

Reactive compatibilization of the PBT/EVA blend by maleic anhydride

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Abstract

This study concerns the reactive compatibilization of the blend of poly(butylene terephthalate) (PBT) and ethylene/vinyl acetate copolymer (EVA) by maleic anhydride (MAH). First, the graft copolymerization of EVA with MAH was investigated using dicumyl peroxide (DCP) as an initiator by melt free radical grafting in a plasticorder (Haake). The concentrations of MAH and DCP were varied from 0 to 3.0 phr and from 0 to 0.4 phr, respectively. EVA-*g*-MAH formed by the grafting reaction of EVA and MAH in the presence of DCP exhibits a significantly lower torque value than EVA bearing no MAH. PBT was blended with thus-obtained EVA-*g*-MAH using the same plasticorder. For comparison, PBT/EVA blend was also prepared. The FTIR spectroscopic studies showed that PBT-*g*-EVA copolymer was formed by the in situ interfacial reaction of MAH grafted onto EVA with the carboxylic and/or hydroxyl groups at the chain ends of PBT in the blend systems. The impact strength of PBT/EVA-*g*-MAH (80/20) blend showed about three-fold increase in comparison with PBT/EVA (80/20) blend due to the enhanced interfacial adhesion by the formation of in situ compatibilizer, i.e. PBT-*g*-EVA copolymer. Also, the morphology of the blends was observed with scanning electron microscope (SEM). © 2001 Published by Elsevier Science Ltd.

Keywords: Reactive compatibilization; PBT; EVA

1. Introduction

A relatively easy and cost-effective way to produce new combinations of properties is blending. However, most blends achieved by melt mixing are immiscible and thus show poor properties. Therefore, compatibilization is demanded to obtain a blend with desired properties. A common way to improve the compatibility and interfacial adhesion between two immiscible polymers is to add block or graft copolymers. Grafting reaction by reactive monomers, such as vinyl silane [1], acrylic acid (AA) [2], or maleic anhydride (MAH) [3,4], on the main chain of a polymer in the presence of peroxide could be achieved. When a graft copolymer possessing functional groups reacts with a polymer, such as poly(butylene terephthalate) (PBT), poly(ethylene terephthalate)(PET), or nylon containing –OH, –COOH or NH₂ groups on the chain end, a desired compatibilizer to improve the compatibility between two different polymers is produced through in situ reaction under the condition of a high temperature and shearing. The compatibilizer produced by the reactive compatibilization exhibits more improved interfacial adhesion in blends than a

common physical compatibilizer. Recently, the reactive compatibilizers have been extensively investigated to overcome the poor properties of blends.

Baker and co-workers reported on a copolymer of styrene and vinylloxazoline as a reactive compatibilizer for the blend of polystyrene with polyethylene containing carboxylic acid [5–7]. Hu and Lindt showed that polypropylene (PP)-*g*-MAH was expected to react with the hydroxyl group of the PBT to form PP-*g*-PBT, but this reaction is reversible and its equilibrium is highly shifted to the reactant side with increasing temperature [8]. Xanthos et al. and Hert [9,10] exhibited that the carboxyl or hydroxyl group of the PBT can react with other functional groups such as MAH, AA, or glycidyl methacrylate (GMA). Kim et al. reported that the PAA homopolymer produced in the process to graft AA onto PP decreased its mechanical properties because of a large difference of the solubility parameter between PP and PAA when the functionalized PP was blended with any polymer bearing the functional groups which can react with AA [11]. Meanwhile, since homopolymerized MAH decomposes at a ceiling temperature of 150°C unlike other functional monomers, the graft reaction practised above 150°C does not generally produce MAH homopolymer [12,13].

Many attempts have been made to improve a low impact strength of PBT by blending a functionalized rubber such as

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Table 1
Characteristics of the PBT and EVA used in this study

Materials	M_n	M_w	T_m (°C)	MFI ^a (g/10 min)	Vinyl acetate contents (%)	Source
PBT	29,400	68,250	225	–	–	SKI
EVA	–	–	87.5	2.5	18	DuPont

^a Melt flow index (in units of g per 10 min); ASTM D 1238, 190°C and 2.16 kg.

ethylene-propylene rubber (EPR) or ethylene-propylene-diene terpolymer (EPDM) with PBT [14–16]. On the other hand, ethylene/vinyl acetate copolymer (EVA) to possess both rubber and resin properties may be expected to improve the impact strength of PBT. Moreover, to our best knowledge, no paper has been reported on the systematic investigation on the reactive compatibilization of the PBT/EVA blends by MAH.

