

# Miscibility and Adhesive Properties of Ethylene Vinyl Acetate Copolymer (EVA)-Based Hot-Melt Adhesives. I. Adhesive Tensile Strength

MOTOTSUGU TAKEMOTO,<sup>1</sup> MIKIO KAJIYAMA,<sup>2</sup> HIROSHI MIZUMACHI,<sup>1</sup> AKIO TAKEMURA,<sup>1</sup> HIROKUNI ONO

<sup>1</sup> Laboratory of Polymeric Materials, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1 Yayoi Itchome, Bunkyo-ku, Tokyo 113-8657, Japan

<sup>2</sup> Institute of Agricultural and Forest Engineering, University of Tsukuba, 1-1 Ten-nodai Itchome, Tsukuba-shi, Ibaraki 305-8572, Japan

Received 6 September 2000; accepted 26 January 2001

**ABSTRACT:** A series of ethylene vinyl acetate copolymers (EVA) were blended with some tackifier resins that are made from wood extracts, and possible relations between their miscibility and properties as hot-melt adhesives (HMA) were investigated. From our previous report on miscibility of various EVA-based HMAs, we chose some blends that represent some of typical miscibility types and measured their adhesive tensile strengths. When the blends were miscible at testing temperatures, the temperature at which the maximum value of adhesive tensile strength was recorded tended to move toward higher temperature as tackifier content of blends increased. This result corresponds to the glass transition temperature ( $T_g$ ) of the blends that became higher as tackifier content of blends increased when blend components were miscible. In terms of HMA performances, we suggest that factors other than miscibility affect absolute values of adhesive tensile strength more directly than miscibility; this idea has to be investigated further in a future study. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 719–725, 2002

**Key words:** EVA; tackifier; hot-melt adhesives; miscibility; adhesive tensile strength

## INTRODUCTION

Hot-melt adhesives (HMA) are polymer blends that are widely used for spreading over substrates in the melt state followed by solidifying after cooling. Thermoplastics, such as ethylene vinyl acetate copolymer (EVA), polyolefin, polyamide, and polyester, are often used as base polymers for HMA. EVA has attracted a great deal of theoretical and experimental attention because it is the most widely used base polymer for HMA in industry. EVA is a flexible and thermally stable

thermoplastic because it does not have more unstable functional groups than the methylene units in its main chain structures. EVA is a random copolymer of ethylene and vinyl acetate (VAc), and a series of EVA with various different VAc content, is readily available. In general, tackifiers are formulated in EVA-based HMA. Addition of tackifiers results in increasing the glass transition temperature ( $T_g$ ) and enhancing the tackiness of adhesives when they are miscible with base polymer because they usually have higher  $T_g$  and lower molecular weights than EVA. Rosin derivatives, which are used as tackifiers in HMA, are prepared from rosin acid and alcohol. Rosin acid is a mixture of abietic acid and its isomers with the C=C double bonds in different

---

Correspondence to: M. Takemoto.

*Journal of Applied Polymer Science*, Vol. 83, 719–725 (2002)  
© 2002 John Wiley & Sons, Inc.

**Table I** EVAs Used in this Study

| Code  | VAc <sup>a</sup> Content<br>(mol %) | MFR <sup>b,c</sup><br>(g/10 min) | Commercial Name | Supplier                    |
|-------|-------------------------------------|----------------------------------|-----------------|-----------------------------|
| EVA10 | 10                                  | 75                               | Evaflex EV640   | Du Pont-Mitsui Polychemical |
| EVA20 | 20                                  | 20                               | Ultracen UE633  | Tosoh Corporation           |
| EVA25 | 25                                  | 400                              | Evaflex EV310   | Du Pont-Mitsui Polychemical |
| EVA32 | 32                                  | 30                               | Ultracen UE750  | Tosoh Corporation           |

<sup>a</sup> Vinyl acetate.

<sup>b</sup> Melt flow rate that indicates viscosity of polymer helps estimating its molecular weight.

<sup>c</sup> Quoted from suppliers' catalogues.

positions. It is easy to oxidize rosin acid at the position of the C=C double bonds. Therefore, rosin acid is often chemically modified by hydrogenation or disproportionation to prevent deterioration. These modified rosin acids are then esterified by some alcohols, including glycerol or pentaerythritol, and used as tackifiers. Terpene phenols are also used as tackifiers in HMA.

