Reactive Compatibilization of the Poly(butylene terephtalate)–EVA Blend by Maleic Anhydride. II. Correlations Among Gel Contents, Grafting Yields, and Mechanical Properties

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ABSTRACT: Correlations among the degree of crosslinking of ethylene vinyl acetate copolymer (EVA), the grafting yield of maleic anhydride (MAH) onto EVA, and the mechanical properties of the blends of poly(butylene terephtalate) (PBT) with EVA-g-MAH were investigated. The EVA was functionalized by melt grafting reaction in the presence of MAH and dicumyl peroxide (DCP) using a plasticorder. The grafting yield of MAH was increased by increasing the concentration of MAH and DCP. The flexural strength of PBT–EVA-g-MAH blends depends on both the grafting yield of MAH and the degree of crosslinking of EVA, while the crosslinked parts of EVA-g-MAH hindered rather than improved the tensile strength regardless of the increase of the grafting yield of MAH. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1305–1310, 2003

Key words: compatibilization; crosslinking; graft copolymers; blends

INTRODUCTION

Polymer blending is one of the most effective and economical methods used to develop new materials that have properties distinct from those of each component.[1,2] However, only few polymer pairs used in blending are miscible and compatible. In general, most of the incompatible polymer pairs necessarily require the use of a compatibilizer, such as a block and graft copolymer, to improve the weak physical properties of the polymer blends.[3–5] The grafting reaction by reactive monomers, such as vinyl silane,[1] acrylic acid,[2] or maleic anhydride (MAH)[3,4] onto the main chain of a polymer in the presence of peroxide is also one of attractive ways of achieving that purpose. 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 -NH$_2$ groups on the chain end, a desired compatibilization between two different polymers is developed through in-situ reaction under conditions of high temperature and shearing. The compatibilizer produced by the reactive compatibilization exhibits improved interfacial adhesion in blends relative to a common physical compatibilizer. Recently, reactive compatibilizers have been extensively investigated to overcome the poor properties of blends, although the number of works addressing reactive compatibilization in a quantitative manner is limited.

PBT is a high melting, semicrystalline polymer with good chemical resistance and processibility, including good tensile strength and flexural modulus. The impact fracture energy of PBT, however, is very low.[6–10] In our previous work, we reported that the impact strength of PBT was vastly improved by blending with MAH-grafted ethylene(vinyl acetate) copolymer (EVA) because of the improved interfacial adhesion between PBT and EVA-g-MAH due to the development of in-situ compatibilization.[11]

The objectives of this study include the investigation of the reactive compatibilization of PBT and EVA through MAH grafting, correlation of the degree of crosslinking of EVA to gel contents, investigation of the grafting yield of MAH onto EVA, and study of the mechanical properties of PBT–EVA-g-MAH blends.

EXPERIMENTAL

Materials

EVA (Elvax 460, MFI = 2.5 g/10min, DuPont, Wilmington, DE) used in this study was a random copolymer of ethylene and vinyl acetate (18%). MAH purchased from SHINYO Pure Chem. (Gunma, Japan) was used without further purification. Dicumyl peroxide (DCP) (Purity 98%) used as an initiator was

TABLE I
Grafting Yield and Gel Contents with DCP and MAH Contents

Exp. No.	$[DCP]_I$ (phr)	$[MAH]_i$ (phr)	$[MAH]_g$ (phr)	Grafting Yield[a] (%)	$[O]_{total}$ (%)	$[O]_{MAH}$ (%)	Gel Contents (%)
1	0.1	0.0	—	—	7.01	0.00	22.5
2	0.1	0.5	0.06	12.0	7.04	0.03	13.0
3	0.1	1.0	0.14	14.0	7.08	0.07	6.10
4	0.1	2.0	0.29	14.5	7.15	0.14	2.30
5	0.1	3.0	0.39	13.0	7.20	0.19	0.00
6	0.2	2.0	0.92	46.0	7.46	0.45	14.9
7	0.3	0.0	—	—	7.01	0.00	29.5
8	0.3	0.5	0.04	8.20	7.03	0.02	27.6
9	0.3	1.0	0.37	37.0	7.19	0.18	25.0
10	0.3	2.0	1.09	54.5	7.54	0.53	17.0
11	0.3	3.0	0.90	30.0	7.45	0.44	13.5
12	0.4	2.0	1.11	55.5	7.55	0.54	27.5

