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Miscibility Between Ethylene Vinyl Acetate Copolymers and Tackifier Resins*

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A series of ethylene vinyl acetate copolymer (EVA) were blended with various kinds of tackifiers and the miscibility between the components was investigated. The miscibility of the blend is illustrated as a phase diagram. The EVA and modified rosin systems tended to have a phase diagram with lower critical solution temperature (LCST), whereas the EVA and petroleum resin systems tended to have that with upper critical solution temperature (UCST). The phase diagrams of EVA/tackifier resins systematically changed as VAc content in the copolymer increased, which is accounted for by the classical Flory-Huggins theory.

Keywords: Hot-melt adhesive; EVA; tackifier; miscibility; phase diagram; UCST; LCST; miscible window; Flory-Huggins theory

INTRODUCTION

Hot-melt adhesives are widely used for spreading over the substrates in the melted state followed by solidifying after cooling. For the base

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polymers of hot-melt adhesives, thermoplastics such as ethylene vinyl acetate copolymer (EVA), polyolefins, polyamides and polyesters are often used. Among them, EVA is the most widely-used hot-melt adhesives in the world. In general, tackifiers are formulated into EVA-based hot-melt adhesives. As tackifiers generally have high glass transition temperature (T_g) and low molecular weight compared with the EVA, addition of tackifiers increases T_g and enhances tackiness of the adhesives, if the two components are miscible. These changes of viscoelastic properties would make adhesion properties adequate for hot-melt adhesives. But if they are immiscible, the particles of tackifier resin would act as a filler in a matrix of EVA. We are investigating the relationship between the viscoelastic properties and the adhesion properties [1–4]. The viscoelastic behavior of the bulk adhesive is much influenced by whether the components are miscible with each other or not. Therefore, it becomes indispensable for us to know the miscibility between the components. Some studies referred to the miscibility between EVA and additives [5, 6], but they were still sporadic. In our previous study, the relationship between the viscoelastic property and adhesion property for the miscible combination of an EVA and a tackifier was investigated [4]. Recently, we have investigated the miscibility between acrylic copolymers and tackifiers [7, 8] and natural rubber and tackifiers [9, 10]. In this article, the miscibility between EVA's and tackifiers is systematically investigated. In the first part of this study, a series of EVA's was blended with various kinds of tackifiers and the miscibility between the components was illustrated in the phase diagrams. Then, the systematic changes of the phase diagrams were qualitatively analyzed according to the Flory-Huggins theory on the basis of the mean-field approximation [11].

EXPERIMENTAL

Materials

The raw materials of commercially-available ethylene vinyl acetate copolymers (EVA's) and tackifier resins were used. As shown in Table I, the contents of vinyl acetate (VAc) in EVA were 10 (Evaflex EV640; Du Pont Mitsui Polychemical Co., Ltd., Tokyo, JAPAN), 20

TABLE I Ethylene vinyl acetate copolymers

<i>Code</i>	<i>Content of vinyl acetate (mol%)^a</i>	<i>M_n^a</i>
VA10	10	18100
VA20	20	27200
VA25	25	14000
VA32	32	23700
VA42	42	20800
VA47	47	17600

^a Quoted from catalogues.

TABLE II Tackifiers used in this study

<i>Tackifier resins^a</i>	<i>Composition^b</i>	<i>M_n^c</i>
Pencil A	pentaerythritol ester of rosin	816
Estergum H	glycerin ester of hydrogenated rosin	705
Foral 105	pentaerythritol ester of perhydrogenated rosin	743
Superester A115	pentaerythritol ester of disproportionated rosin	784
YS Polystar T130	terpene phenolic copolymer	765
Clearon K4090	hydrogenated terpene oligomer	793
Escorez 1102	aliphatic petroleum (C5) resin	1280
Escorez 1310	aliphatic petroleum (C5) resin	570
Escorez 2101	petroleum (C5/C9) resin	850

^a Commercial names.

^b Quoted from catalogues.

^c Determined from GPC.

(Ultracene UE633; Tosoh Corp., Mie, JAPAN), 25 (Evaflex EV310; Du Pont Mitsui Polychemical Co., Ltd.), 32 (Ultracene UE750; Tosoh Corp.), 42 (Ultracene UE760; Tosoh Corp.) and 47 (Evaflex EV47x; Du Pont Mitsui Polychemical Co., Ltd.) mol%, respectively. The tackifiers used in this study are listed in Table II. Detailed properties were described in our previous papers [9, 10].