In considering properties of blended materials, including various adhesives, it is necessary to determine the miscibility of blends because miscibility must have great influence on phase structure, physical properties, and bulk performance in many practical situations. The relation between viscoelasticity and adhesive properties of EVA/tackifier resin blends has been studied by our group<sup>1–5</sup> and others.<sup>6,7</sup> The blends of EVA/tackifier resin are classified into four types in terms of miscibility: (1) completely immiscible system, (2) system that has lower critical solution temperature (LCST), (3) system that has upper critical solution temperature (UCST), and (4) completely miscible system. These four types of blend are referred to as “immiscible type,” “LCST type,” “UCST type,” and “miscible type,” respectively. We reported the following conclusion regarding the miscibility and thermal properties of various EVA/tackifier resin blends based on a qualitative analysis of the mean-field approximation in our previous paper;<sup>8</sup> phase diagrams of EVA/tackifier resin blends systematically changed as VAc content in the copolymer increased. This phenomenon is easy to interpret in terms of classical Flory–Huggins theory based on the mean-field approximation.

In this study, we discuss possible relations between miscibility and adhesive tensile strength of EVA/tackifier resin blends, using wood as adherends, over a wide range of temperature. From our previous study,<sup>8</sup> we chose blends that represent some of the typical miscibility types just men-

tioned; one is blended with rosin derivatives and the other with terpene phenol resin as tackifiers.

## EXPERIMENTAL

### Materials

EVAs used in this study are listed in Table I. VAc content in EVAs were 10 (Evaflex EV640/Du Pont-Mitsui Polychemical Company, Ltd., Tokyo, Japan), 20 (Ultracen UE633/Tosoh Corporation Company, Ltd., Mie, Japan), 25 (Evaflex EV310/Du Pont-Mitsui Polychemical), and 32 (Ultracen UE750/Tosoh Corporation) mol %, respectively. These EVAs are referred to as EVA10, EVA20, EVA25, and EVA32, respectively. EVA20 has higher molecular weight than the other EVAs. Tackifier resins used in this study are listed in Table II. Estergum H (Arakawa Chemical Industries Company, Ltd., Osaka, Japan) is the glycerin ester of hydrogenated rosin, and YS Polystar T130 (Yasuhara Chemical Company, Ltd., Hiroshima, Japan) is the terpene phenolic copolymer (phenol: 25%). Estergum H was mixed with all EVAs, whereas YS Polystar T130 was mixed with EVA10 and EVA20, as shown in Table II.

### Preparation of Test Specimens

Kaba wood (*Betula Maximowicziana* Regal.) was used as adherends. The dimensions of wood are shown in Figure 1. Test specimens for adhesive tensile strength test were prepared according to the conditions that are presented in Figure 1. Adhesion temperature and pressure were 160°C and 1 MPa, respectively. These specimens were conditioned at 20°C (65% relative humidity) for ~ 1 week before testing to ensure adhesives had completely reached the equilibrium state.

### Measurement of Adhesive Tensile Strength

Measurement of adhesive tensile strength was conducted with an Orientec Tensilon UCT-5T

**Table II Tackifiers Used in this Study**

| Commercial Name               | $M_w^a/M_n^b$   | $T_g/^\circ\text{C}^c$ | Phase Diagram <sup>d</sup> for EVA/Tackifier Blend |                |                       |                       | Main Component                            |
|-------------------------------|-----------------|------------------------|--|----------------|-----------------------|-----------------------|---|
|                               |                 |                        | EVA10/ $T_c^e$                                     | EVA20/ $T_c^e$ | EVA25/ $T_c^e$        | EVA32/ $T_c^e$        |   |
| Estergum H <sup>g</sup>       | 856/705 (1.21)  | 44.2                   | Immiscible   | LCST/110       | LCST/140              | Miscible              | Glycerin ester of hydrogenated rosin      |
| YS Polystar T130 <sup>h</sup> | 1132/765 (1.48) | 78.7                   | UCST/170   | Miscible       | Miscible <sup>f</sup> | Miscible <sup>f</sup> | Terpene phenolic copolymer (phenol : 25%) |

<sup>a</sup> Weight average molecular weight determined from GPC.

<sup>b</sup> Number average molecular weight determined from GPC.

<sup>c</sup> Glass transition temperature determined from GPC. Temperatures are in Celsius scale.

<sup>d</sup> Temperature range of phase diagrams is 60–170°C.

<sup>e</sup> Critical temperatures shown in phase diagram.

