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Description	

Transfer of a low-molecular-weight compound between two immiscible polymers

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Abstract

We investigated plasticizer transfer between poly(ethylene-*co*-vinyl acetate) (EVA) and poly(lactic acid) (PLA) and its temperature dependence using laminated films comprising EVA and PLA, each containing equal amounts of a plasticizer (i.e., diethyl phthalate (DEP) or dibutyl phthalate (DBP)). Because the miscibility between PLA and DEP is better than that between EVA and DEP, a large amount of DEP was detected in the PLA film after annealing the laminated films at 80°C; i.e., some DEP moved from the EVA film to the PLA film. Furthermore, more DEP migrated to the PLA film at 130°C, suggesting that the difference in the interaction parameter with DEP between PLA and EVA is more pronounced at higher temperatures. In laminated films containing DBP, the DBP content in each film was almost equal after annealing at 80°C, although DBP migrated from the PLA film to the EVA film at 130°C.

Introduction

Polymer blending has developed as the polymer industry has progressed because it is one of the easiest ways of improving several polymer properties. Therefore, a great deal of effort has been put into optimizing various polymer blends.[1-5] Recently, advanced techniques have been proposed using interesting phenomena such as: (1) miscibility change or segregation behavior (concentration gradient) under a temperature gradient[6,7] or velocity gradient, i.e., a flow field;[8,9] (2) orientation correlation between matrix polymer chains and low-molecular-weight compounds dissolved in a polymer;[10-12] and (3) selective localization of a third component in an immiscible blend.[13-18] In the present study, we focused on the selective localization of a third component and its temperature dependence using a plasticizer as the low-molecular-weight compound in an immiscible polymer pair comprising poly(lactic acid) (PLA) and poly(ethylene-*co*-vinyl acetate) (EVA).

Localization and/or migration of a third component between phases has been reported mostly in immiscible rubber blends,[13-15,] and is usually considered to be an unfavorable phenomenon in the rubber industry. For example, the uneven distribution of a curative[14,15] and/or accelerator[13] directly results in a marked cure imbalance between the phases. Such uneven distribution occurs in not only low-molecular-weight compounds but also fillers.[16-18] Recently, Kuhakongkiat et al. proposed a new technique for controlling the temperature-dependent distribution of plasticizers in immiscible blends comprising ethylene-*co*-propylene rubber (EPR) and elastomeric polyisobutylene (PIB).[19] They found that bis(2-ethylhexyl) adipate (DOA), which acts as a plasticizer for both rubbers, localized in the EPR at low temperatures and in the PIB at high temperatures. In other words, the DOA concentration in each rubber phase is dependent on the ambient temperature. Therefore, blends in which EPR is the matrix phase have a low modulus in winter and high modulus in summer. Doan et al. found a similar phenomenon in an immiscible rubber blend containing a tackifier.[20] Such interphase transfer is also expected in damping materials that exhibit large values of loss tangent (*tan* δ) over a wide temperature range, because the plasticizer distribution in phase-separated blends affects the glass transition temperature (T_g) and the dynamic mechanical properties of each phase. We used PLA and EVA in the present study, because the T_g of PLA is slightly higher than room temperature and that of EVA is lower than room temperature. This situation has a capability for the blend to show good damping properties over a wide temperature range near room temperature. Up to now, various studies on PLA/EVA blends have been carried out, especially to improve the mechanical toughness of PLA by the EVA addition.[21-26] Although PLA sometimes shows partial miscibility with EVA,[27] at which the vinyl acetate content in EVA is high, it is basically known as immiscible blends. Therefore, the compatibilization is the key factor for the studies, such as addition of compatibilizer,[24] transesterification,[25] and peroxide modification.[26] However, the application to damping materials has not been studied to the best of our knowledge.

