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The effect of PS–GMA as an *in situ* compatibilizer on the morphology and rheological properties of the immiscible PBT/PS blend

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Poly(styrene-*co*-glycidyl methacrylate) (PS–GMA) is used as an *in situ* compatibilizer for incompatible (or immiscible) blends of poly(butylene terephthalate) (PBT) and polystyrene (PS). The epoxy group in PS–GMA reacts with the carboxylic acid group in PBT, thus PS-*graft*-PBT copolymer is formed and acts as a compatibilizer between PS and PBT during the melt blending. The degree of the reaction is investigated by the observation of the torque change with time at various temperatures, since the torque is directly related to the amount of graft copolymer formed in the mixer. But, the actual temperature in the mixer is higher than the specific setting temperature due to the viscous heating and exothermic reaction with time. Thus, the torque, as obtained from a torque rheometer, must be appropriately compensated based on the reference temperature, which becomes more useful in finding a relationship between the degree of the reaction and the amount of graft copolymer formed. Rheological behaviour of blends having *in situ* compatibilizer was investigated by dynamic oscillatory shearing measurement. It is shown that as the amount of graft copolymer formed during blending increases, the viscosity at low shear rates increases but the degree of shear thinning is not pronounced. For polymer alloys prepared at the setting temperature of 230°C, the finer morphology was obtained when more than 5 phr PS–GMA was added to PBT/PS blend, but this amount of PS-GMA decreased to 3 phr when the setting temperature in the mixer was increased to 240°C since at higher temperature more graft copolymer can be formed.

(Keywords: compatibility; graft copolymer; rheology)

INTRODUCTION

Polymer alloys consisting of two or more components have been used in many advanced materials for obtaining unique physical properties that cannot be obtained from the constituent polymers alone[1–4]. In order to make polymer alloys from an incompatible polymer mixture, a compatibilizer (or emulsifier) must be used to improve the interfacial adhesion. There are generally two methods of compatibilization: physical compatibilization and chemical compatibilization. The former technique utilizes a pre-made block or graft copolymer whose constituent component is compatible (or miscible) with each component in the blend. In this method, a block or graft copolymer can be located at the interface between two immiscible phases since the enthalpic contribution becomes dominant over entropy loss[5–7]. Many theories[8–12] suggest that in order to reduce significantly the interfacial tension between the phases, a block copolymer having larger molecular weight is more efficient than one having smaller molecular weight. But, as the molecular weight of a block copolymer becomes larger, only part of it can go to the interface and the rest stays in the bulk phase owing to the higher possibility of micelle formation of a block copolymer[13–16]. Another difficulty is that in physical compatibilization a block copolymer cannot reach the interface easily owing to its high viscosity and rather short processing time since polymer alloys are usually prepared by extruder or compounding machine. Thus, although much work[5–7,17–20] has been done in this area, physical compatibilization is not widely used for commercial production of polymer alloys.

The chemical compatibilization technique utilizes the reaction between reactive groups, making *in situ* graft (or block) copolymer during melt blending by extruder or internal mixer[3,21–23]. This copolymer acts as a compatibilizer between two immiscible polymer blends and stays near the interface since the reaction between functional groups occurs easily near the interface. Polymer alloys prepared by this technique have a very fine morphology and broader interface. Moreover, this fine morphology can persist under the very high shear stress found during the injection moulding process. These alloys are commercially available, for example, NORYL GTX (impact-modified nylon/PPE [poly(1,4-dimethyl-2,6-phenylene ether)]) and TRIAX (nylon/ABS (acrylonitrile-*co*-butadiene-*co*-styrene)). In order to obtain this kind of

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alloy each polymer must have a specific reactive group, and both must react within 2–3 min if the extrusion or compounding time is considered. Three pairs of reactive groups are now used in industry although many possible alternatives can be considered[3,21–23]. The first pair uses the reaction between the anhydride group and amine (or amide) group as in GTX. The amine group is usually found at the chain end in nylon. Thus, when an anhydride group is introduced to the other polymer, one can obtain polymer alloys with good physical properties. Polymer alloys using nylon and maleic-anhydride-modified polypropylene (and/or ethylene–propylene rubber or PPE) can be classified in this group[24–28]. The second pair uses the reaction between the epoxy group and carboxylic acid group[29,30]. Note that polyesters such as poly(butylene terephthalate) and poly(ethylene terephthalate) have a carboxylic acid group at the chain end. The last pair utilizes the reaction between the oxazoline group and anhydride (or carboxylic acid) group[31,32], but this pair is not widely used in industry.