The objective of this study is to investigate the reactive compatibilization of PBT and EVA by MAH, and to identify the formation of PBT-*g*-EVA copolymer as an in situ compatibilizer by the reaction of hydroxyl groups and/or carboxylic groups at the chain ends of PBT and MAH grafted onto EVA in the presence of DCP as an initiator. Also, morphology and impact strength of PBT/EVA-*g*-MAH and PBT/EVA blends were measured to investigate the compatibilizing effects of the PBT-*g*-EVA copolymer.

2. Experimental

2.1. Materials

Table 1 lists the materials in this study. EVA (Du Pont, Elvax 460, MFI = 2.5 g/10 min) used in this study was a random copolymer of ethylene and vinyl acetate (18%). MAH purchased from Shinyo Pure Chemical was used without further purification. Dicumyl peroxide (DCP, purity 98%) used as an initiator was purchased from Aldrich, and its half-lifetime at the melt grafting temperature (175°C) was about 1.45 min. PBT was a commercial product of Sunkyong Inc., Korea, (SKYTON 1100C). The PBT contains, at its chain ends, 0.063 eq/kg of hydroxyl groups and 0.041 eq/kg of carboxylic groups, and its number and weight average molecular weights were 29,400 and 68,250, respectively.

2.2. Melt grafting and blend preparation

EVA was dried prior to use in an oven for 5 h at 70°C. The EVA was functionalized in the presence of MAH and

DCP using a plasticorder (HAAKE Rheocord 9000, 85 cm³) equipped with cam rotors. The melt grafting reaction was carried out under the conditions that the rotor speed was 50 rpm, the set temperature 175°C, and the reaction time 10 min. EVA was mixed with MAH before adding DCP for inhibiting pre-crosslink of EVA. The concentration of MAH was varied from 0.5 to 3.0 phr, and that of DCP from 0.1 to 0.4 phr. Torque–time behaviours were measured during reaction. Table 2 summarizes the composition of DCP and MAH used for the grafting reaction. 60 g of EVA was fed into the plasticorder for the grafting reaction. PBT was dried before blending at 120°C for 24 h, and EVA-*g*-MAH at 70°C for 5 h. PBT/EVA (80/20 w/w) and PBT/EVA-*g*-MAH blends (80/20 w/w) were prepared using the plasticorder with 50 rpm of rotor speed, 240°C of set temperature, and 10 min of reaction time.

2.3. Measurements

Extraction of the PBT-*g*-EVA copolymer is similar to those reported by Pilati [17]. Preliminary solubility tests showed that PBT was soluble in dichloroacetic acid (DCAA) at room temperature, but EVA was insoluble in DCAA [18]. About 5 g of PBT/EVA6 and PBT/EVA5 blends were added to 100 ml DCAA, respectively, and stirred at room temperature for three days. The suspensions were filtered off. The clear solution obtained was precipitated with water. The precipitate obtained was washed with water and dried in a vacuum oven until constant weight. To confirm the presence of PBT-*g*-EVA copolymer from these samples obtained by the extraction, FTIR spectra were recorded on Nicolet 710 FTIR spectrometer. Also, the blended samples were pressed into sheets with 2 mm thickness using compression moulding machine for further testing and measurements. Notched Izod impact tests were carried out using Izod impact tester (Uheshima, IM-103) at room temperature. The dimensions of the specimens for the Izod impact tests were 65 × 12 × 2 mm³ with a notched 0.25 mm in radius. Morphologies of the cryogenically fractured surfaces in liquid nitrogen were examined by scanning

Table 2
Composition of DCP and MAH used for the grafting reaction

Notation	EVA	EVA1	EVA2	EVA3	EVA4	EVA5	EVA6	EVA7
MAH (phr)	0	2	2	2	2	2	0	2
DCP (phr)	0	0	0.05	0.1	0.2	0.3	0.3	0.4

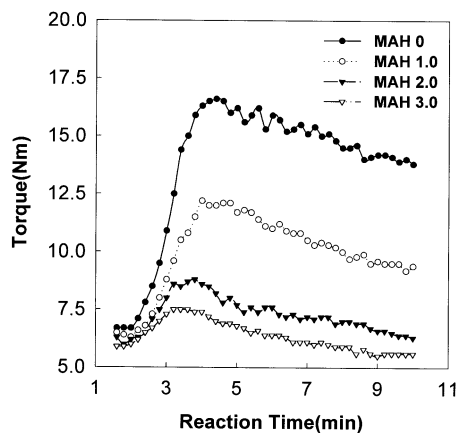


Fig. 1. Rheographs of EVA as a function of MAH concentration (DCP: 0.1 phr).

electron microscopy (SEM; JEOL, JSM-6100). The fractured surface of the specimens was treated by coating with gold prior to the SEM examination. Insoluble parts extracted from the melt grafted EVA in boiling xylene for 12 h were dried in a vacuum oven at 60°C according to ASTM D2765-68 (method A) standard. The insoluble parts were weighed for measuring gel contents.