In this study, we applied annealing procedure only beyond the melting point of EVA to avoid the effect of crystallinity and slow diffusion in PLA at low temperature. However, the current experimental results about the effect of annealing temperature on the transfer phenomenon would demonstrate the importance of the concept for the material design.

Moreover, we employed two types of phthalic esters to examine the effect of the plasticizer species on the transfer phenomenon. Since the plasticizers that we used are conventional materials with similar structure but having different solubility parameter, the comparison between the plasticizers will provide the fundamental information on the material design.

Experimental

Materials

The polymers used in the present study were commercially available PLA (Lacea H280, Mitsui Chemicals, Inc., Japan) and EVA (Evaflex EV360, Dupont-Mitsui Polychemicals Co., Ltd., Japan). The PLA comprised 12% D-lactic acid units, and was therefore not crystalline. The number- and weight-average molecular weights of the PLA—evaluated by size-exclusion chromatography as a polystyrene standard—were $M_n = 1.5 \times 10^5$ and $M_w = 2.7 \times 10^5$, respectively. The EVA comprised 25 wt.% vinyl acetate. Its density at room temperature was 950 kg/m^3, its melt flow rate at 190°C was 2 g/10 min, and its melting point was 77°C. The EVA had an $M_n = 6.3 \times 10^4$ and an $M_w = 2.5 \times 10^5$, as determined using a polystyrene standard. The thermal and rheological properties of PLA[28,29] and EVA[30,31] have been described in detail previously.

We used two plasticizers—diethyl phthalate (DEP) and dibutyl phthalate (DBP), both purchased from Daihachi Chemical Industry Co., Ltd., Japan—without further purification. The Hansen solubility parameters of DEP and DBP were reported to be 20.5 and 19.0 (MJ/m^3)$^{0.5}$, respectively.[32] The glass transition temperatures are -90.0 for DEP and -95.5°C for DBP.[33]

Sample preparation

We prepared plasticized EVA and PLA samples using a 30 cc Labo Plastomill 10M100 internal mixer (Toyo Seiki Seisaku-sho, Ltd., Japan) for 3 min at a blade rotation speed of 30 rpm. The mixing temperatures were 180°C for the PLA blends and 130°C for the EVA blends. We vacuum-dried pellets of the PLA blend at 80°C for 4 h prior to melt-mixing to avoid hydrolysis. The plasticizer constituted 5, 10, 15, or 20 parts per hundred of resin (phr). We compressed the obtained mixtures into flat films (0.3-mm-thick) using a compression-molding machine at 130°C under 30 MPa.

The plasticizer transfer experiments were performed using PLA and EVA, both containing 10 phr of a plasticizer (DEB or DBP). As illustrated in Figure 1, the plasticized PLA and EVA films were laminated together. We applied slight manual pressure only to ensure perfect lamination. After the perfect contact of the films, the pressure was removed. The laminated films were then annealed at 80 or 130°C for various periods such as 1, 4, and 9 hours without any pressure, after which both polymers were in the non-crystalline rubbery state. The film thickness hardly changed (no flow) even after 9 hours at 130°C because of the high viscosity at this temperature. To confirm the reversibility of plasticizer transfer, we annealed one set of laminated films at 130°C for 4 h, then further annealed them at 80°C for 4 h. After annealing, we separated the films and stored them at room temperature for 3 days to homogenize the plasticizer distribution in the films prior to characterization. We confirmed that both surfaces provide the same IR spectra.

