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In situ copolymerization and compatibilization of polyester and polystyrene blends. II. Thermally and chemically induced reaction and mechanical properties

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Abstract

The basic studies of in situ compatibilization process between polystyrene (PS) and polybutylene terephthalate (PBT) are carried out by adding various functionalized polystyrenes with mono, di, tetra hydroxy functions. The tensile mechanical properties of these in situ compatibilized blends are investigated. It is important to control the thermal degradation of PBT during the high temperature processing in order to generate the reaction between the functionalized polystyrene and PBT and result in the improvement in their mechanical properties. However, the excess degradation deteriorates the tensile properties of the in situ copolymerized and compatibilized polymer blends. It is found that the usage of Titanium butoxide (TNBT) was effective to promote the thermal degradation of PBT and the copolymerization of PBT with the functionalized polystyrenes. On the other hand, Triphenyl phosphite (TPP) was used to prevent the excess thermal degradation and induce the possible end capping reaction of PBT. The addition of 5% PS-F4 (tetra functionalized polystyrene) in PS/PBT 10/90 blend at 270°C with 1% TPP exhibits the best improvement in the elongation at break among the mono-, di- and tetra-functionalized polystyrenes. The increase of amount of the functionalized polystyrenes into the PS/PBT blends decreased the elongation to break, the yield strength, and the energy to break. More functional groups in the functionalized polystyrenes are more effective in promoting in situ compatibilization. Furthermore, the one-step mixing in which all the ingredients were blended together for 10 min has better elongation to break than the two steps mixing. The detailed characterization of rheological, morphological and mechanical properties of various blends of functionalized PS/PBT and PS/PBT with different functionalized polystyrenes and the additives are described. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Functionalized polystyrene; Polybutylene terephthalate; Degradation

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1. Introduction

A major improvement in mechanical properties of various polyamide and polyester blends by using in situ copolymerization technique has been reported in various patents and papers [1–10]. Ide and Hasegawa [1] first introduced nylon 6/polypropylene blend compatibilized by formation of nylon–PP copolymer using polypropylene-*grafted*-maleic anhydride. The blend exhibited a finely dispersed phase of nylon and resulted in superior tensile strength and elongation at break. Since then, many attempts have been made to modify polyamides by adding the small amount of rubber particles grafted with maleic anhydride [2–6]. In 1986, Crespy et al. [6] reported the improvement of mechanical properties of the blends of Nylon 66 and ethylene-propylene-diene-*grafted*-maleic anhydride (EPDM-*g*-MA). They investigated the effect of different levels of grafting MA in the range of 0–10% to the rubber component of their mechanical properties. Maximum tensile strength of molded test parts was observed at 6% MA grafted to rubber. In the case of modification of polyester blends, the in situ copolymerization between carbodiimide functionalized polyphenylene ether (PPE) and polybutylene terephthalate (PBT) in a twin screw extruder was developed by Han and Gately [7]. They found that the reactive compatibilization increased the notched impact strength of the PPE/PBT blend. High levels of PPE bound to PBT were demonstrated by selective solvent extraction. Kobayashi et al. [8] also investigated the reactive blend of PET and PPE with 0.5–5.0 parts of epoxidized liquid polybutadiene and 7.5% oxirane oxygen in a twin screw extruder. The blend demonstrated better impact strength than the blend with

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neat polybutadiene. Similarly, blends of PBT with glycidyl methacrylate grafted ethylene propylene diene copolymer (EPDM-*g*-GMA) were investigated by Olivier [9] and Pratt et al. [10]. The blends of PBT and EPDM-*g*-GMA showed a better-notched impact strength than the blend with neat EPDM. These studies mentioned above provide the possible in situ reaction and compatibilization of polymer grafted with maleic anhydride and epoxidized polymers with polyamide and polyesters. The resultant reactive blends exhibit the improvement in their tensile properties and impact strength. The former compatibilization may be generated by the hydrogen bonding between the carboxyl group in maleic anhydride and amino group in polyamide [1,9,10]. In the latter case, it was speculated that the interaction between the epoxy group in the epoxydized polymers and the carboxyl group in polyesters which generated by thermal degradation [11,12]. The degradation is the important key to induce both grafting on the polymers and the in situ reaction to be compatible during mixing. On the other hand, the excess degradation of polyamide and polyester will result in their poor mechanical properties [13–15]. Therefore, it is important to control the level of thermal degradation in order to obtain the optimum reaction to be compatible and improve their mechanical properties. The various chemical strategies have been described as to prevent the excess degradation of polyesters due to the residual catalysts [16,17]. Two effective methods have been reported: to extend the polyester chains by a coupling agent [18–20]; and to cap the carboxylic acid group of polyester [21–23].

In this paper, the in situ compatibilization process between polystyrene (PS) and polybutylene terephthalate (PBT) is described by adding various functionalized polystyrenes. The thermal analysis, characterization of reaction as well as the tensile properties of these blends are investigated. As described above, we made efforts to find the effects of thermal degradation of PBT component during high temperature processing on their mechanical properties. The effects of the additives to control copolymerization and degradation are described.

2. Materials

The materials used in this study from commercial suppliers were polybutylene terephthalate (PBT) (Hoechst Celanese Corporation, Celanex 2002), polystyrene (Dow Chemical Corporation, Styron 615 APR). The functionalized polystyrene's (PS-F's), including tetra-, di- and mono-phenol functional group (PS-F4, PS-F2, PS-F1), were prepared by Dr Quirk and his co-workers of Institute of Polymer Science at University of Akron by means of anionic polymerization as described in the preceding paper [23].

Titanium butoxide (TNBT) and Triphenyl phosphite (TPP) supplied by Aldrich Chemical Company were used as catalyst and stabilizer.

3. Experimental

3.1. Blending

Binary blends of PS/PBT, PS-F/PBT and ternary blends of PS/PBT/PS-F were prepared in the Mini-Max injection molder (Model CS-183 MMX, Custom Scientific Instruments Inc.) at 250 and 260°C.

3.2. Thermo gravimetric analysis

The weight loss and degradation temperatures of parent polymers and thermally treated polymers were determined by thermo gravimetric analysis (TGA, DuPont 9900) at a heating rate of 20°C/min from 100 to 500°C. Samples of approximately 15 mg were placed in the TGA sample holder. The experiments were carried out in the air. The temperatures of 0.3 and 5 wt% weight loss were determined.

3.3. Scanning electron microscopy

Phase morphologies of the fracture surface of the blends and parent polymers were studied by a scanning electron microscope (SEM, ISI model SX-40). Each fracture surface of the blends and parent polymers was prepared in liquid nitrogen. The samples were coated with gold-palladium alloy by using a coating sputter (Polaron E5400). The number average diameter of the dispersed phase was calculated from the SEM microphotographs.

3.4. Rheological properties

The steady state shear viscosities of PS, PBT and each of functionalized polystyrenes were measured by a Rheometrics Mechanical spectrometer(RMS-800) with cone-plate mode in the range of shear rates from 0.01 to 10 s^{-1}. To avoid excess degradation during the viscosity measurement the dynamic viscosities of PS and PBT at 270°C with 1% TNBT and 1% TPP for various thermal treatments were also measured by using a Rheometrics Mechanical Spectrometer with the parallel plate mode. The circular shaped specimens for the steady shear and dynamic viscosity measurement were prepared by compression molding at 180°C for PS and 240°C for PBT.

The PBT and PS specimens for determining the zero shear viscosity were prepared for various thermal treatments in a Mini-Max injection molder. In general, it is difficult to determine the level of degradation, the molecular weight and its distribution of PBT by GPC. Therefore, we attempt to discuss the degree of thermal degradation in terms of the changes in zero shear viscosity. The periods of thermal treatment were varied in the range of 10–60 min TNBT and TPP were mixed with PS and PBT, respectively, for 10, 30, 45, and 60 min at 270°C. The circular plate specimens were prepared by injecting the melt into the circular mold. A parallel plate viscometer was used to measure the zero shear viscosity at the frequencies of 0.1–100ω.

3.5. Mechanical properties

The dumbbell specimens of the blends were prepared by the Mini-Max injection molder. The gauge length of the tensile specimen is 7.9 mm and the diameter is 1.3 mm. The mechanical properties of various blends and thermally treated parent polymers were measured by the tensile tester (Monsanto T10) at a cross head speed of 5 mm/min at room temperature.