Methods

Evaluation of Miscibility

EVA and tackifier resin were individually dissolved in chlorobenzene, blended at a ratio of 90:10, 70:30, 50:50, 30:70, and 10:90 by weight, respectively, and cast on glass plate. They were dried *in vacuo* and kept in a desirable temperature at least for 24 hours and then visually observed as to whether they were uniform or not. We decided that the clear blends were miscible at that temperature. These

procedures were repeated in the temperature range from 60°C to 180°C. To confirm the miscibility as decided above, blending was also done in a melt stage at 140°C for about 20 minutes in a blender equipped with thermal and mixing speed controllers. The films were prepared by spreading the polymer blends between Teflon[®] sheets and hot-pressing at 140°C. The films were allowed to cool in air before removing from the Teflon[®] sheets. A spacer was used to keep the polymer film thickness at about 0.3–0.35 mm. The films thus made were employed for microscopic observation and thermal analysis.

Measurement of Thermal Properties

Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 at a heating rate of 20°C • min⁻¹ in helium to investigate the glass transition temperature (T_g) and melting point (T_m) of the blends and their components. T_g of some blend films were confirmed by dynamic mechanical analysis (DMA) which were carried out using a Perkin Elmer DMA7 at 10 Hz in a three-point bending mode at a heating rate of 3°C • min⁻¹ under nitrogen.

RESULTS AND DISCUSSION

Phase Diagrams

Phase diagrams of EVA/tackifier resins were classified into four types. They were (i) miscible-type where an EVA and a tackifier were miscible at any blending ratio from 60°C to 180°C, (ii) LCST-type which had a lower critical solution temperature, (iii) UCST-type which had an upper critical solution temperature and (iv) immiscible-type where an EVA and a tackifier were immiscible so far as we observed. In some series of EVA/tackifier resin systems, phase diagrams systematically changed as the content of vinyl acetate in EVA increased. Phase diagrams of EVA/Escorez 1310 are shown in Figure 1. The VA10/Escorez 1310 system gave a phase diagram of upper critical solution temperature (UCST) type, where the blends were immiscible (opaque) below 70°C and changed to miscible (transparent) at higher temperature.

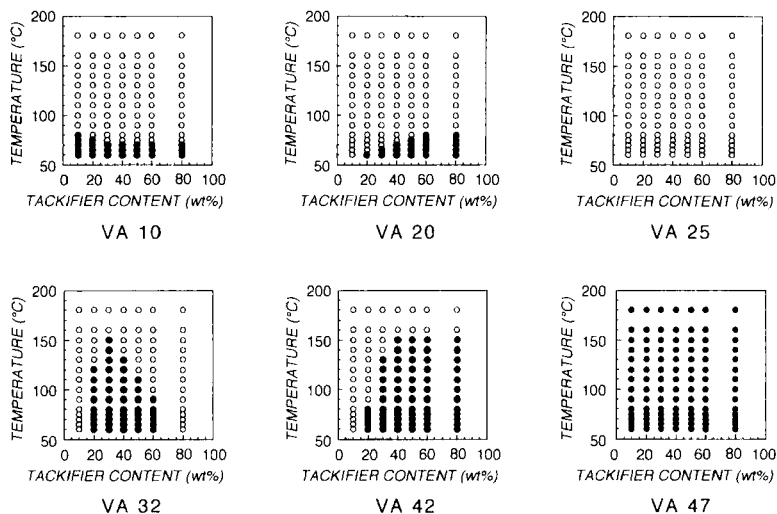


FIGURE 1 Phase diagrams of EVA/Escorez 1310. ○: transparent (miscible) and ●: opaque (immiscible).

The phase diagram of EVA/Escorez 1310 systematically changes as VAc content in the copolymer increases, except for the VA25/Escorez 1310 system. As shown in Table I, the number average molecular weight of VA25 is lower than for the other EVA's. We think that the low molecular weight depresses the immiscible region below room temperature. The critical temperatures (T_c) of the UCST phase diagrams are elevated as the VAc content increases. Finally, for the VA47/Escorez 1310 system, all the blends were immiscible at any temperature between 60°C and 180°C, irrespective of the tackifier content. Other EVA/petroleum resin systems also gave phase diagrams of the UCST-type at 25–42 mol% of VAc content. On the contrary, EVA/modified rosin systems gave phase diagrams of the lower critical solution temperature (LCST) type, where the blends were miscible at room temperature and changed to immiscible at higher temperature. Typical phase diagrams are shown in Figure 2 and the summarized results are listed in Table III.