Furthermore, it should be noted that it is no difficulty for the film separation. This is reasonable because the interfacial thickness of the system is quite thin due to the large difference in the solubility parameter, which is theoretically predictable.[34,35]

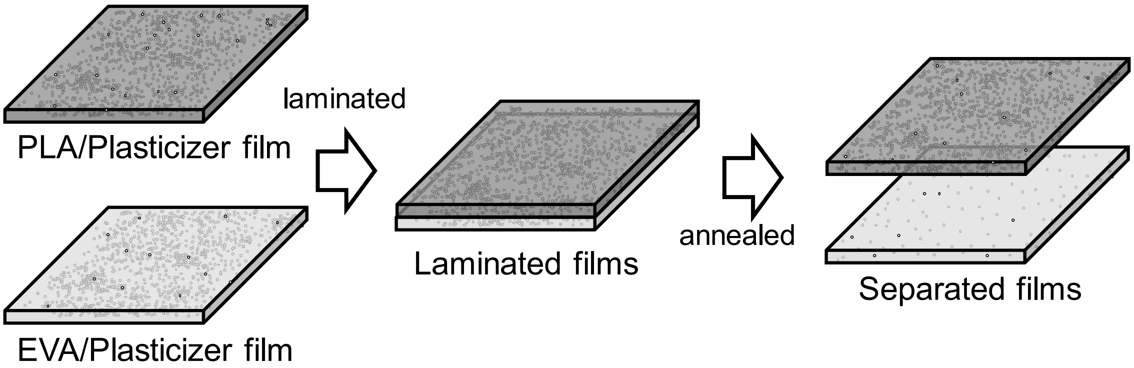

Figure 1 Schematic illustration of the plasticizer transfer experiment.

Measurements

Dynamical mechanical properties

We investigated the dependence on temperature of the tensile storage modulus (E') and the loss tangent ($tan\ \delta$) of rectangular specimens (5-mm-wide; 20-mm-long; 0.3-mm-thick) using a Rheogel E4000-DVE dynamic mechanical analyzer (UBM Co., Ltd., Japan) in the temperature ranges 0–100°C for the PLA and plasticized PLA films, and −80–40°C for the EVA and plasticized EVA films. The heating rate was 2°C/min, and the applied frequency was 10 Hz. The peak temperature in the $tan\ \delta$ curve was taken to be the T_g.

Fourier-transform infrared (FTIR) spectroscopy

The attenuated total reflection (ATR) infrared spectra were collected using a Spectrum 100 FT-IR instrument (PerkinElmer Inc., MA, USA) with KRS-5 as an ATR plate. The intensity of a characteristic absorbance peak at 1123 $\mathrm{cm^{-1}}$ was used to determine the plasticizer content of the EVA films; a calibration curve was constructed from EVA films containing various amounts of the plasticizer for this purpose.

Results and Discussion

Characteristics of polymers containing plasticizer

Prior to evaluation of the transfer phenomenon, we examined the effect of the plasticizer on the dynamic mechanical properties of a film made from each polymer. Figure 2 shows the temperature dependence of the tensile storage modulus (E') and loss tangent ($\tan \delta$) at 10 Hz of the pure polymers and the polymers with 5 or 10 phr of DEP. The peak temperature of $\tan \delta$ in the glass-to-rubber transition region—i.e., T_g—decreased following the addition of DEP, for both PLA and EVA. The plasticization phenomenon by DEP was already reported elsewhere.[36,37] The peak width was hardly affected by the addition of DEP for both systems, suggesting a narrow relaxation time distribution, i.e., good miscibility. In the case of the EVA blends, however, the peak was broad even for pure EVA. This broad relaxation mode is ascribed to various amorphous chains having different mobilities, such as floating chain, cilia chain, loop chain, and tie chain, as reported previously,[38-41] although the crystallinity of the EVA is not so high (ca. 15 %, calculated from the heat of fusion evaluated by the DSC measurement[30]). Moreover, we found that E' in the glassy region was enhanced by the addition of DEP; i.e., DEP acted as an antiplasticizer in the glassy region (the numeric data are shown in Table 1), although it showed plasticizing effect around at T_g. This may be important because antiplasticized systems have reduced thermal expansion.[42] The E' in the glassy region in the PLA system decreased by the addition of 10 phr of DEP, which is a typical behavior for a plasticized polymer.[43,44] However, the small addition, 5 phr, of DEP seems to enhance the modulus slightly.

