universal testing machine (UTM) according to the standard methods.

Figs. 13 shows the tensile strength of the PBT-PA blends with EGMA content. In Fig. 13, it is found that the tensile strength of the 30/70 PBT-PA blend increases with increase

![Fig. 11. Extrudate swell ratio of the PBT-PA and PBT-PA-EGMA 10 phr blends: (△) PBT-PA; (○) PBT-PA-EGMA 10 phr.](image)

![Fig. 12. Torque change with mixing time at a temperature 240°C: (a) PA; (b) PA with EGMA 10 phr; (c) 50/50/10 PBT-PA-EGMA; (d) 50/50 PBT-PA; (e) PBT with EGMA 10 phr; (f) PBT.](image)

![Fig. 13. Tensile strength with EGMA content for the PBT-PA blends: (▼) 70/30 PBT-PA; (○) 50/50 PBT-PA; (●) 30/70 PBT-PA.](image)
of EGMA up to 2 phr, while tensile strength of the blend in which EGMA content is higher than 2 phr decreases with increase of EGMA content.

Fig. 14 shows the tensile elongation with EGMA content. In Fig. 14, the tensile elongation of the 30/70 PBT-PA blend increases with the increase of EGMA, reach a maximum when EGMA content is equal to 10 phr. For the 50/50 and 70/30 PBT-PA blends, the tensile elongation increase rapidly with EGMA content up to 2 phr, then increases slowly more than 2.0 phr EGMA were added.

4. Conclusions

Reactive blends of the PBT and PA compatibilized with EGMA copolymer were prepared by twin screw extruder. Morphological, thermal, rheological, and mechanical properties of the blends were investigated using scanning electron microscopy, differential scanning calorimetry, advanced rheometric expansion system, and universal testing machine.

From the results of thermal analysis by DSC, the melting point of the 30/70 PBT-PA blend increases with the increase of EGMA, which suggests that the increase of the compatibility in the 30/70 PBT-PA blend.

From the results of mechanical properties, it was found that the tensile strength of the 30/70 PBT-PA blend increased with the increase of EGMA up to 2 phr, while tensile strength of the blend in which EGMA content is higher than 2 phr decreases with the increase of EGMA content.

From the results of morphological, thermal, rheological, and mechanical properties for the PBT-PA-EGMA blends, it is concluded that the EGMA could be used as a compatibilization role in the blends.

Acknowledgment

This work was supported by Samyang Corporation.

References


Huang, C.-C. and F.-C. Chang, 1997a, Reactive compatibilization of polymer blends of polybutylene Terephthalate (PBT)/polyamide-6,6 (PA-6,6): 1. Rheological and thermal properties, *Polymer* **38**, 2135.

Huang, C.-C. and F.-C. Chang, 1997b, Reactive compatibilization of polymer blends of polybutylene Terephthalate (PBT)/polyamide-6,6 (PA-6,6): 2. Morphological and mechanical pro-
properties, *Polymer* **38**, 4287.