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Description	

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

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1 **Abstract**

2   We investigated plasticizer transfer between poly(ethylene-*co*-vinyl acetate) (EVA)

3 and poly(lactic acid) (PLA) and its temperature dependence using laminated films

4 comprising EVA and PLA, each containing equal amounts of a plasticizer (i.e., diethyl

5 phthalate (DEP) or dibutyl phthalate (DBP)). Because the miscibility between PLA and

6 DEP is better than that between EVA and DEP, a large amount of DEP was detected in the

7 PLA film after annealing the laminated films at 80°C; i.e., some DEP moved from the

8 EVA film to the PLA film. Furthermore, more DEP migrated to the PLA film at 130°C,

9 suggesting that the difference in the interaction parameter with DEP between PLA and

10 EVA is more pronounced at higher temperatures. In laminated films containing DBP, the

11 DBP content in each film was almost equal after annealing at 80°C, although DBP

12 migrated from the PLA film to the EVA film at 130°C.

13

1   **Introduction**

2   Polymer blending has developed as the polymer industry has progressed because it is one

3   of the easiest ways of improving several polymer properties. Therefore, a great deal of

4   effort has been put into optimizing various polymer blends.[1-5] Recently, advanced

5   techniques have been proposed using interesting phenomena such as: (1) miscibility

6   change or segregation behavior (concentration gradient) under a temperature gradient[6,7]

7   or velocity gradient, i.e., a flow field;[8,9] (2) orientation correlation between matrix

8   polymer chains and low-molecular-weight compounds dissolved in a polymer;[10-12] and

9   (3) selective localization of a third component in an immiscible blend.[13-18] In the present

10   study, we focused on the selective localization of a third component and its temperature

11   dependence using a plasticizer as the low-molecular-weight compound in an immiscible

12   polymer pair comprising poly(lactic acid) (PLA) and poly(ethylene-*co*-vinyl acetate)

13   (EVA).

14   Localization and/or migration of a third component between phases has been reported

15   mostly in immiscible rubber blends,[13-15,] and is usually considered to be an unfavorable

16   phenomenon in the rubber industry. For example, the uneven distribution of a curative[14,15]

17   and/or accelerator[13] directly results in a marked cure imbalance between the phases. Such

18   uneven distribution occurs in not only low-molecular-weight compounds but also

19   fillers.[16-18] Recently, Kuhakongkiat et al. proposed a new technique for controlling the

20   temperature-dependent distribution of plasticizers in immiscible blends comprising

21   ethylene-*co*-propylene rubber (EPR) and elastomeric polyisobutylene (PIB).[19] They

22   found that bis(2-ethylhexyl) adipate (DOA), which acts as a plasticizer for both rubbers,

1   localized in the EPR at low temperatures and in the PIB at high temperatures. In other

2   words, the DOA concentration in each rubber phase is dependent on the ambient

3   temperature. Therefore, blends in which EPR is the matrix phase have a low modulus in

4   winter and high modulus in summer. Doan et al. found a similar phenomenon in an

5   immiscible rubber blend containing a tackifier.[20] Such interphase transfer is also expected

6   in damping materials that exhibit large values of loss tangent (*tan δ*) over a wide

7   temperature range, because the plasticizer distribution in phase-separated blends affects

8   the glass transition temperature (T_g) and the dynamic mechanical properties of each phase.

9   We used PLA and EVA in the present study, because the T_g of PLA is slightly higher than

10   room temperature and that of EVA is lower than room temperature. This situation has a

11   capability for the blend to show good damping properties over a wide temperature range

12   near room temperature. Up to now, various studies on PLA/EVA blends have been carried

13   out, especially to improve the mechanical toughness of PLA by the EVA addition.[21-26]

14   Although PLA sometimes shows partial miscibility with EVA,[27] at which the vinyl acetate

15   content in EVA is high, it is basically known as immiscible blends. Therefore, the

16   compatibilization is the key factor for the studies, such as addition of compatibilizer,[24]

17   transesterification,[25] and peroxide modification.[26] However, the application to damping

18   materials has not been studied to the best of our knowledge.

19   In this study, we applied annealing procedure only beyond the melting point of EVA

20   to avoid the effect of crystallinity and slow diffusion in PLA at low temperature. However,

21   the current experimental results about the effect of annealing temperature on the transfer

22   phenomenon would demonstrate the importance of the concept for the material design.