<sup>f</sup> Not used in this study.

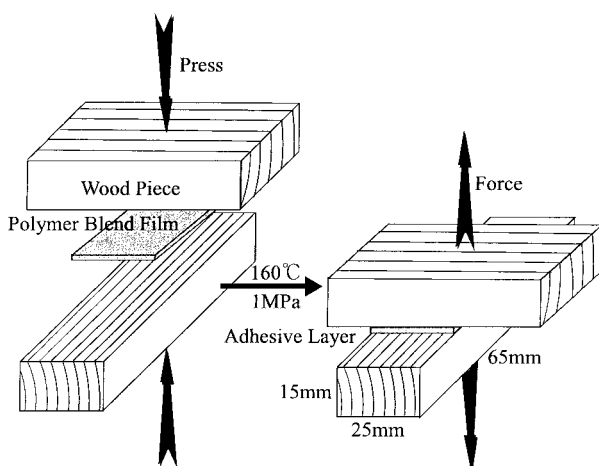
<sup>g</sup> Product of Arakawa Chemical Industries Company, Ltd.

<sup>h</sup> Product of Yasuhara Chemical Company, Ltd.

with a cross-head speed of 50 mm/min, at the temperatures of  $-20$ ,  $0$ ,  $20$ ,  $40$ , and  $60^\circ\text{C}$ . Test results are an average of five measurements under each same condition.

### Measurement of Glass Transition Temperature

Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 at a heating rate of  $20^\circ\text{C}/\text{min}$  in helium to investigate the glass transition temperatures ( $T_g$ ) and melting point ( $T_m$ ) of the blends and their components. The  $T_g$ s of some blend films were confirmed by dynamic mechanical analysis (DMA), which was carried out with a Perkin Elmer DMA7 at 10 Hz in a three-point bending mode at a heating rate of  $3^\circ\text{C}/\text{min}$  under nitrogen.

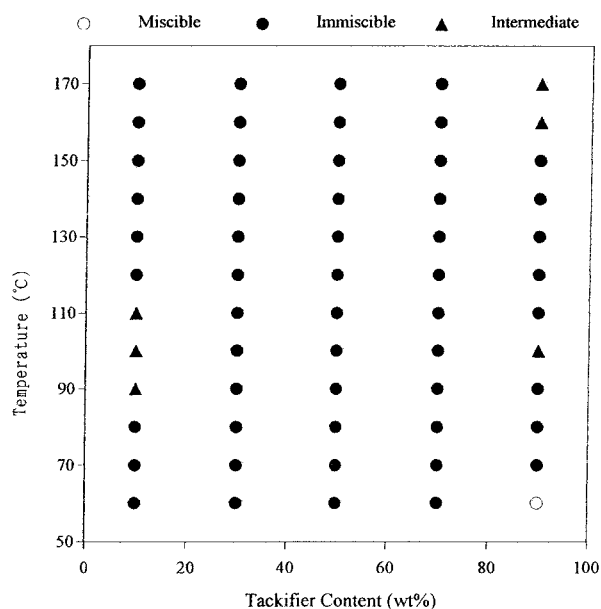


**Figure 1** Dimensions of test specimen for adhesive tensile strength test.

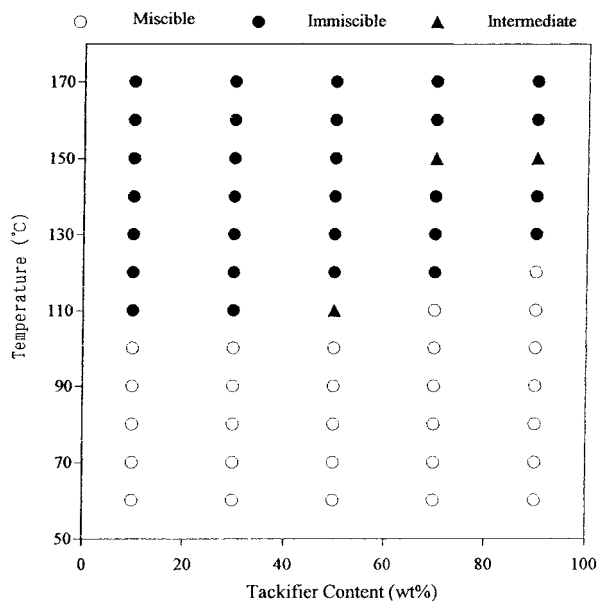
## RESULTS AND DISCUSSION

### Phase Diagrams

Phase diagrams of EVA/estergum H system are shown in Figures 2–5. Blends of EVA10/estergum H are the immiscible type, whereas those of EVA20 and EVA25/estergum H are the LCST type, and EVA32/estergum H is the miscible type. Critical temperatures ( $T_c$ ) for the EVA20 and EVA25/estergum H system are 110 and  $140^\circ\text{C}$ , respectively. In other words, the miscible zone of these phase diagrams becomes wider and wider

