Journal of Elastomers and Plastics

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What is This?

Thermoplastic elastomer by reactive blending of poly(butylene succinate) with ethylene-propylene-diene terpolymer and ethylene-1-butene rubbers

Kittisak Jantanasakulwong, David Rohindra, Keisuke Mori, Keiichi Kuboyama and Toshiaki Ougizawa

Abstract

Poly(butylene succinate) (PBS) was melt blended with maleic anhydride–grafted ethylene-propylene-diene terpolymer (EPDM-MAH) and maleic anhydride–grafted ethylene-1-butene copolymer (EB-MAH) to obtain thermoplastic elastomers (TPEs) containing a biodegradable polyester. PBS/EB-MAH blend showed lower modulus and excellent strain recovery compared to PBS/EPDM-MAH blend due to the smaller rubber particle size. Tensile strength of PBS/EPDM-MAH blend was found to be significantly improved by annealing because of the increased interfacial reaction between PBS matrix phase and EPDM dispersed phase and the increased cross-linking in EPDM. As the result, it was found that the annealing process is effective for the improvement of the mechanical properties of PBS/MAH-grafted rubber blends.

Keywords

Thermoplastic elastomer, poly(butylene succinate), reactive blending, maleic anhydride, ethylene-propylene-diene terpolymer, ethylene-1-butene

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Introduction

Recently, thermoplastic elastomers (TPEs) have attracted much attention because of its ease in melt processing and the advantage of reprocessability of used products. TPEs exhibit both the processing characteristics of thermoplastics and the elastomeric properties like thermoset rubbers and have been replacing vulcanized rubbers in some applications. Because of its ease in reprocessing, TPEs are regarded as environmentally friendly materials compared to the vulcanized rubbers.

Thermoplastic vulcanizates (TPVs) consisting of cross-linked rubber particles dispersed in thermoplastic matrix are also reprocessable. To improve the compatibility between the rubber and the thermoplastic through interfacial reactions and to induce the cross-linking of the rubber, some chemicals have been added to the blend during melt mixing. Dicumyl peroxide[1–3] have been used as initiator, dibutyl tin oxide[4] and dibutyltin dilaurate[5] as catalyst for transesterification, N, N'-m-phenylene-bis-maleimide[6] as coupling agent, and hexamethylenediamine carbamate,[7,8] phenolic resin[9] and tin chloride[9] as cross-linking agent in the rubber phase. However, these chemicals sometimes lead to cross-linking in the thermoplastic matrix phase. To avoid the cross-linking of the thermoplastic matrix phase, a rubber material grafted with an organic compound that can react with the thermoplastic matrix phase has been used to induce the interfacial reaction. Glycidyl methacrylate,[10] allyl(3-isocyanate-4-tolyl),[10] and maleic anhydride (MAH)[11–13] are some examples of the grafted organic compounds on rubbers. Generally, MAH is grafted on to a rubber in molten state at high temperature.[14] However, MAH has low reactivity and then it is difficult to generate free radicals on MAH.[14–16] Alternatively, MAH can also be grafted onto a rubber by dissolving the rubber and MAH in a solvent with the addition of peroxide for generating active sites.[12,13] Furthermore, many rubbers have also been grafted with MAH such as ethylene-propylene-diene terpolymer (EPDM),[17] ethylene-propylene rubber,[18,19] and natural rubber.[20,21] As for MAH, it has also been grafted onto various copolymers[18–27] and thermoplastic materials such as ethylene vinyl-acetate copolymer,[22] polyethylene,[28,29] and polypropylene.[23,30] The polymer blending with MAH-grafted copolymer have been studied by many researchers.[11,13,18,20,28,30]

As a thermoplastic matrix polymer, a biodegradable or a bio-based polymer, which is produced from renewable sources, is a promising candidate for an environmentally friendly material. Therefore, TPVs prepared by a biodegradable polymer can combine advantages of reprocessability and environmental friendliness of the matrix phase. Nevertheless, not many studies have been reported on TPVs using biodegradable polymers.[1,31,32] Among the several biodegradable or bio-based polymers, poly(L-lactic acid) and polycaprolactone have been used to develop new TPVs. However, TPVs consisting of biodegradable polymers with excellent properties have not been achieved so far. Poly(butylene succinate) (PBS) is a biodegradable polymer and its mechanical properties are similar to polypropylene.[33] Although PBS has been produced from petroleum-based 1,4-butanediol and petroleum-based succinic acid, truly bio-based PBS has also been developed and will be soon available from bio-based renewable resources.[34,35] Therefore, PBS will be a suitable material as a thermoplastic matrix polymer for TPV.