In chemical compatibilization, the amount of reactive groups becomes very important in determining the morphology and thus the final physical properties. When this amount is small, only a little graft copolymer is formed. In this situation, the final physical properties of polymer alloys can be expected to be relatively poor due to minimal compatibilization effect. On the other hand, when the amount of reactive groups is too high, graft copolymer with very large molecular weight or even crosslinked copolymer can be formed, which makes these copolymers stay in the bulk phase rather than move to the interface. Therefore, one cannot make a polymer alloy with the desired physical properties in this extreme case.

Recently, Macosko and coworkers[30] have studied the chemical reaction kinetics of copolymer formation between carboxylic-acid-terminated polystyrene (PS–COOH) and epoxy-terminated poly(methyl methacrylate) (PMMA–E). They found that the coupling reaction between carboxylic acid and epoxy at 180°C is rather slow due to the low diffusion coefficient. Also, they found that the reaction rate is very important in the formation of the initial morphology, but once the initial morphology is formed, the reaction rate is little affected by mixing.

Many research groups[29,31,32] have used the torque rheometer, such as a Brabender Plasticorder or a Haake rheometer, to check the reactivity between the functional groups. During the torque measurement in this kind of rheometer, the temperature inside the mixer is usually higher than the specific setting temperature due to the exothermic heat from reaction and viscous heating. Thus, in order to study the degree of reaction quantitatively the torque obtained directly from the torque rheometer at the specific setting temperature must be appropriately compensated using the reference temperature.

In this paper, we investigate the effect of *in situ* compatibilizer of poly(styrene-*co*-glycidyl methacrylate) (PS–GMA) on the final morphology and rheology of the immiscible polymer blends of poly(butylene terephthalate) (PBT) and polystyrene (PS). Note that the epoxy group in PS–GMA reacts easily with the carboxylic acid group in PBT at higher temperatures above the melting point of PBT, thus a PBT-*graft*-PS is formed and acts as a compatibilizer between PBT and PS. Also, the torque data obtained from the torque rheometer are appropriately compensated using the reference temperature and are discussed in terms of the amount of graft copolymer and rheological properties of the blend.

EXPERIMENTAL

Materials

The PS employed in this study was a commercial grade (GP-125) of Miwon Petrochemical Co., Korea. Its number average molecular weight (M_n) and the polydispersity index (M_w/M_n) were 55 000 and 3.6, respectively, as determined by calibration curves for standard polystyrenes using gel-permeation chromatography (g.p.c.).

The PBT employed in this study was a commercial grade (HV 1010) of LG Chemical Co., Korea. The intrinsic viscosity (IV) was 1.0 dl^{-1} g^{-1} in mixed solvent of phenol and tetrachloroethane (60/40 volume ratio) at 25°C. With the Mark–Houwink relationship ($IV = 7.39 \times 10^{-5} M_v^{0.871}$) and polydispersity of 2.2 measured from g.p.c., M_n of PBT was calculated to be 25 000. The amount of carboxylic acid in PBT was determined to be 63 eq/10^6 g using the end-group titration method. Thus, there are approximately 1.6 carboxylic acid units per chain based on M_n.

The PS–GMA employed in this study was kindly donated by LG Chemical Co., Korea, and was prepared by suspension polymerization. A typical procedure for suspension polymerization of PS–GMA is as follows. Styrene monomer (1960 g), glycidyl methacrylate (40 g) and 2.8 l water were added to a glass reactor. The suspension agents used were poly(vinyl alcohol) (4.5 g) and tricalcium phosphate (5 g) and the initiator was a combination of 11 g of benzoyl peroxide and 1 g of lauryl peroxide. In order to control the molecular weight of polymer, 10 g of α-methyl styrene dimer was added as a chain transfer agent. The temperature at the reactor was slowly increased from room temperature to 90°C for 1 h and the initial polymerization occurred at this temperature for 4 h. Later, the reaction temperature was increased further to 110°C for 20 min and the reaction was completed at this temperature for 1.5 h. The speed of the stirrer was about 700 rev min^{-1}. Beads of PS–GMA with average particle size of 0.84 mm were obtained and were washed several time by water and filtered by a centrifuge. Finally, they were dried at 80°C for 8 h.

The M_n and polydispersity index of PS–GMA synthesized were 46 000 and 2.5, respectively, obtained from g.p.c., and the amount of GMA in PS–GMA was 2.0 wt% determined from ^{13}C n.m.r. Thus, about 6.4 epoxy units are present in each PS–GMA chain.