[a] The grafting yield is defined as the ratio of concentration of grafted MAH to initial MAH, $[MAH]_g/[MAH]_i$

purchased from Aldrich (St. Louis, MO). Its half-life at the melt grafting temperature (175°C) was about 1.45 min. PBT is a commercial product of Sunkyong Inc., Korea, (SKYTON 1100C, Suwon, Korea). The PBT contains, at its chain ends, 0.063 eq/kg hydroxyl groups and 0.041 eq/kg carboxylic groups, and its number and weight average molecular weights were 29,400 and 68,250, respectively.

Melt grafting and blend preparation

EVA was dried prior to use in an oven for 5 h at 70°C. The EVA was functionalized into EVA-g-MAH through grafting by MAH in the presence of DCP in a plasticorder (HAAKE Rheocord 9000, 85 cm³) equipped with cam rotors, at a 50 rpm rotor speed, and a 175°C set temperature. The reaction time was 10 min. EVA was mixed with MAH before adding DCP to inhibit pre-crosslinking of EVA. PBT and EVA-g-MAH were dried before blending at 75°C for 15 h. PBT/crosslinked EVA (80 : 20 w/w) (without MAH) and PBT/EVA-g-MAH (80 : 20 w/w) blends were prepared using the plasticorder at 50 rpm rotor speed, 230°C set temperature, and 10 min reaction time. The blend composition was fixed at 80 wt % of PBT.

Measurements

The functionalized EVA samples were purified to determine the grafting amounts of MAH by dissolving them in boiling xylene, and then by precipitating them in acetone. The unreacted monomer and homopolymer of MAH were dissolved in acetone. The precipitate obtained was washed several times with acetone and dried in a vacuum oven until a constant weight was obtained. The grafting yield of MAH was determined by an elemental analyzer (Carlo Erba, EA1108)

from measuring the oxygen content of MAH grafted onto EVA. The relations are as follows:

