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Polymer 42 (2001) 6661–6668

polymer

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Preparation of poly(butylene terephthalate)/oxazoline containing polystyrene graft copolymer through melt-blending and their application as a compatibilizer in polycarbonate/polystyrene blend

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Received 20 December 1999; received in revised form 15 August 2000; accepted 25 September 2000

Abstract

The polybutylene terephthalate (PBT)/oxazoline containing polystyrene (RPS) graft copolymer was prepared through melt reaction of PBT and RPS. The formation of the PBT/RPS graft copolymer was noticed by the increase in torque during melt blending in a Haake Buchler internal mixer and also confirmed by the observation of Fourier transform infrared spectroscopy (FT-IR) after the extraction of RPS from the PBT/RPS mixture. The compatibilized polycarbonate (PC)/polystyrene (PS) blends with the pre-made PBT/RPS graft copolymer were prepared by melt blending in the internal mixer. The morphologies of these blends were examined by the transmission electron microscope (TEM). The compatibilized PC/PS blends showed finer morphologies than the uncompatibilized blend. Tensile properties of these blends were also investigated. © 2001 Published by Elsevier Science Ltd.

Keywords: Polycarbonate; Polystyrene; Polybutylene terephthalate

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1. Introduction

There is commercial interest in multiphase polymer blends because of their commercial versatility [1]. The majority of known polymers are usually immiscible with each other. The immiscible polymer blends show a large interfacial tension in the melt, which makes it difficult to disperse the components properly and to drive coalescence of phase morphology at low stress or quiescent condition. It generally leads to poor interfacial adhesion at the interface of each phase in the solid state, which results in poor mechanical properties. Compatibilization for these immiscible polymer blends can be achieved either by the addition of block and graft copolymers or by in-situ formation of copolymer during the processing, which can act as interfacial agents at the interface. The term of compatibilization means the modification process of interfacial properties in an immiscible polymer blend, leading to lower interfacial tension between the two phases or stabilization against the phase coalescence. Various compatibilization methods have been reported. One of most popular methods is to add a third component, which can act as an interfacial agent at the interface. Block or graft copolymer is generally used as a third component. Although addition method is very effective in compatibilization, there are some difficulties in the synthesis of such block or graft copolymers. Such method requires relatively large amount of block or graft copolymer and they usually quite expensive. As an alternative way to compatibilize immiscible polymer blends, in-situ compatibilization has been frequently applied. The in-situ compatibilizer could be formed via interfacial reaction between functional groups of added polymeric components, i.e. reactive compatibilization. The in-situ compatibilizer synthesized from suitably functionalized polymers can offer a number of advantages over the separate addition type previously described [2]. Some of them are as follows: Copolymers formed by the in-situ reaction would preferentially locate at the interface between two polymers since they can meet at the interface. Often as little as 0.5–2.0 wt% copolymer is sufficient to achieve stabilization in reactive compatibilization. Therefore it could be not only cost-efficient but also effective.

Polycarbonate (PC) has been one of highly growing engineering plastic materials. PC has several merits such as its high transparency, high impact resistance and good heat

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PII: S0032-3861(01)00103-3

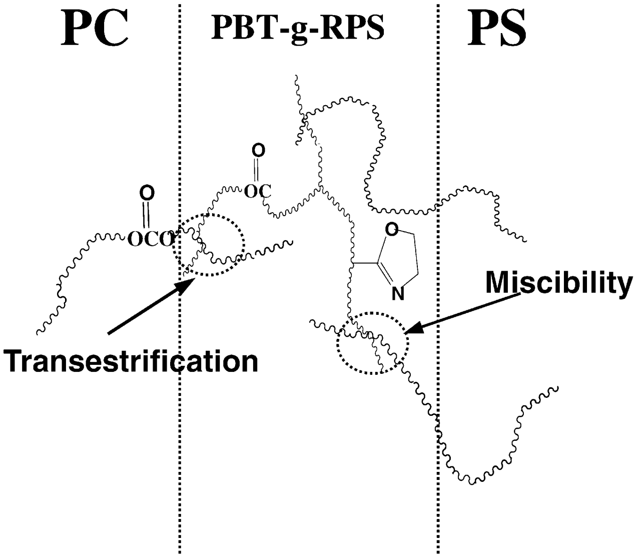


Fig. 1. Schematic illustration for the compatibilization of the PC/PS blend by using the PBT/RPS graft copolymer.

resistance and so on. However it is known that there are difficulties in processing due to its high melt viscosity and sensitivity of impact strength on temperature especially for thick product. In order to overcome these demerits, several types of PC blends with other polymers have been developed. The PC/acrylonitrile–butadiene–styrene (ABS) blends are one example of the commercialized PC blends. The PC/ABS blend exhibits not only excellent fluidity and impact property but also cost-efficient characteristics enough to compensate for demerits of PC material. The PC/polystyrene (PS) blend has been also commercialized but its market has not been developed so largely. The reason is that there are no specific merits either in cost or in physical properties compared to PC/ABS alloy. However, developments of environmental friendly materials and thin wall products for packaging materials of electronic goods have become important recently. Along with this trend, the PC/PS blends have been developed with excellent flame retardancy and high fluidity [3]. Several studies on the compatibilization of PC/PS blend have been reported [4–7]. Many of these studies focused on the synthesis of PC/PS copolymer. However, the synthesis of the PC/PS copolymer is difficult and complicated, because of the difference in polymerization mechanism of PC and PS.