Torque rheometer

In order to investigate the extent of reaction between carboxylic acid and epoxy group, an internal mixer (Brabender Plasticorder) with capacity of 30 cm^3 and speed of 50 rev min^{-1} was used. Before mixing, all polymers were vacuum dried at 120°C for 2 h. PBT/PS blends, with blend ratios of 75/25, 50/50 and 25/75 wt/wt, were prepared using various amounts of PS–GMA (0 to 10 phr (parts per hundred parts blend by weight)) at two different setting temperatures of 230 and 240°C.

Differential scanning calorimetry

In order to check whether or not the crystallinity of the PBT phase in PBT/PS blends changes with the amount of PS–GMA added, a differential scanning calorimetry (Perkin-Elmer DSC 7 series) was used. Prior to measurement, baseline correction was obtained using two empty pans. In order to prevent thermal degradation, nitrogen gas was circulated around the sample pan. Each sample, of about 15 mg, was first heated to 250°C with a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$, annealed for 3 min and quenched to room temperature with a cooling rate of $200^{\circ}\mathrm{C\,min^{-1}}$. The heating rate was $10^{\circ}\mathrm{C\,min^{-1}}$ under nitrogen atmosphere. The second heating run was used to determine the heat of fusion of blends.

Dynamic mechanical thermal analyser

Storage modulus (E') and loss tangent ($\tan\delta$) for blends were measured using a dynamic mechanical thermal analyser (DMTA, model MK-11, Polymer Laboratories) with a single cantilever at a frequency of 1 Hz and a heating rate of $3^{\circ}\mathrm{C\,min^{-1}}$. The sample was prepared using a compression moulding machine and the dimension of the specimen was 15 mm × 5 mm × 2 mm.

Rheological measurement

In order to compensate the torque data using the reference temperature, the activation energy and viscosity of each blend must be obtained. The complex viscosities (η^*) of blends at various angular frequencies (ω) were measured using a Rheometrics Dynamic Spectrometer (RDS II) with 25 mm circular discs under oscillatory shear mode at several temperatures.

Morphology

The domain size of the dispersed phase of each blend was measured by scanning electron microscopy (Hitachi S-570). The specimen was sharply cracked by razor at room temperature.

RESULTS AND DISCUSSION

Torque change for blends

Plots of torque and actual temperature in the internal mixer *versus* mixing time at the setting temperature of 240°C for 75/25 PBT/PS blend are given in *Figure 1a* without PS–GMA, and in *Figure 1b* with 5 phr of PS-GMA. It can be seen from *Figure 1* that the actual temperature in the mixer increased rapidly during a short time interval, but it reached about 245°C, which is higher than the setting temperature, due to viscous heating of the polymer even if there was no reaction. When the reaction between carboxylic acid group in PBT and epoxy group in PS–GMA occurred, a maximum in torque appeared at about 3.5 min and the torque value at 15 min was higher than that of the blend without PS–GMA. It is noted that the actual temperature in the mixer reached about 248°C. This is due to viscous heating of highly viscous PBT-*graft*-PS copolymer formed during the reaction, in addition to the exothermic heat of reaction. According to Chikanari *et al.*[33], the rate constant for the reaction between carboxylic acid in PBT and the epoxy group is about 10 times higher than that between the hydroxyl group (–OH) in PBT and the epoxy group. Thus, the main reaction between PBT and PS–GMA is due to the former reaction, and the occurrence of this reaction was detected by an increase in the torque appearing near 3.5 min, which is given in *Figure 1b*. Note that ring-opening or crosslinking reaction between epoxy groups themselves in PS–GMA did not occur at this temperature since there is no sign of torque increase during the experimental time-scale as shown in *Figure 2*. It should be mentioned that the viscosity of PS–GMA is lowest among blend components due to low molecular weight (M_w = 115 000), thus the torque of PS–GMA at a given temperature is about half that of neat PBT.

From *Figure 1*, one must compensate the torque obtained directly from the internal mixer using the reference temperature since the temperature inside the

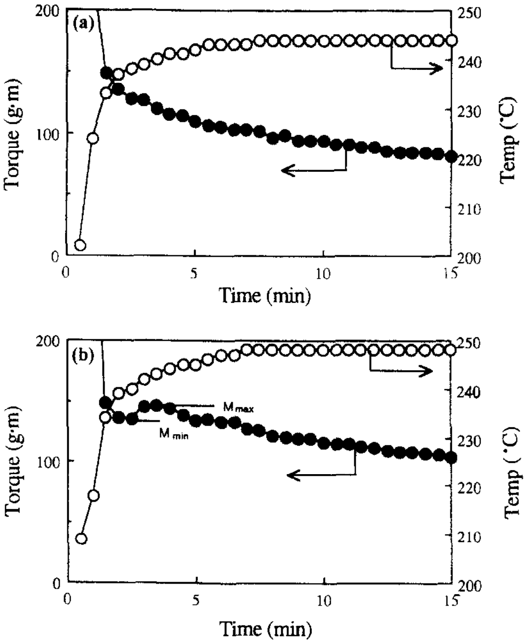

Figure 1 Variation of torque and temperature in the internal mixer with mixing time at the setting temperature of 240°C for 75/25 PBT/PS blends (a) without PS–GMA and (b) with 5 phr of PS–GMA