In this article, new TPV and TPE were developed by melt-blending of PBS with maleic anhydride–grafted EPDM (EPDM-MAH) and maleic anhydride grafted ethylene-1-butene copolymer (EB-MAH). Their morphology and properties were investigated. To the best of our knowledge, this is the first attempt on the reactive blending of PBS with rubbers having excellent mechanical properties.

Experimental

Materials

PBS with a trade name of Bionolle was kindly provided by Showa HighPolymer Co., Ltd., of which the melting point is 115°C and the melt flow index is 3.7 g/10 min at 190°C. EPDM-MAH (MAH content = 1 wt%, ethylidene norbornene (ENB) content = 8.1 wt% and ethylene content = 52 wt%) was kindly supplied by Mitsubishi Chemical Corp., Japan. and maleic anhydride–grafted EB-MAH (MAH content = 1 wt% and 1-butene content = 20 wt%) was supplied by Mitsui Chemicals Inc., Japan. The chemical structures of EPDM-MAH and EB-MAH are presented in Figure 1(a) and (b), respectively.

Sample preparation

PBS was blended with one of the two kinds of rubbers, EPDM-MAH and EB-MAH, by melt mixing in compositions of 40/60 at 160°C. The sample was mixed at the rotation speed of 100 rpm for 10 min using a mini max molder (Model CS-183MM-065; Custom Scientific Instruments Inc., USA.).

Measurements

Phase determination. The blended samples (0.01 g) were immersed in 1 ml of toluene at room temperature for at least 24 h. Toluene is a good solvent for EPDM and EB rubbers, while not for PBS. The components of matrix and the dispersed phase were checked from the residual component.

Measurement of tensile properties. The dumbbell-shaped samples for the tensile test were prepared by compression molding at 170°C for 3 min. The gage length, width, and thickness of the sample were 10, 2, and 0.5 mm, respectively. Tensile properties of the blends were measured using tensile tester (Tensilon UTM-II-20; Orientec Co., Ltd, Japan.) at room temperature with a crosshead speed of 10 mm/min. The strain recovery test was also performed. After the preset strain of 100% was attained, the crosshead was returned to the original position at the same speed.

Scanning electron microscopy (SEM). SEM (SM-200; Topcon Corp, Japan.) was used to investigate the morphology of the blends. The samples were broken in liquid nitrogen, then the fracture surface of the samples was sputter-coated with gold and scanned with an acceleration voltage of 10 kV.
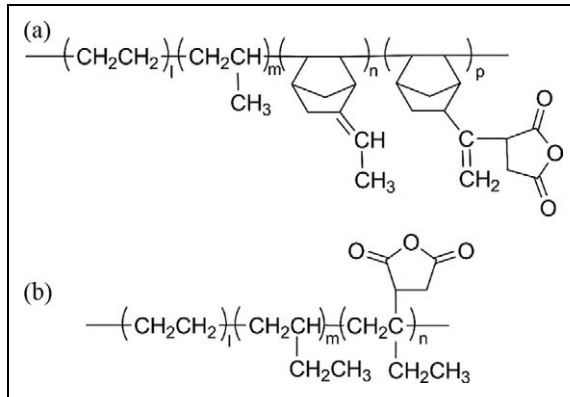
Figure 1. Chemical structures of (a) EPDM-MAH and (b) EB-MAH. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer.

Differential scanning calorimetry (DSC). Thermal behaviors of PBS, rubbers, and blended samples were measured by DSC (DSC6200; Seiko instruments Inc, Japan.). A sample was heated in an aluminum pan from -100 to $150°C$ under nitrogen gas flow at a heating rate of $10°C/min$.

Fourier transform infrared spectroscopy (FTIR). The interfacial reaction between PBS and MAH-grafted rubber was measured by FTIR (FT/IR-480plus; Jasco Corp, Japan.). Films of samples were prepared by hot press molding at $170°C$. The IR spectra were recorded in the range of 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Degree of cross-link measurement. The samples (0.5 g) covered by nickel net were dissolved in chloroform at $25°C$ for 24 h and then the residual samples in the nickel net were dried at $60°C$ for 24 h in order to remove the solvent. The gel percentage was calculated by Eq. 1.

$$Gel(\%) = \frac{W_d - W_n}{W_o} \times 100 \qquad (1)$$

Where W_d, W_n, and W_o are the weight of the dried sample with nickel net after dissolution, the weight of the nickel net, and the initial weight of the sample, respectively.