3. Results and discussion

3.1. Melt grafting of MAH onto EVA

Torque rheometry. Torque rheometry has frequently been used to monitor chemical reaction during reactive melt mixing. The torque–time behaviours of the EVA–MAH–DCP and the EVA–DCP system were investigated under the same reaction conditions. Fig. 1 shows rheographs of EVA as a function of MAH concentration when DCP content was fixed at 0.1 phr. The concentration of the MAH varied from 0 to 3.0 phr. An increase in the MAH concentration led to a significantly lower torque value than EVA bearing no MAH.

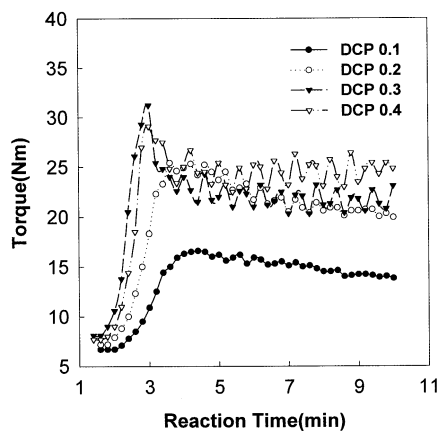


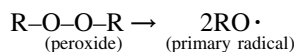
Fig. 2. Rheographs of EVA as a function of DCP concentration (MAH: 0 phr).

This implies the formation of EVA-g-MAH due to the graft reaction of EVA and MAH in the presence of DCP. For higher DCP concentration over 0.1 phr, torque rise by peroxide-induced crosslinking of EVA after attainment of the minimum steady torque was not largely changed, as shown in Fig. 2. In the presence of a MAH, however, the maximum torque value of EVA containing DCP showed a noticeable increase, as shown in Fig. 3. The results mean that the reactive processing of EVA in the presence of DCP and MAH in a plasticorder leads to the formation of the modified EVA such as MAH-grafted EVA, and crosslinked EVA, and thus crosslinking of EVA may be competitive with grafting reaction.

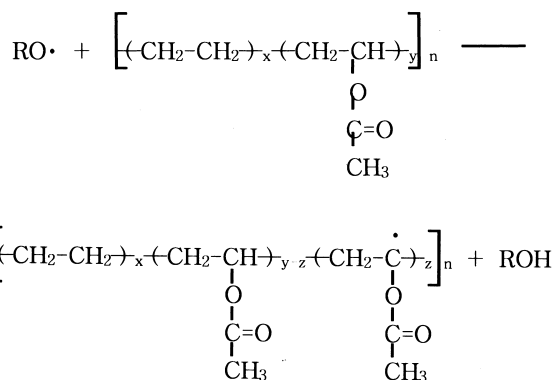
Fig. 4 shows the effects of MAH and DCP concentration on the gel contents of EVA after rheocorder experiments. As is expected, the gel contents of EVA were increased with increasing the concentration of DCP, but were decreased with increasing the concentration of MAH. Ghosh et al. reported in their study on the modification of low density polyethylene (LDPE) by graft copolymerization with some acrylic monomers that the nature and degree of variations of torque with time during the reactive processing leading to significant grafting of PE were characteristically dependent on the nature of monomer and dose levels of the monomer and DCP used for grafting [19].

Mechanism of grafting and crosslinking by DCP. When molten EVA is sheared in the presence of DCP and MAH at 175°C using a plasticorder, the sequence of reaction that would occur is as follows:

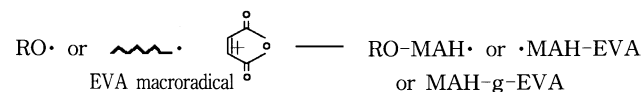
(a) Formation of the initiator radical



(b) Radical transfer reactions occurring between the primary radical and EVA used