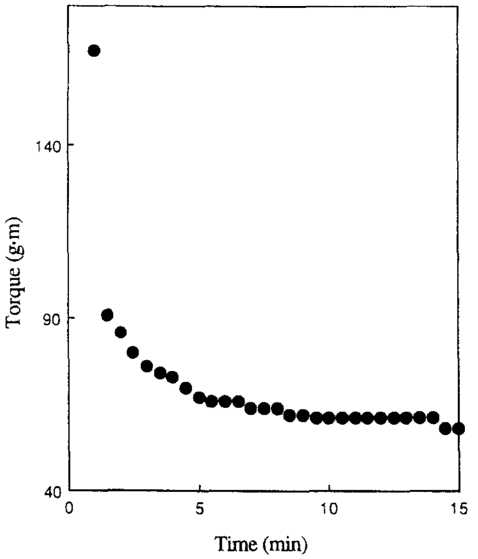

Figure 2 Torque change with mixing time for PS–GMA alone at the setting temperature of 230°C

internal mixer is not the same as the setting temperature. Note that torque is a function of viscosity of molten polymer which, in turns, depends upon temperature. This compensation method was suggested long ago by Goodrich and Porter[34,35].

The shear stress (τ) of molten polymer can be expressed by shear rate ($\dot{\gamma}$) using a power law when the shear rate is relatively large:

$$\tau = K\dot{\gamma}^n \tag{1}$$

where n is the power-law index and K is a function of temperature, which can be given by an Arrhenius equation at higher temperatures:

$$K = K_0 \exp(\Delta E/RT) \tag{2}$$

in which ΔE is the activation energy, R is the gas constant, and T is the absolute temperature.

In the internal mixer, since shear rate is proportional to mixer speed (N) ($\dot{\gamma} \propto N$) and torque (M) is proportional to shear stress ($M \propto \tau$), we have:

$$M = C\exp(\Delta E/RT)N^n \tag{3}$$

where C is a constant independent of temperature and mixer speed.

When N is constant, one obtains the temperature dependence of torque from equation (3):

$$M(T_{\mathrm{ref}}) = M(T)\exp[(\Delta E/R)(1/T_{\mathrm{ref}} - 1/T)] \tag{4}$$

where $M(T_{\mathrm{ref}})$ is the reduced torque value calculated at the reference temperature.

In order to use equation (4), the activation energy must be known. This can be obtained if the viscosity of each blend is measured at various temperatures since viscosity can also be expressed by the Arrhenius relationship:

$$\eta(T_{\mathrm{ref}}) = \eta(T)\exp[(\Delta E/R)(1/T_{\mathrm{ref}} - 1/T)] \tag{5}$$

Note that because the temperature dependence of shear viscosity can change with shear rate, the shear rate in the internal mixer must be fixed. However, owing to the very complex rotor geometry in the Brabender internal mixer used in this study, shear rate may change with each position in the mixer[36,37]. Shear rate (in rev s^{-1}) at each position of the Brabender internal mixer is given by:

$$\dot{\gamma} = 2\pi RN/(60h) \tag{6}$$

where R is the radius of the rotor blade and changes with position, and h is the gap between the mixer wall and rotor blade. Apparent shear rate ($\dot{\gamma}_{\mathrm{app}}$) inside the Brabender internal mixer used in this study is assumed to be $17.5\,s^{-1}$ (or equivalently, $\omega = 17.5\,\mathrm{rad\,s^{-1}}$ due to the Cox–Merz rule), which is the average of the maximum shear rate, $\dot{\gamma}_{\max}$ of $29.7\,s^{-1}$ obtained using $R = 1.7$ cm and $h = 0.3$ cm, and the minimum shear rate, $\dot{\gamma}_{\min}$ of $5.23\,s^{-1}$ obtained using $R = 1$ cm and $h = 1$ cm.