These systematic changes of the phase diagrams were qualitatively analyzed according to our previous paper [8] based on the Flory-

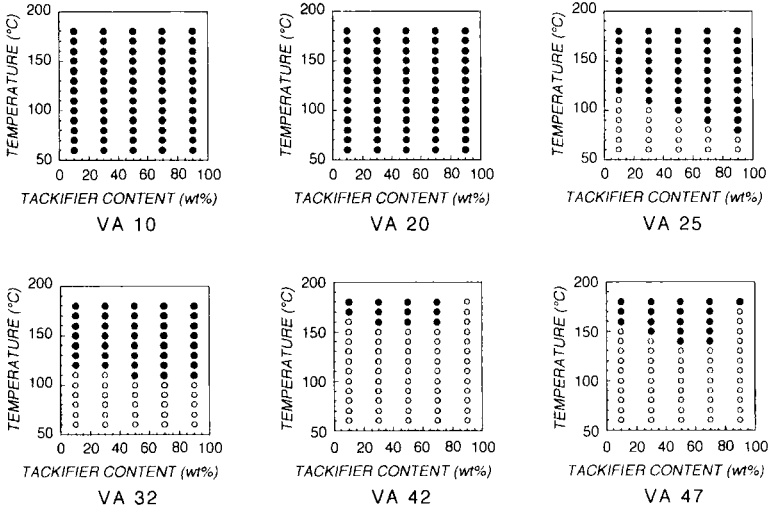


FIGURE 2 Phase diagrams of EVA/Pencil A. The symbols are the same as in Figure 1.

TABLE III Types of phase diagrams for EVA and tackifier resin systems^a

Component	VA10	VA20	VA25	VA32	VA42	VA47
Pencil A	I	I	L	L	L	L
Estergum H	I	L	L	M	M	M
Foral 105	L	L	L	M	M	M
Superester A115	L	L	L	M	M	M
YS Polystar	M	M	M	M	M	M
T130	U	M	M	M	M	U
Clearon	U	M	M	M	M	U
K4090	U	M	M	M	M	U
Escorez 1102	I	I	U	U	I	I
Escorez 1310	U	U	M	U	U	I
Escorez 2101	I	I	U	U	U	I

^a I: Immiscible at 60–180°C; U: UCST; L: LCST; M: Miscible at 60–180°C.

Huggins theory [11]. Binodal curves can be expressed by the following equations:

$$\chi_{\text{blend}} = A_{\text{blend}} + \frac{B_{\text{blend}}}{RT} \quad (1)$$

$$\frac{1}{T_{bn}} = \frac{1}{T_c^\infty} \left\{ 1 - \frac{1}{2A(\phi_1 - \phi_2)} \left[\frac{1}{m_2} \ln \frac{\phi_1}{\phi_2} - \frac{1}{m_1} \ln \frac{1 - \phi_1}{1 - \phi_2} \right] \right\} \quad (2)$$

$$2 \left(\frac{1}{m_1} - \frac{1}{m_2} \right) (\phi_1 - \phi_2) + \left[2 - \frac{(\phi_1 + \phi_2)}{m_1} \right] \ln \frac{1 - \phi_1}{1 - \phi_2} + \frac{(\phi_1 + \phi_2)}{m_2} \ln \frac{\phi_1}{\phi_2} = 0 \quad (3)$$

$$\frac{1}{T_c^\infty} = - \frac{AR}{B} \quad (4)$$

where χ_{blend} is the overall segmental interaction parameter for a copolymer and tackifier resin pair, A_{blend} and B_{blend} are constants, R is the gas constant ($= 8.3143 \text{ J} \bullet \text{K}^{-1} \bullet \text{mol}^{-1}$), T_{bn} is the binodal temperature, T_c^∞ is the critical temperature where the number of segments in the copolymer is infinity, ϕ_1 and ϕ_2 are volume fraction (in this study volume fraction is estimated as the same as weight fraction) of the tackifier in the two phases and m_1 and m_2 are the number of segments in EVA and tackifier, respectively. Here we estimate that m_1 and m_2 are one-thirtieth of the number-average molecular weight of the components, because the molecular weight of an ethylene unit is roughly about thirty. We can calculate a set of ϕ_1 and ϕ_2 from Eq. (3) and then put some values of A and T_c^∞ in Eq. (2) to obtain a series of trial values for T_{bn} . Until an adequate set of T_{bn} , ϕ_1 and ϕ_2 resulted, this procedure was repeated. In principle, the curve fitting can be done for the experimentally-observed phase diagrams, but in this study it was rather difficult to determine the strict values of the parameters. Figure 3 shows the results of curve fitting for the EVA/Escorez 1310 system by the trial and error method. As the melting points (T_m) of the blends measured by DSC were in good agreement with the clearing points of the VA10/Escorez 1310 system when the tackifier content was between 0 and 30 wt%, deviation from the calculated value was caused by the crystalline nature of VA10. But the deviation observed in the VA32/Escorez 1310 system shows the limitation of this method. The approximate χ_{blend} values obtained are summarized in Table IV.