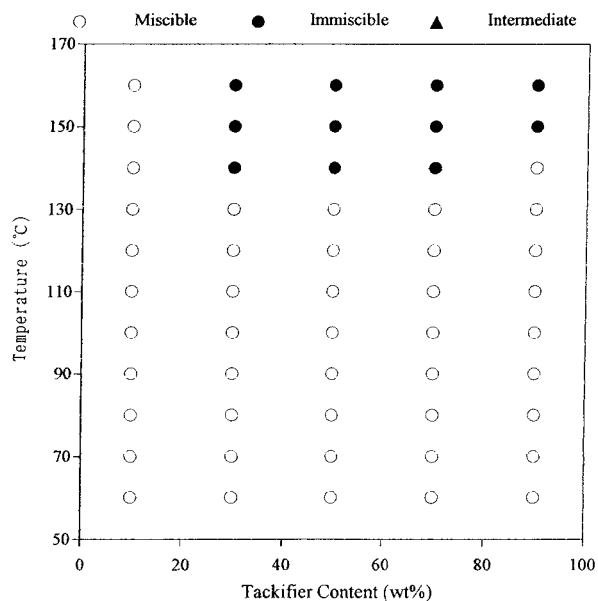


**Figure 2** Phase diagram for EVA10/estergum H. Key: (○) miscible; (●) immiscible; (▲) intermediate.

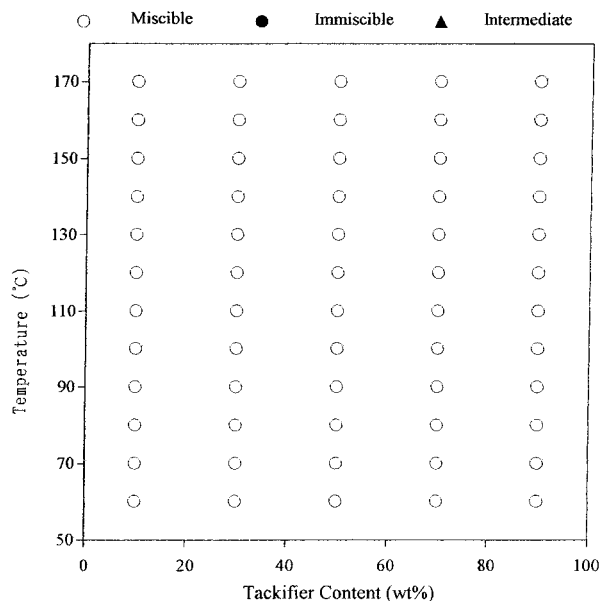


**Figure 3** Phase diagram for EVA20/ester gum H. Key: (○) miscible; (●) immiscible; (▲) intermediate.

as VAc content in EVA increases. These facts imply that EVA/ester gum H system is basically of the LCST type, and  $T_c$  becomes gradually higher as VAc content in EVA increases. In this interpretation,  $T_c$  must be  $< 60^\circ\text{C}$  in EVA10/ester gum H, whereas  $T_c$  must be  $> 170^\circ\text{C}$  in EVA32/ester gum H. We must recognize that the temperature range of phase diagrams in this study is limited to 60–170°C.