(c) Addition of MAH to primary radical or the EVA macroradical



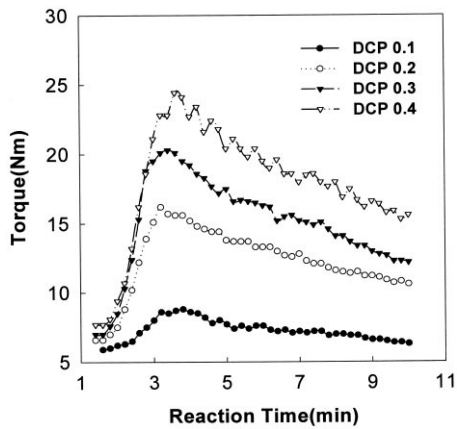
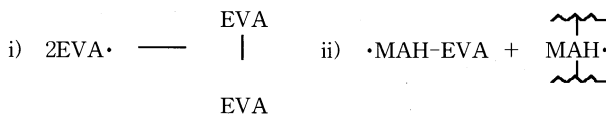


Fig. 3. Rheographs of EVA as a function of DCP concentration (MAH: 2.0 phr).

(d) Crosslinking by mutual termination of the grafted-propagating chains or EVA macroradicals



3.2. Identification of PBT-g-EVA by extraction

It is not easy to identify the characteristic peaks of MAH, which is grafted onto EVA, because EVA and MAH possess the same C=O group. Fig. 5 shows the IR spectra of EVA and EVA-g-MAH (here, EVA5). Consequently, extractions were performed to verify the formation of the PBT-g-EVA copolymer, which would be obtained by the reactive compatibilization of the blends of PBT and EVA-g-MAH. The PBT separated from PBT/EVA5 blend after extraction showed some turbidity in DCAA unlike for the pure PBT or PBT/EVA6 blend solutions in DCAA, suggesting the presence of PBT-g-EVA. It may be assumed that the PBT

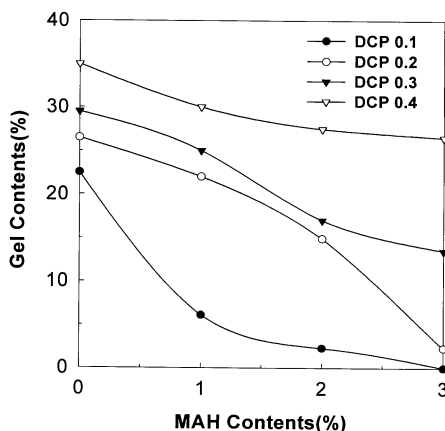


Fig. 4. Gel contents of EVA as a function of MAH and DCP concentration.

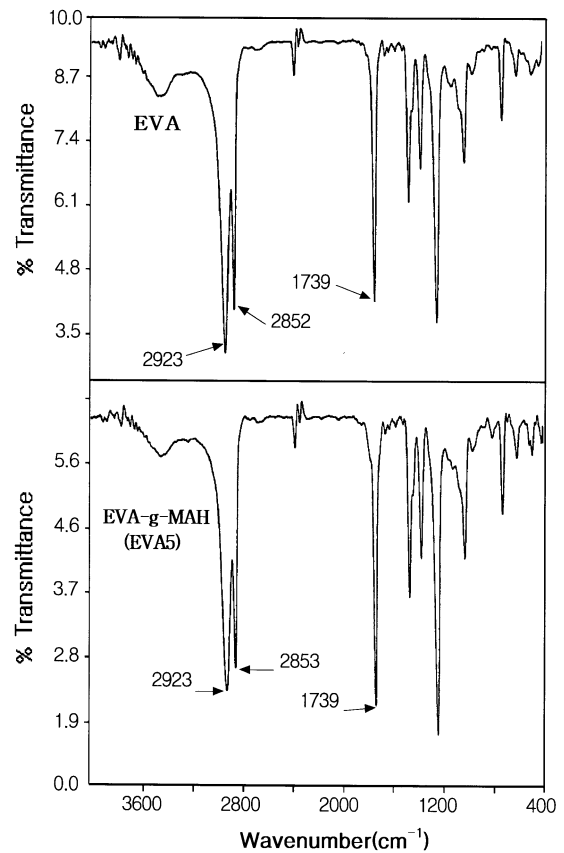


Fig. 5. FTIR spectra of the pure EVA and MAH-grafted EVA (EVA5).

solution in DCAA after extraction from PBT/EVA5 blend contain a partially dissolved PBT-g-EVA in DCAA. The turbidity may imply that whole of the graft copolymer cannot be dissolved in DCAA. The PBT separated from PBT/EVA5 and PBT/EVA6 blends by extraction was characterized using FTIR spectrometer. The results are shown in Fig. 6. It should be noted here that EVA5 is EVA-g-MAH but EVA6 has been prepared in the absence of MAH, as seen in Table 2. Two distinct characteristic peaks due to the C–H stretch of ethylene groups of EVA appeared at 2923 and 2852 cm⁻¹ in the spectrum of the PBT separated from PBT/EVA5 blend, but they are not seen in the pure PBT and PBT/EVA6 blend. This proves that MAH grafted onto EVA in the presence of DCP reacted with the hydroxyl and/or carboxyl groups at the end groups of PBT to form PBT-g-EVA copolymer as an in situ compatibilizer.