In the present paper, the polybutylene terephthalate (PBT)/oxazoline containing polystyrene (RPS) graft copolymer was investigated as a compatibilizer in the PC/PS blend. RPS is the reactive polystyrene with oxazoline functionality. Schematic diagram for this compatibilizing concept is illustrated in Fig. 1. It is well known that oxazoline functional group can react with carboxylic acid, amine, anhydride and epoxy functional groups [8–12]. It has been also reported that the carboxylic acid end groups of PBT could react easily with oxazoline functional groups in the melt state, leading to form the copolymers [13].

On the other hand, studies for the reactive compatibilization between PBT and other polyesters [14] and between PC and other polyesters [15] through transestrification reaction were carried out. Generally, it has been reported that the transestrification reaction between PC and PBT rapidly occurred in the melt state [16–22]. In this case, most of reaction occurs at the main chains of PC and PBT.

This compatibilization method by using PBT/RPS graft copolymer has several advantages. Both PBT and RPS are commercially available products. The PBT/RPS graft copolymer can be developed using common extrusion process so that it can be operated in a solvent-free process.

2. Experimental

2.1. Materials

The RPS used is a copolymer of vinyl oxazoline and styrene which has 5 wt% vinyl oxazoline. The RPS material was purchased from Nippon Schokubai Co. The PBT resin was obtained from SK Chemical Co. The molecular weight of the PBT was measured by G.P.C. using polystyrene calibration. Materials used in this study are commercially available polymers and their details are listed in Table 1.

2.2. Preparation of the graft copolymers

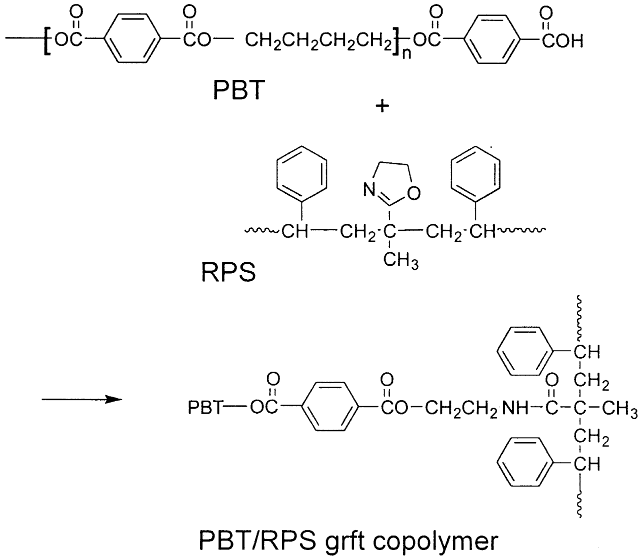
The PBT/RPS graft copolymers were prepared in a Haake

Table 1
Materials used in this study (Shichoon Lee et al.)

Material	Designation	Molecular weight		Maker	Grade	Remarks
		$\overline{M}$n	$\overline{M}$w			
Polycarbonate	PC	15,000	27,000	Teijin Chem. Co.	Panlite, L-1250W	
Polystyrene	PS	82,000	218,000	Cheil Ind. Inc.	Starex HF2660	
oxazoline containing Polystyrene	RPS	61,300	156,000	Nippon Schokubai Co.	Epocros RPS1005	Oxazoline content[a]: 5 wt%
Polybutylene Terephthalate	PBT	22,000	77,000	SK Chem. Co.	Skyton 1100C	Concentration[b] of acid end group: 0.98 mol/10^6

[a] Reported by the supplier.

[b] Measured by acid titration analysis.



Scheme 1.

Buchler internal mixer, which has a 69 cm^3 mixing head with roller blades. Possible reaction scheme of the graft copolymerization shows for the following (Scheme 1). The mixer was operated with 50 g loading at 50 rpm and 230°C and the torque was recorded under these conditions. After 10 min of melt blending, the blend samples were taken out and quenched in ice water to freeze the blend morphology. These graft copolymers were crushed and added in the PC/PS blends as the compatibilizer.

2.3. Melt blending

PC/PS and PC/PS/graft copolymer blends were melt blended with a composition of 70 PC/30 PS by weight by varying amount of premade 50 PBT/50 RPS graft copolymer. These blends were prepared in a Haake Buchler internal mixer. The mixer was operated for 10 min at 50 rpm and 250°C.

2.4. FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectra were observed on Perkin Elmer 1769X spectrometer in the film state in order to examine the graft copolymerization in PBT/RPS blend after the melt blending. For verifying the compatibilizing effects of this graft copolymer, the soluble fraction in the PC/PS/graft copolymer blends was removed by using methylene chloride/tetrahydrofuran 5/5 solvent mixture and the extracted parts were examined by FT-IR spectroscopy.