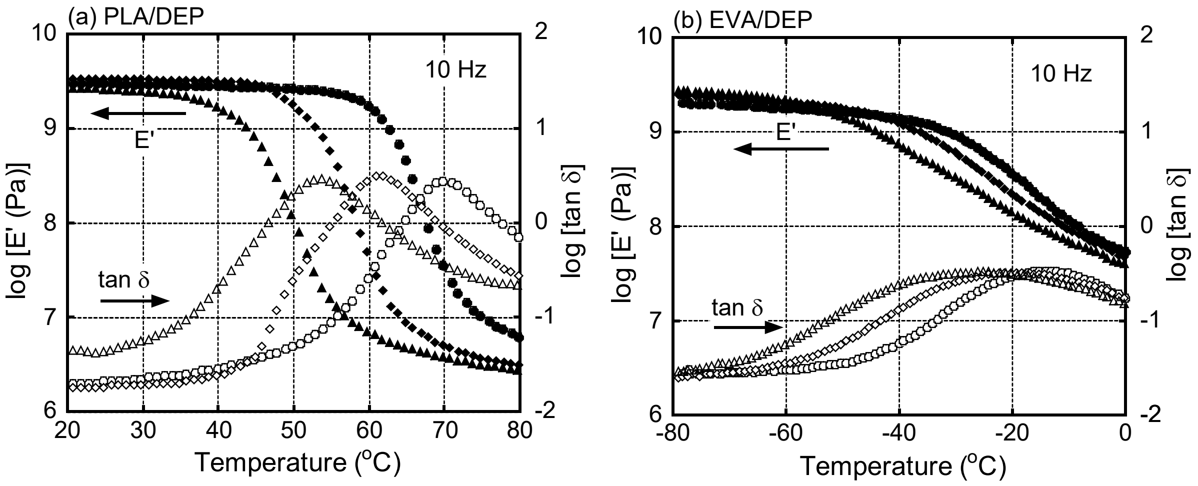

Figure 2 Temperature dependence of tensile storage modulus (E') and loss tangent (*tan δ*) at 10 Hz of (a) polylactic acid (PLA) and (b) poly(ethylene-*co*-vinyl acetate) (EVA) films containing various amounts of diethyl phthalate (DEP); (circles) 0 phr, (diamonds) 5 phr, and (triangles) 10 phr.

Figure 3 shows the dynamic mechanical properties for the blends with DBP. The results were almost the same as those with DEP for each composition, although the PLA film containing 10 phr of DBP had a slightly broader relaxation peak. The width of tan δ peak, as the full-width at half-maximum (FWHM), was plotted as a function of the weight fraction of a plasticizer in Figure 4. The results suggest that the concentration fluctuation of DBP in PLA is more pronounced than that of DEP,[38-40] indicating that DBP has poor miscibility with PLA compared with DEP. We also detected the antiplasticizer phenomenon in the EVA/DBP systems in Figure 3 (see Table 1).