3.3. Morphological observation

Fig. 7 shows the SEM micrographs of the fractured surfaces of the PBT/EVA-g-MAH blends. The notations are described in Table 2. The MAH contents was fixed at 2 phr. The DCP concentration is higher in the order EVA1 < EVA2 < EVA3 < EVA4 < EVA5. One can see that the particle size of the dispersed phase (here, EVA-g-MAH) was reduced from 5–10 to 0.5–1 μm as the EVA-g-MAH was prepared with

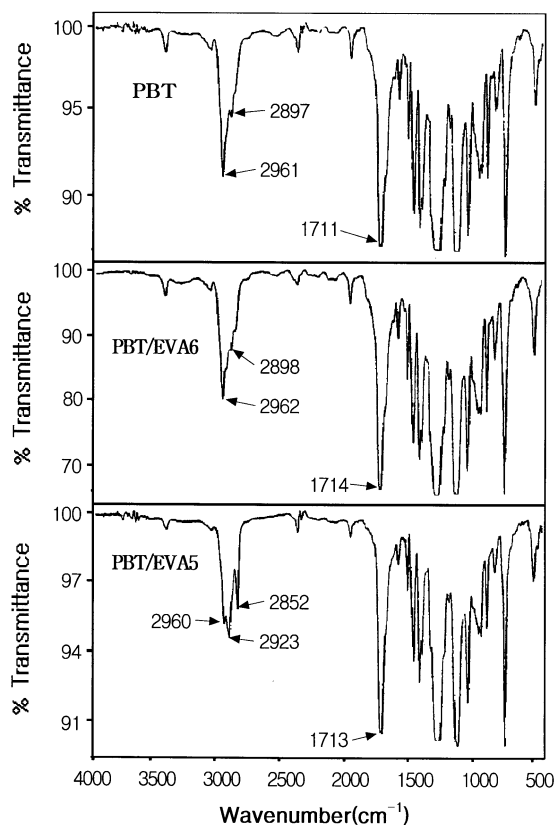


Fig. 6. FTIR spectra of the pure PBT, the PBT separated from PBT/EVA5 and PBT/EVA6 blends by extraction.

higher concentration of DCP and were blended with PBT. The average particle size of the dispersed phase was about 5.70, 1.68, 1.68 and 1.70 μm for EVA1, EVA2, EVA4, and EVA5, respectively, suggesting that the morphology was not strongly dependent on the DCP concentrations. The average particle size of the dispersed phase for EVA3 was also 1.68 μm , though data are not shown here. Careful inspection of the morphology, however, indicates that the phase boundaries between PBT matrix and EVA4 or EVA5 domain became less clear than EVA1 or EVA2 domain. The result means that the interfacial adhesion in the PBT/EVA blends becomes better as DCP concentrations are higher. The enhanced interfacial adhesion may be due to either the in situ formation of the PBT-g-EVA copolymer by the potential reactivity of MAH with the hydroxyl group of PBT at the interface of the blends [20–22], or intermolecular dipole–dipole interaction between the carbonyl oxygen in MAH of the EVA-g-MAH and the hydrogen in the hydroxyl group of PBT [23]. Based on the FTIR spectra of the extracted PBT shown in Fig. 6, the morphological feature is believed to be attributed to the formation of the in situ compatibilizer, i.e. PBT-g-EVA copolymer, which would achieve a reactive compatibilization on the PBT/EVA-g-MAH blends, instead of a physical compatibilization such as intermolecular dipole–dipole interaction. The result of Fig. 6 also indicates that the reactive compatibilization takes place more effectively as DCP concentration is higher, due to higher reactivity, even under the same amount of MAH contents, i.e. 2 phr.