The overall segmental interaction parameter, χ_{blend} , for a blend of a $(A_y B_{1-y})_{m_2} / T_{m_1}$ system, where A , B and T refer to vinyl acetate, ethylene and tackifier, respectively, can be expressed by the following

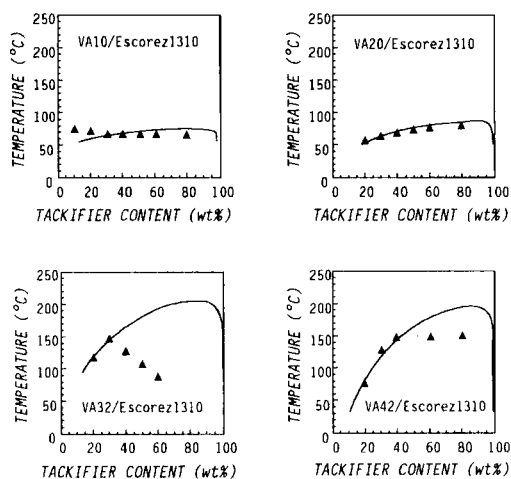


FIGURE 3 Binodal curve and cloud point of EVA/Escorez 1310 calculated according to Eqs. (1)–(4). –: binodal curve from Table IV and ▲: cloud point from Figure 1.

TABLE IV χ parameters of EVA and tackifier resin systems^a

Tackifier resins	EVA	T_c^x (°C)	A	B
Pencil A	VA25	60	0.025	– 69
	VA32	100	0.085	– 264
	VA42	160	1.1	– 3960
	VA47	120	0.03	– 98
Foral 105	VA10	90	0.1	– 302
	VA20	90	0.095	– 287
	VA25	65	0.0125	– 35
Escorez 1310	VA10	97	– 0.3	923
	VA20	127	– 0.15	499
	VA32	569	– 0.02	140
	VA42	727	– 0.02	166

^a $\chi = A + B/RT$.

equation [12]:

$$\begin{aligned} \chi_{\text{blend}} &= y\chi_{AT} + (1 - y)\chi_{BT} - y(1 - y)\chi_{AB} \\ &= y^2\chi_{AB} + y(\chi_{AT} - \chi_{BT} - \chi_{AB}) + \chi_{BT} \end{aligned} \quad (5)$$

where χ_{ij} is the interaction parameter of each combination of segment. And if χ_{ij} is expressed by

$$\chi_{ij} = A_{ij} + B_{ij}/RT \quad (6)$$

then the overall A_{blend} and B_{blend} should also be expressed by the quadratic equation:

$$\begin{aligned} A_{\text{blend}} &= yA_{AT} + (1-y)A_{BT} - y(1-y)A_{AB} \\ &= y^2A_{AB} + y(A_{AT} - A_{BT} - A_{AB}) + A_{BT} \end{aligned} \quad (7)$$

$$\begin{aligned} B_{\text{blend}} &= yB_{AT} + (1-y)B_{BT} - y(1-y)B_{AB} \\ &= y^2B_{AB} + y(B_{AT} - B_{BT} - B_{AB}) + B_{BT} \end{aligned} \quad (8)$$

A_{AB} and B_{AB} are calculated to be about -0.0007 and $2.4 \text{ J} \cdot \text{mol}^{-1}$, respectively, from Table IV by plotting A_{blend} B_{blend} vs. y (VAc fraction), followed by calculation of A_{AB} and B_{AB} by the least squares method, respectively. These values are lower than those which have been reported by Shimoi *et al.* [13] and Cruz-Ramos *et al.* [14] Because the tackifier resins used in this study are large and bulky molecules and EVA contains long linear molecules compared with another component, the values of the parameters obtained according to a simple lattice model have little physical significance. But the general trends are qualitatively explained. Figure 4 is the schematic illustration of the VAc content (y) dependence of χ_{blend} , A_{blend} and B_{blend} for the $(A_y B_{1-y})_{m_2} / T_{m_1}$ system. As χ_{blend} are expressed by the quadratic equation of y , the existence of a miscible window is expected. The VAc content (y) dependence of $T_c^\infty (= -B_{\text{blend}}/A_{\text{blend}} R)$ for EVA/Escorez 1310, Pencil A and Foral 105 systems are illustrated in Figure 5, suggesting the existence of a miscible window. The inclination that the EVA and modified rosin systems tend to be of the LCST-type,