2.5. Determination of bound RPS onto PBT and fraction of reacted RPS in PBT/RPS blends

The PBT/RPS blends were dissolved in methylene chloride/tetrahydrofuran 5/5 solvent mixture for 2 days. In this solvent mixture, RPS is readily soluble whereas PBT and PBT/RPS graft copolymer are insoluble at room temperature. Insoluble fractions were filtered by centrifugal machine. This extraction procedure was repeated twice to ensure that all unreacted RPS are removed. The bound RPS onto PBT in the extracted products was determined by FT-IR in the film state. The calibration curve was obtained on the basis of various compositions of the PBT/RPS blends. As seen in Fig. 2, the 1493 cm^{-1} peak region is due to phenyl ring stretching of RPS and the peak at 1504 cm^{-1} due to PBT appears. Both peaks will not be dependent on the reaction. Thus the ratio of two peaks can be related to the concentration ratio. Of these peaks, detailed observations reveal that the peak at 1504 cm^{-1} slightly overlaps with 1493 cm^{-1}, whereas the peak at 1493 cm^{-1} is due to RPS only. Therefore, the ratio of two absorbance peaks should be written by Eq. (3)

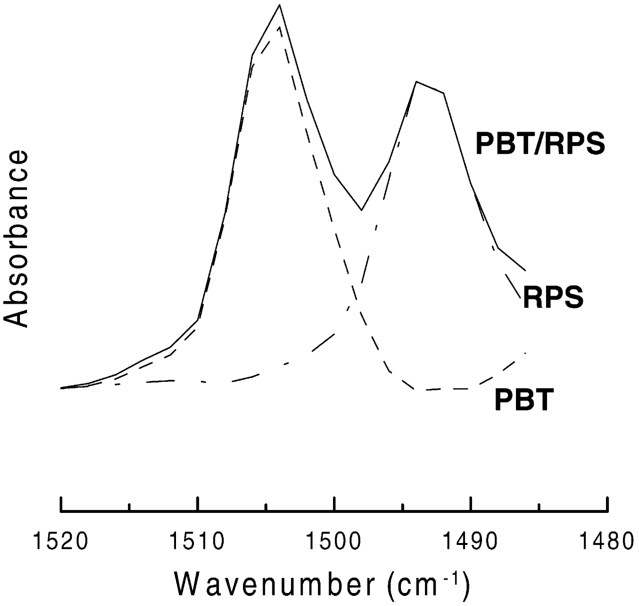


Fig. 2. Part of the infrared spectrum used calibration.

$$A_{1504} = k_a C_{\mathrm{PBT}} + k_b C_{\mathrm{RPS}}, \tag{1}$$

$$A_{1493} = k_c C_{\mathrm{RPS}}, \tag{2}$$

$$A_{1504}/A_{1493} = k_1 C_{\mathrm{PBT}}/C_{\mathrm{RPS}} + k_2, \tag{3}$$

where C_{PBT} and C_{RPS} are the weight concentration of PBT and RPS, respectively.

The calibration curve in Fig. 3 which was fitted using linear regression, yields the relation $A_{1504}/A_{1493} = 0.3618 C_{\mathrm{PBT}}/C_{\mathrm{RPS}} + 0.0473$ with regression coefficient $R^2 = 0.997$. The ratio of bound RPS onto PBT in the extracted part, $C_{\mathrm{RPS}}/C_{\mathrm{PBT}} \times 100$, was determined by above Eq. (3). The fraction of the reacted RPS to the RPS feeding composition at various compositions could be calculated by

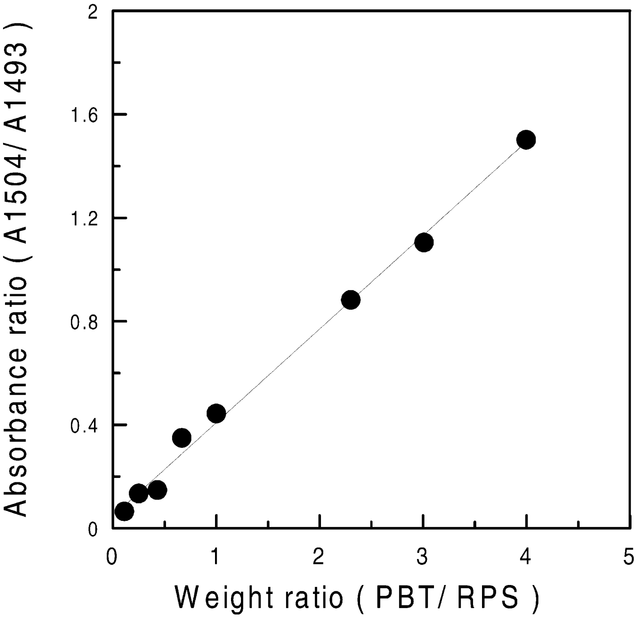


Fig. 3. Calibration curve of the ratio of the absorbances of two peaks.