Results and discussion

Phase determination

The TPV obtained by polymer blending, the matrix phase of the blend should be a thermoplastic polymer, and the component of the matrix phase was checked by dissolving the blend into a solvent. Figure 2 shows a picture of the immersed
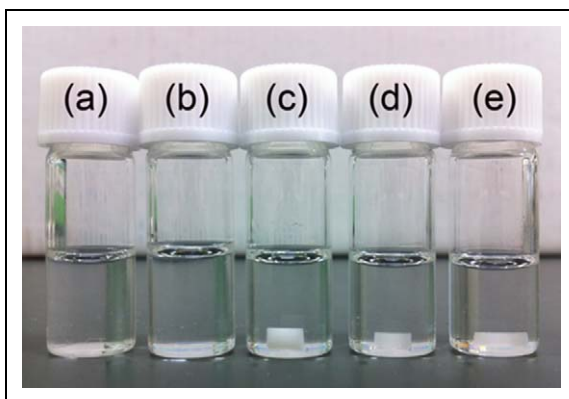
Figure 2. Picture of (a) EPDM-MAH, (b) EB-MAH, (c) PBS, (d) PBS/EPDM-MAH, and (e) PBS/EB-MAH blends immersed into toluene at 25°C for 24 h. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate).

rubbers, PBS, and the blended samples in toluene for 24 h. EPDM-MAH and EB-MAH completely dissolved into toluene (Figure 2(a) and (b)), while PBS was insoluble (Figure 2(c)). Both the PBS/EPDM-MAH and PBS/EB-MAH blends were also insoluble in toluene, and the shape of the samples did not change (Figure 2(d) and (e)). If the matrix is rubber, then the uncross-linked rubber matrix gets dissolved or the cross-linked rubber becomes swollen to form a gel in toluene. These behaviors were not observed in both blends. Moreover, it was also confirmed that the sample was reprocessable by melting. From the facts, it was suggested that the blend did not consist of cross-linked rubber matrix but of PBS matrix phase. The result shown in Figure 2 (a)-(e) indicated that the morphology of these blends probably is co-continuous or sea-island structure with rubber dispersed phase and PBS matrix phase.

Morphology

The PBS/EB-MAH and PBS/EPDM-MAH blends showed finer morphology, while the PBS/EB and PBS/EPDM blends without MAH showed larger dispersed phase, which was recognized by the visual inspection. Figure 3 shows the SEM fracture surface images of PBS/EPDM-MAH and PBS/EB-MAH blends. The images of both blends showed the sea-island phase separated structures. Considering the result of the phase determination experiment, it was confirmed that in both blends the rubber particles were dispersed in PBS matrix. The EB-MAH rubber particle was much smaller than EPDM-MAH. It was suggested that the EB-MAH was more compatible with PBS than EPDM-MAH. The holes observed in the EPDM-MAH blend were due to the removal of some rubber particles from the fracture surface during
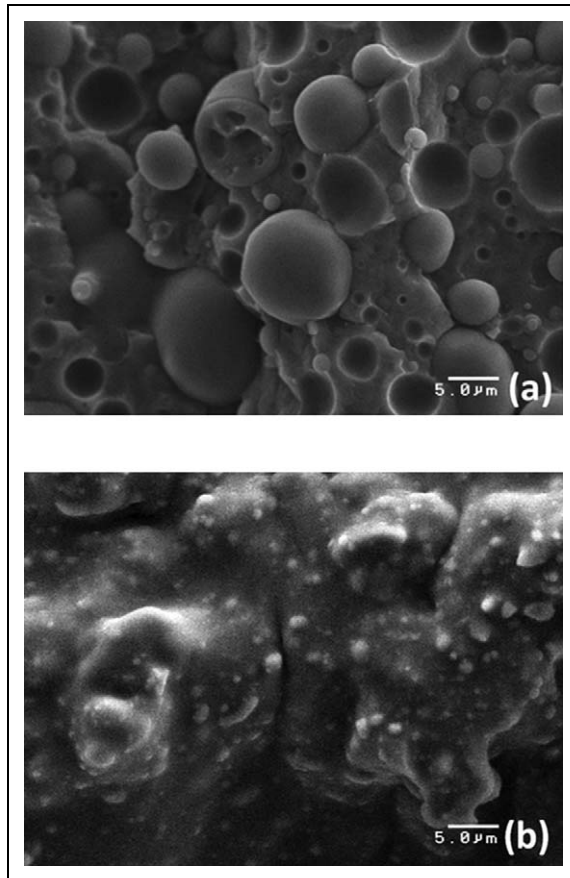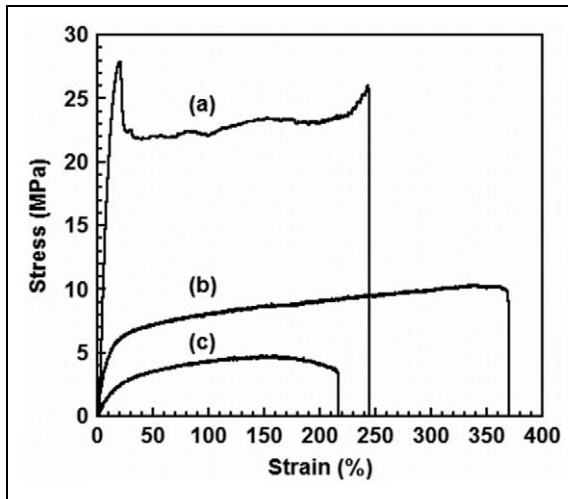
Figure 3. SEM images of fracture surface of (a) PBS/EPDM-MAH and (b) PBS/EB-MAH blends. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate); SEM: scanning electron microscope.

cracking. It might be attributed to low interfacial adhesion between the PBS matrix and the rubber dispersed phase.