4. Results and discussion

4.1. Characterization of thermally, mechanically and chemically induced degradation

The melting point of the PBT used in this study is determined at 226.2°C by a differential scanning calorimeter (DSC). However, PBT tends to degrade easily at 260°C [15–17] as well as PS-F's. On the other hand, the in situ reaction between PBT and the hydroxy groups of PS-F's requires the adequate degradation of PBT in order to initiate a reaction to the hydroxy group of functionalized polystyrenes. The neat molten polyesters such as PBT and PET at high temperature can undergo transesterification and hydrolysis in the presence of moisture or residual catalyst such as TNBT which is generally used as a catalyst for synthesizing PBT by promoting the transesterification reaction [13–16]. There are several papers published on this subject [19–22]. It was found that the excess thermal degradation of PBT and excess transesterification reactions in polyester blends yielded poor mechanical properties such as reduction in the impact strength [19] and less chemical and thermal resistance [25,26]. Therefore, it is important to control the level of degradation and transesterification to improve the mechanical properties of those blends. The extensive chemical strategies have been developed in order to retard the ester-exchange reaction in PBT by using organophoshorous compounds such as phosphites for PC/PBT blend [15], phosphonates [27] and phosphates [28]. Cheung et al. [29] found that the stabilizer combined with phosphite and carbodiimide inhibited the transesterification in the blends of PAr/PC/PET at 300°C and could retain the substantial fraction of the crystallinity. Van Bennekom et al. [30,31] also reported the studies of transesterification of PC/PBT blends with tripheny phosphite. In this study, triphenyl phosphite (TPP) was used as a stabilizer to prevent the excess degradation of PBT.

Hence, it is important to determine the level of degradation of PBT by adding the stabilizer and the catalyst. It is difficult to determine the level of degradation of PBT such as the change in molecular weight and molecular weight distribution by GPC etc. In this study, we determined the change of zero shear viscosities of PBT and PS with varying thermal treatments and additives by RMS with the parallel plates mode. The effects of degradation and addition of TPP and TNBT on stability and mechanical properties of neat polymers and blends were investigated by TGA, SEM and tensile test. The same processing conditions are conducted for the ternary blends of PS/PBT/PS-F4 that will be described in the later section.

4.2. Rheological properties

4.2.1. PBT and PS with TNBT and TPP for various thermal treatments

The dynamic viscosities of neat PBT with 1% TNBT and 1% TPP under varying heat treatment periods at 270°C as a function of frequency are shown in Fig. 1(a)–(c). All the curves show Newtonian behavior at low frequencies. From these results, the zero shear viscosities are determined.

The zero shear viscosities of PBT at 270°C as a function of heat treatment with various additives are shown in Fig. 2. The PBT with 1% TNBT shows lower viscosity than the neat one. It indicates that TNBT promotes the degradation of PBT during the thermal treatment. The viscosity curve of PBT with 1% TPP shows higher viscosity than the neat PBT. We speculate that the coupling reaction may occur when TPP acts as a condensation agent during the thermal treatment. According to the mechanism of the coupling reaction described in Ref. [24], the viscosity of PBT increases with increasing molecular weight during the period of 20 min thermal treatment. However, the viscosity of PBT with 1% TPP decreases by the same order as the neat PBT for 60 min thermal treatment. It means that the thermal degradation may be more dominant than the coupling reaction during the longer thermal treatment period.

The dynamic viscosities of PS with 1% TPP for varying heat treatments at 270°C decrease with increasing the period of thermal treatment. In comparison to the dynamic viscosities of PBT with the additives, all the curves exhibit non-Newtonian behavior even for 60 min treatment. The plateau region is slightly broadened with increasing the periods of thermal treatment, which indicates the broader molecular weight distribution. However, the effects of treatment periods on the viscosity of PS and the addition of TPP are not significant in comparison to those of PBT. Fig. 3 exhibits the zero shear viscosity of PS at 270°C as a function of heat treatment time with and without TPP. It shows that the addition of TPP on PS does not influence the viscosity of PS.

4.2.2. Functionalized polystyrenes

The steady state shear viscosities of series of functionalized polystyrene as well as all the neat PBT and PS were determined by using the cone plate rheometer at 250 and 270°C in the range of shear rates from 0.01 to 10 s^{-1}, which correspond to the estimated shear rate (3 s^{-1}) of the Mini-Max molder. As shown in Fig. 4, the shear viscosities of functionalized polystyrenes are lower than those of the parent polymers. They also show more significant non-Newtonian and shear shinning behavior than those of the parent polymers due to the bulky functional groups. The

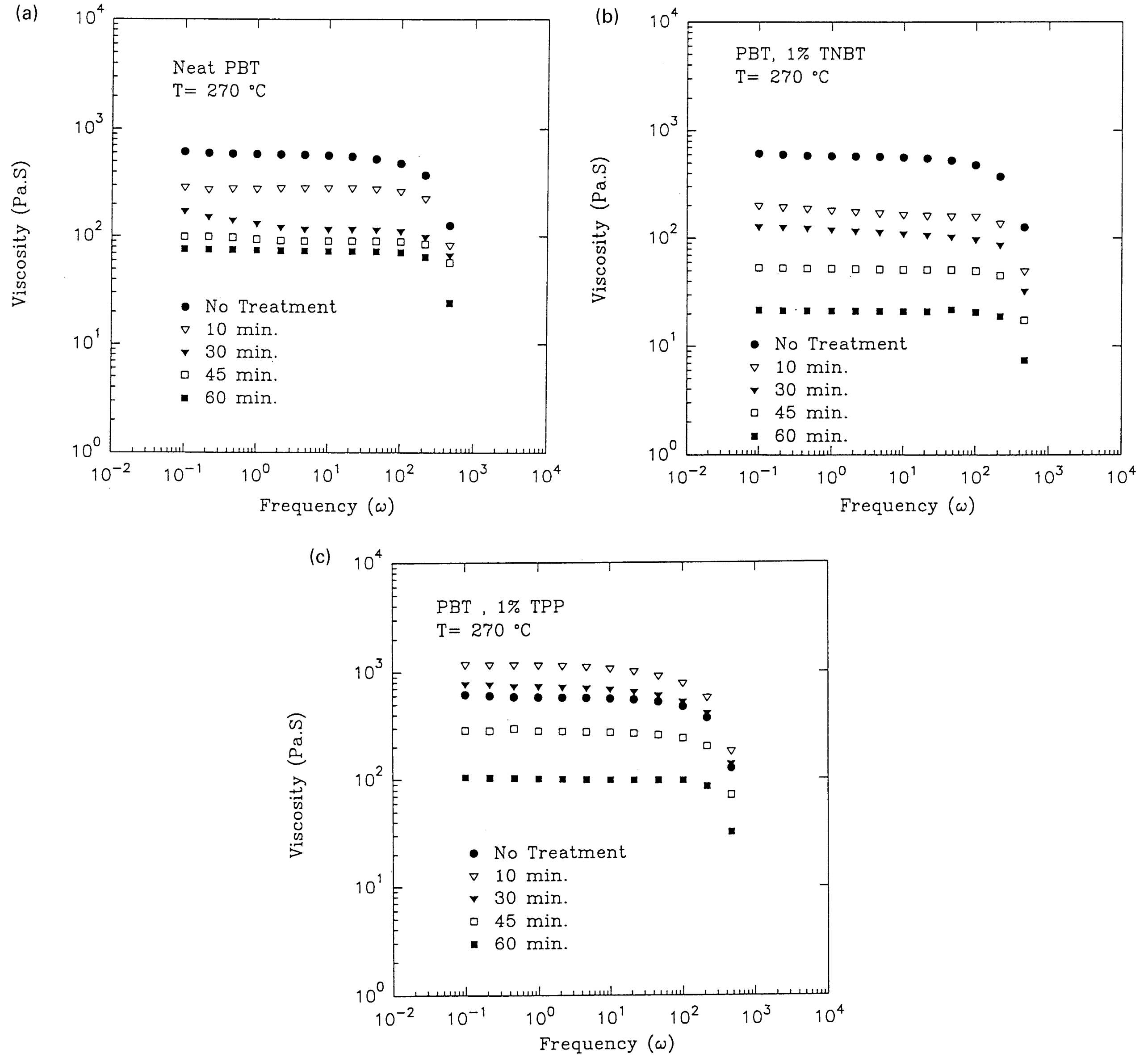


Fig. 1. (a) The dynamic viscosity vs. frequency of neat PBT for various heat treatments. (b) The dynamic viscosity vs. frequency of PBT with 1% TNBT with various thermal treatments. (c) The dynamic viscosity vs. frequency of PBT with 1% TPP for various thermal treatments.

temperature dependency of the shear viscosity of each of the functionalized polystyrene is relatively similar to each other. It is interesting to note that the increase of functional groups increases the shear viscosity at both 250°C and 270°C. The order of shear viscosities is; PS-F4 > PS-F2 > PS-F1.

4.3. Thermal stability and mechanical properties

The weight loss of PBT and PS treated thermally for 10 min at 270°C with 1% TPP or 1% TNBT were determined as a function of temperature. Table 1 shows the temperatures of weight loss at 0.3 and 5 wt% for neat PS, PBT and the treated PS's and PBT's. The temperature at 0.3 wt% weight loss indicates the initial degradation point since it is the least weight loss. PBT with 1% TNBT at 270°C for 10 min degraded earlier than all the other treated ones. On the contrary, the addition of 1% TPP into PBT at 270°C for 10 min has more heat resistance than that without TPP. These results correspond to the least viscosity reduction of PBT with 1% TPP as shown in Fig. 2. PS with 1% TPP at 270°C for 10 min shows slightly higher temperatures at 0.3 and 5 wt% weight losses than the other ones. However, the addition of TPP into PS doesn't influence the heat resistance significantly in comparison to that of PBT. These results are consistent with the results of shear and dynamic viscosity measurements.