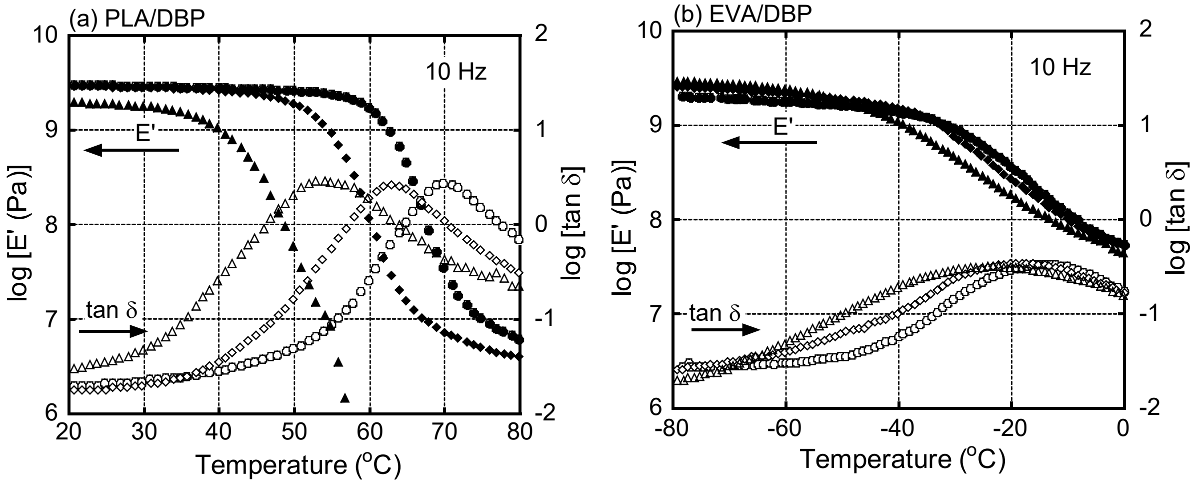

Figure 3 Temperature dependence of tensile storage modulus (*E'*) and loss tangent (*tan δ*) at 10 Hz for (a) polylactic acid (PLA) and (b) poly(ethylene-*co*-vinyl acetate) (EVA) films containing various amounts of dibutyl phthalate (DBP); (circles) 0 phr, (diamonds) 5 phr, and (triangles) 10 phr.

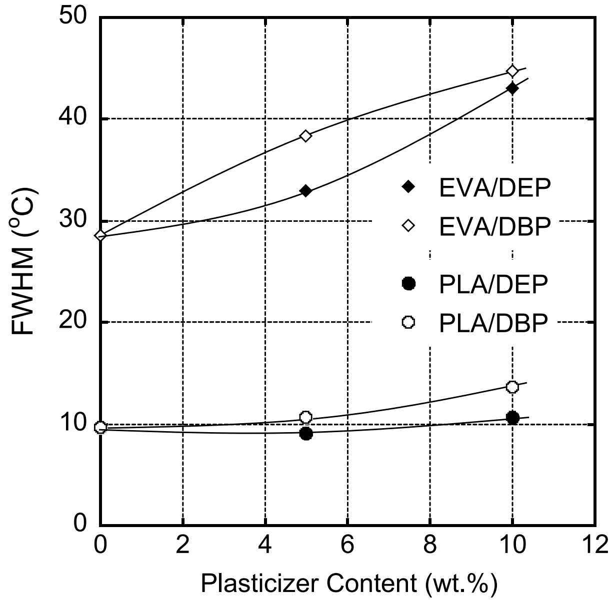

Figure 4 Full-width at half-maximum (FWHM) of tan *δ* peak as a function of the plasticizer content.

Table 1 *E'* in the glassy region, T_g, and FWHM for the samples

	E' (GPa)	T_g (°C)	FWHM (°C)
PLA	2.99	69.8	9.6
PLA/DEP (5 phr)	3.34	62.9	9.1
PLA/DEP (10 phr)	2.63	52.9	10.7
PLA/DBP (5 phr)	2.90	61.9	10.6
PLA/DBP (10 phr)	1.93	52.7	13.7
EVA	2.05	-15.2	28.6
EVA/DEP (5 phr)	2.48	-20.3	33.0
EVA/DEP (10 phr)	2.78	-26.3	43.1
EVA/DBP (5 phr)	2.59	-21.3	38.3
EVA/DBP (10 phr)	2.97	-26.2	44.8

E': Values in the glassy region (at 23 °C for PLA and -80°C for EVA)

T_g: Peak temperature of tan δ

As shown in Table 1, the T_g values of both polymers decreased following addition of the plasticizer as reported previously.[31,36,37,45] Because the T_g of PLA is higher than that of EVA, the T_g shift was more pronounced for the PLA systems (T_g's of the plasticizers are significantly low as mentioned in the experimental part), which is predicted by blending rules such as the Fox equation and the Gordon–Taylor equation.[39,46] The difference in the plasticizing effect between DEP and DBP was not obvious. This is reasonable because the difference in T_g between DEP and DBP is not significant as compared with the T_g difference between the plastics and plasticizers.