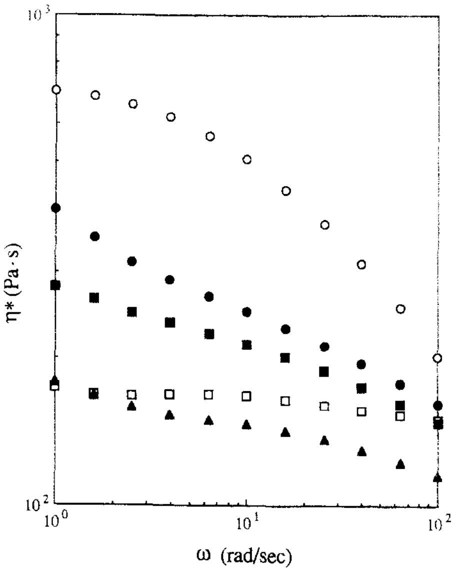

Figure 3 Plots of complex viscosity (η^*) *versus* angular frequencies (ω) at 252°C for neat PBT and PS, and PBT/PS/PS–GMA blends with different amounts of PS–GMA prepared by mixer at the setting temperature of 240°C: □, PBT; ○, PS; ▲, 75/25/0; ■, 75/25/2; ●, 75/25/5

Table 1 Activation energies (ΔE) (kcal $\mathrm{mol^{-1}}$) at $\omega = 17.5\,\mathrm{rad\,s^{-1}}$ calculated from viscosity data for neat PBT and PS, and PBT/PS/PS–GMA blends prepared at two different setting temperatures

Setting temperature (°C)		PBT/PS				
	PS–GMA (phr)	100/0	75/25	50/50	25/75	0/100
230	0	17.0	18.0	18.1	13.6	13.4
	5		18.2	20.5	12.8	
	10		18.2	20.6	13.2	
240	0	17.0	17.2	18.3	12.2	13.4
	3		18.0	18.5	12.4	
	5		19.2	21.2	12.5	
	10		19.2	22.3	10.0	

Plots of complex viscosity (η^*) *versus* angular frequencies (ω) for neat PS and PBT, and PBT/PS/PS–GMA blends, which were all prepared by the internal mixer at a setting temperature of 240°C, are given in *Figure 3*. It is seen in *Figure 3* that neat PBT shows Newtonian behaviour while neat PS shows shear thinning. The complex viscosity of 75/25 PBT/PS blends without PS-GMA is lower than that of constituent components PBT and PS at higher frequencies. According to Han[38], the viscosity of immiscible polymer blends changes with their morphology and a minimum viscosity can be found at a certain blend composition when a domain can be elongated easily in the matrix. Note that in the 75/25 PBT/PS blend, PS became the domain structure and might be elongated easily owing to its high elasticity compared to PBT. As the amount of PS–GMA increases, both viscosity and the degree of shear thinning increase since more PBT-*graft*-PS copolymer is formed due to reaction.

The activation energies, which were calculated using several values of η^* measured between 235 and 260°C at $\omega = 17.5\,\mathrm{rad\,s^{-1}}$, for blends having different compositions of PBT, PS and PS–GMA are given in *Table 1*. Note that the slope in plots of $\ln \eta^*$ *versus* $1/T$ becomes $\Delta E/R$ (see equation (5)). It is gratifying to find in *Table 1* that the activation energy varies little with the amount of PS–GMA when the blend ratio of PBT/PS is fixed. Thus, the amount of PBT-*graft*-PS copolymer formed during reaction is not the main factor affecting ΔE at $\omega = 17.5\,\mathrm{rad\,s^{-1}}$ rather ΔE depends mainly upon the blend ratio of PBT/PS. The activation energy of the 25/75 PBT/PS blend was quite different from that of the 75/25 and 50/50 PBT/PS blends. This is because the matrix

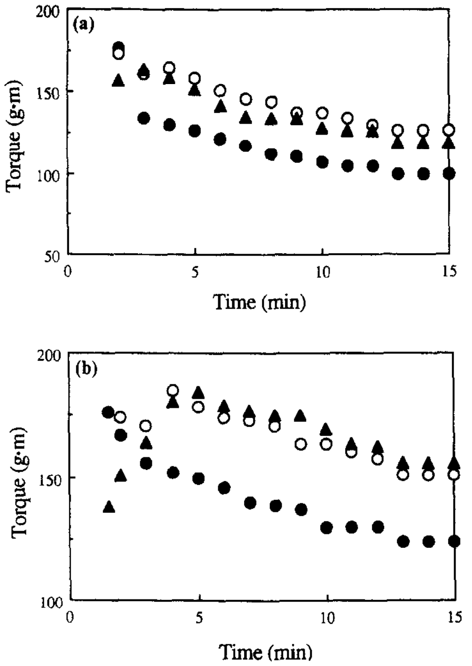

Figure 4 Torque change with mixing time for 75/25 PBT/PS blends with three different amounts of PS–GMA: (a) without torque compensation; and (b) with torque compensation using the reference temperature of 230°C. Amount of PS–GMA in the blends: ●, 0 phr; ○, 5 phr; ▲, 10 phr