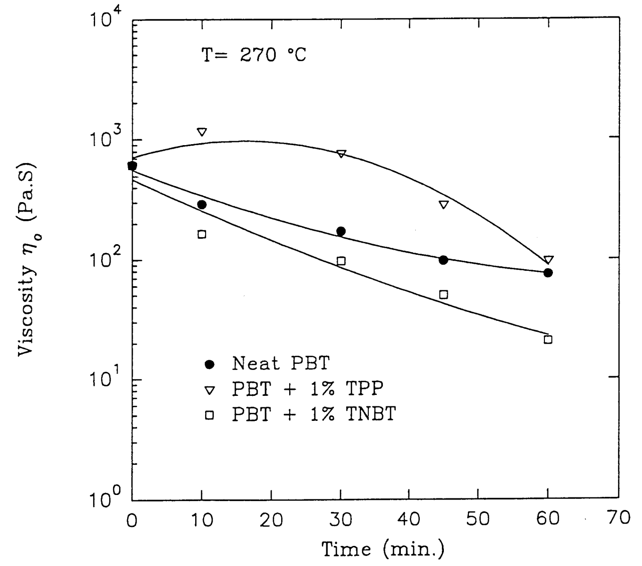


Fig. 2. The zero viscosity of PBT prepared at 270°C as a function of thermal treatment time with various additives.

The effect of addition of TPP and TNBT on their stress–strain curves of neat PBT and treated PBT are shown in Fig. 5. PBT with TNBT shows brittle behavior. On the other hand, PBT with TPP for 10 min mixing and heat treatment shows a little decrease in elongation at break; but has a larger tensile strength at break than that without TPP.

Hence we can conclude that the PBT treated for 10 min with 1% TNBT exhibits the most degradation. The PBT with 1% TPP with the short heat treatment (less than 20 min) can prevent the further degradation that causes the brittle mechanical behavior.

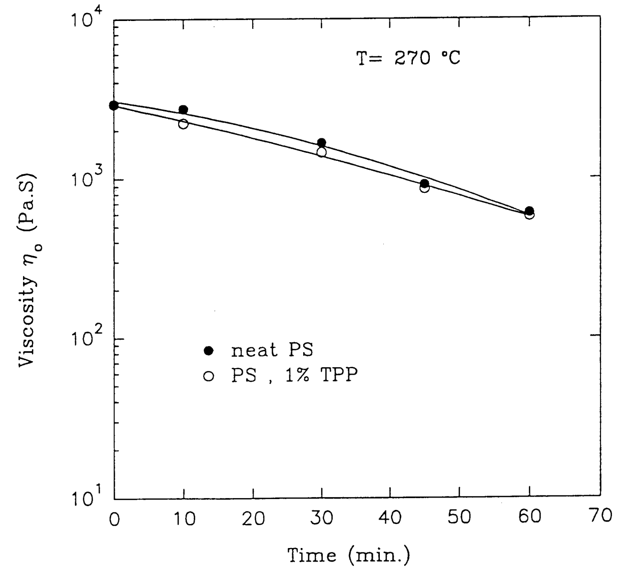


Fig. 3. The zero shear viscosity of PS at 270°C as a function of thermal treatment time with various additives.

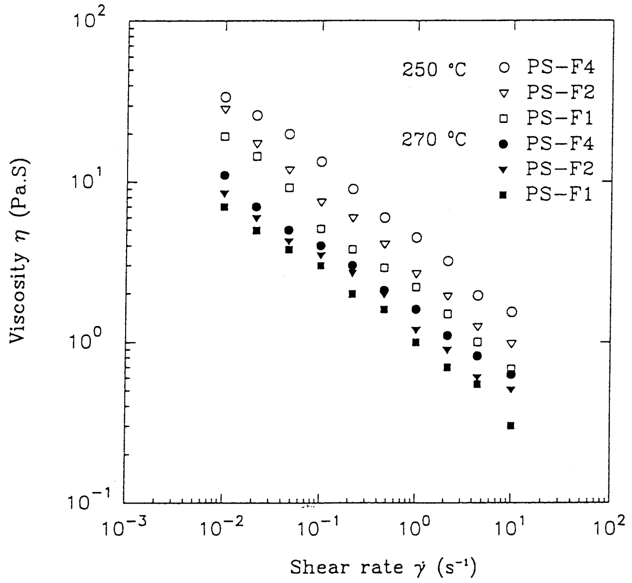


Fig. 4. The shear viscosity vs. shear rate of the functionalized polystyrenes.

4.4. In situ copolymerization of PS/PBT blends with PS-F

4.4.1. Phase morphology of various PS/PBT/PS-F blends

The phase morphology of immiscible blends of PS and PBT was observed by a scanning electron microscope. The size of the dispersed phase of PS in the matrix of PBT of PS/PBT 10/90 blend at 250°C is smaller than that at 270°C as shown in Fig. 6(a) and (b). The higher viscosity of the matrix PBT at 250°C than at 270°C attributes to the smaller size of the dispersed phase [32,33]. The effect of the addition of 1% TPP on the morphology of PS/PBT 10/90 blends for 10 min is shown in Fig. 6(c) and (d). The size of dispersed phase of the blends with TPP is smaller than that without TPP at 250 and 270°C, respectively. The size of dispersed phase of the blend mixed at 250°C is still finer than at 270°C. As stated before, the viscosity of PBT increases at the beginning of 20 min mixing time due to the chain extension reaction. Therefore, we speculate that the higher viscosity matrix with 1% TPP attributes to form a finer dispersed phase.

Fig. 7(a)–(d) show the SEM micrographs of fracture surface of PS/PBT 10/90 blends with 5% and 10% PS-F4 blended for 10 min at 250 and 270°C, respectively. The size

Table 1
The temperatures of weight loss of treated polymers

Polymers	0.3 wt% loss	5 wt% loss
PBT	331.4	377.8
PBT, 207°C, 10 min	305.4	363.1
PBT, 207°C, 10 min 1% TPP	313.3	366.8
PBT, 270°C, 10 min 1% TNBT	296.4	369.8
PS	282.5	324.2
PS, 270°C, 10 min	260.1	318.7
PS, 270°C, 10 min 1% TPP	275.0	321.6

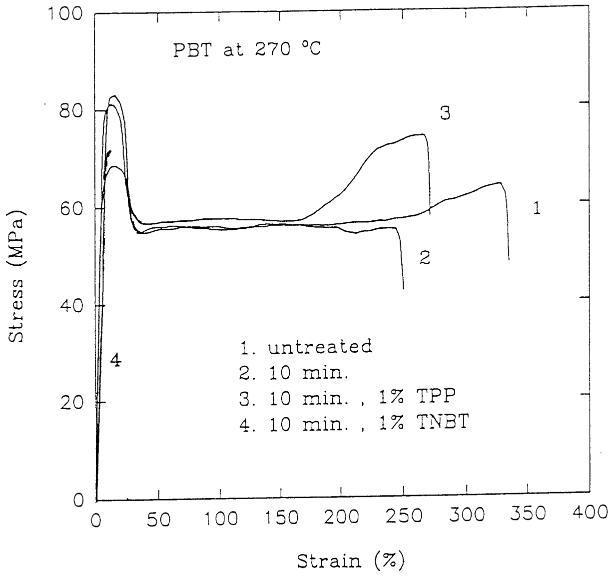


Fig. 5. The stress–strain curves of PBT prepared with the additives at 270°C.

of dispersed phase increases with the addition of PS-F4 at 250 and 270°C. We speculate that the 10 min thermal treatment is not sufficient enough to induce the reaction between PS-F4 and PBT at 270°C. This result agrees with the DSC results of PS-F4/PBT 25/75 blends and FTIR spectra demonstrated in our preceding paper [24]. However, the effect of addition of 1% TPP in the PS/PBT 10/90 blends with various contents of PS-F4 for 10 min on their phase morphology are shown in Fig. 8(a)–(d). The size of the dispersed phase of the blends with TPP is significantly smaller than that without TPP at 250 and 270°C. We have to point out that the scale bar shown in the photographs in Fig. 8 is much smaller than the one shown in Fig. 7. These photographs demonstrate the drastic reduction of the dispersed phase. Similarly, we observed the fracture surfaces of various blends of PBT, PS and the three different polystyrenes functionalized with mono-, di- and tetrahydroxy groups with 1% of TPP. The size of the dispersed phase of PS/PBT 10/90 blends with the different functionalized polystyrenes and the temperature are plotted in Fig. 9. It demonstrates that the most significant reduction of the size of the dispersed phase was obtained by adding 1% TPP into the ternary blends of PS, PBT with 5 wt% of PS-F4. By increasing the number of hydroxy groups of the functionalized polystyrenes from mono, and di to tetra, the size of the dispersed phase reduced most effectively at 5 wt% of PS-F4 with 1% TPP at 270°C. We conclude that the in situ copolymerization occurs most between PS-F4 and PBT with 1% TPP, and then resulting in the in situ compatibilization of PS/PBT blends. It is noted that TPP plays an important role in reducing the size of the dispersed phase in comparison with those of the blends without TPP. The addition of TPP will not only prevent the excess degradation of PBT by chain extension reaction, but also can act as a coupling agent between PS-F4 and PBT to promote the in situ copolymerization as mentioned in Ref. [24].