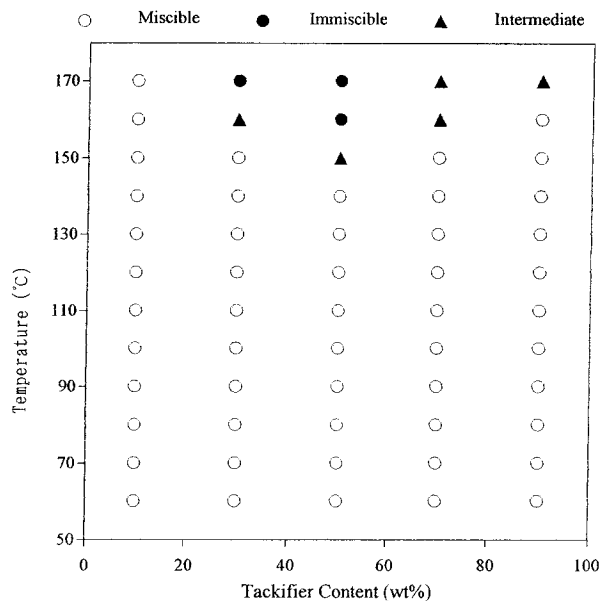


**Figure 4** Phase diagram for EVA25/ester gum H. Key: (○) miscible; (●) immiscible; (▲) intermediate.

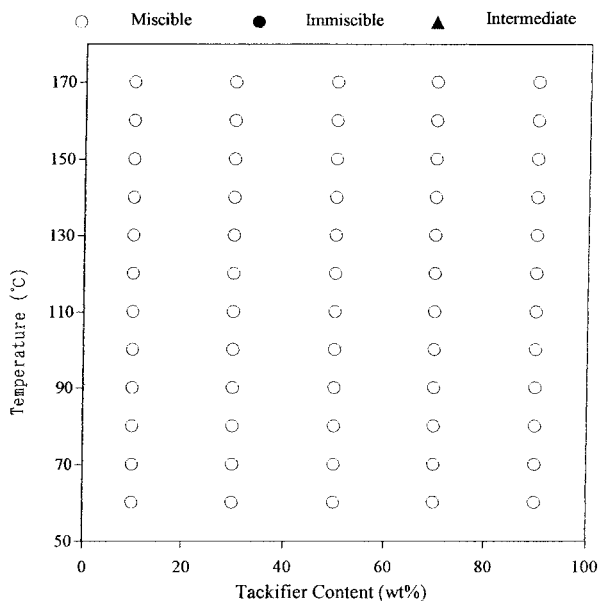


**Figure 5** Phase diagram for EVA32/ester gum H. Key: (○) miscible; (●) immiscible; (▲) intermediate.

Also, phase diagrams of EVA/YS Polystar T130 are shown in Figures 6 and 7. Blends of EVA10/YS Polystar T130 are the LCST type ( $T_c$ , 160°C) and that of EVA20/YS Polystar T130 is the miscible type. These phase diagrams suggest that EVA/YS Polystar T130 is basically the LCST type, and LCST becomes gradually higher as VAc content



**Figure 6** Phase diagram for EVA10/YS Polystar T130. Key: (○) miscible; (●) immiscible; (▲) intermediate.



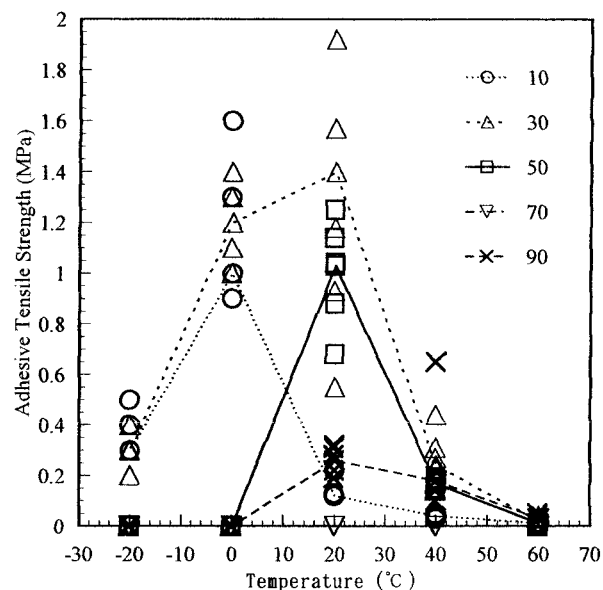
**Figure 7** Phase diagram for EVA20/YS Polystar T130. Key: (○) miscible; (●) immiscible; (▲) intermediate.

in EVA increases, just as in the EVA/estergum H systems.

The miscible zone of phase diagrams for EVA/YS Polystar T130 system is much larger than that of the EVA/estergum H system. This fact has to be investigated further in detail with infrared spectroscopy in a future study.