1   Moreover, we employed two types of phthalic esters to examine the effect of the

2   plasticizer species on the transfer phenomenon. Since the plasticizers that we used are

3   conventional materials with similar structure but having different solubility parameter,

4   the comparison between the plasticizers will provide the fundamental information on the

5   material design.

6

7   **Experimental**

8   **Materials**

9   The polymers used in the present study were commercially available PLA (Lacea

10   H280, Mitsui Chemicals, Inc., Japan) and EVA (Evaflex EV360, Dupont-Mitsui

11   Polychemicals Co., Ltd., Japan). The PLA comprised 12% D-lactic acid units, and was

12   therefore not crystalline. The number- and weight-average molecular weights of the

13   PLA—evaluated by size-exclusion chromatography as a polystyrene standard—were M_n

14   $= 1.5 \times 10^5$ and $M_w = 2.7 \times 10^5$, respectively. The EVA comprised 25 wt.% vinyl acetate.

15   Its density at room temperature was 950 kg/m^3, its melt flow rate at 190°C was 2 g/10

16   min, and its melting point was 77°C. The EVA had an $M_n = 6.3 \times 10^4$ and an $M_w = 2.5 \times$

17   10^5, as determined using a polystyrene standard. The thermal and rheological properties

18   of PLA[28,29] and EVA[30,31] have been described in detail previously.

19   We used two plasticizers—diethyl phthalate (DEP) and dibutyl phthalate (DBP), both

20   purchased from Daihachi Chemical Industry Co., Ltd., Japan—without further

21   purification. The Hansen solubility parameters of DEP and DBP were reported to be 20.5

22   and 19.0 (MJ/m^3)$^{0.5}$, respectively.[32] The glass transition temperatures are -90.0 for DEP

1   and -95.5°C for DBP.[33]

2

3   **Sample preparation**

4   We prepared plasticized EVA and PLA samples using a 30 cc Labo Plastomill

5   10M100 internal mixer (Toyo Seiki Seisaku-sho, Ltd., Japan) for 3 min at a blade rotation

6   speed of 30 rpm. The mixing temperatures were 180°C for the PLA blends and 130°C for

7   the EVA blends. We vacuum-dried pellets of the PLA blend at 80°C for 4 h prior to melt-

8   mixing to avoid hydrolysis. The plasticizer constituted 5, 10, 15, or 20 parts per hundred

9   of resin (phr). We compressed the obtained mixtures into flat films (0.3-mm-thick) using

10   a compression-molding machine at 130°C under 30 MPa.

11   The plasticizer transfer experiments were performed using PLA and EVA, both

12   containing 10 phr of a plasticizer (DEB or DBP). As illustrated in Figure 1, the plasticized

13   PLA and EVA films were laminated together. We applied slight manual pressure only to

14   ensure perfect lamination. After the perfect contact of the films, the pressure was removed.

15   The laminated films were then annealed at 80 or 130°C for various periods such as 1, 4,

16   and 9 hours without any pressure, after which both polymers were in the non-crystalline

17   rubbery state. The film thickness hardly changed (no flow) even after 9 hours at 130°C

18   because of the high viscosity at this temperature. To confirm the reversibility of plasticizer

19   transfer, we annealed one set of laminated films at 130°C for 4 h, then further annealed

20   them at 80°C for 4 h. After annealing, we separated the films and stored them at room

21   temperature for 3 days to homogenize the plasticizer distribution in the films prior to

22   characterization. We confirmed that both surfaces provide the same IR spectra.

1 Furthermore, it should be noted that it is no difficulty for the film separation. This is

2 reasonable because the interfacial thickness of the system is quite thin due to the large

3 difference in the solubility parameter, which is theoretically predictable.[34,35]