following relation (4)

$$\text{Fraction of reacted RPS} = \frac{C_{\text{RPS}}}{C_{\text{PBT}}} \times \frac{\text{PBT feed composition}}{\text{RPS feed composition}}. \qquad (4)$$

2.6. Acid titration analysis

Amount of carboxylic acid in PBT and the PBT/RPS graft copolymers was measured by acid titration analysis. About 0.1 g of the PBT/RPS graft copolymers was dissolved in 10 ml hot benzyl alcohol, cooled and titrated with 0.1 N benzyl alcoholic NaOH using phenol red as indicator. The amount of reacted acid end group and that of oxazoline groups in a RPS chain at each composition were calculated. Assuming that the amount of carboxylic acid generated by 10 min melt blending was negligible, following relations were given.

$$\text{R}_{\text{COOH}} + \text{C}_{\text{COOH}} = \text{N}_{\text{COOH}}, \qquad (5)$$

$$\text{R}_{\text{ox}} + \text{C}_{\text{ox}} = \text{N}_{\text{ox}}, \qquad (6)$$

$$\text{R}_{\text{COOH}} = \text{R}_{\text{ox}}, \qquad (7)$$

where C_{COOH} is the concentration of acid end group unreacted, R_{COOH} is concentration of acid end group reacted, N_{COOH} is concentration of acid end group at feed composition, C_{ox} is concentration of oxazoline groups unreacted, R_{ox} is concentration of oxazoline groups reacted and N_{ox} is the concentration of oxazoline groups at feed composition.

2.7. Differential scanning calorimetry (DSC)

The changes of T_g in the PC/PS blends and their compatibilized blends were measured at the scanning rate 10°C min^{-1} using Du Pont DSC 2910 model.

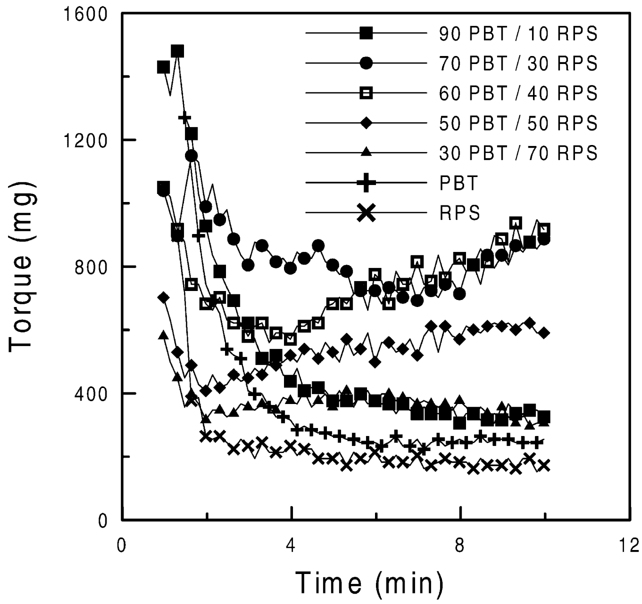


Fig. 4. Torque–time relationships for the PBT/RPS blends.

2.8. TEM analysis

Besides PC/PS blend and PC/PS/graft copolymer blends, the morphologies of the PBT/RPS graft copolymer were observed by Jeol JEM-2000EX transmission electron microscopy (TEM). For this purpose, two-stage staining method was employed. First, specimens were stained in a 2% solution of OsO_4 for 48 h and ultra-thin slices were cut using a Reichert–Jung Ultra-cut Microtome at room temperature. The thin sections were further stained by vapor of a 0.5% RuO_4 solution for 30 min. The apparent particle diameter was determined by digitizing TEM photomicrographs. The weight average particle diameter of the dispersed phase was calculated from the analysis of 300 to 500 particles using an image analysis software program. Weight average diameters of the dispersed phase were calculated as follows

$$D_w = \frac{\sum N_i D_i^2}{\sum N_i D_i},$$

where N_i is the number of particles having the diameter of D_i.

2.9. Tensile test

The tensile properties for these blends were measured. The specimens were prepared by cutting the line in the compression molded sheet at 250°C with gauge length 40 mm, width 10 mm and 1 mm thickness. Tensile tests were carried out on a Shimadzu Universal Tensile Machine at the strain rate 1 mm min^{-1}. The maximum tensile