$$[O]_{total} - [O]_{EVA} = [O]_{grafted\ MAH}$$

$$[O]_{grafted\ MAH} \times [(C + H)/O]_{MAH} = [C + H]_{grafted\ MAH}$$

$$[O]_{grafted\ MAH} + [C + H]_{grafted\ MAH} = [MAH]_{EVA-g-MAH}$$
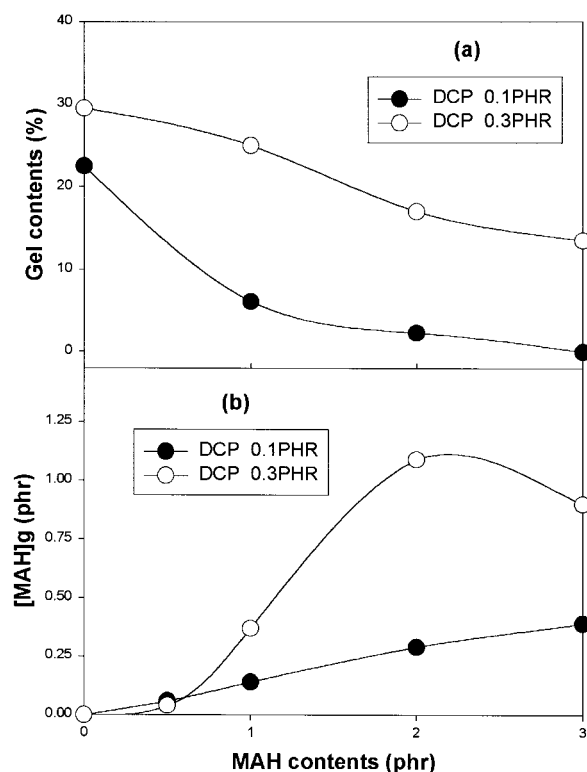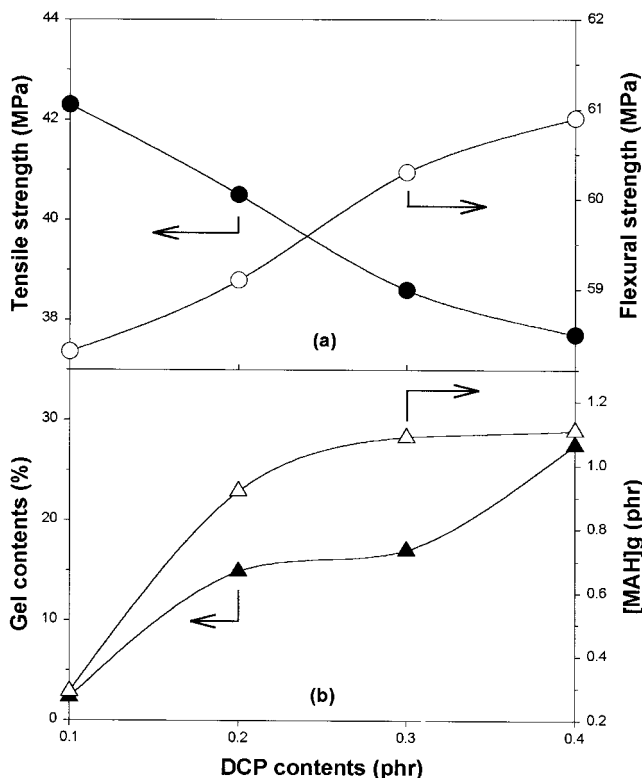

Figure 1 Variation of (a) gel content (%) of EVA and (b) grafting yield with MAH contents (phr) at two different DCP contents (0.1 and 0.3 phr).

Figure 2 Variation of (a) tensile and flexural strength and (b) gel content (%) and grafting yield of PBT–EVA-g-MAH blends (80/20) with DCP content (MAH: 2.0 phr).

The blended samples were compression molded into a sheet of 2 mm thickness for further studies. The tensile and flexural properties were measured with a universal test machine (Hounsfield HL25) at room temperature, according to ASTM D638 and ASTM D790, respectively. Crosshead speeds of 5 mm/min for tensile properties and 1 mm/min for flexural properties were used in measurements. Morphologies of the cryogenically fractured surfaces of the specimens were coated with gold and subjected to SEM study. The crosslinked parts of EVA extracted from boiling xylene for 12 h were dried in a vacuum oven at 60°C, according to ASTM D2765-68 (Method A). These were weighed to estimate gel contents. Table I summarizes the grafting yields and the gel contents determined in this way.

RESULTS AND DISCUSSION

### Effects of MAH and DCP concentration on grafting yield and gel content

The grafting yields of MAH and the gel contents of crosslinked EVA as functions of the initial concentrations of MAH are illustrated in Figure 1. As the concentration of MAH was increased from 0.5 phr to 3.0 phr, the gel contents were decreased regardless of DCP contents (0.1 or 0.3 phr). Upon increasing the

MAH concentration, however, the grafting yield of MAH was gradually increased when the DCP content was 0.1 phr. However, when the DCP content was 0.3 phr, the grafting yield of MAH increased, showed a maximum around 2 wt % MAH content, and then decreased. The grafting yield, like the gel content, was higher when the DCP content was higher.