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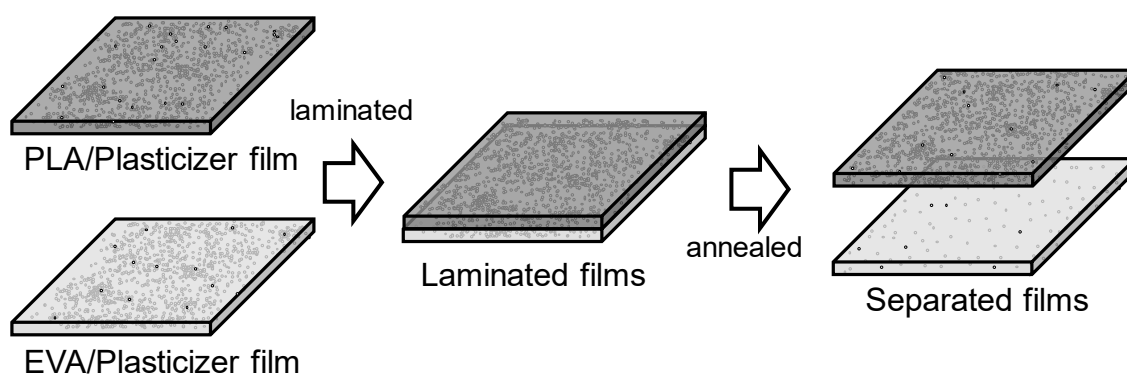
6 Figure 1 Schematic illustration of the plasticizer transfer experiment.

7

8 **Measurements**

9 *Dynamical mechanical properties*

10   We investigated the dependence on temperature of the tensile storage modulus (E')

11 and the loss tangent (*tan δ*) of rectangular specimens (5-mm-wide; 20-mm-long; 0.3-mm-

12 thick) using a Rheogel E4000-DVE dynamic mechanical analyzer (UBM Co., Ltd.,

13 Japan) in the temperature ranges 0–100°C for the PLA and plasticized PLA films, and

14 −80–40°C for the EVA and plasticized EVA films. The heating rate was 2°C/min, and the

15 applied frequency was 10 Hz. The peak temperature in the *tan δ* curve was taken to be

16 the T_g.

17

18 *Fourier-transform infrared (FTIR) spectroscopy*

1   The attenuated total reflection (ATR) infrared spectra were collected using a

2   Spectrum 100 FT-IR instrument (PerkinElmer Inc., MA, USA) with KRS-5 as an ATR

3   plate. The intensity of a characteristic absorbance peak at 1123 cm^{-1} was used to determine

4   the plasticizer content of the EVA films; a calibration curve was constructed from EVA

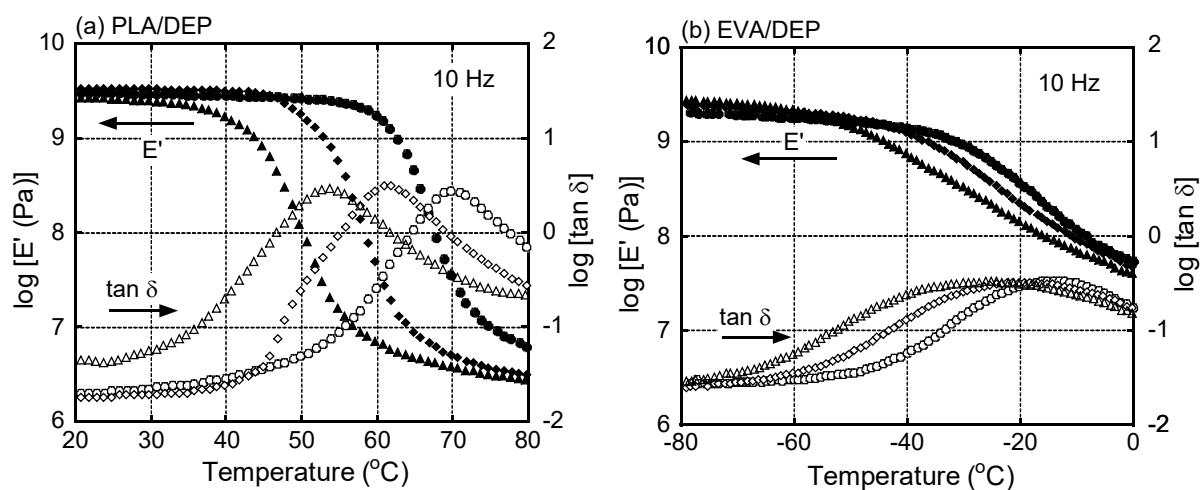5   films containing various amounts of the plasticizer for this purpose.

6

7   **Results and Discussion**

8   **Characteristics of polymers containing plasticizer**

9   Prior to evaluation of the transfer phenomenon, we examined the effect of the

10   plasticizer on the dynamic mechanical properties of a film made from each polymer.

11   Figure 2 shows the temperature dependence of the tensile storage modulus (E') and loss

12   tangent (*tan δ*) at 10 Hz of the pure polymers and the polymers with 5 or 10 phr of DEP.