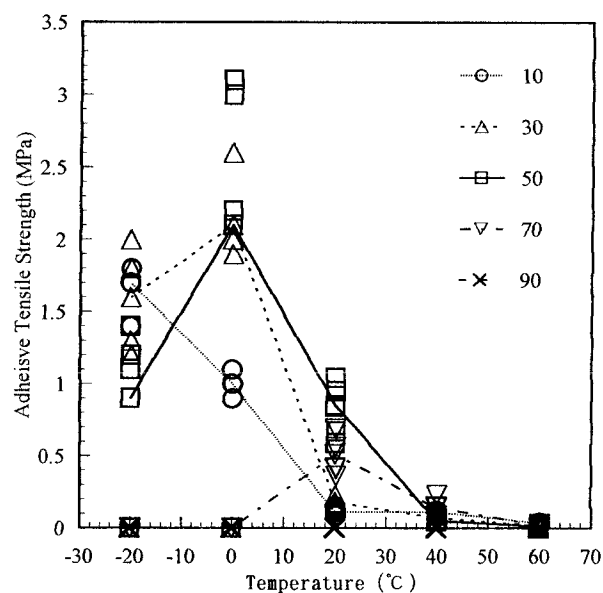
#### Adhesive Tensile Strengths of EVA/Estergum H Blends

The temperature dependence of adhesive tensile strength for blends of EVA10, EVA20, EVA25, and EVA32 with estergum H are shown in Figures 8–11, respectively. In the cases of EVA20, EVA25, and EVA32/estergum H blends, whose phase diagrams are of the LCST type (miscible at testing temperatures), the temperature at which the maximum value of adhesive tensile strength was recorded tended to move toward higher temperature as tackifier content of blends increased. This result corresponds to the fact that the  $T_g$ s of blends became higher as tackifier content of blends increased when blend components were miscible, as measured by DSC and shown in Figure 12. These results also correspond to the viscoelasticity of blends and we are going to report on the viscoelasticity in the following paper. The peaks of adhesive tensile strength were at  $\sim 0$ – $20^\circ\text{C}$ , and these blends became very weak at temperatures  $> 40^\circ\text{C}$ . This result is probably because

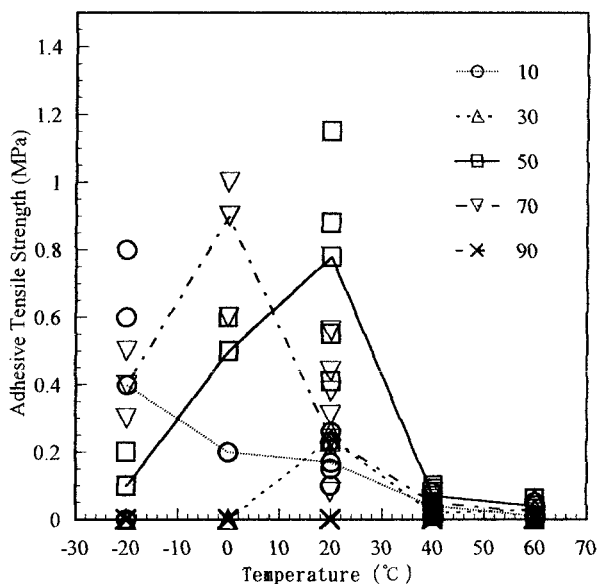


**Figure 8** Temperature dependence of adhesive tensile strength for EVA10/estergum H. Tackifier content: (○) 10 wt %; (Δ) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

the  $T_g$  of estergum H is  $\sim 40^\circ\text{C}$ , so solidified adhesive layers will become soft at temperatures  $> 40^\circ\text{C}$ . Absolute values of adhesive tensile strength for EVA25/estergum H blends were lower than the other blends, which may corre-



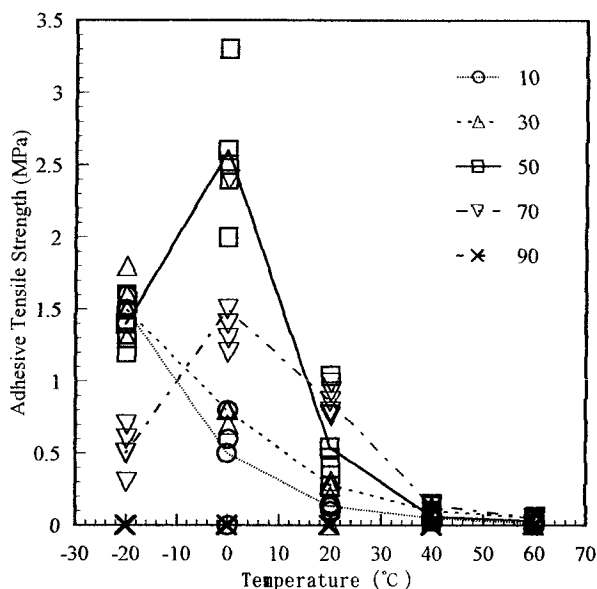
**Figure 9** Temperature dependence of adhesive tensile strength for EVA20/estergum H. Tackifier content: (○) 10 wt %; (Δ) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.