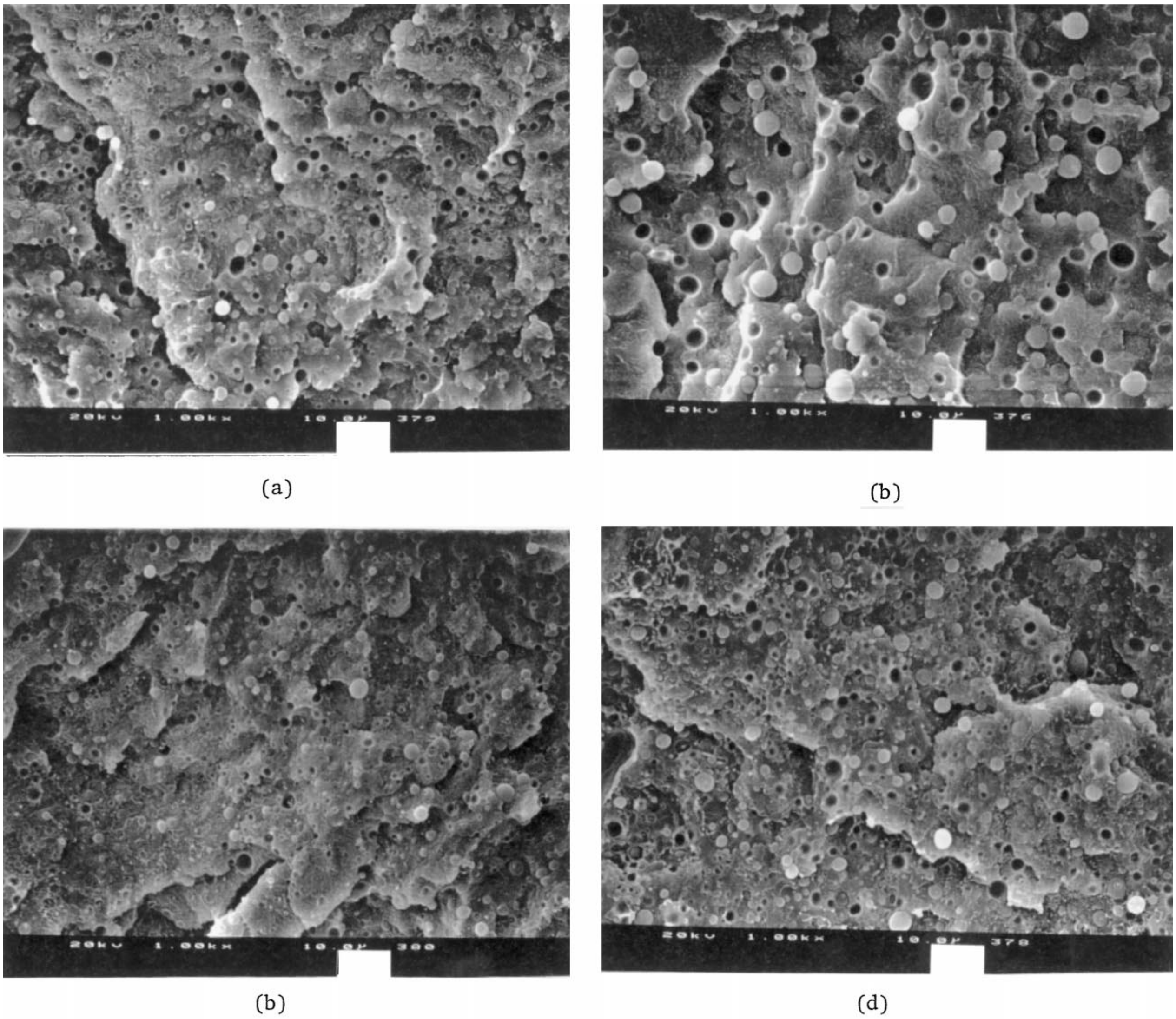
The DSC data and FTIR spectra indicate the low level of the alcoholysis reaction in the PS-F4/PBT blend treated for 10 min. The high-level reaction of the alcoholysis may occur in the blends treated for 60 min. However, the thermal treatment for 60 min will induce the excess thermal degradation of PBT that will cause its brittle mechanical property. Thus we attempt to promote a coupling reaction without the excess thermal degradation. The reaction will take place between the hydroxyl end group of PS-F4 and the carboxylic acid end group of PBT. We presume that the copolymer formed by the coupling reaction will have a higher molecular weight than that from the alcoholysis reaction since the latter is generated from the chain scission of PBT. Thereby the copolymer formed from the coupling reaction may be a more effective compatibilizer than the latter because of its superior anchoring efficiency [34]. We conclude that the in situ copolymerization reduces the size of the dispersed phase in the blends as an effect of induced compatibilization. However, the size of the dispersed phase of the blends prepared at 270°C is smaller than that at 250°C. It is due to the fact that the copolymer formed by the coupling reaction may form the higher molecular weight, resulting in the higher viscosity than that of homopolymer. Therefore, the lower viscosity at the high temperature will enhance the copolymer chains to diffuse into the interface. In other words, the driving force for the domain formation of copolymer will limit the emulsifying activity of the copolymer [35].

Fig. 9 shows that the dispersed phase of blends with 10 wt% PS-F4 is larger than that of blends with 5 wt% PS-F4. We speculate that the unreacted PS-F4 will disperse in the homopolymer as inert particles, and thus the blends including unreacted PS-F4 form a larger dispersed phase of PS than that of blends with 5 wt% PS-F4. A similar observation for addition of block copolymer into their homopolymers was discussed in our previous paper [36]. Although the content of PS-F4 is increased, the size of dispersed phase of PS increases by increasing the amount of PS-F4 added. There is a possible interchain or intrachain reaction of hydroxyl groups in PS-F4, which will form an inert particle in a similar way as described above. The molecular weight and the molecular weight distribution of neat functionalized polystyrenes before and after processing at 270°C for 10 min are listed in Table 2. The results indicate that the molecular weight of each homopolymer decreases after processing, and the molecular weight distribution becomes broader. It suggests that no interchain reaction takes place to increase the molecular weight.

4.5. Mechanical properties of neat polymers and various blends

4.5.1. Neat polymers and binary blends

The tensile properties of PS in this study exhibit: a high



(a) (b)

(b) (d)

Fig. 6. SEM micrographs of PS/PBT 10/90 blends for 10 min: (a) at 250°C; (b) at 270°C; (c) at 250°C with 1% TPP for 10 min; and (d) at 270°C for 10 min with 1% TPP.

Young's modulus (1260 MPa) and tensile strength (90.5 MPa); and a brittle behavior (9% elongation at break). The tensile properties of PBT ascertained the ductile behavior with 340% elongation at break after undergoing yielding and necking, as well as lower Young's modulus (1100 MPa) and break strength (60 MPa). It was too brittle to determine the tensile properties of the neat functionalized polystyrenes. We intended to prepare the dumbbell shaped specimen of each functionalized polystyrene; but these materials were too brittle to be removed from the mold without breaking.

Fig. 10 exhibits the tensile properties of the PS/PBT10/90 blends prepared with different mixing temperatures with and without 1% TPP. The blends without 1% TPP at 250 and 270°C become brittle due to the immiscible phase of PS and the poor adhesion between the PS phase and the PBT matrix. However, the addition of 1% TPP shows a significant improvement. The brittle behavior of PS/PBT blends was transformed to be ductile by adding 1% TPP. The blend prepared with 1% TPP at 250°C shows 52% elongation at break; whereas the blend prepared at 270°C shows lower elongation at break (43%). As seen in the SEM photographs (Figs. 6–8), the blends with 1% TPP shows a smaller size of the dispersed PS phase than that without 1% TPP. The smaller size of the dispersed phase attributes to the longer elongation at break than those of blends without 1% TPP. The higher elongation at break may also be originated from the effects of the addition of TPP in the PBT phase. It shows that PBT with 1% TPP has a larger elongation at break than those without 1% TPP. It is due to the coupling reaction that occurred while mixing TPP and less degradation of PBT. The yield strength and modulus of the blends with TPP do not change significantly in comparison with the blends without TPP.