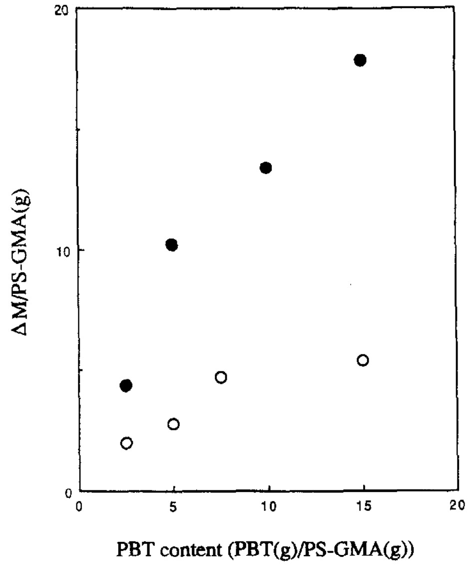

Figure 5 Plots of ΔM normalized by the amount of PS–GMA *versus* the amount of PBT at two different reference temperatures: ○, 230°C; ●, 240°C

was PS in the former blend while the matrix became PBT in the latter two blends. Note that ΔE of neat PBT is 17.0 kcal mol^{-1} which is larger than that of neat PS (13.4 kcal mol^{-1}). It should be mentioned that ΔE depends upon ω (or $\dot{\gamma}$) when ω (or $\dot{\gamma}$) is higher than its critical value ω_c. Usually, ΔE becomes smaller as ω increases since the power law index decreases with increasing ω. For example, when ΔE of neat PS was calculated at lower ω (i.e. based on the zero shear viscosity), this is 22.5 kcal mol^{-1}, which is about twice that calculated based on $\omega = 17.5\,\mathrm{rad\,s^{-1}}$. Note that ΔE of neat PBT changes very little with ω due to Newtonian behaviour.

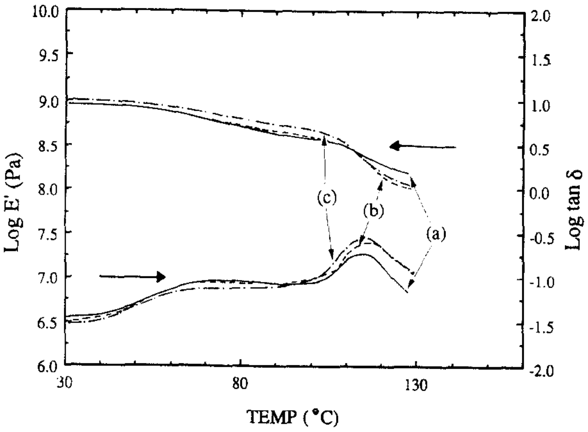

Figure 6 Plots of storage modulus (E') and loss tangent ($\tan\delta$) *versus* temperature for 75/25 PBT/PS blends with various amounts of PS–GMA: (a) 0 phr; (b) 5 phr; (c) 10 phr

For the 75/25 PBT/PS blend having various amounts of PS–GMA the behaviour of the torque obtained directly from the internal mixer at a setting temperature of 230°C is different from that reduced to the reference temperature of 230°C using temperature compensation; this is shown in *Figure 4*. As the amount of PS–GMA increases, both torque value and torque increment ($\Delta M = M_{\max} - M_{\min}$) increase. Here, $M_{\max}$ and $M_{\min}$ are the maximum and minimum torque values, respectively (see *Figure 1b*). When torque is not compensated, as shown in *Figure 4a*, the value of ΔM for the blend having 5 phr PS–GMA seems to be larger than that for the blend having 10 phr PS–GMA; however, when torque is properly compensated, as given in *Figure 4b*, the value of ΔM for the former blend is clearly smaller than that for the latter blend. Thus, it can be concluded that when the value of ΔM is not larger, which is the case for the blend having a small amount of PS–GMA, torque must be appropriately compensated in order to investigate a relationship between the rate of reaction and the amount of PBT-*graft*-PS copolymer formed during reaction.