Ghosh et al.,[12] in their study of the modification of low density polyethylene (LDPE) by graft copolymerization with some acrylic monomers, reported 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 the monomer and the dose levels of the monomer and DCP used for grafting. Vainio et al.[13] also reported the effect of the initial concentration of peroxide and ricinoloxazoline maleinate (OXA) on the grafting yield. They showed that when the initial concentration of peroxide and OXA was increased, the grafting yield of OXA onto PP increased appreciably.[13]

In our previous work, we proposed possible reaction mechanisms for the shearing of the molten EVA in the presence of DCP and MAH at 175°C in plasticorder.[11] It was suggested that crosslinking, either by mutual termination of the grafted-propagating chains or by EVA macroradicals, is the termination step of
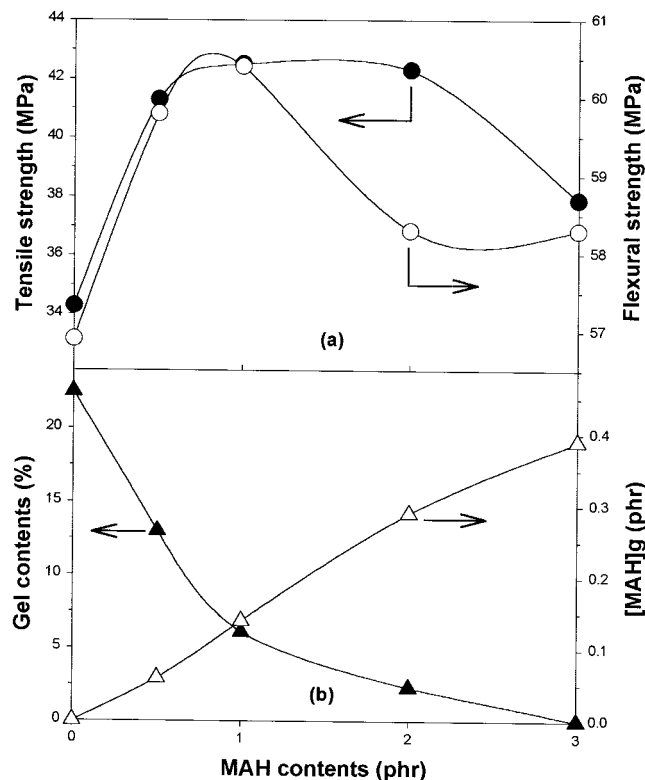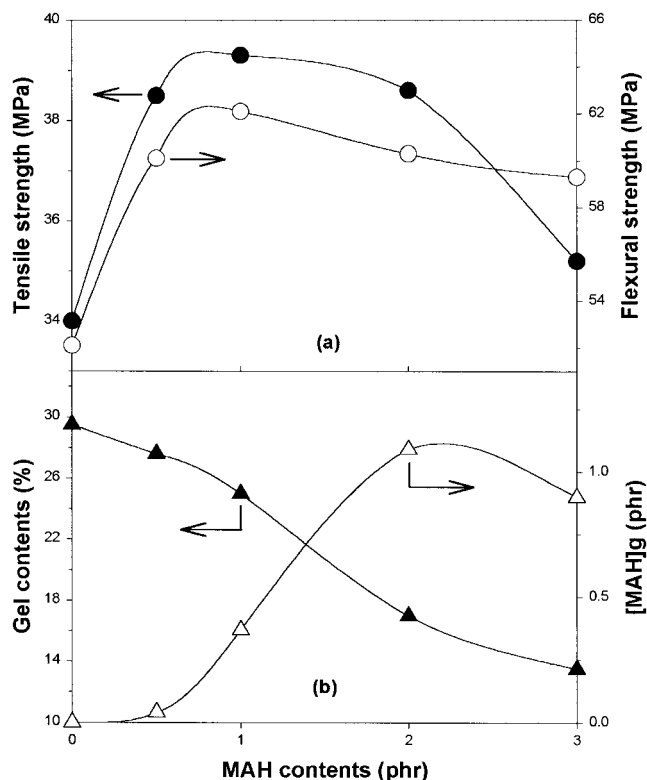