The tensile properties of the PS/PBT 25/75 blend are similar to that of PS; but exhibit a higher modulus and

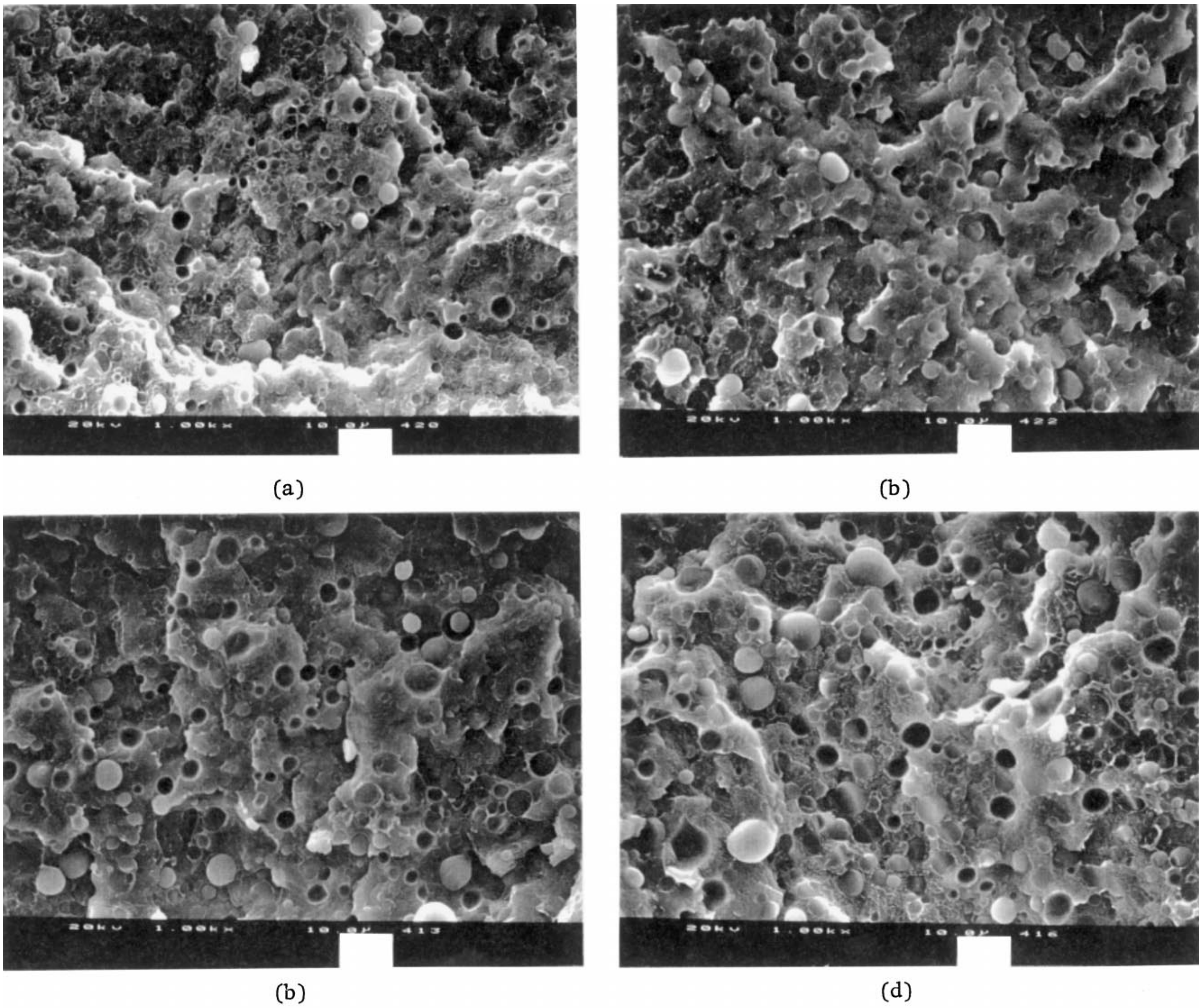


Fig. 7. SEM micrographs of PS/PBT 10/90 blends prepared at: (a) 250°C with 5% PS-F4; (b) 250°C with 10% PS-F4; (c) 270°C with 5% PS-F4; and (d) 270°C with 10% PS-F4 for 10 min.

tensile strength than the other blends. On the other hand, the PS-F4/PBT 25/75 blend shows more ductile behavior than the PS/PBT blend. Although the modulus of PS-F4/PBT blend is slightly lower than that of the PS/PBT blend, the elongation to break is significantly improved. We surmise that the un-reacted PS-F4 will be present as inert particles in the PBT matrix thereby resulting in less ductile properties of PBT. It is interesting to note that the addition of TPP enhances the ductile behavior and the tensile strength. It may be because of a lesser degradation of PBT by adding 1% TPP [16–22]. As discussed above, the addition of TPP can prevent the excess degradation of PBT [16–22]. On the contrary, the addition of TNBT promotes the degradation of PBT. Therefore, the stress–strain curve of PS-F4/PBT blend shows lower tensile strength and elongation at break.

4.5.2. Ternary blends

The typical stress–strain curves of PS/PBT 10/90 blend with various contents of PS-F4 at 250°C are shown in Fig. 11. These figures demonstrate the change from brittle to ductile behavior with the addition of PS-F4. However, the elongation to break of the blends with 5% PS-F4 became more than those of the other blends. We speculate that the improvement may be attributed to the smallest size of the dispersed phase as shown in Fig. 9.

Furthermore, the significant effects of the addition of 1% TPP on the tensile properties of PS/PBT/PS-F4 blends prepared at 270°C are shown in Fig. 12. The addition of 1% TPP made the PS/PBT10/90 blends transformed from brittle to ductile behavior. It is particularly significant in the blend with 5% of PS-F4. This result is consistent with the SEM photographs shown in Figs. 6 and 8. It indicates that the copolymer promotes in situ compatibilization in PS/PBT blend during mixing, and results in the better adhesion and elongation to break.

Previously we investigated the effects of addition of

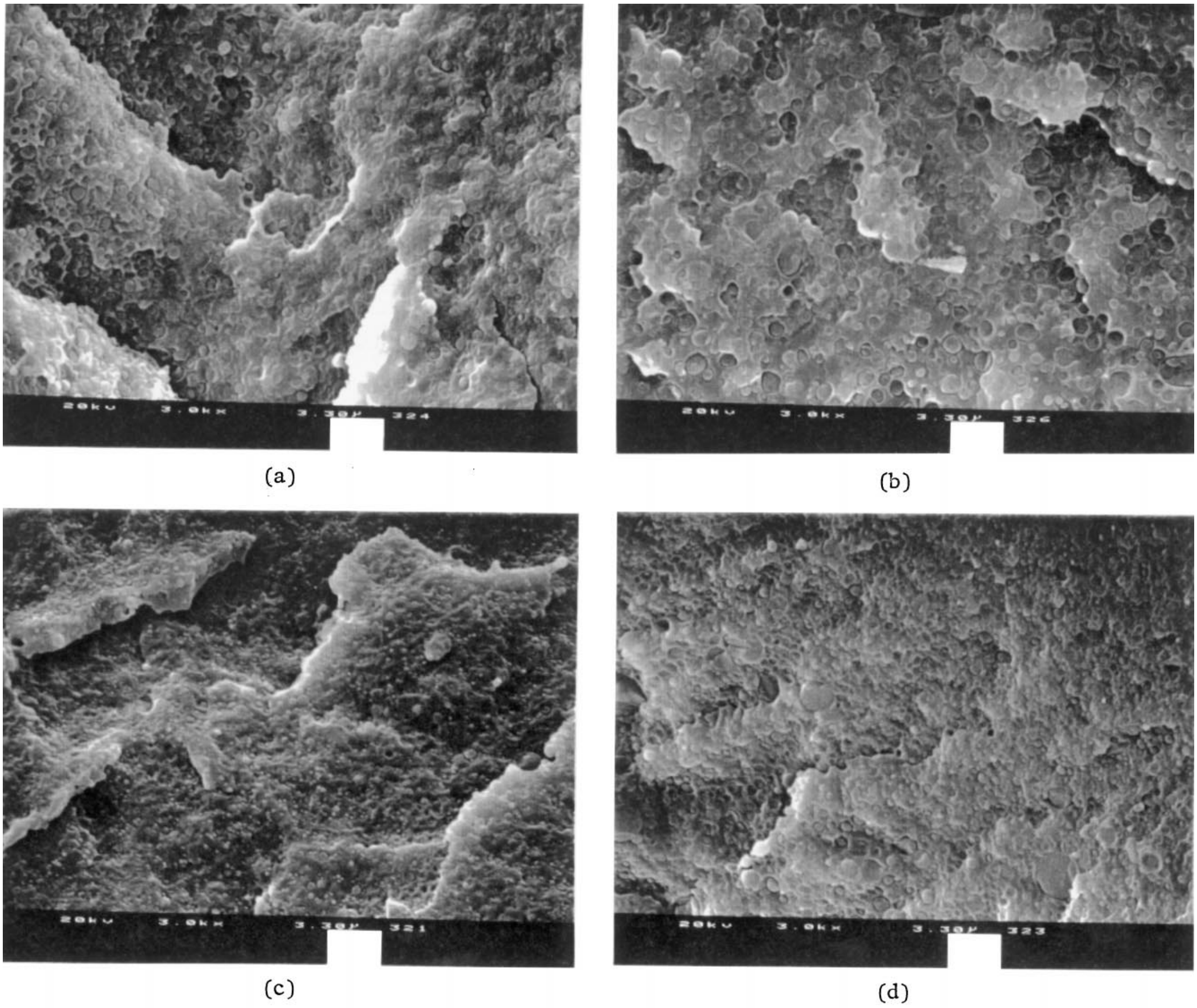


Fig. 8. SEM micrographs of PS/PBT 10/90 blends prepared at: (a) 250°C with 5% PS-F4; (b) 250°C with 10% PS-F4; (c) 270°C with 5% PS-F4; and (d) 270°C with 10% PS-F4 for 10 min with 1% TPP.