The ATR spectra of EVA films with various amounts of a plasticizer are shown in Figure 5. Because the sample films were in the rubbery state at room temperature, they showed perfect contact with the ATR crystal. The absorption at 1123 cm^{-1}, indicated by the arrows in the figure, can be ascribed to the stretching vibration of O=C–O,[47] which is weak for pure EVA because of the low concentration of carbonyl groups. The inset figure reveals that the absorbance was proportional to the plasticizer content with negligible experimental error, indicating that the peak can be used to determine the content of the plasticizer in the EVA film separated after annealing.

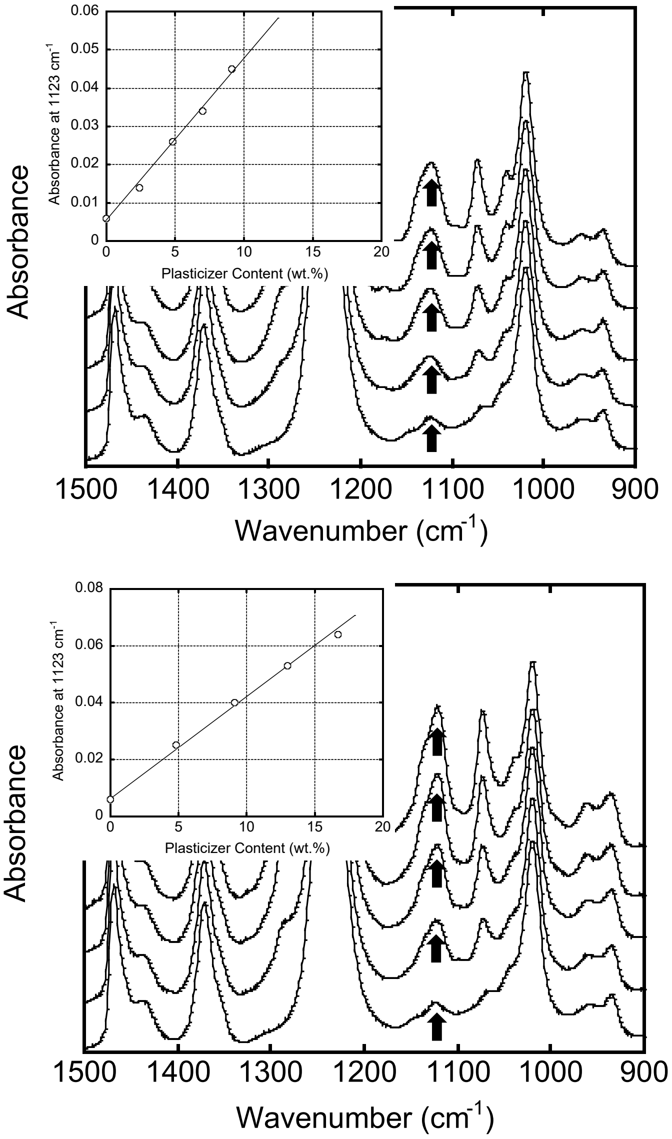

Figure 5 Attenuated total reflection–Fourier-transform infrared (ATR-FT-IR) spectra of poly(ethylene-*co*-vinyl acetate) (EVA) films with various amounts of (top) diethyl phthalate (DEP) and (bottom) dibutyl phthalate (DBP). The small figure represents the absorbance at 1123 cm^{-1} as a function of a plasticizer.