Figure 5 shows that ΔM normalized by the amount of PS–GMA increases almost linearly with the ratio of PBT/PS–GMA and the value obtained at the higher temperature is higher than that obtained at lower temperature. Since the average number (1.6) of carboxylic acid units per PBT chain is smaller than that (6.4) of epoxy units per PS–GMA chain, more graft copolymers, due to reaction between two functional groups, are expected to be formed as the amount of PBT in the blend increases. Also, since this reaction occurred faster at the higher mixing temperature (240°C), the torque increment becomes larger. It can be expected from *Figure 5* that when torque is appropriately compensated the degree of graft reaction can be directly correlated with normalized ΔM.

Dynamic mechanical properties

Plots of storage tensile modulus (E') and loss tangent ($\tan\delta$) *versus* temperature for 75/25 PBT/PS blends having various amounts of PS–GMA are given in *Figure 6*. It can be seen that as the amount of PS–GMA increases, values of E' near 100°C increase. This suggests that as the amount of PS–GMA increases, more

Table 2 Heat of fusion (ΔH_f) and relative crystallinity of PBT phase in PBT/PS/PS–GMA blends prepared at the setting temperature of 230°C

(PBT/PS/PS–GMA)	ΔH_f ($J g^{-1}$)	Relative crystallinity[a]
100/0/0	43.2	100
75/25/0	29.4	91.8
75/25/5	27.3	88.5
75/25/10	28.7	97.5

[a] Relative crystallinity = ΔH_f of blend/[(wt% of PBT in blend) (ΔH_f of neat PBT)]

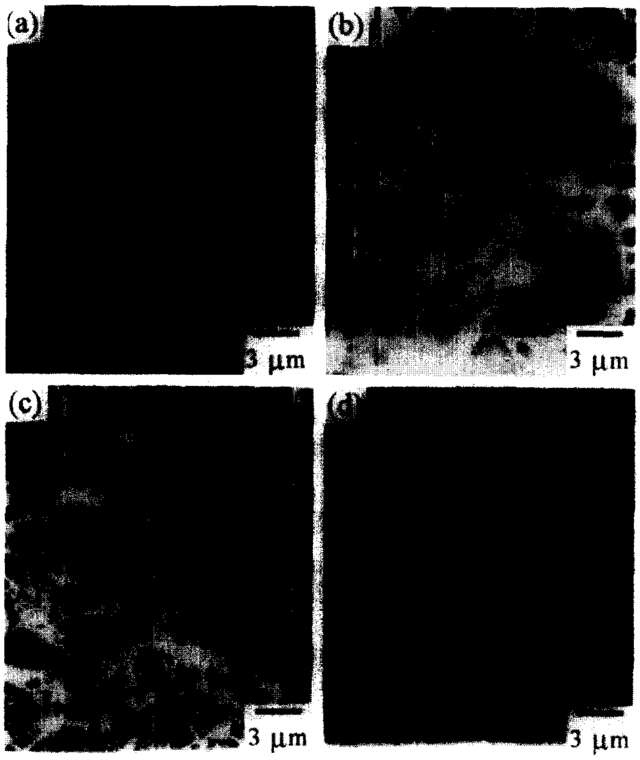

Figure 7 Scanning electron micrographs of a fractured surface made at ambient temperature for 75/25 PBT/PS blends prepared at the setting temperature of 230°C with various amounts of PS–GMA: (a) 0 phr; (b) 0.5 phr; (c) 2 phr; (d) 5 phr

PBT-*graft*-PS copolymer is formed. It should be pointed out that the increase in E' near 100°C is not due to a change in relative crystallinity of PBT phase in the blend since the heat of fusion of PBT phase in the 75/25 PBT/PS blend measured by d.s.c. does not change greatly with the amount of added PS–GMA, which is demonstrated in *Table 2*. Also, the glass transition of PS phase, which appeared near 120°C, increases slightly with increasing amount of PS–GMA.

Morphology of PBT/PS/PS–GMA blend

Morphologies of the fractured surface of the 75/25 PBT/PS blend prepared by mixer at a setting temperature of 230°C with different amounts of PS–GMA are given in *Figure 7*. It can be shown that (i) when there is no PS–GMA in the blend, the average domain size of the disperse phase is about 3 μm and the interfacial adhesion between dispersed and matrix phases turns out to be poor (*Figure 7a*); (ii) when only 0.5 phr of PS–GMA is added the average domain size decreases to about 2.5 μm, but from the fracture surface this blend shows good interfacial adhesion since PBT-*graft*-PS acts as a compatibilizer between two immiscible blends (*Figure 7b*); (iii) as the amount of PS–GMA increases further, the domain size decreases significantly (*Figure 7c*); and (iv) finally, one cannot see the difference between the disperse and matrix phase (*Figure 7d*) when the amount of added PS–GMA is greater than 5 phr.