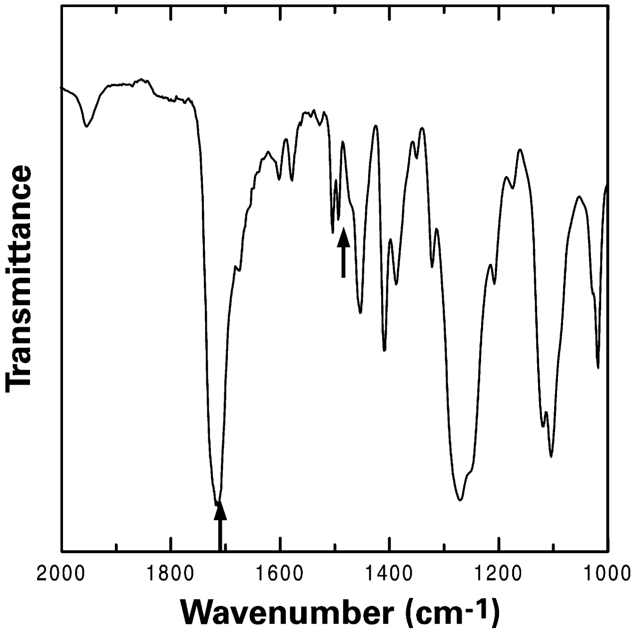


Fig. 5. FT-IR spectrum of extracted parts of the PBT/RPS blends.

strength and strain at break were obtained. Each tensile value reported was the average of five tests.

3. Results and discussions

3.1. The PBT/RPS graft copolymer

Fig. 4 shows the torque variations during melt blending for the different compositions in PBT/RPS blends. There are variations for the different compositions in PBT/RPS blends. Torque levels of all these blends at around 10 min of mixing time were higher than those of PBT and RPS homo-polymers. The torque was slowly increasing after a few minute at the compositions of 70 PBT/30 RPS and 50 PBT/50 RPS. On the contrary, torque shows the steady value at the 90 PBT/10 RPS and 30 PBT/70 RPS. It is considered that the increase in torque is the indication of coupling reaction. Similar result was reported by Baker and coworker [23].

After the solvent extraction of RPS from the 50 PBT/50 RPS blend, FT-IR spectrum of the extracted part was examined as shown in Fig. 5. It is evident that there is a carbonyl stretching peak at 1714 cm^{-1} due to PBT and a phenyl ring stretching peak of RPS components at 1493 cm^{-1}. Thus, it can be concluded that RPS reacts with PBT. However, it was not possible to confirm the occurrence of characteristic N–H stretching band at around 3450 cm^{-1} attributable to the amide groups, which should be generated by the reaction between oxazoline with carboxylic acid. It might be due to the overlapping of the absorption bands by the carboxylic end groups in unreacted PBT.

Figs. 6(a) and (b) show the TEM photographs of the PBT/RPS melt blend. Fig. 6(a) is for the 70 PBT/30 RPS blend and Fig. 6(b) for the 30 PBT/70 RPS blend. Note that the light area represents the PBT phase, while the dark area defines the RPS phase stained with ruthenium tetraoxide. Fig. 6(a) shows that the average domain size in the PBT matrix is about 200 nm and Fig. 6(b) shows the approximately 100 nm finer PBT domains dispersed in the RPS matrix. Such fairly fine dispersed domains imply that the PBT/RPS graft copolymer is generated.

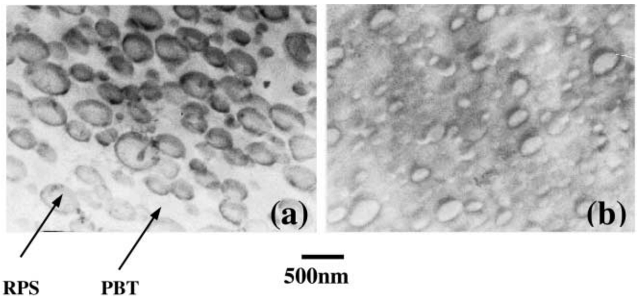


Fig. 6. TEM photograph of the PBT/RPS blends. (a) 70 PBT/30 RPS (b) 30 PBT/70 RPS.

Fig. 7 shows the ratio of bound RPS onto PBT and the fraction of reacted RPS. The ratio of bound RPS onto PBT, $C_{\mathrm{RPS}}/C_{\mathrm{PBT}}$, stays almost constant within experimented RPS compositions. However the fraction of reacted RPS decreases rapidly as the RPS composition increases. Even though the reaction occurred, the PBT/RPS blends were immiscible and the reaction would take place at the interface of PBT/RPS blends [24]. Therefore, the extent of reaction would depend on the interfacial area formed during melt blending. The interfacial area per unit volume of the blends might not be appreciably changed in reactive blend with increasing RPS composition. Thus, the ratio of bound RPS onto PBT would be nearly constant as shown in Fig. 7. Table 2 shows that there is considerable amount of acid end

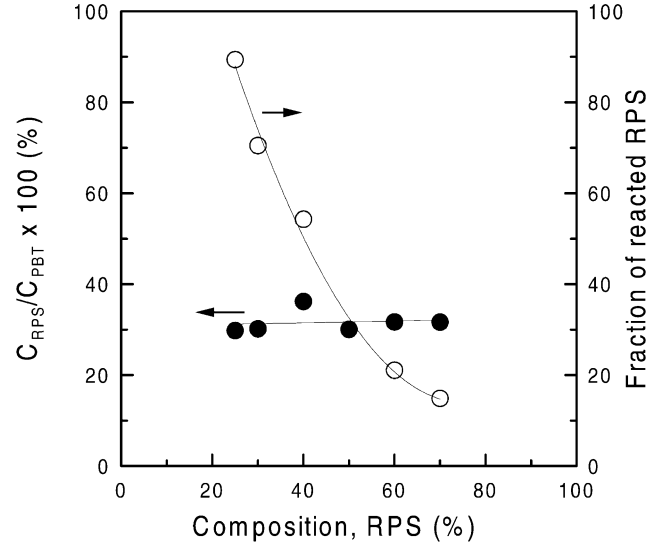


Fig. 7. $C_{\mathrm{RPS}}/C_{\mathrm{PBT}}$ and the fraction of reacted RPS for each RPS composition.