Mechanical properties

Figure 4 shows the stress–strain curves of PBS, PBS/EPDM-MAH, and PBS/EB-MAH blends. PBS showed high modulus, tensile strength, and elongation at break, while PBS blended with EPDM-MAH and EB-MAH showed lower modulus and tensile strength than PBS, respectively. Figure 5 shows the strain recovery curves of PBS, PBS/EPDM-MAH, and PBS/EB-MAH blends. The PBS/EPDM-MAH and PBS/EB-MAH blends showed more superior strain recovery ($\sim 40\%$ and $\sim 70\%$, respectively) than PBS ($\sim 20\%$).

Figure 4. Stress–strain curves of (a) PBS, (b) PBS/EPDM-MAH, and (c) PBS/EB-MAH blends. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate).
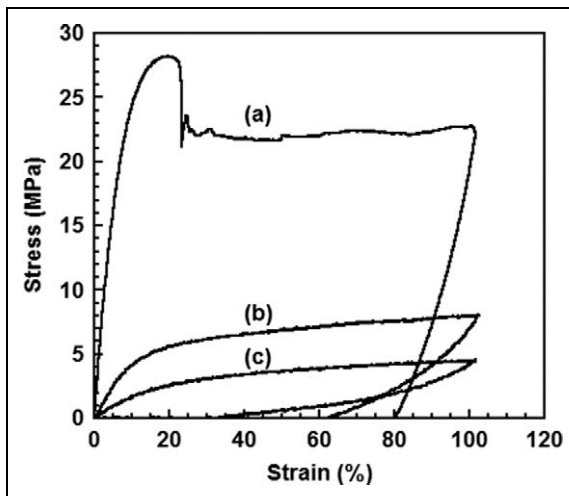
Figure 5. Strain recovery curves for (a) PBS, (b) PBS/EPDM-MAH, and (c) PBS/EB-MAH blends. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate).

Influence of annealing on mechanical properties

From the SEM images shown in Figure 3, the removal of rubber particles was observed, and this indicates the low interfacial adhesion between thermoplastic matrix phase and rubber dispersed phase. It was expected that annealing process at high temperature would increase the interfacial adhesion. However, the higher annealing temperature than 170°C may induce thermal decomposition of PBS. Therefore, the blends were annealed at 170°C for 0, 10, 30 and 60 min to improve the interfacial adhesion where the interfacial reaction was expected to proceed, and mechanical properties were analyzed by tensile test. Figure 6 shows the stress–strain curves of annealed PBS/EPDM-MAH and PBS/EB-MAH blends of different annealing times. The PBS/EB-MAH blend showed lower tensile strength, elongation at break, and modulus than the PBS/EPDM-MAH blend. Tensile strength and elongation at break of both blends increased with increasing annealing time, and tensile strength extremely increased in the PBS/EPDM-MAH. The annealing effect on strain recovery of PBS/ EB-MAH and the PBS/EPDM-MAH blends is shown in Figure 7. The PBS/EPDM-MAH and PBS/EB-MAH with annealing showed the improvement in strain recovery of about 10%. The samples after measurement were retained at room temperature for 1 week, and the PBS/EB-MAH sample showed a slow recovery to 90%. Moreover, both the PBS/EPDM-MAH and PBS/EB-MAH blends annealed at 170°C for 60 min were reprocessable by melting. The excellent strain recovery of PBS/EB-MAH blend with annealing was due to the consequence of (i) the better elasticity of EB rubber, (ii) small rubber particle size, and (iii) the increased interfacial adhesion by annealing. The mechanism of elastic recovery in a TPV has been explained by the existence of non-yielded ligament of plastic matrix phase between rubber particles in the stretching direction even at highly deformed states at which almost the matrix is yielded by the stress concentration, and it acts as joint region for interconnecting rubber particles.[36] The interfacial adhesion between the two phases and the decreasing of rubber particles size in TPVs led to more effective stress localization, and then the elastic recovery improved.[37] Therefore, this may also be the reason why the PBS/EB-MAH showed better elastic recovery.