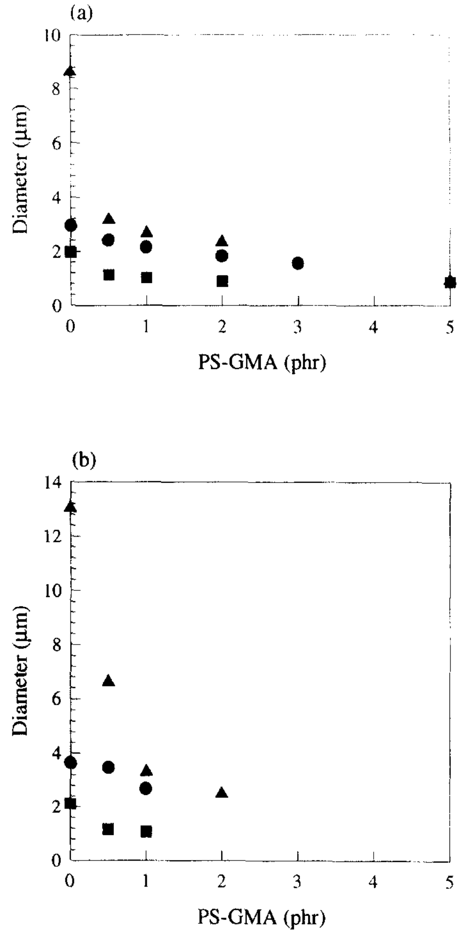

Figure 8 Plots of the number-average diameter of the dispersed phase *versus* the amount of PS–GMA for PBT/PS blends prepared at two different setting temperatures: (a) 230°C; (b) 240°C. PBT/PS blend ratios: ●, 75/25; ▲, 50/50; ■, 25/75

The reduction in domain size with increasing the amount of PS–GMA for three blend ratios of PBT/PS prepared at two different setting temperatures, 230 and 240°C, is given in *Figures 8a* and *b*, respectively. It is shown in *Figure 8a* that distinct phase-separated domains are not visible at this magnification when the amount of PS–GMA added is greater than 5 phr. When the mixing temperature in the internal mixer increases from 230 to 240°C, the trend in decreasing domain size for three different blend ratios with increased amount of PS–GMA is similar to that for blends prepared at 230°C. It can be seen in *Figure 8b* that very fine morphology, where distinct phase-separated domains are not visible at this magnification, was obtained when the amount of PS–GMA added is greater than 3 phr. It should be noted that the domain size of 50/50 PBT/PS blend without PS–GMA prepared by mixer at the setting temperature of 240°C is about 13 μm, which is larger than that for the blend prepared at 230°C (9 μm). This is mainly due to a larger difference in viscosity between the disperse phase of PS and matrix of PBT at 240°C compared to that at 230°C.

It is very interesting to find in *Figure 8* that as the amount of PS–GMA added to the blend increases, the domain size decreases very rapidly for the 50/50 PBT/PS blend while it decreases rather slowly for the other two blends (i.e. 75/25 and 25/75 PBT/PS blends). This phenomenon can be explained by Taylor's equation[39]: at a given shearing force a large domain can be deformed and broken into smaller domain sizes more easily than is the case with a smaller domain.

CONCLUSIONS

In this study, we have shown that PS–GMA acts efficiently as a compatibilizer between two immiscible polymer blends of PBT and PS since the epoxy units in PS–GMA react with the carboxylic acid group in PBT, and PBT-*graft*-PS copolymer is formed.

It is pointed out that for a relatively small increase in torque (e.g. less than 50 g m) measured by the internal mixer, it is necessary to compensate for the temperature effect on torque in order to find a relationship between the degree of reaction and the amount of graft copolymer formed. This compensation can be calculated using the activation energy at a certain shear rate or frequency corresponding to that in the internal mixer when the viscosity at each blend is measured at various temperatures. The major parameter affecting the activation energy of blends calculated at $\omega = 17.5\,\mathrm{rad\,s^{-1}}$ was the blend ratios of PBT/PS, not the amount of PS–PMA added. When ΔM is normalized by the amount of PS–GMA, it increases almost linearly with the amount of PBT.

The finer morphology was obtained for PBT/PS blends prepared at the setting temperature of 230°C when the amount of PS–GMA is greater than 5 phr, while this amount decreased to 3 phr for blends prepared at the setting temperature of 240°C.

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