Table 2
Amount of acid end group and oxazoline groups in PBT/RPS graft copolymers (Shichoon Lee et al.)

Feed composition (PBT[a]/RPS)	Concentration of acid end group unreacted[b] (mol/10^6 g)	Concentration of acid end group reacted (mol/10^6 g)	Amount of oxazoline groups reacted in a RPS chain (%)
70/30	0.55	0.13	0.100
50/50	0.30	0.19	0.084
30/70	0.13	0.16	0.052

[a] Concentration of acid end group of neat PBT: 0.98 mol/10^6 g.

[b] Measured by acid titration analysis.

group in PBT/RPS graft copolymers at each composition. Those mean only partial limited amounts among these reactive groups would participate in the reaction. The reacted ratio among oxazoline groups in a RPS chain shows in Table 2. As the PBT composition increases, the reacted ratio of oxazoline groups gets higher. At 70 PBT/30 RPS compositions, larger amount of RPS may react with PBT. However at 30 PBT/70 RPS composition, there is less amount of reactive acid end group compared with that of oxazoline groups because the number of acid end group in the PBT is far less than those of oxazoline groups of RPS as shown in Table 1. It is difficult to induce more reaction. Thus considerable amount of unreacted RPS will exist at such compositions. On the contrary, unreacted PBT might be presented excessive at 90 PBT/10 RPS compositions. Such unreacted compositions would make an effect considerably on the melt viscosity of their blends. This result is consistent with the results of torque observations for the different compositions.

3.2. Compatibilization of PC/PS blends with the PBT/RPS graft copolymer

The evidence of transestrification reaction can be established from solubility tests coupled with infrared analysis [16–17]. The melt blended 70 PC/30 PS blend with 10 wt% graft copolymer which is premade 50 PBT/50 RPS graft copolymer, was extracted by previously mentioned procedure. Devaux and coworkers [16–19] reported that an exchange reaction took place between PC and PBT, within even short reaction time lead to the production of block copolyesters with reduced solubility. In that solvent mixture, PC, PS and RPS are completely soluble whereas PBT remains insoluble. In the extracted parts by centrifugation, it is expected that there would be unreacted PBT and copolymers formed by tranestrification reaction, which would be PC/PBT or PC/PBT/RPS copolymers. The FT-IR spectrum of extracted parts is shown in Fig. 8. There are carbonyl stretching peaks at 1772 and 1714 cm^{-1} attributable to PC and PBT, respectively, and a new infrared absorption peak is found at around 1740 cm^{-1}. This peak is considered to be a characteristic peak of an aromatic ester structure generated by ester exchange reaction as reported by Devaux and coworkers [16]. Also phenyl ring stretching peak of RPS appeared at 1493 cm^{-1}. This confirms the evidence of the existence of RPS components in the extracted parts. The presence of the RPS component in the extracted part is due to the PBT/RPS graft copolymer and the graft copolymer generated by the reaction between the PBT/RPS copolymer and PC. Thus it can be inferred that even small amount of the copolymer with three components, PC, PBT and RPS, was in-situ generated by transesterification during the melt blending.

The changes of glass transition temperature (T_g) for the blend components with adding PBT/RPS graft copolymer were measured by DSC. It was reported that T_g for each phase shifted inward in the PC/PBT blend [22]. Fig. 9 shows the T_g for the PC/PS and PC/PS/graft copolymer blends. The T_g of PC phase in the PC/PS/graft copolymer decreases gradually with adding PBT/RPS graft copolymer. Such feature could be interpreted that PBT was dissolved in PC phase since PBT has partial miscibility with PC, and appreciable amount of transestrification reaction has occurred between PC and PBT.