PS/PBT block copolymer into the blends of PS/PBT on the tensile properties [36]. The 10% addition of various block copolymers synthesized by the anionic polymerization enhanced the tensile properties such as elongation to break. We attempt to compare the results of tensile properties of the in situ compatibilized blends with our previous results of blends with block copolymers. The blends with various contents of PS-F4 at 270°C with 1% TPP show better elongation at break (150%) than those (60%) with 10% block copolymer. We conclude that a higher temperature promotes more reaction and easier diffusion of the copolymer into the interface due to its low viscosity at high temperature. On the other hand, the addition of functionalized polymer or block copolymers in the PS/PBT blends at 250°C had little influence on their mechanical properties because of insufficient adhesion or anchoring effect caused by the low concentration of the copolymer on the interface. The difference in the viscosity of blends at 250°C from that at 270°C will enhance a faster diffusion of copolymers to reach the interface than at 270°C.

Heikens et al. [37] reported the effects of addition of *block* and *graft* copolymers into the immiscible blends on their mechanical properties and morphology. They found that the addition of *graft* copolymer of polystyrene-*g*-(ethylene-propylene) (PS-*g*-EP) enhances the impact strength of PS/EP blends much more than polystyrene and low-density polyethylene *graft* copolymer (PS-*g*-LDPE) in the PS/LDPE blends. They concluded that the influence of the addition of PS-*g*-EP copolymer on PS/EP blend is more than that of PS-*g*-LDPE copolymer due to the lack of crystallinity of the EP segment in PS-*g*-EP copolymer as compared with the LDPE segment in the PS-*g*-LDPE copolymer in PS/LDPE blend. They suggested that the crystalline LDPE grafted chains would be too rigid to follow the applied deformation and were unable to maintain adhesion between the dispersed phase and the matrix. A similar

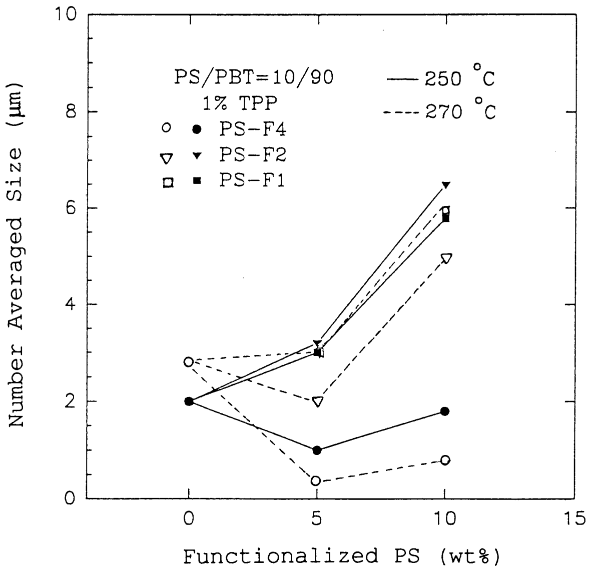


Fig. 9. Number averaged size of dispersed phase in PS/PBT 10/90 blends as a function of contents of functionalized polystyrenes at 250 and 270°C.

explanation can be applied to the results in our previous study [36] of PS-*b*-PBT copolymer in PS/PBT blend. The aromatic group of the PBT segment in the PS-*b*-PBT copolymer will be too rigid to deform and act as an adhesion between the interface of PS and PBT components in the blend.

On the contrary, Fig. 12(a) demonstrates that the improvement in elongation to break by adding 5% PS-F4 in PS/PBT blend is better than a 10% addition. This result corresponds to the reduction of the size of the dispersed phase as discussed before. However, in the case of the addition of *block* copolymers, the addition of 10% copolymer improves the elongation at break more than the addition of 5 and 25% copolymer. They speculated that the 5% addition would not be sufficient enough to enhance the adhesion on the interface and that the 25% addition would create a new domain of the copolymers separated from the dispersed phase of the blends. The diffusion of *block* copolymer would be much slower than the functionalized polystyrene because of its higher viscosity. Fig. 12(b) exhibits the effect of the periods of thermal treatments at 270°C on the tensile properties of the PS/PBT 10/90 blends with 5% PS-F4 and 1% TPP. It demonstrates that the longer thermal treatment will increase the level of reaction including in situ compatibilization and degradation. The 60 min thermal treatments cause severe degradation leading to poor tensile properties. It suggests that the best tensile properties such as elongation to break and tensile strength can be obtained by the 10 min thermal treatment at 270°C with 1% TPP.

Table 2
The characteristic data of neat functionalized polystyrenes before and after processing at 270°C for 10 min

		M_w	M_n	M_w/M_n	IV
PS-P4	(neat)	22 987	20 817	1.104	0.162
	(after processing)	17 973	15 169	1.185	0.135
PS-F2	(neat)	18 198	17 328	1.050	0.138
	(after processing)	15 874	14 007	1.133	0.124
PS-F1	(neat)	14 706	14 097	1.043	0.118
	(after processing)	12 134	10 949	1.108	0.103

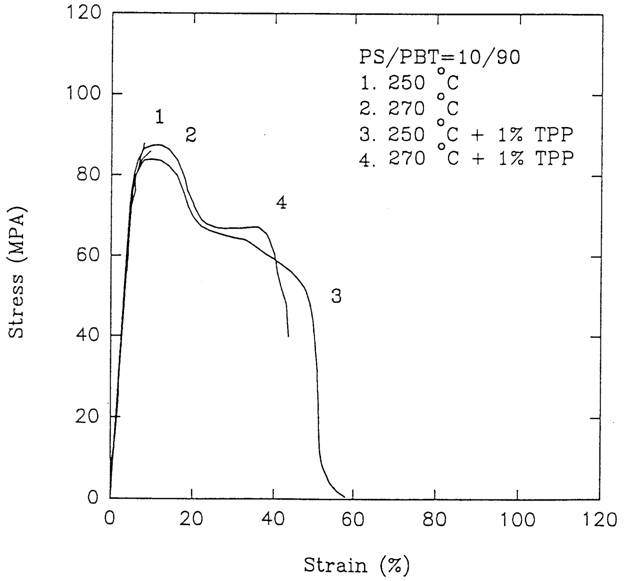


Fig. 10. The typical stress–strain curves of PS/PBT 10/90 blends prepared at different temperatures with and without 1% TPP.

Similarly, the effect of different functionality on the tensile properties was investigated by varying the number

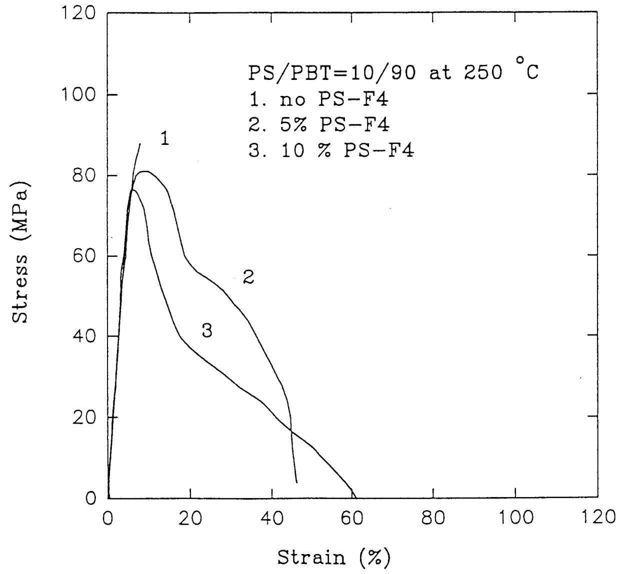


Fig. 11. The stress–strain curves of PS/PBT 10/90 blends prepared at 250°C with various PS-F4 content.