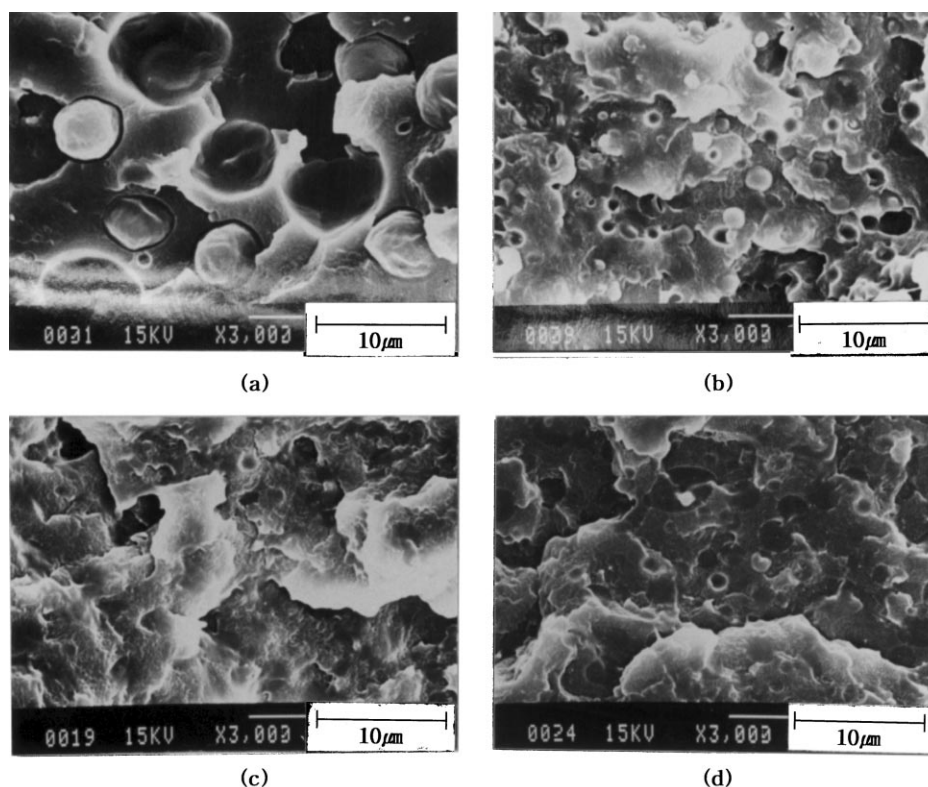


Fig. 7. SEM micrographs of fractured surface of: (a) PBT/EVA1, (b) PBT/EVA2, (c) PBT/EVA4, and (d) PBT/EVA5 blends.