As seen in Fig. 10, domain size of the dispersed PS phase

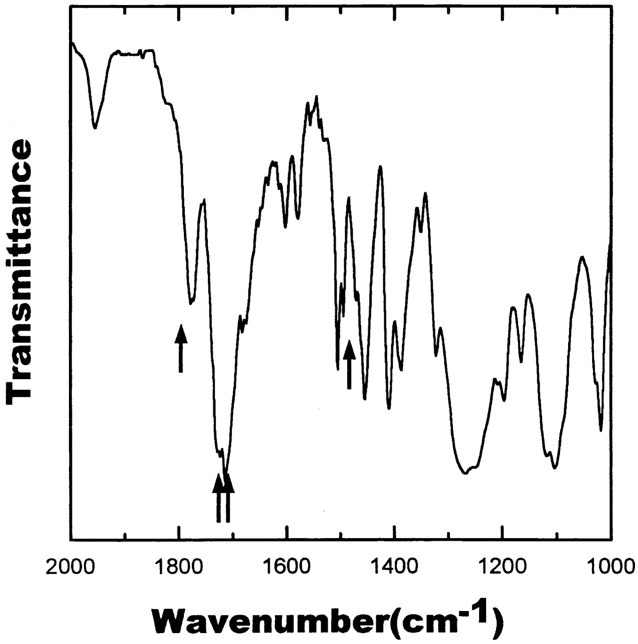


Fig. 8. FT-IR spectrum of the extracted parts of the 70 PC/30 PS blend with 10 wt% PBT/RPS graft copolymer.

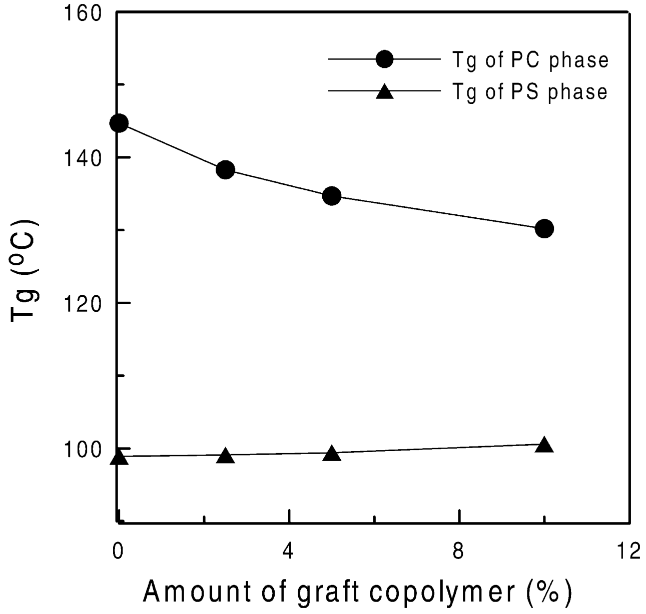


Fig. 9. T_g variations of the 70 PC/30 PS blend with varying amounts of the 50 PBT/50 RPS graft copolymer.

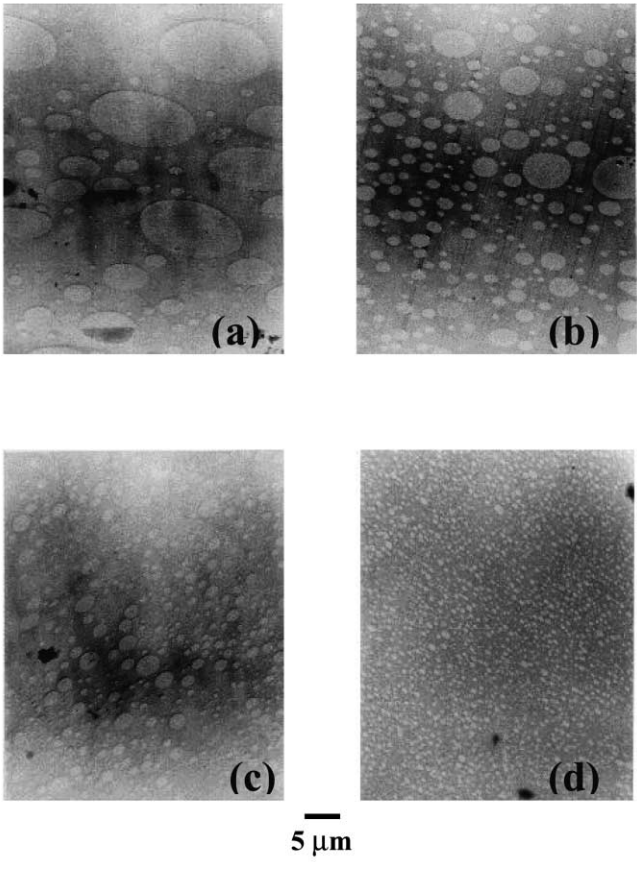


Fig. 10. TEM photographs of the 70 PC/30 PS blend with the 50 PBT/50 RPS graft copolymer blend. (a) 0 wt% (b) 1 wt% (c) 2.5 wt% (d) 10 wt%.