Figure 3 Variation of (a) tensile and flexural strength and (b) gel content (%) and grafting yield of PBT–EVA-g-MAH blends (80/20) with MAH content (DCP: 0.1 phr).

the reaction. This step would occur after the addition of MAH to the primary radical of peroxide, or when the EVA macroradical formed by transfer reactions of the peroxide radical to EVA. The compatibilization of PBT and EVA can occur by 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, or by intermolecular dipole-dipole interaction between the carbonyl oxygen in the MAH of the EVA-g-MAH and the hydrogen in the hydroxyl group of PBT. Based on this mechanism of the grafting of MAH and the crosslinking of EVA by DCP, the decrease of gel content of EVA as a function of MAH under a constant DCP content suggests the increase of the grafting yield, since the degree of crosslinking and its grafting yield are determined by the concentration of MAH and the kinetics of the addition of MAH to the EVA macroradical and the mutual termination of the grafted-propagating chains or EVA macroradicals. When EVA-g-MAH is blended with PBT, the morphological and mechanical properties of the blends are influenced by either the grafting yield or the degree of crosslinking of EVA. This will be discussed in detail below.

Correlations among degree of crosslinking, grafting yield, and mechanical properties

This section discusses the ways in which the gel contents and the grafting yield of EVA-g-MAH affect the tensile and flexural strength of PBT–EVA-g-MAH blends. Figure 2 shows that the gel content and the grafting yield increase with increasing DCP content. In this case, the MAH content was fixed at 2.0 phr. In Figure 2, the tensile strength decreased and the flexural strength increased with the increase of the gel contents and the grafting yield. Mechanical properties of crosslinked polymeric materials are usually improved with an increase in the degree of crosslinking. Thus, it is the flexural strength of the PBT–EVA-g-MAH blend are apparently influenced by the crosslinked components of EVA-g-MAH, although the tensile strengths are not. This implies that tensile and flexural properties are achieved through different response mechanisms to a given stress. The flexural strength depends on both the grafting yield of MAH and the degree of crosslinking of EVA, while the tensile strength is hindered rather than improved by the crosslinking of EVA-g-MAH, in spite of the increase in the grafting yield of MAH. This may be due either to the increased interfacial concentration of EVA-g-MAH or to the restriction of molecular motion by crosslinked EVA.

Figure 3 shows the variation of tensile and flexural strength with the grafting yield and gel content of PBT–EVA-g-MAH blends with 0.1 phr DCP content. The gel content, a measure of the degree of crosslink-


Figure 4 Variation of (a) tensile and flexural strength and (b) gel content (%) and grafting yield of PBT–EVA-g-MAH blends (80/20) with MAH contents (DCP: 0.3 phr).

ing of EVA-g-MAH, was gradually decreased with increasing MAH content. Again the tensile strength and the flexural strength showed an initial increase up to 2.0 phr and 0.1 phr MAH contents, respectively, but thereafter these decreased, in spite of a steady increase of the grafting yield of MAH. These results may be attributed to the possibility of some optimum concentration of PBT-g-EVA copolymer formed by the in-situ reaction between MAH grafted onto EVA and the hydroxyl and/or carboxyl groups at the end of PBT around a certain MAH content. Although the concentration of MAH grafting onto EVA increases, the compatibility of PBT-g-EVA might always be limited because of the concentration of the end groups of PBT. Figure 4 shows trends similar to those shown in Figure 3. The grafting yield of MAH and the degree of crosslinking (gel content) at 2.0 phr MAH loading are greater at 0.3 phr DCP content (Fig. 4) than those at 0.1 phr DCP content (Fig. 3).

It should be noted from Figures 3 and 4 that the mechanical properties of the PBT–EVA-g-MAH blends are higher than those of PBT–crosslinked EVA blends without MAH, regardless of DCP and MAH contents.