13   The peak temperature of *tan δ* in the glass-to-rubber transition region—i.e., T_g—decreased

14   following the addition of DEP, for both PLA and EVA. The plasticization phenomenon

15   by DEP was already reported elsewhere.[36,37] The peak width was hardly affected by the

16   addition of DEP for both systems, suggesting a narrow relaxation time distribution, i.e.,

17   good miscibility. In the case of the EVA blends, however, the peak was broad even for

18   pure EVA. This broad relaxation mode is ascribed to various amorphous chains having

19   different mobilities, such as floating chain, cilia chain, loop chain, and tie chain, as

20   reported previously,[38-41] although the crystallinity of the EVA is not so high (ca. 15 %,

21   calculated from the heat of fusion evaluated by the DSC measurement[30]). Moreover, we

22   found that E' in the glassy region was enhanced by the addition of DEP; i.e., DEP acted

1   as an antiplasticizer in the glassy region (the numeric data are shown in Table 1), although

2   it showed plasticizing effect around at T_{g}. This may be important because antiplasticized

3   systems have reduced thermal expansion.[42] The E' in the glassy region in the PLA system

4   decreased by the addition of 10 phr of DEP, which is a typical behavior for a plasticized

5   polymer.[43,44] However, the small addition, 5 phr, of DEP seems to enhance the modulus
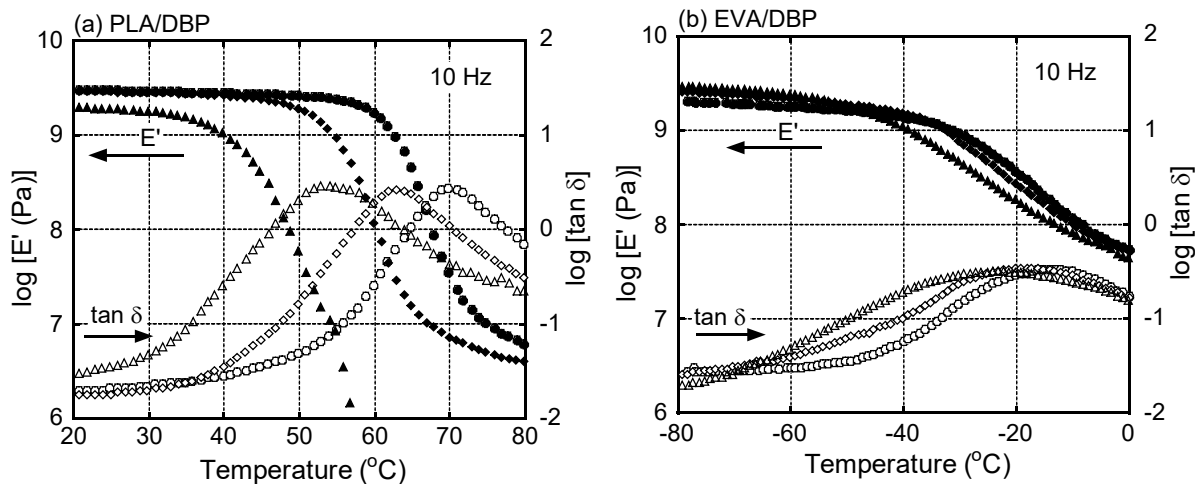
6   slightly.

7

8

9   Figure 2   Temperature dependence of tensile storage modulus (E') and loss tangent (*tan*
10   *δ*) at 10 Hz of (a) polylactic acid (PLA) and (b) poly(ethylene-*co*-vinyl acetate) (EVA)
11   films containing various amounts of diethyl phthalate (DEP); (circles) 0 phr, (diamonds)
12   5 phr, and (triangles) 10 phr.

13

14   Figure 3 shows the dynamic mechanical properties for the blends with DBP. The

15   results were almost the same as those with DEP for each composition, although the PLA

16   film containing 10 phr of DBP had a slightly broader relaxation peak. The width of tan δ

17   peak, as the full-width at half-maximum (FWHM), was plotted as a function of the weight

18   fraction of a plasticizer in Figure 4. The results suggest that the concentration fluctuation

19   of DBP in PLA is more pronounced than that of DEP,[38-40] indicating that DBP has poor