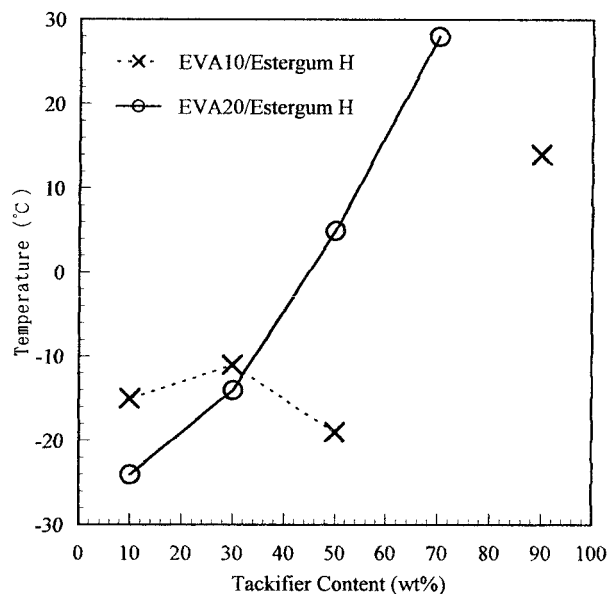
**Figure 10** Temperature dependence of adhesive tensile strength for EVA25/estergum H. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

spond to the lower molecular weight of EVA25 compared with the other blends.

As for EVA10/estergum H blends, the phase diagram is of the immiscible type (immiscible at testing temperatures) and less clear tendencies of adhesive tensile strength in terms of tackifier



**Figure 11** Temperature dependence of adhesive tensile strength for EVA32/estergum H. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.



**Figure 12** Glass transition temperature for EVA10 and EVA20/estergum H. Key: (×) blends of EVA10 and estergum H; (○) blends of EVA20 and estergum H.

content than the other EVA/estergum H blends were observed. But, adhesive tensile strength showed a maximum at  $\sim 0$ – $20^\circ\text{C}$  and became very weak at temperatures  $> 40^\circ\text{C}$ , as did the other EVA/estergum H blends.

#### Adhesive Tensile Strengths for EVA/YS Polystar T130 Blends

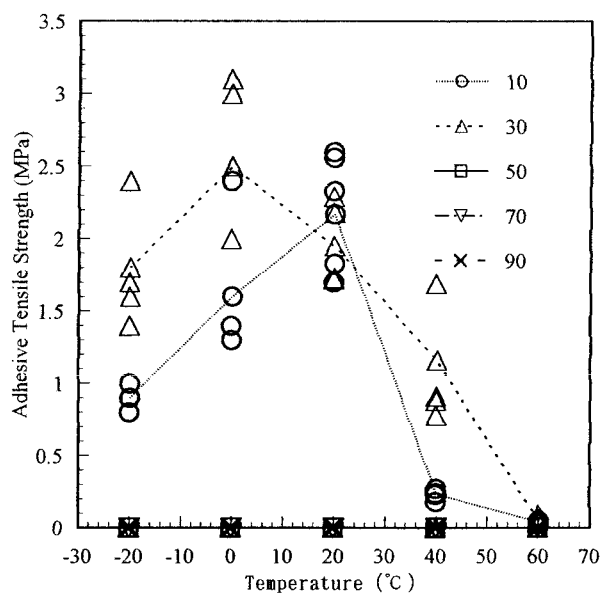
The temperature dependence of adhesive tensile strength for EVA10 and EVA20/YS Polystar T130 blends is shown in Figures 13 and 14, respectively. Phase diagrams of these blends are of the LCST type and miscible type, respectively, which mean all blends are miscible at all testing temperatures in the study. When tackifier content was 10–30%, values of adhesive tensile strength showed maxima at  $0$ – $20^\circ\text{C}$ . This result corresponds to the fact that the  $T_g$ s of the blends became higher as tackifier content of blends increased when blend components were miscible, the same as with the EVA/estergum H system. For all blends, tensile strength showed mostly high values when testing temperatures were  $< 20^\circ\text{C}$ . Otherwise, adhesive tensile strength became relatively weak at higher temperature for all conditions, especially  $> 60^\circ\text{C}$ . This result is somewhat different from that for the EVA/estergum H system because the  $T_g$  for YS Polystar T130 is higher than that of Estergum H.