## Annealing effect on interfacial adhesion

In the SEM images of nonannealed PBS/EPDM-MAH and PBS/EB-MAH blends, the rubber particles were observed, and some of the particles were removed from PBS fracture surface as shown in Figure 3(a) and (b). The annealed PBS/EPDM-MAH and PBS/ EB-MAH blends showed smooth fracture surface as shown in Figure 8(a) and (b), and the removing of rubber particles was not observed. The smooth fracture surface indicates that the fracture did not occur at the interface of matrix and dispersed phases by freeze fracture in liquid nitrogen. Such a change in SEM fracture surface image by increasing of the interfacial adhesion has also been reported.[38] From the result, it was suggested that the annealing at 170°C for 60 min improved interfacial adhesion between PBS and EPDM-MAH or EB-MAH rubber.

To check the reaction by the annealing, the reacted component of PBS/EB-MAH and PBS/EPDM-MAH with annealing at 170°C for 60 min was extracted by dissolving in
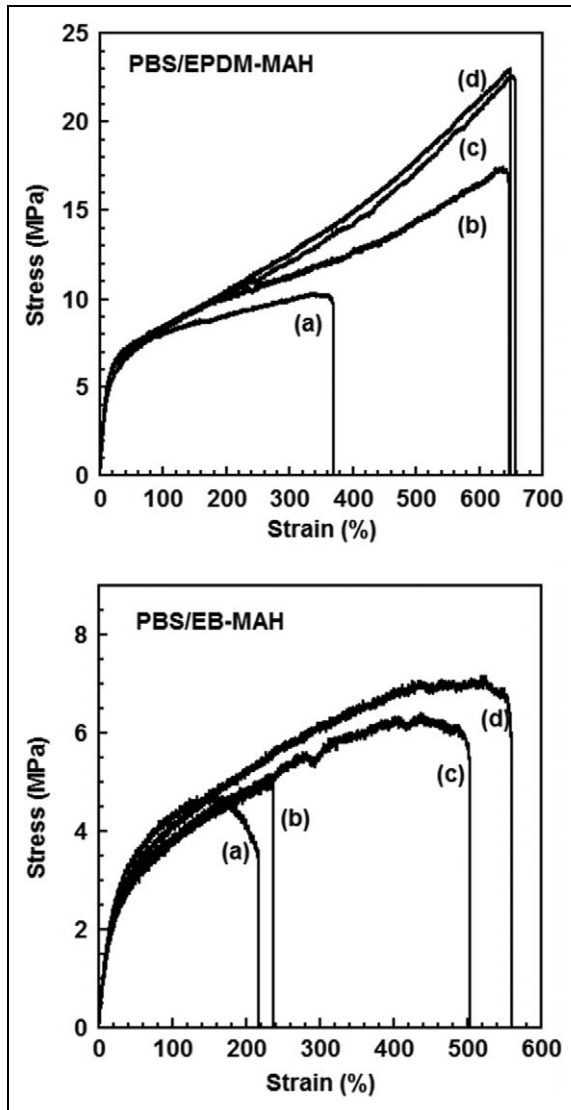
Figure 6. Stress–strain curves of PBS/EPDM-MAH and PBS/EB-MAH blends annealed at 170°C for (a) 0, (b) 10, (C) 30, and (d) 60 min. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate).

chloroform for removing of unreacted PBS and rubbers phase. Although PBS, EPDM, and EB can dissolve in chloroform, insoluble gel fractions remained after the extraction. These residual gel fractions were suggested to be the cross-linked samples, which was
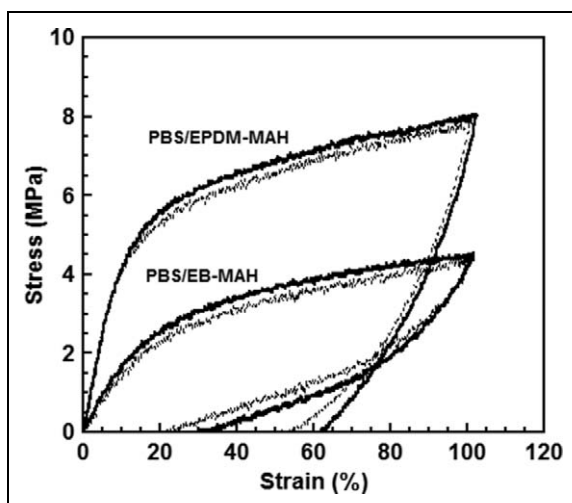
Figure 7. Strain recovery curves for PBS/EPDM-MAH and PBS/EB-MAH blends without annealing (bold line) and with annealing (thin line). EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate).