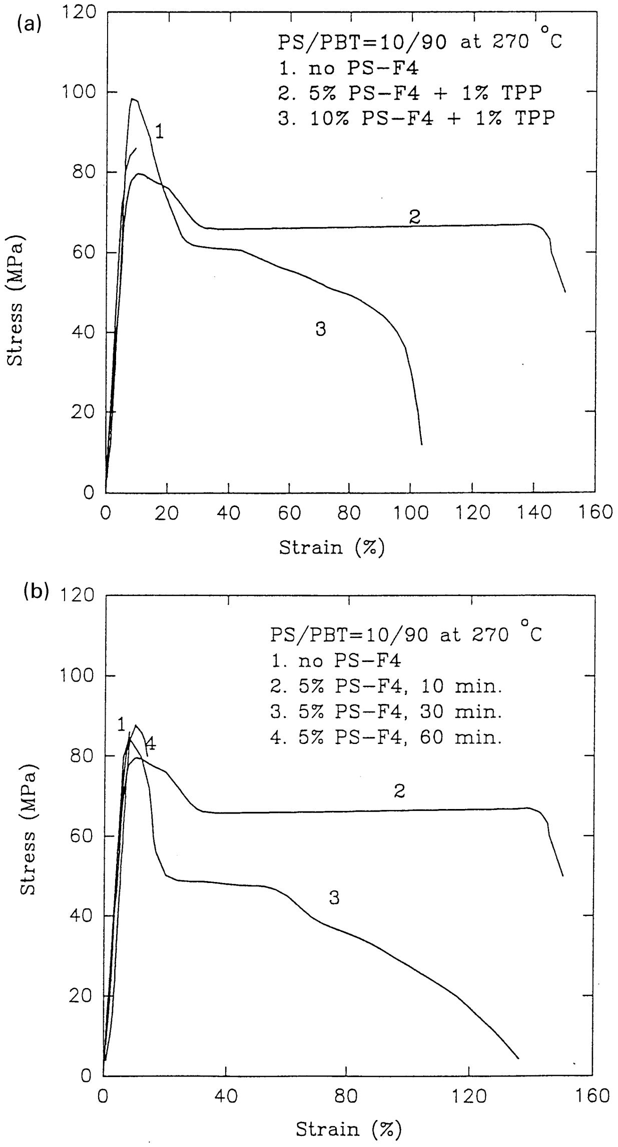


Fig. 12. (a) The stress–strain curves of PS/PBT 10/90 blends prepared at 270°C with 1% TPP and various PS-F4 content. (b) The stress–strain curves of PS/PBT 10/90 blends prepared at 270°C with 5% PS-F4 and 1%TPP for varying thermal treatments.

of functionality such as mono-, di- and tetra-functionalities as discussed in Ref. [24]. Fig. 13(i)–(iv) demonstrates the tensile properties of PS/PBT 10/90 blends prepared at 250 and 270°C with 1% TPP with the various contents of functionalized polystyrenes(PS-F1, PS-F2 and PS-F4), which include: the elongation to break, modulus, yield strength and the energy to break. The addition of 5% PS-F4 is the most effective and PS-F1 the least effective in enhancing the elongation at break. In order to compare the number of functional group per unit molecular weight, the following calculations are conducted:

$$\text{PS-F} \qquad \frac{\text{functional group no.}}{\text{molecular weight}}$$

$$\text{PS-F4} \qquad \frac{4}{21\,000} = 1.9 \times 10^{-4}$$

$$\text{PS-F2} \qquad \frac{2}{17\,000} = 1.2 \times 10^{-4}$$

$$\text{PS-F1} \qquad \frac{1}{14\,000} = 0.7 \times 10^{-4}$$

These values suggest that PS-F4 has more functional groups than PS-F2 and PS-F1 per unit weight. Therefore, PS-F4 is more effective in enhancing the elongation at break. More functional groups will promote more in situ copolymerization during blending which acts a compatibilizer in the PS/PBT blends. Fig. 13(i) also shows that the addition of 5% PS-F is better than the addition of 10% PS-F in improving the elongation at break. It agrees with the results of the smallest size of dispersed phase as shown in Fig. 9.

Fig. 13(ii) shows the lower bound curves of modulus of the blends with various functionalized polystyrenes from the other tensile properties except the addition of PS-F2. The modulus of the blends with the addition of 10% PS-F tends to increase more than the addition of 5%. Fig. 13(iii) exhibits little difference in yield strength among the various types of functionalized polystyrenes. However, the addition of PS-F4 is always more favorable than the other PS-F in improving the yield strength. Fig. 13(iv) shows the results of energy to break as a function of the content of functionalized polystyrenes. The tendency of these curves is similar to the one shown in Fig. 13(i). We also investigated the tensile properties of PS/PBT 25/75 blends at 250 and 270°C, respectively, with various contents of PS-F4 with 1% TPP. The results are similar to the previous result of PS/PBT 25/75 blend with various contents of copolymer BS3 as discussed in our previous paper [36]. All the blends show brittle behavior even after the addition of 25% *block* copolymer, BS3 or the functionalized polystyrene, PS-F4. It may be due to the fact that the in situ formed copolymer or the synthesized copolymer cannot saturate the larger interface between the PS phase and PBT phase than that of PS/PBT 10/90 blends due to the low degree of reaction or low diffusion.

The stress–strain curves of PS/PBT 10/90 blends with various PS-F4 contents at 270°C with 1% TPP for the two steps mixing are shown in Fig. 14. The PBT and various contents of PS-F4 were mixed first with 1% TPP for 5 min, and then 10% polystyrene was added and mixed for an additional 5 min. The addition of 5 or 10% PS-F4 changes the brittle behavior to ductile behavior. However, the elongation at break shown in Fig. 14 is better than that in Fig. 12. Both the blends shown in these two figures were prepared under the same composition and processing conditions. The difference in the elongation at break may be originated from the different mixing times for polystyrene. A longer mixing time as shown in Fig. 14, i.e. 10 min, may break up the dispersed phase of PS into the finer size of dispersed phase, and result in better tensile properties.