1   miscibility with PLA compared with DEP. We also detected the antiplasticizer

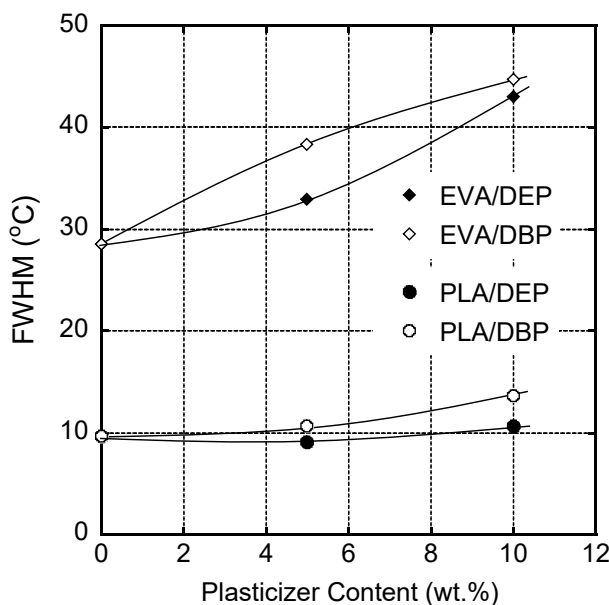2   phenomenon in the EVA/DBP systems in Figure 3 (see Table 1).

3

4

5   Figure 3 Temperature dependence of tensile storage modulus (*E'*) and loss tangent (*tan*
6   *δ*) at 10 Hz for (a) polylactic acid (PLA) and (b) poly(ethylene-*co*-vinyl acetate) (EVA)
7   films containing various amounts of dibutyl phthalate (DBP); (circles) 0 phr, (diamonds)
8   5 phr, and (triangles) 10 phr.

9

10

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

13

14

1 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

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

3 T_g: Peak temperature of tan δ

4

5   As shown in Table 1, the T_g values of both polymers decreased following addition of

6 the plasticizer as reported previously.[31,36,37,45] Because the T_g of PLA is higher than that

7 of EVA, the T_g shift was more pronounced for the PLA systems (T_g's of the plasticizers

8 are significantly low as mentioned in the experimental part), which is predicted by

9 blending rules such as the Fox equation and the Gordon–Taylor equation.[39,46] The

10 difference in the plasticizing effect between DEP and DBP was not obvious. This is

11 reasonable because the difference in T_g between DEP and DBP is not significant as

12 compared with the T_g difference between the plastics and plasticizers.

13

14   The ATR spectra of EVA films with various amounts of a plasticizer are shown in

15 Figure 5. Because the sample films were in the rubbery state at room temperature, they

16 showed perfect contact with the ATR crystal. The absorption at 1123 cm^{-1}, indicated by

17 the arrows in the figure, can be ascribed to the stretching vibration of O=C–O,[47] which is

18 weak for pure EVA because of the low concentration of carbonyl groups. The inset figure

1   reveals that the absorbance was proportional to the plasticizer content with negligible

2   experimental error, indicating that the peak can be used to determine the content of the

3   plasticizer in the EVA film separated after annealing.

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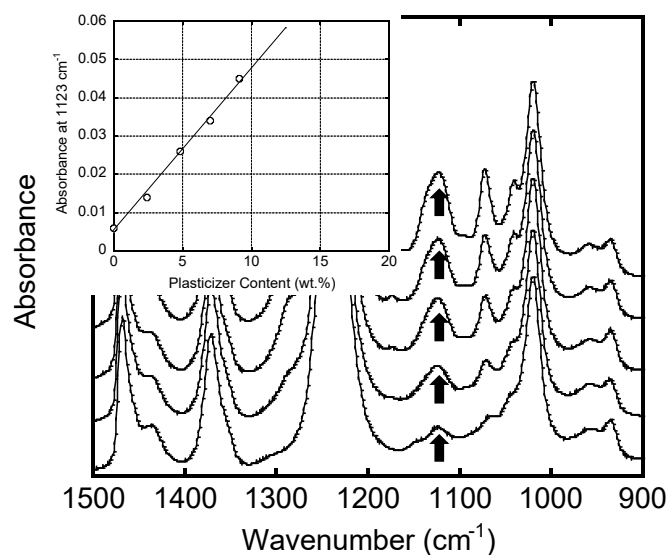
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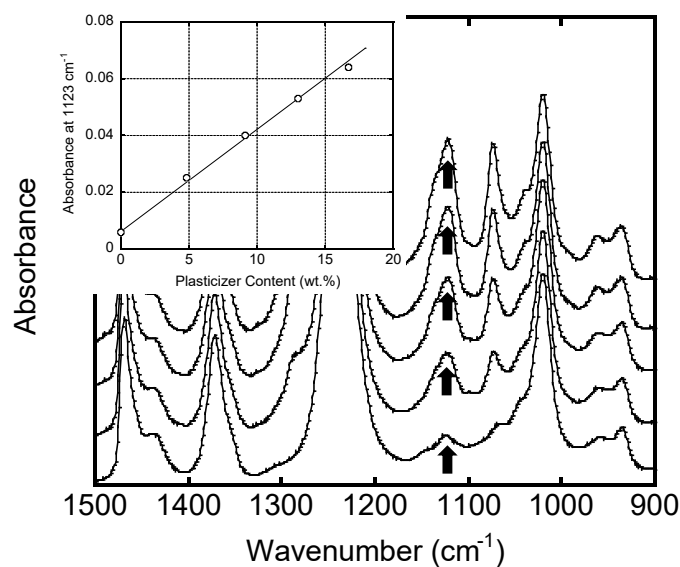
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7   Figure 5 Attenuated total reflection–Fourier-transform infrared (ATR-FT-IR) spectra of