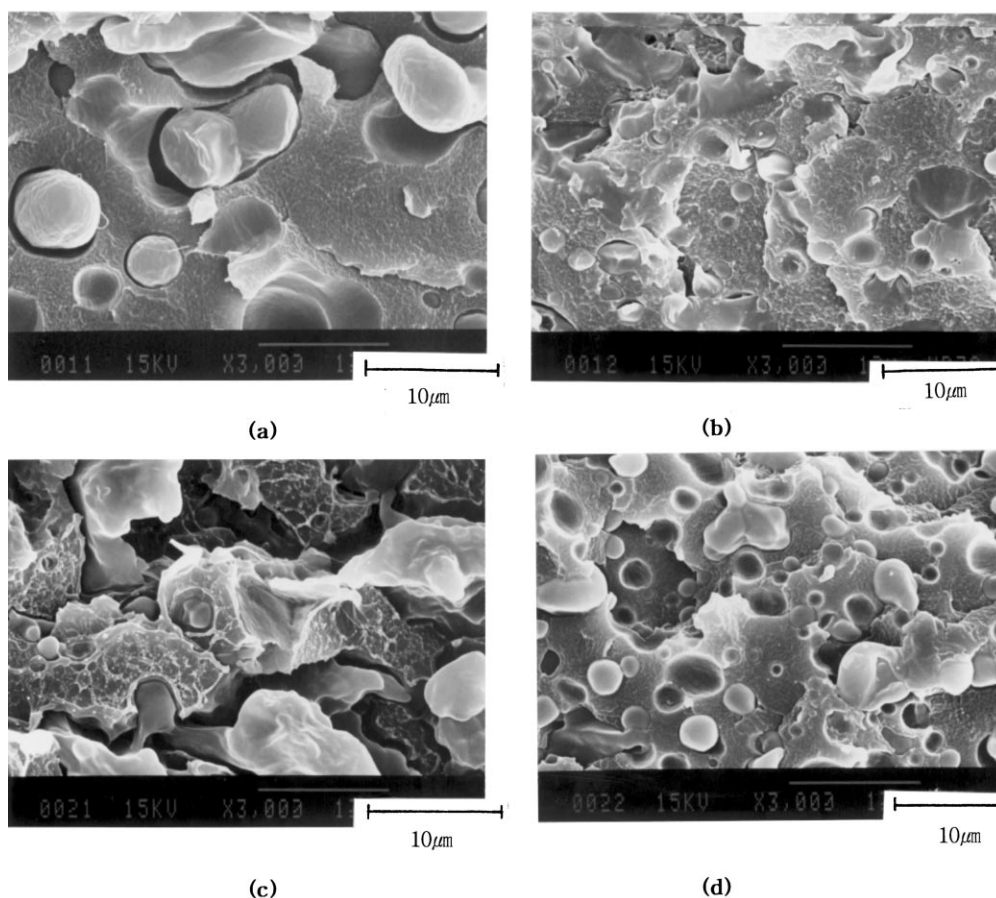


Fig. 8. SEM micrographs of fractured surface of PBT/EVA blends with different DCP and MAH contents. (a) DCP (0.1 phr), MAH (0.0 phr); (b) DCP (0.1 phr), MAH (0.5 phr); (c) DCP (0.3 phr), MAH (0.0 phr); and (d) DCP (0.3 phr), MAH (0.5 phr).

Fig. 8 shows the SEM micrographs of PBT/EVA blends with or without MAH in the presence of DCP. Even when MAH contents are lower, say, 0.5 phr, the dispersed particles were smaller by adding MAH, regardless of DCP concentrations, 0.1 or 0.3 phr. The result also suggests the compatibilization effect in the PBT/EVA blends by MAH. The compatibilizing effect of MAH was more clearly seen when DCP contents was lower, i.e. 0.1 phr. When DCP contents were higher in the absence of MAH, the morphology of the blend might be governed by the crosslinking of EVA by DCP. In this case, not much clear compatibilization effect was observed.

Usually, the morphology of polymer blends is mainly affected by both interfacial tension and viscosity ratio between matrix and domains. The interfacial tension may be dependent on the reactivity of the carboxyl end groups of PBT with MA, which is directly related to the concentrations of the functional groups. The SEM results in Fig. 8 suggests that both the interfacial tension and the viscosity determine the morphology of PBT/EVA or PBT/EVA-g-MAH blends in this work. The effect of the viscosity ratio between matrix and domains should not be negligible, especially when DCP contents are higher in the absence of MAH, since the increase of concentration of

DCP resulted in the increase of torque and gel content, then viscosity.

It may be assumed that the crosslinking of EVA and the grafting of MAH onto EVA take place competitively and simultaneously by adding DCP. The morphology shown in Fig. 7, however, implies that the grafting of MAH onto EVA, then in situ grafting of PBT with the EVA-g-MAH may dominate over the crosslinking of EVA, when adding all amounts of DCP with high MAH contents, i.e. 2.0 phr. Then, the increased interfacial adhesion by the formation of the in situ graft copolymer, PBT-g-MAH-EVA, governs the final morphology of the blends, rather than the crosslinking of EVA by DCP does. In addition, the shear rate may be also one of essential factors to govern the morphology of the blends. In general, the size of crosslinked rubber phases are strongly dependent on the shear rate for dynamically vulcanized rubber blends. A constant shear rate was applied in this work by adjusting the rotational speed of the mixer at 50 rpm. Further studies are now underway to reveal the effect of the shear rate on the morphology, depending on the DCP and MAH contents. It should be mentioned that it was difficult to control the morphology with smaller particle size than 1.68 μm by the amount of DCP and MAH in this work.

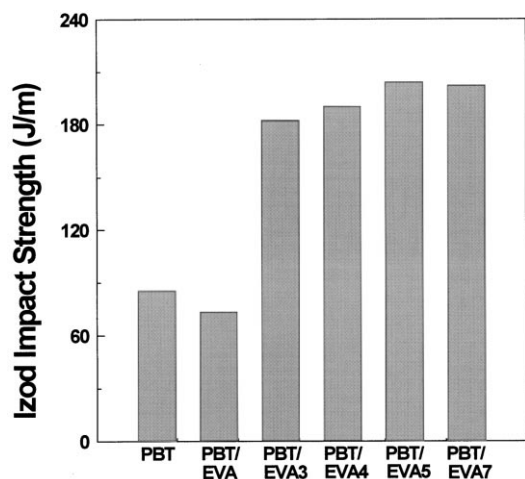


Fig. 9. Impact strength of PBT (80 wt%) in PBT/MAH-grafted EVA blends (at 23°C).