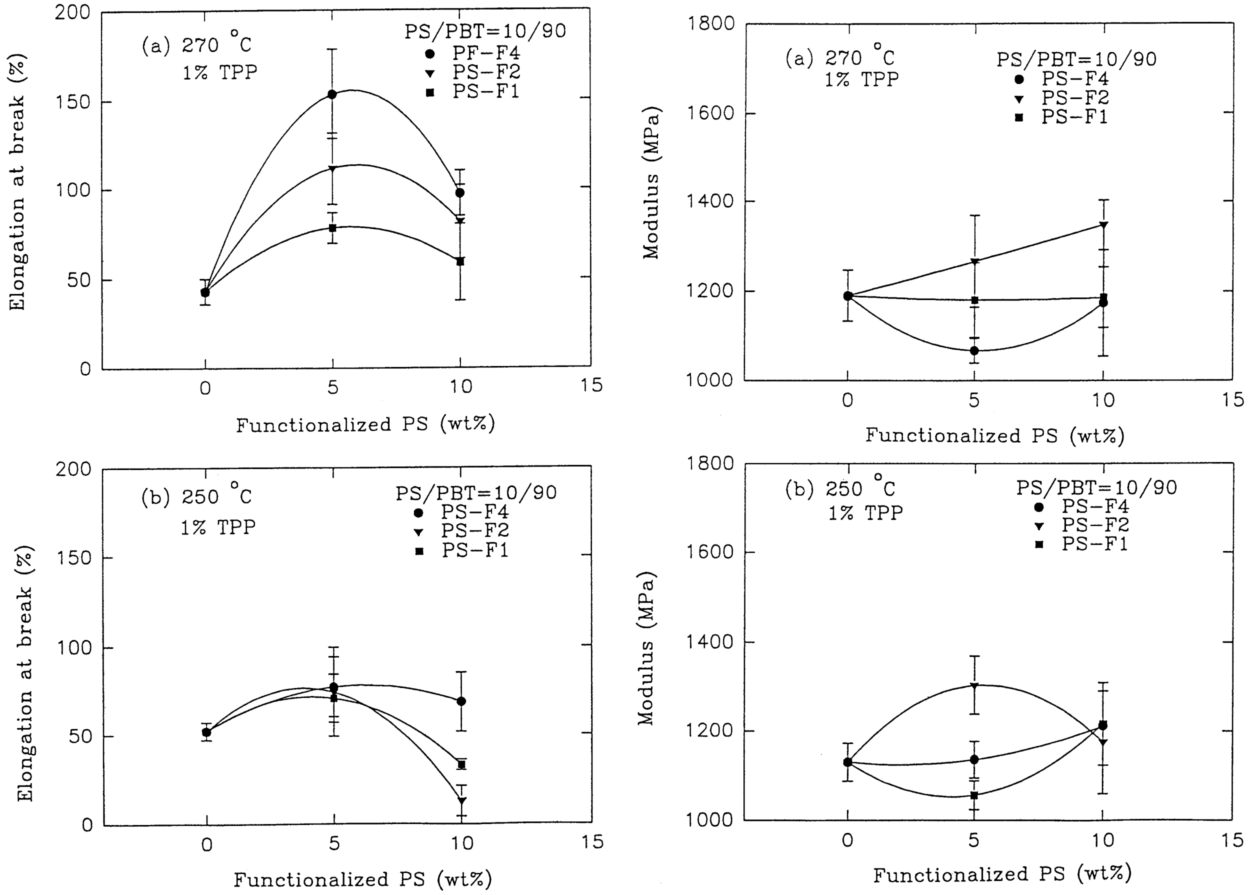


Fig. 13. (i) Elongation at break of PS/PBT 10/90 blends as a function of various PS-F's content prepared at: (a) 270°C; (b) 250°C. (ii) Young's modulus of PS/PBT 10/90 blends as a function of various PS-F's content at: (a) 270°C; (b) 250°C. (iii) Yield strength of PS/PBT 10/90 blends as a function of various PS-F's content prepared at: (a) 270°C; (b) 250°C. (iv) Energy to break of PS/PBT 10/90 blends as a function of various PS-F's content prepared at: (a) 270°C; (b) 250°C.

5. Conclusions

The in situ compatibilization of the ternary blends were studied with varying number of functional groups, the additives, concentration and processing conditions. Our conclusions are as follows:

1. From the results of the Rheological property measurements, TGA, SEM, and tensile test the addition of 1% TNBT promotes the thermal degradation of PBT. On the other hand, the addition of 1% TPP can prevent it in a 20 min heat treatment at 270°C.
2. SEM micrographs reveal that PS/PBT 10/90 blend at 250°C show a finer dispersed phase than the blend at 270°C. In the ternary blends, the dispersed phase of PS/PBT/PS-F 10/90/5 and 10/90/10 blends at 270°C are finer than the ones at 250°C. Furthermore, the addition of 10% PS-F4 in PS/PBT blends shows a larger dispersed phase in blends than by the of 5% PS-F4. The addition of PS-F4 in PS/PBT blends reduces the size of the dispersed phase more than the addition of PS-F2. The blends with PS-F2 also exhibit a finer dispersed phase than that with PS-F1.
3. It is important to control the thermal degradation of PBT in order to improve the tensile properties of PS/PBT10/90 blends. The addition of 5% PS-F4 in PS/PBT 10/90 blend at 270°C with 1% TPP for 10 min heat treatment exhibits the best improvement in the elongation at break.
4. More numbers of functional groups of the functionalized polystyrenes are more effective in promoting in situ compatibilization, i.e. they promote compatibilization in the following order, PS-F4 > PS-F2 > PS-F1.
5. The elongation at break, yield strength, and the energy to break of PS/PBT/PS-F blends at 270°C is better than that at 250°C. The elongation at break, yield strength, and energy to break of PS/PBT/PS-F blends were deteriorated by increasing the concentration of PS-F, i.e. the mechanical properties with 5% addition of PS-F is better than that with 10%.
6. The addition of PS-F4 has little effect on the brittle behavior of PS-F4/PBT25/75 blend.
7. When the period of heat treatment is longer than 10 min, the elongation at break of the PS/PBT/PS-F4 10/90/5 blend at 270°C with 1% TPP decreases. Furthermore, one-step mixing wherein all the ingredients were blended together

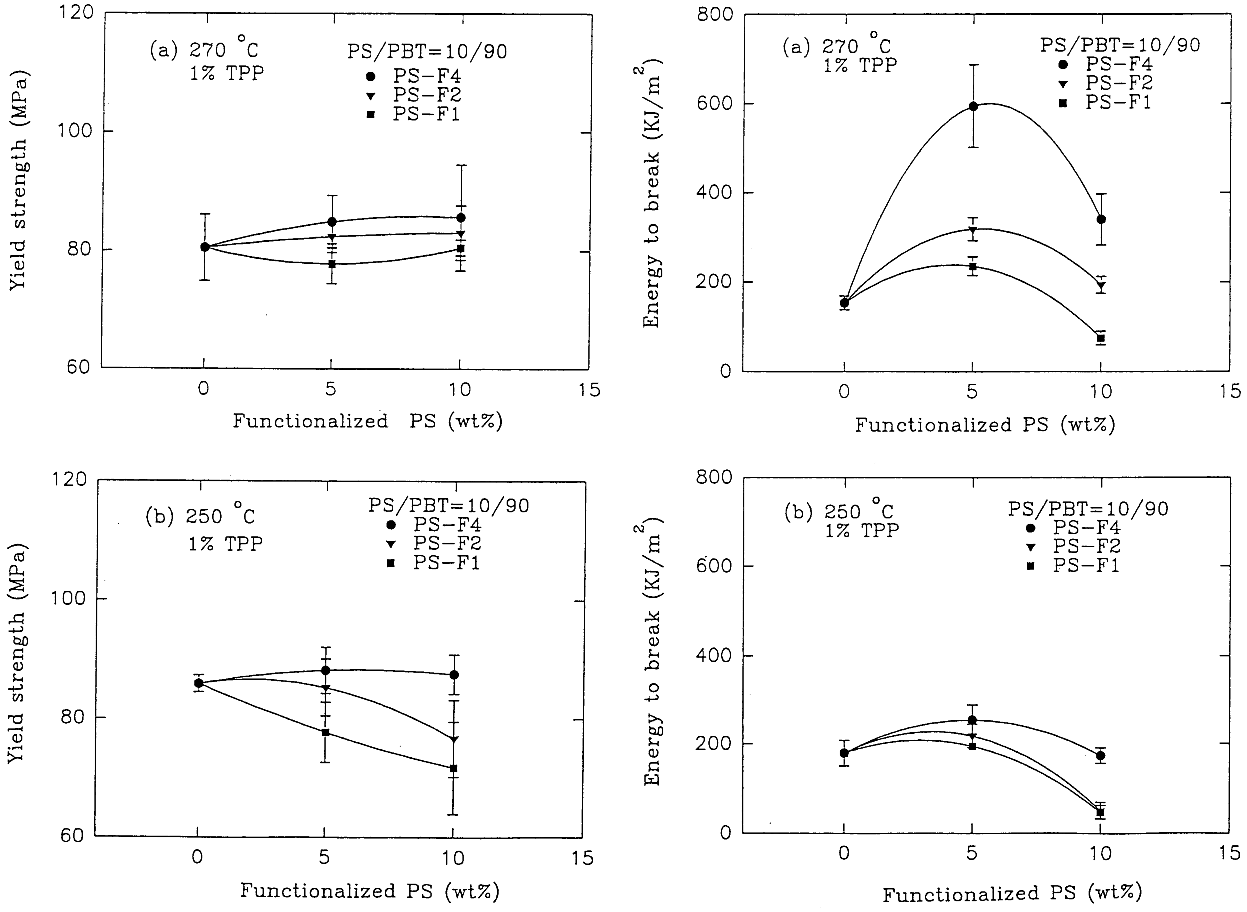


Fig. 13. (*continued*)

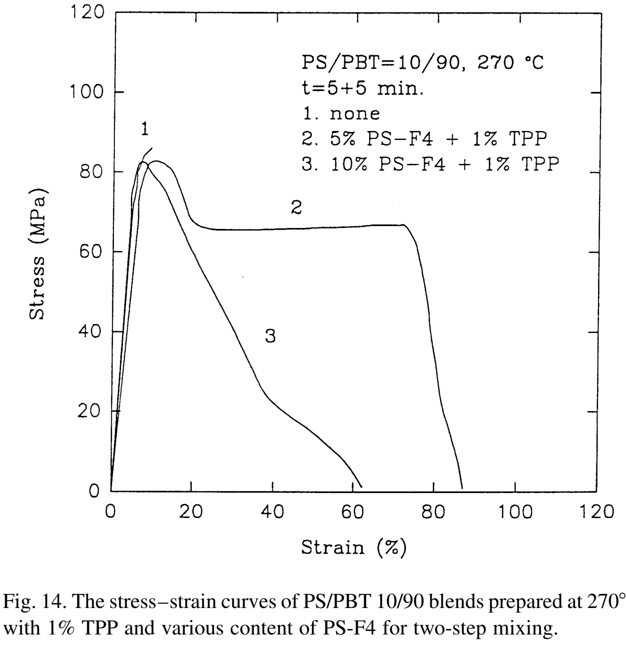


Fig. 14. The stress–strain curves of PS/PBT 10/90 blends prepared at 270°C with 1% TPP and various content of PS-F4 for two-step mixing.

for 10 min demonstrates a better elongation at break than the two-step mixing, where PS-F4/PBT was mixed first for 5 min followed by mixing with 10% PS for an additional 5 min.

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