8   poly(ethylene-*co*-vinyl acetate) (EVA) films with various amounts of (top) diethyl

9   phthalate (DEP) and (bottom) dibutyl phthalate (DBP). The small figure represents the

10   absorbance at 1123 cm^{-1} as a function of a plasticizer.

11

12   **Interphase transfer of plasticizer**

1   After annealing the laminated films for various periods, the films were separated to

2   characterize the plasticizer content by the dynamic mechanical analysis (DMA). When

3   annealing for 1 hour at 80°C of laminated films, each containing 10 phr of DBP at first,

4   T_g of the separated PLA film was slightly (< 1°C) higher than that of the separated one

5   after annealing for 4 hours. Furthermore, the T_g of the separated PLA film annealed for 9

6   hours was the same with that after annealing for 4 hours. These results demonstrate that

7   the plasticizer distribution is in the equilibrium condition after at least 4 hours. This is

8   attributed to the thin (300 μm) films with low T_g even for the PLA film because of the

9   plasticizing effect. Therefore, we annealed various laminated films for 4 hours at either

10   80°C or 130°C.

11   Figure 6 shows the temperature dependence of *tan δ* of the separated films containing

12   DEP. It is apparent that the T_g of the PLA film decreased, whereas that of the EVA film

13   increased. These results demonstrate that the DEP migrated from the EVA to the PLA film

14   during annealing; i.e., DEP prefers PLA to EVA. This phenomenon can be attributed to

15   the difference in miscibility. The solubility parameter of EVA is calculated by the

16   summation of the contributions from ethylene and vinyl acetate units. It was found to be

17   around 18.8 $(MJ/m^3)^{0.5}$, whereas PLA shows a relatively high value,[48] 21.9 $(MJ/m^3)^{0.5}$. As

18   a result, DEP prefers PLA, whereas DBP tends to stay in EVA. Furthermore, it should be

19   noted that the extent of DEP transfer—i.e., the T_g shift—was enhanced during the high-

20   temperature annealing, suggesting that the difference in the interaction parameter between