formed during both the mixing process and the annealing process. Deuri and Bhowmick also found a gel of raw EPDM rubber after extraction by the solvent, and this gel content increased with aging time without any compounding ingredients.[39] It is well known that the rubber without compounding ingredients also forms a cross-link by thermal aging.[39] Figure 9 shows the DSC heating curves of PBS and annealed blend samples of PBS/EPDM-MAH and PBS/EB-MAH. DSC curves of the EPDM and EB rubber showed a broad endothermic peak around 60°C, which corresponded to the melting of crystal in rubbers[40,41] (Figure 9(d)). The DSC heating curves of extracted component of annealed samples (Figure 9(c)) showed similar behavior with that of the blended samples with annealing (Figure 9(b)), which showed both the crystal melting peaks of rubbers and PBS. However, the melting peak intensity of PBS was found to decrease, and it was due to a few amount of crystalline PBS. The result that the residual gel of annealed samples contained both rubber and PBS indicates that the reaction occurred not only in the rubber phase but also at the interface between the PBS matrix phase and the rubber dispersed phase.

Figure 10 shows FTIR spectra of the neat polymers, the blended samples with annealing at 170°C for 60 min and the solvent-extracted annealed samples by chloroform at 25°C for 24 h. The absorption bands at 1,720 cm^{-1} and 1,163 cm^{-1} represented the carbonyl (C=O) and ether groups (C–O–C) of PBS, respectively.[42] In the EPDM-MAH and EB-MAH rubbers, the absorption band of C=O of MAH was located at 1,709 cm–1.[43] The spectra of annealed PBS/EPDM-MAH and PBS/EB-MAH showed the combined absorption bands of PBS and rubbers. Complication in the spectrum arose
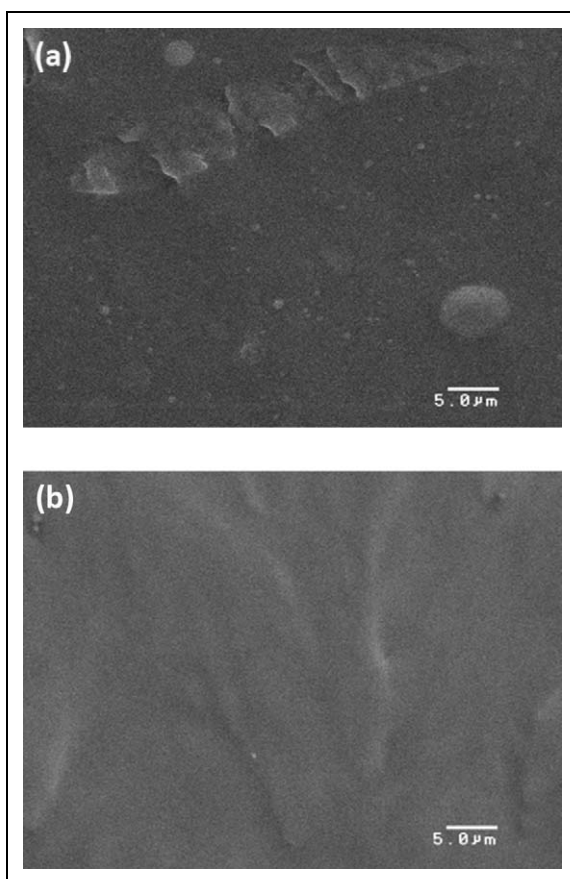
Figure 8. SEM pictures of fracture surface of (a) annealed PBS/EPDM-MAH and (b) annealed PBS/EB-MAH blends at 170°C for 60 min. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate); SEM: scanning electron microscope.