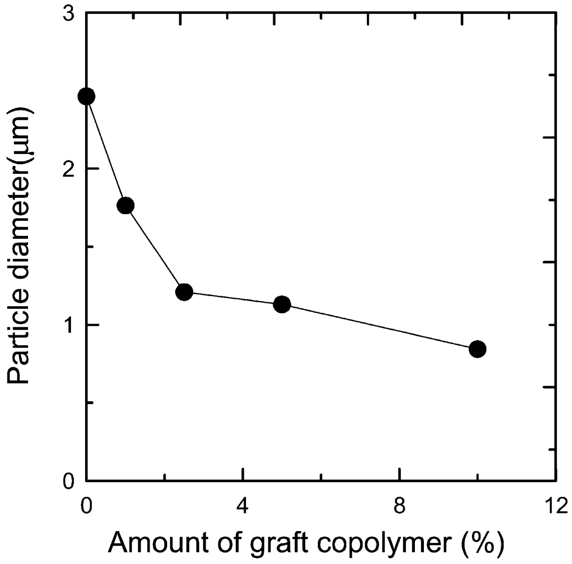


Fig. 11. Weight average particle diameter in the 70 PC/30 PS blend with the 50 PBT/50 RPS graft copolymer.

in the PC/PS/graft copolymer blends is reduced with adding the PBT/RPS graft copolymer compared with that of 70 PC/30 PS blend. The weight average particle diameter, which was calculated from image analysis, is shown in Fig. 11. As the amount of the PBT/RPS graft copolymer increases, the particle size gets considerably smaller than that of uncompatibilized PC/PS blend. Steep decrease is clearly seen up to content of 2.5 wt% of the graft copolymer. Further decrease in the domain size is continuously seen up to the 10 wt% graft copolymer. This behavior has been frequently observed when the immiscible blends were compatibilized with block or graft copolymer.

The beneficial effect of the graft copolymer on the dispersion and interfacial adhesion of PC/PS blends was examined

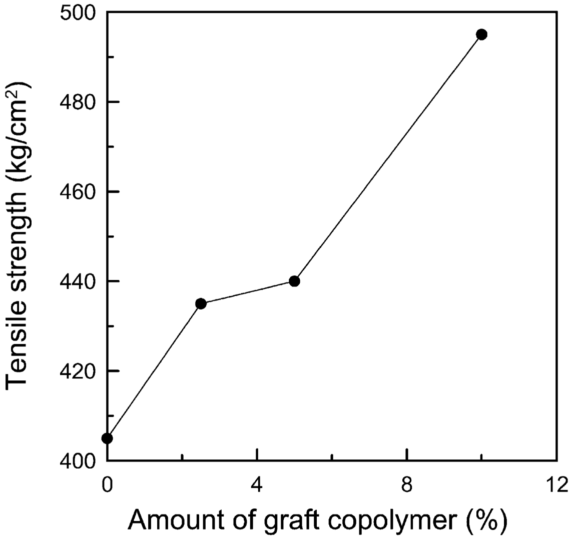


Fig. 12. Effect of the 50 PBT/50 RPS graft copolymer on tensile strength in the PC/PS/graft copolymer blend.

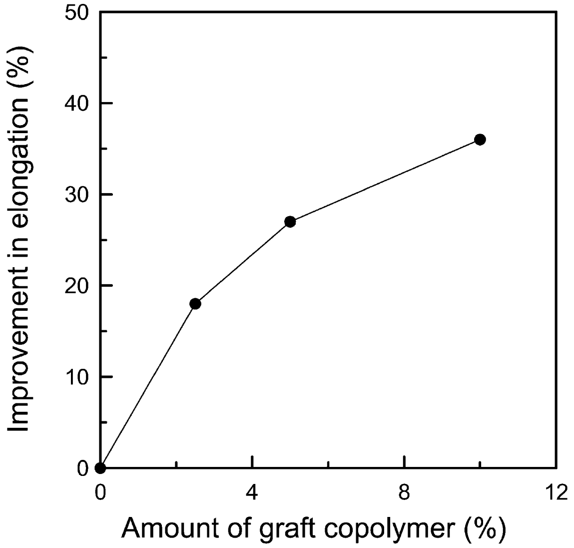


Fig. 13. Effect of the 50 PBT/50 RPS graft copolymer on relative tensile elongation in the PC/PS/graft copolymer blend.

by the observance of the tensile properties of the blends. Fig. 12 shows the effect of the PBT/RPS graft copolymer on the tensile strength of the 70 PC/30 PS blend. Tensile strength has a low value for the uncompatibilized blend and increases appreciably as the amount of the PBT/RPS graft copolymer increases. Similar result shows in the tensile elongation. As the amount of the PBT/RPS graft copolymer increases, elongation increases continuously as shown in Fig. 13. This result is because the PBT/RPS graft copolymer enhanced the interfacial adhesion of PC and PS phase in the PC/PS blend.

4. Conclusions

The PBT/RPS graft copolymer was introduced as a compatibilizer in the PC/PS blends. Observations of torque increase of the PBT/RPS blends during melt blending and FT-IR experiments revealed the occurrence of the PBT/RPS graft copolymer by reaction between carboxylic end groups of PBT and oxazoline functional groups of RPS. The compatibilization of PC/PS blend using the PBT/RPS graft copolymer was achieved. The morphologies of the PC/PS/graft copolymer blends were considerably finer compared to that of the comparable uncompatibilized blend. Tensile strength and relative elongation increased as the amount of the PBT/RPS graft copolymer increased. This also indicates that the PBT/RPS graft copolymer makes it possible to successfully compatibilize the PC/PS blends.

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