3.4. Impact strength

Fig. 9 shows the Izod impact strength of the pure PBT and the blends of PBT with EVA and EVA-g-MAH. The sample notations are described in Table 2. While the impact strength of PBT/EVA (80/20) blend was slightly smaller in comparison with that of the pure PBT, that of PBT/EVA-g-MAH (80/20) blends showed about three-fold increase, regardless of DCP concentrations. Fig. 10 shows the Izod impact strength of the blends of PBT with EVA-g-MAH as a function of MAH and DCP concentration. The Izod impact strength of the PBT/EVA-g-MAH blends was increased with increasing the concentration of MAH for a given concentration of DCP, but it was slightly decreased when 3.0 phr of MAH was added. The increase in the MAH concentration increases not only the amount of the MAH grafted onto the EVA but also that of the residual

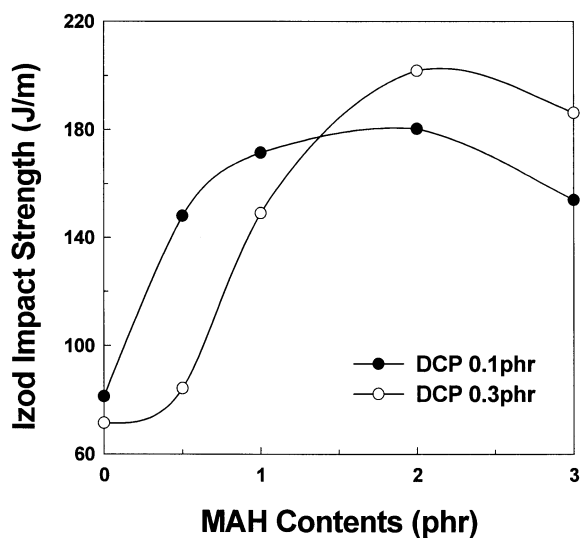


Fig. 10. Impact strength of PBT/MAH-grafted EVA (80/20) as a function of MAH and DCP concentration (at 23°C).

MAH [24,25]. The former favours the formation of the desired graft copolymer, PBT-g-EVA, whereas the latter achieves the opposite effect. This is because the residual MAH monomer can also react with the PBT, probably at a higher rate than the MAH-grafted EVA, due to its much greater mobility. As a result, the amounts of the PBT-g-EVA formed will be reduced, which may cause a decrease in the impact strength of the blends. The difference in the impact strength can be related to the morphology of blends in terms of particle size of dispersed phases but the relationship is not clearly seen in this work, since the dependence of the particle size on the DCP under the same MAH concentrations (2.0 phr) are not large, as already seen in Fig. 7. The difference in the interfacial adhesion, as shown in Fig. 7, however, may be closely related to the difference in the impact strength of blends. Comparison of Figs. 7 and 9 clearly shows that the blends exhibiting better interfacial adhesion exhibit higher impact strength (compare PBT/EVA4 and PBT/EVA5 with PBT/EVA1 blend).

It should be also noted from Fig. 10 that the impact strength of blends of PBT with EVA blends crosslinked with lower DCP contents (0.1 phr) is higher than that with higher DCP contents (0.3 phr), when no MAH was present or the MAH contents are low. When MAH contents are higher, however, the impact strength of blends of PBT with higher DCP contents are higher on increasing DCP contents. These results clearly indicate that the formation of in situ graft copolymer between PBT and EVA-g-MAH by DCP plays a more effective role to increase the impact strength rather than the crosslinking of EVA by DCP does, as discussed for the morphology.

4. Conclusions

It was found that the amounts of the MAH grafted onto EVA in the presence of DCP were dependent on the concentrations of MAH and DCP, which influence final torque values in the torque–time behaviours because of the competitive reaction of the grafting and crosslinking of EVA. When EVA5 was blended with PBT, the in situ compatibilizer, i.e. PBT-g-EVA, was obtained from the reaction of MAH grafted onto EVA and the hydroxyl groups and/or carboxylic groups at the chain ends of PBT. The PBT-g-EVA in the blend was also confirmed from the PBT separated by extraction using FTIR spectrometer. The Izod impact strength of the PBT/EVA (80/20) blend appeared to a slight decrease in comparison with that of the pure PBT, whereas that of PBT/EVA-g-MAH (80/20) blends showed about three-fold increase. The result is attributed to the fact that the formation of the PBT-g-EVA copolymer was achieved in this blend system. Also, the SEM micrographs showed that the particle size of the dispersed phase (MAH grafted EVA) was reduced from about 5–10 to about 0.5–1 μm due to the reactive compatibilizing effects when

EVA4 or EVA5 obtained at a higher concentration of DCP was blended with PBT.

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