when the carbonyl band in the reactive groups and ether band in PBS overlapped. To overcome this complication, unreacted PBS in the blend was extracted by dissolving in chloroform. It was expected that if no reaction took place between PBS and the rubber, then PBS should be completely removed from the residual rubber, and the FTIR spectrum of the solvent-extracted annealed fractions will have no contribution from PBS. However, the extracted annealed fractions showed two weak absorption bands of C=O and C–O–C of PBS at 1,720 cm^{-1} and 1,163 cm^{-1}, respectively (Figure 10(c)). These bands were found in the extracted annealed fractions of both blends. From these results, it was suggested that PBS molecules were involved in the interfacial reaction, and the result agreed with that of DSC.
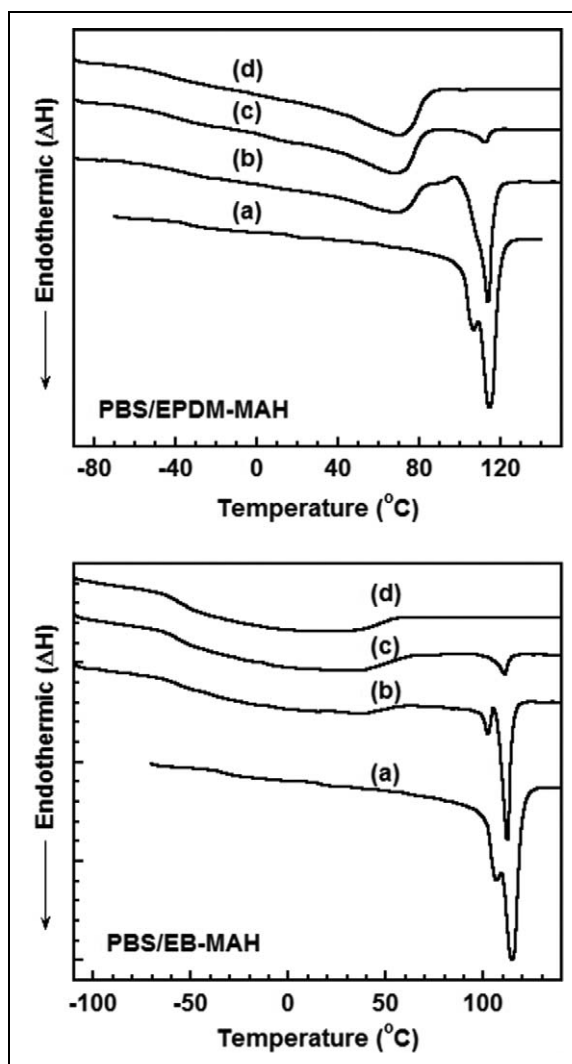
Figure 9. DSC heating curves of (a) neat PBS, (b) blend samples with annealing at 170 °C for 60 min, (c) solvent-extracted fractions of annealed samples, and (d) neat rubbers. DSC: Differential scanning calorimetry; PBS: poly(butylene succinate)

It is known that MAH can react with both hydroxyl group and carboxyl group under suitable condition[44] (the expected chemical reactions are shown in Figure 11), but the reactivity of MAH is low.[14–16] Consequently, the annealing induced the additional reaction between terminal groups of PBS and MAH, and it led to the formation of cross-linking structure at the interface. However, the annealing process may increase not only the interfacial reaction but also the cross-linking inside of the rubber phase.
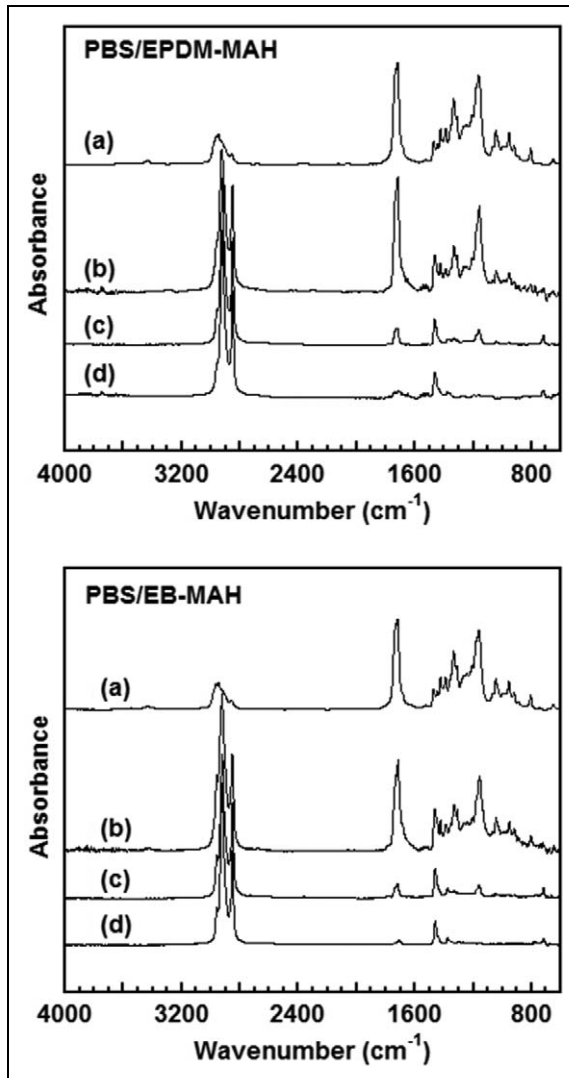
Figure 10. FTIR absorption spectra of (a) neat PBS, (b) blend samples with annealing at 170 °C for 60 min, (c) solvent-extracted fractions of annealed samples and (d) neat rubbers. FTIR: Fourier transform infrared; PBS: poly(butylene succinate).