Morphology

In our previous work,[11] we showed by SEM micrographs that when the DCP content was higher in the
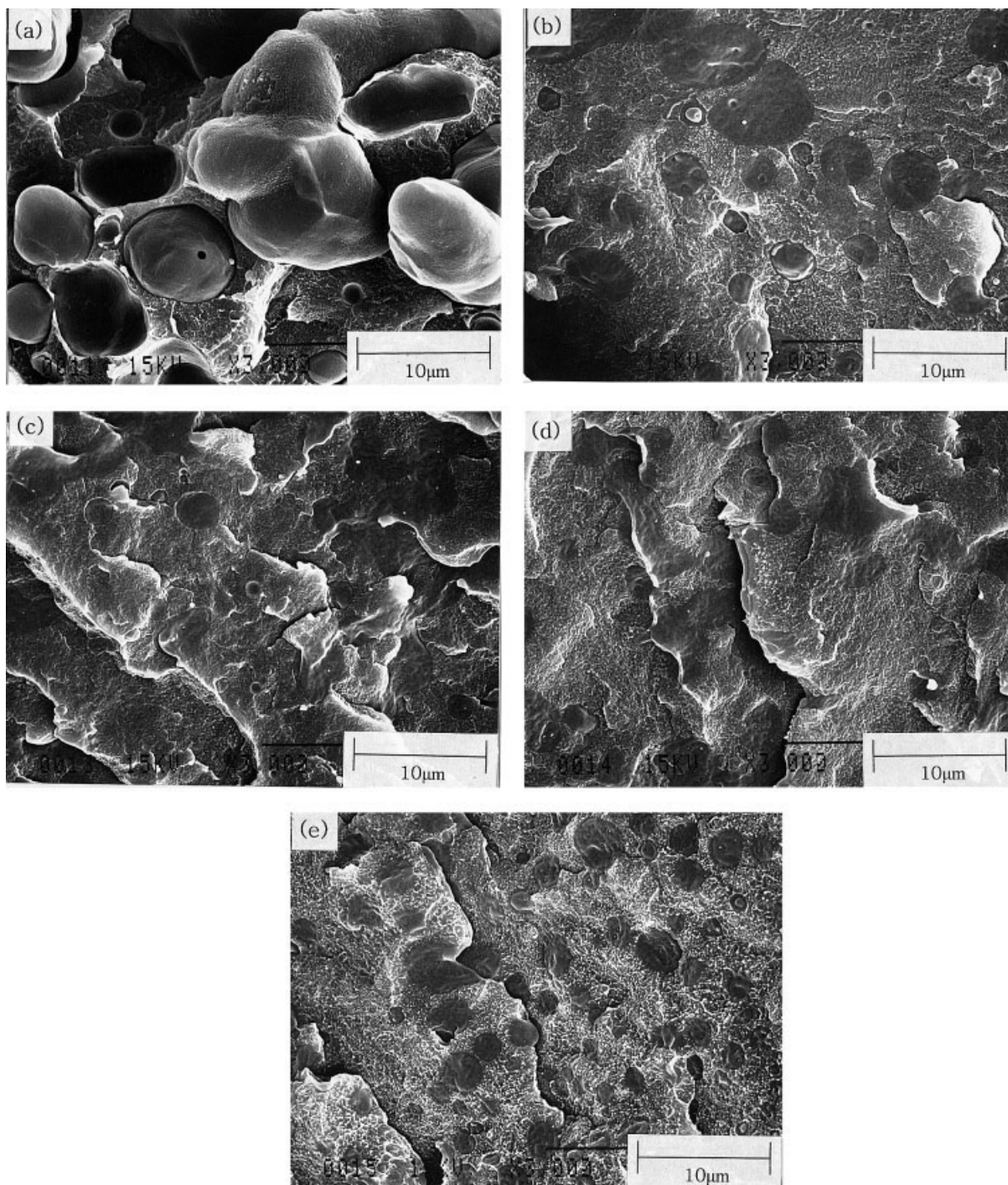
Figure 5 SEM micrographs of fractured surface of PBT–EVA-g-MAH blends (80/20) with 0.1 phr DCP with different MAH contents: (a) 0 phr, (b) 0.5 phr, (c) 1.0 phr, (d) 2.0 phr, (e) 3.0 phr.