### Miscibility and Adhesive Tensile Strengths

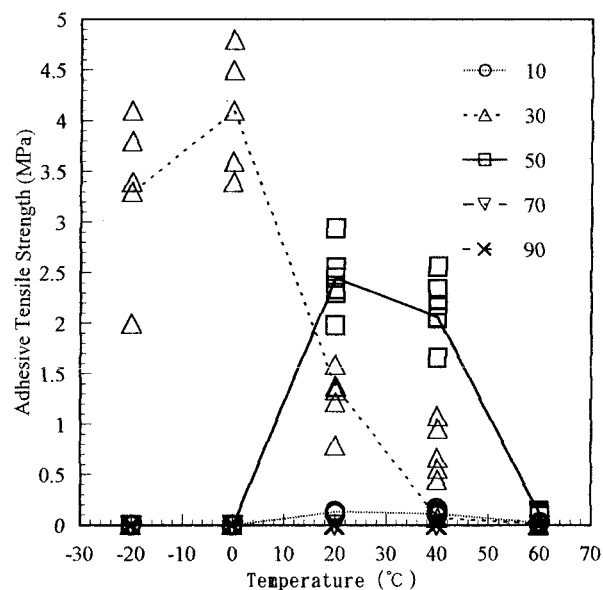
In terms of the miscibility–adhesive tensile strength relationship, no significant tendencies caused by the miscibility of the blend components were observed for all blends. Therefore, we consider that miscibility does not affect adhesive tensile strength of the blends directly, as far as these results are concerned. Other factors that affect adhesive tensile strength have to be investigated.

### CONCLUSIONS

Measurements of adhesive tensile strength for the EVA/tackifier resin system, which basically has lower critical solution temperatures (LCST), were conducted. When a system was miscible at testing temperatures, the temperature at which the maximum value of adhesive tensile strength was recorded tended to move toward higher temperature as tackifier content of blends increased. This result is supposed to correspond to the fact that the glass transition temperature rose up toward higher temperatures as tackifier content increased, when components are miscible with each other. As for absolute values of adhesive tensile strength, no clear tendencies due to the difference of miscibility of the blends were observed. When tackifier content was ~ 30–50%, blends showed



**Figure 13** Temperature dependence of adhesive tensile strength for EVA10/YS Polystar T130. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.



**Figure 14** Temperature dependence of adhesive tensile strength for EVA20/YS Polystar T130. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

mostly high tensile strength at  $< 20^{\circ}\text{C}$ . Otherwise, at  $> 40\text{--}60^{\circ}\text{C}$ , all blends showed little adhesive tensile strength because of the low  $T_g$  of the tackifier.

We acknowledge Du Pont-Mitsui Polychemical Company, Ltd., Tosoh Corporation Company, Ltd., Arakawa Chemical Industries Company, Ltd., and Yasuhara Chemical Company, Ltd. for donating materials used in this study.

### REFERENCES

- Mizumachi, H.; Tsukiji, M.; Konishi, Y.; Tsujita, A. *J Adhesion Soc Jpn* 1976, 12, 378.
- Mizumachi, H.; Hatano, Y.; Kamei, T.; Yamagishi, Y. *Mokuzai Gakkaishi* 1979, 25, 288.
- Hatano, Y.; Tomita, B.; Mizumachi, H. *Holtsforschung* 1986, 40, 255.
- Turreda, L. D.; Hatano, Y.; Mizumachi, H. *Holtsforschung* 1991, 45, 371.
- Turreda, L. D.; Sekiguchi, Y.; Takemoto, M.; Kajiyama, M.; Hatano, Y.; Mizumachi, H. *J Appl Polym Sci* 1998, 70, 409.
- Shih, H. H.; Hamed, G. R. *J Appl Polym Sci* 1997, 63, 323.
- Shih, H. H.; Hamed, G. R. *J Appl Polym Sci* 1997, 63, 333.
- Takemoto, M.; Karasawa, T.; Mizumachi, H.; Kajiyama, M. *J Adhesion* 2000, 72, 85.