Interphase transfer of plasticizer

After annealing the laminated films for various periods, the films were separated to characterize the plasticizer content by the dynamic mechanical analysis (DMA). When annealing for 1 hour at 80°C of laminated films, each containing 10 phr of DBP at first, T_g of the separated PLA film was slightly (< 1°C) higher than that of the separated one after annealing for 4 hours. Furthermore, the T_g of the separated PLA film annealed for 9 hours was the same with that after annealing for 4 hours. These results demonstrate that the plasticizer distribution is in the equilibrium condition after at least 4 hours. This is attributed to the thin (300 μm) films with low T_g even for the PLA film because of the plasticizing effect. Therefore, we annealed various laminated films for 4 hours at either 80°C or 130°C.

Figure 6 shows the temperature dependence of *tan δ* of the separated films containing DEP. It is apparent that the T_g of the PLA film decreased, whereas that of the EVA film increased. These results demonstrate that the DEP migrated from the EVA to the PLA film during annealing; i.e., DEP prefers PLA to EVA. This phenomenon can be attributed to the difference in miscibility. The solubility parameter of EVA is calculated by the summation of the contributions from ethylene and vinyl acetate units. It was found to be around 18.8 $(MJ/m^3)^{0.5}$, whereas PLA shows a relatively high value,[48] 21.9 $(MJ/m^3)^{0.5}$. As a result, DEP prefers PLA, whereas DBP tends to stay in EVA. Furthermore, it should be noted that the extent of DEP transfer—i.e., the T_g shift—was enhanced during the high-temperature annealing, suggesting that the difference in the interaction parameter between PLA-DEP and EVA-DEP was more pronounced at the high temperature.

The DEP content of each separated film was estimated from the T_g shift measured by

DMA (the calibration curve is shown in Supporting information 1) and FT-IR spectra, which was summarized in Table 2. The results obtained by FT-IR spectroscopy corresponded well with those estimated by DMA.