21   PLA-DEP and EVA-DEP was more pronounced at the high temperature.

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

1 DMA (the calibration curve is shown in Supporting information 1) and FT-IR spectra,

2 which was summarized in Table 2. The results obtained by FT-IR spectroscopy

3 corresponded well with those estimated by DMA.
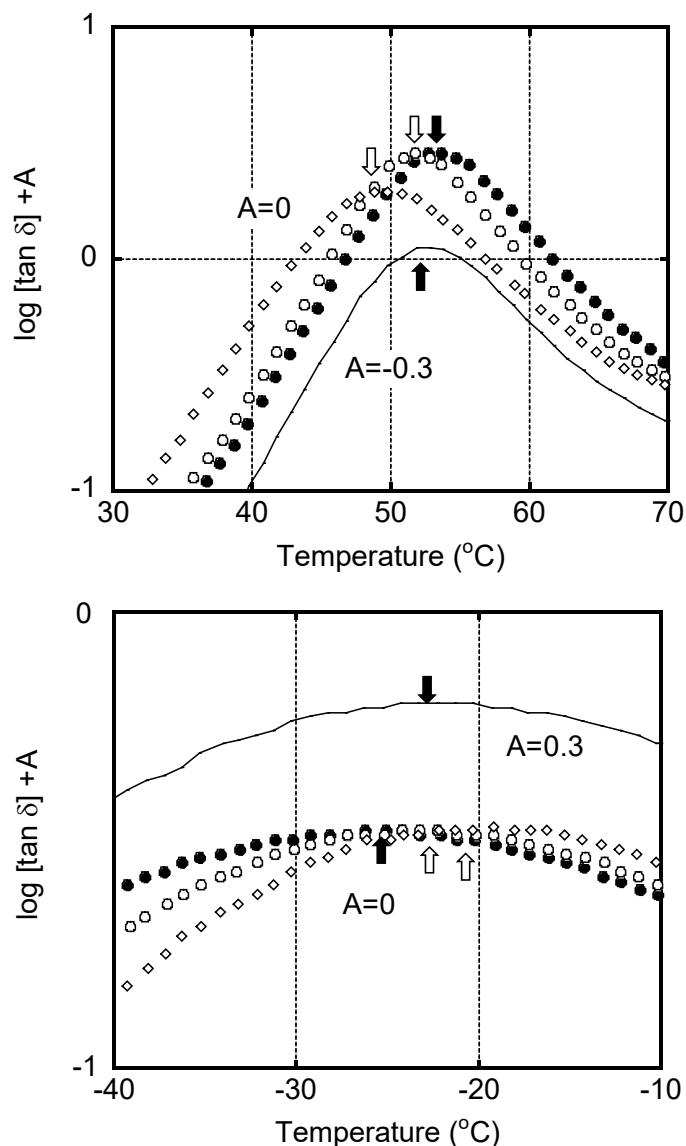
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5
6 Figure 6 Temperature dependence of loss tangent (*tan δ*) at 10 Hz of (top) polylactic acid
7 (PLA) and (bottom) poly(ethylene-*co*-vinyl acetate) (EVA) films; (closed circles) before
8 lamination (10 phr of DEP), (open circles) separated film after annealing at 80°C, and
9 (open diamonds) separated film after annealing at 130°C. In the figure, the data for the
10 separated film after multi-annealing histories—i.e., annealing at 80°C followed by
11 annealing at 130°C—are shown as a solid line with a vertical shift.

12

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

1 130°C for 4 hours were annealed for a further 4 hours at 80°C. As indicated by the solid

2 line in Figure 6, the T_g of the separated films—which indicates the amount of DEP in the

3 films—was determined by the final annealing temperature. The data are also listed in

4 Table 2. The results confirm that the annealing period was enough to achieve equilibrium.

5

6 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 80°C	10.7 phr	8.0 phr	7.8 phr
After annealing at 130°C	12.4 phr	6.2 phr	6.6 phr
After re-annealing at 80°C using the sample annealed at 130°C	10.6 phr	8.1 phr	—

7 * FT-IR spectra are shown in Supporting Information 2

8

9 The same experiments were performed using DBP as the plasticizer, and the results

10 are summarized in Table 3. The films annealed at 80°C contained almost the same amount

11 of DBP—i.e., 10 phr—suggesting that the interaction parameter between PLA and DBP

12 was similar to that between EVA and DBP at this temperature. However, we detected DBP

13 transfer from the PLA film to the EVA film during annealing at 130°C, which was the

14 opposite direction to that observed in the DEP system. This indicates that DBP prefers

15 EVA to PLA at this temperature. These results demonstrate that the extent and direction

16 of plasticizer transfer across the boundary between the immiscible PLA and EVA films

1 are markedly affected by the plasticizer and the ambient temperature.

2

3 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	—

4 * FT-IR spectra are shown in Supporting Information 2

5

6 **Conclusions**

7 We investigated the interphase transfer of a plasticizer between PLA and EVA using

8 laminated films at 80 and 130 °C. The extent and direction of plasticizer transfer, which

9 were estimated from the FT-IR spectra and the T_g shift measured by DMA, were

10 dependent on the annealing temperature and the plasticizer. Furthermore, the plasticizer

11 transfer phenomenon was reversible; i.e., the plasticizer content in each polymer film was

12 determined by the final annealing temperature. These phenomena can be attributed to the

13 temperature dependence of the difference in the interaction parameter with the plasticizer

14 between PLA and EVA. Because the transfer of low-molecular-weight compounds such

15 as plasticizers is also expected in blends, this information will be useful for the future

16 development of functional immiscible blends.

17

Acknowledgements

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