Influence of annealing on cross-linking

To check the cross-linking in the rubber phase, the degree of cross-linking was determined by dissolving the blends into chloroform at 25°C for 24 h. Cross-linked components were not dissolved in this solvent. Annealing time dependence of the gel content of PBS/EPDM-MAH, EPDM-MAH, PBS/EB-MAH and EB-MAH are presented in
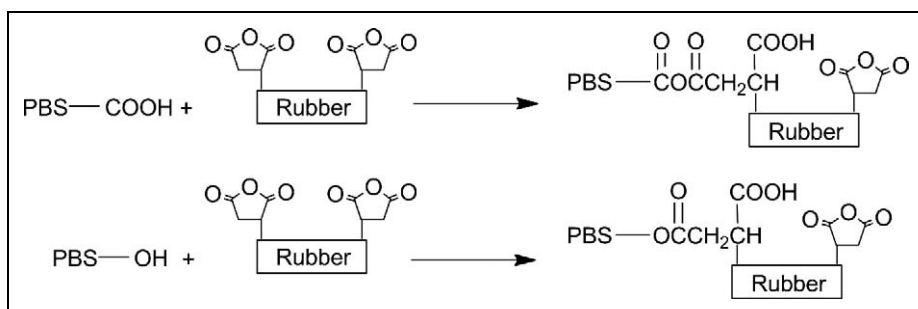
Figure 11. Expected reactions of PBS terminal groups and MAH group of rubber. MAH: maleic anhydride; PBS: poly(butylene succinate).
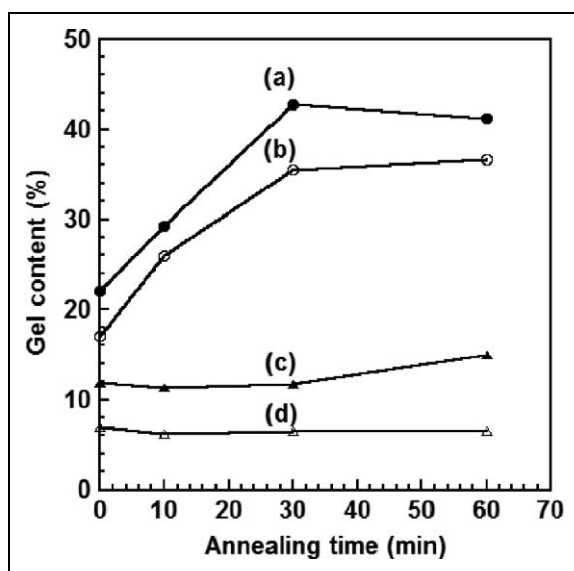
Figure 12. Variation in gel percentages with annealing time at 170°C in (a) PBS/EPDM-MAH, (b) EPDMMAH, (c) PBS/EB-MAH and (d) EB-MAH. EPDM-MAH: maleic anhydride–grafted ethylene-propylene-diene terpolymer; EB-MAH: maleic anhydride–grafted ethylene-1-butene copolymer; PBS: poly(butylene succinate).

Figure 12. PBS/EPDM-MAH blend and EPDM-MAH (Figure 12(a) and (b)) showed that the gel content after dissolving in chloroform increased with the annealing time. The PBS/EB-MAH blend (Figure 12(c)) showed slight increase in gel content, while the EB-MAH (Figure 12(d)) showed almost no change in the annealing time. Formation of interfacial cross-linking between the PBS matrix and the rubber dispersed phase during melt-mixing process was also suggested from the result because both blended samples showed higher amount of gel contents than the rubbers alone even at the

annealing for 0 min. It was suggested that the increased gel content by the annealing was due to the increase in both the cross-linking of rubber and the interfacial reaction between PBS and the rubbers at the interface. EPDM without cross-linking agent has low reactivity to form cross-link, but the reactivity increases by the increasing of aging temperature and time.[39] The higher gel content of the annealed PBS/EPDM-MAH blend than the annealed PBS/EB-MAH blend was attributed to the diene unit in EPDM. EB-MAH rubber was not cross-linked by the annealing at 170°C for 60 min. The slightly increased gel content of annealed PBS/EB-MAH blend suggested the increased interfacial cross-link by the annealing. It was indicated that the increasing of both the cross-linking of rubber and the interfacial cross-link by annealing were the reasons for the improvement of mechanical properties of PBS/MAH-grafted rubber blends.

Conclusions

New TPEs of PBS/EPDM-MAH and PBS/EB-MAH with excellent tensile strength and strain recovery properties were successfully developed by the reactive blending and the annealing. Both blends showed the phase-separated morphology, where the rubber particles were dispersed in the PBS matrix. The mechanical properties of them were improved by the annealing. The annealing process was found to have a twofold effect; it improved the interfacial adhesion through the reaction between the PBS terminal groups and the MAH group of the rubbers and also promoted cross-linking of EPDM rubber. The improved tensile strength of the PBS/EPDM-MAH blend was due to the high cross-linking of interfacial and rubber phase, while the PBS/EB-MAH blend showed the better strain recovery because of the increased interfacial cross-link, the presence of small rubber particle dispersed in the PBS matrix, and the better elasticity of EB rubber.

Funding

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