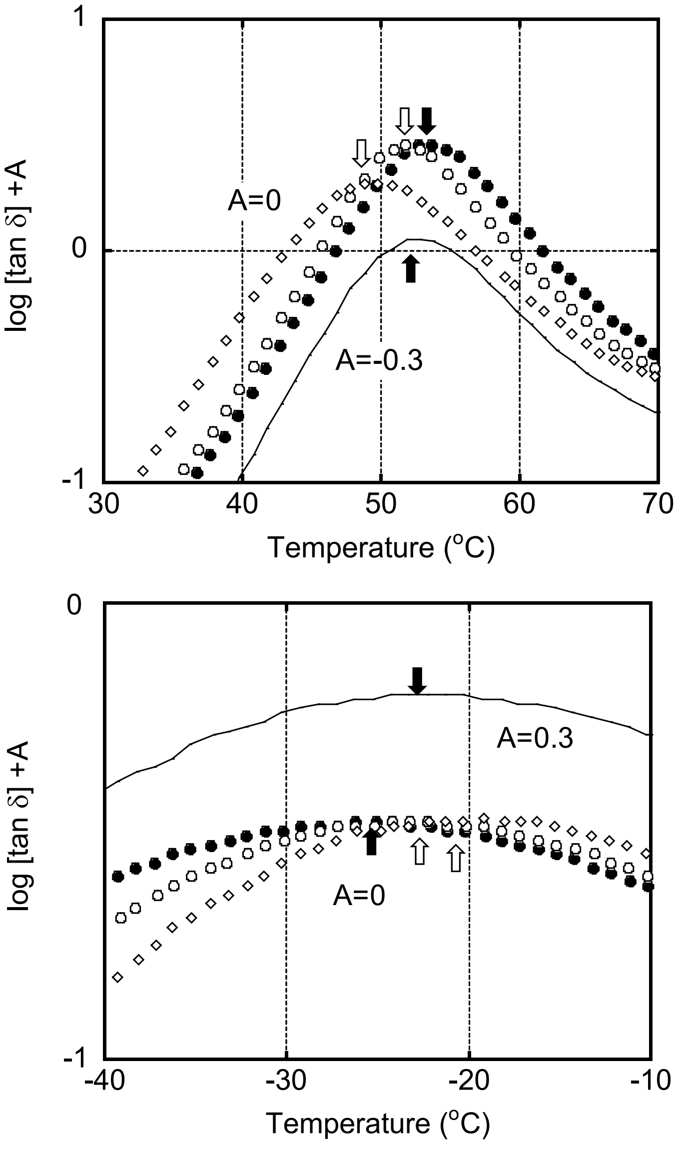

Figure 6 Temperature dependence of loss tangent (*tan δ*) at 10 Hz of (top) polylactic acid (PLA) and (bottom) poly(ethylene-*co*-vinyl acetate) (EVA) films; (closed circles) before lamination (10 phr of DEP), (open circles) separated film after annealing at 80°C, and (open diamonds) separated film after annealing at 130°C. In the figure, the data for the separated film after multi-annealing histories—i.e., annealing at 80°C followed by annealing at 130°C—are shown as a solid line with a vertical shift.

To confirm the effect of the annealing temperature, the laminated films annealed at

130°C for 4 hours were annealed for a further 4 hours at 80°C. As indicated by the solid line in Figure 6, the T_g of the separated films—which indicates the amount of DEP in the films—was determined by the final annealing temperature. The data are also listed in Table 2. The results confirm that the annealing period was enough to achieve equilibrium.

Table 2 Diethyl phthalate (DEP) content in the films

	DEP content in PLA estimated by DMA	DEP content in EVA evaluated by DMA	DEP content in EVA evaluated by FT-IR*
Without lamination (initial content)	10 phr	10 phr	10 phr
After annealing at 80ºC	10.7 phr	8.0 phr	7.8 phr
After annealing at 130ºC	12.4 phr	6.2 phr	6.6 phr
After re-annealing at 80ºC using the sample annealed at 130ºC	10.6 phr	8.1 phr	—

* FT-IR spectra are shown in Supporting Information 2

The same experiments were performed using DBP as the plasticizer, and the results are summarized in Table 3. The films annealed at 80°C contained almost the same amount of DBP—i.e., 10 phr—suggesting that the interaction parameter between PLA and DBP was similar to that between EVA and DBP at this temperature. However, we detected DBP transfer from the PLA film to the EVA film during annealing at 130°C, which was the opposite direction to that observed in the DEP system. This indicates that DBP prefers EVA to PLA at this temperature. These results demonstrate that the extent and direction of plasticizer transfer across the boundary between the immiscible PLA and EVA films are markedly affected by the plasticizer and the ambient temperature.

Table 3 Dibutyl phthalate (DBP) content in the films

	DBP content in PLA estimated by DMA	DBP content in EVA evaluated by DMA	DBP content in EVA evaluated by FT-IR*
Without lamination (initial content)	10 phr	10 phr	10 phr
After annealing at 80°C	9.8 phr	11.0 phr	10.3 phr
After annealing at 130°C	7.9 phr	13.6 phr	12.0 phr
After re-annealing at 80°C using the sample annealed at 130°C	9.1 phr	10.9 phr	—

* FT-IR spectra are shown in Supporting Information 2

Conclusions

We investigated the interphase transfer of a plasticizer between PLA and EVA using laminated films at 80 and 130 °C. The extent and direction of plasticizer transfer, which were estimated from the FT-IR spectra and the T_g shift measured by DMA, were dependent on the annealing temperature and the plasticizer. Furthermore, the plasticizer transfer phenomenon was reversible; i.e., the plasticizer content in each polymer film was determined by the final annealing temperature. These phenomena can be attributed to the temperature dependence of the difference in the interaction parameter with the plasticizer between PLA and EVA. Because the transfer of low-molecular-weight compounds such as plasticizers is also expected in blends, this information will be useful for the future development of functional immiscible blends.

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