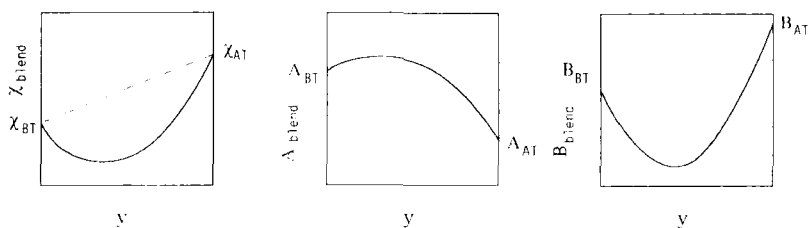


FIGURE 4. Schematic illustration of the y dependence of χ_{blend} , A_{blend} and B_{blend} for $(A_y B_{1-y})_{m_2} / T_{m_1}$ system.

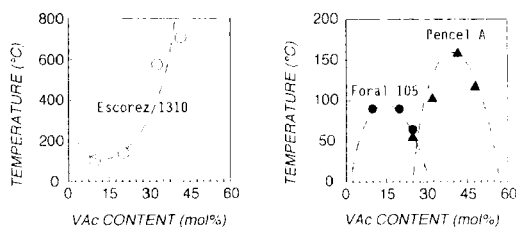


FIGURE 5 VAc content dependence of critical temperature for EVA: Escorez 1310 (○), Pencil A (▲) and Foral 105 (●).

whereas the EVA and petroleum resin systems tend to be of the UCST-type, might be caused by the polarity of the tackifier, but this is only circumstantial evidence.

Glass Transition Temperatures

Glass transition temperature (T_g) is determined from the second heating scan of the DSC thermogram of the blend film in this section. Typical T_g 's of the LCST- and UCST-type blends are shown with their phase diagrams in Figures 6 and 7, respectively. T_g of the LCST-type blend acts as if the blend is miscible. As shown in Figure 6, T_g increased as the tackifier content increased. In case of the UCST-type blend, T_g is almost constant irrespective of the tackifier content. This behavior is the same as that of immiscible blends. Indeed, the two components of the UCST-type blends are immiscible at low

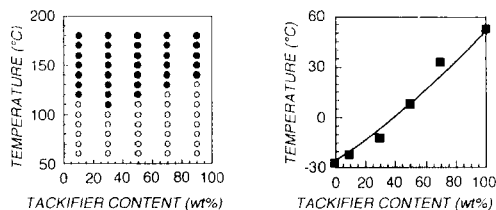


FIGURE 6 Phase diagram (left figure) and glass transition temperature (right figure) for VA20/Estergum H.

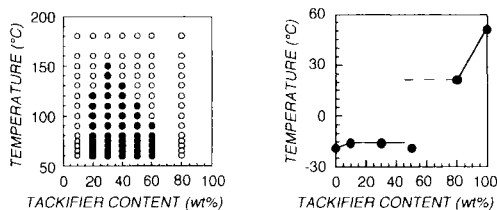


FIGURE 7 Phase diagram (left figure) and glass transition temperature (right figure) for VA32/Escorez 1310.

temperature. Generally, two T_g's, corresponding to each component, are observed in an immiscible blend but, unfortunately, the T_g of the quantitatively minor component was not detected in the VA32/Escorez 1310 system (Fig. 7). The results of dynamic mechanical analysis of the UCST-type blend films had the same tendencies. We think that the tackifier-rich phase is dispersed in a matrix of EVA-rich phase so that we can detect only the transition of a matrix by our DMA equipment. Further investigation will be done in future with discussion of the adhesion properties. The effect of phase structure on adhesive joint strength was rather weaker than that of VAc content. Of course, the phase structure affects viscoelastic properties and the adhesive property was very much affected by the viscoelastic properties of the adhesives. But the maximum value of joint strength at 20°C was recorded when EVA20 was used. Further discussion will be forthcoming in the future paper.

CONCLUSIONS

A series of ethylene vinyl acetate copolymers (EVA) were blended with various kinds of tackifiers and the miscibility between the components was illustrated by phase diagrams which were classified into: (i) miscible-type, (ii) LCST-type, (iii) UCST-type and (iv) immiscible-type. The EVA and modified rosin systems tended to be of the LCST-type, whereas the EVA and petroleum resin systems tended to be of the UCST-type. The phase diagrams of EVA/tackifier resins systematically changed as VAc content in the copolymer increased, which is accounted for by the classical Flory-Huggins theory.

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