absence of MAH, the morphology of the blend was governed by the crosslinking of EVA by DCP, and thus no clear compatibilization effect was observed. The reactive compatibilization in the morphological sense was clearly observed when MAH was used in the presence of DCP. It was observed that the particle size of the dispersed phase (i.e. EVA-g-MAH) was reduced in PBT–EVA-g-MAH blends. It is quite inter-

esting to note, however, that the particle size was not much changed with DCP contents, even though more effective compatibilization was observed due to higher reactivity, with the same MAH content. The reason the control of morphology with particle size smaller than a certain value (i.e. around 1.68 μm) by the DCP and MAH was not possible was not explained clearly due to lack of sufficient data.[11]

Figure 5 shows typical SEM micrographs of fractured surfaces of blends of PBT with EVA-g-MAH by 0.1 phr of DCP, with varying MAH content. Considering the observation of the previous article and of Figure 5 of the present article, we attempted to further establish a quantitative relationship between optimum MAH contents in the presence of DCP and the morphology (particle size) in the reactive compatibilization of polymer blends. In our previous work, the particle size of crosslinked EVA dispersed in PBT was approximately 8–16μm.[11] A poor interfacial adhesion was found with traces that the dispersed phase was pulled out, whereas the morphology of PBT–EVA-g-MAH blends with various contents of MAH show good interfacial adhesion with a smaller particle size of 1–7μm. As MAH concentration was increased, however, the particle size of EVA-g-MAH was not changed much once they became smaller than around 1.68 μm. On increasing the concentration of MAH and DCP, the morphological properties of PBT–EVA-g-MAH blends never showed a remarkable difference in domain size and interfacial adhesion.[14–16]

The above observation suggests that the result is certainly related to the inverse relationship between increased grafting yield and decreased gel contents with increasing the MAH content, regardless of DCP content. It is reasonable to suspect that the reactive compatibilization by the formation of in-situ grafting of PBT with EVA-g-MAH takes place competitively and simultaneously with the crosslinking of EVA and the grafting of MAH onto EVA. It may be considered that the maximum compatibilization of the PBT-g-MAH-EVA take place at a certain MAH content, thus producing the best mechanical properties, as already shown in Figures 3 and 4. To the best of our knowledge, this is the first report to reveal a quantitative relationship between the optimum MAH content in the presence of DCP for optimum properties and the morphology of the reactive compatibilization of polymer blends.

CONCLUSIONS

This article has described the correlations among the gel contents of crosslinked EVA, the grafting yield of EVA-g-MAH, and the mechanical properties of the blends of PBT with EVA-g-MAH. As the concentration of MAH was increased from 0.5 phr to 3.0 phr, the gel content was decreased regardless of DCP content (0.1 or 0.3 phr). On increasing the MAH concentration,

however, the grafting yield of MAH was gradually increased when the DCP content was 0.1 phr. However, when the DCP content was 0.3 phr, the grafting yield increased only to a maximum of around 2 wt % MAH content, and thereafter went down. It was also found that the grafting yield and the gel content were higher at higher DCP content. The tensile strength decreased but flexural strength increased with the increasing gel contents and grafting yield. The mechanical properties of crosslinked polymeric materials are usually improved with the degree of crosslinking. As a result it was noticed that the flexural strength of the PBT–EVA-g-MAH blend is apparently influenced by the crosslinked components of EVA-g-MAH, while the tensile strength is not.

Reactive compatibilization by the formation of in-situ grafting of PBT with EVA-g-MAH takes place competitively and simultaneously with the crosslinking of EVA and the grafting of MAH onto EVA. It was considered that the maximum formation of the PBT-g-MAH-EVA take place at a certain MAH content, producing the best reactive compatibilization in the PBT–EVA-g-MAH blend and thus the highest mechanical properties.

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