

Miscibility and Adhesive Properties of EVA-Based Hot-Melt Adhesives. II. Peel Strength

MOTOTSUGU TAKEMOTO,¹ MIKIO KAJIYAMA,² HIROSHI MIZUMACHI,¹ AKIO TAKEMURA,¹ HIROKUNI ONO¹

¹ 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

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

Received 12 October 2000; accepted 19 February 2001

ABSTRACT: A series of ethylene vinyl acetate copolymers (EVA) were blended with some tackifier resins that were 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 the typical miscibility types and investigated their peel strengths. When the blends were miscible at testing temperatures, the temperature at which the maximum value of peel strength was recorded tended to move toward higher temperature as tackifier content of blends increased. This result corresponds to the storage modulus of the blends whose curves tended to move toward higher temperature as tackifier content of blends increased when blend components were miscible as well as their maximum values of $\tan \delta$, or glass transition temperatures. It was characteristic for peel strength that there existed second peaks on peel strengths curves at $\sim 100^\circ\text{C}$, which adhesive tensile strengths for the blends did not have. In terms of relationship between miscibility and HMA performances, we suggest that there are several factors other than miscibility that affect absolute values of peel strength more directly than miscibility; this idea has to be investigated further in the a future study.
© 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 726–735, 2002

Key words: EVA; tackifier; hot-melt adhesives; miscibility; peel 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. In particular, EVA has attracted a great deal of theoretical and experimental atten-

tion because it is the most widely used base polymer for HMA in industry. EVA is a flexible and thermally stable thermoplastics because it does not have more unstable functional groups than the methylene units in terms of chemical structure. 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 leads to increasing the glass transition temperature (T_g) and enhancing tackiness of adhesives when they are miscible with base polymer because they usually have higher T_g and lower molecular weights

Correspondence to: M. Takemoto.

Journal of Applied Polymer Science, Vol. 83, 726–735 (2002)
© 2002 John Wiley & Sons, Inc.

Table I EVAs Used in this Study

Code	VAc ^a Content (mol %)	MFR ^{b,c} (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

^a Vinyl acetate.

^b Melt flow rate, which indicates that the viscosity of polymers help in estimating their molecular weights.

^c Quoted from suppliers' catalogues.

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 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 derivatives, such as hydrogenated terpene or terpene phenol, 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 group¹⁻⁵ and others.^{6,7} 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:⁸ 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 peel strength of EVA/tackifier resin blends, using polyethylene terephthalate (PET) films as adherends, over a wide range of temperature. From our previous study,⁸ we chose blends that represent some of typical miscibility types which just mentioned; one is blended with rosin derivatives and the others with terpene derivatives as tackifiers.

EXPERIMENTAL

Materials

EVAs used in this study are listed in Table I. VAc contents 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 blends. Tackifier resins used in this study are listed in Table II. Clearon K-4090 (Yasuhara Chemical Company, Ltd., Hiroshima, Japan) is hydrogenated terpene resin, YS Polystar T130 (Yasuhara Chemical Company, Ltd.) is terpene phenolic copolymer (phenol: 25%), and Estergum H (Arakawa Chemical Industries Company, Ltd., Osaka, Japan) is glycerol ester of hydrogenated rosin. Estergum H was mixed with all EVAs, whereas Clearon K-4090 and YS Polystar T130 were mixed with EVA10 and EVA20, as shown in Table II. We chose these combination of blends to investigate how our results show differences between when the blends were miscible and when the blends were immiscible.

Table II Tackifiers Used in this Study

Commercial Name	M_w^a/M_n^b	$T_g, ^\circ\text{C}^c$	Phase Diagram ^d for EVA/Tackifier Blend				Main Component
			EVA10/ T_c^e	EVA20/ T_c^e	EVA25/ T_c^e	EVA32/ T_c^e	
Clearon K-4090 ^g	1419/793 (1.79)	41.8	UCST/170	Miscible	Miscible ^f	Miscible ^f	Hydrogenated terpene Resin
YS Polystar T130 ^g	1132/765 (1.48)	78.7	LCST/150	Miscible	Miscible ^f	Miscible ^f	Terpene phenolic Copolymer (phenol: 25%)
Estergum H ^h	856/705 (1.21)	44.2	Immiscible	LCST/110	LCST/140	Miscible	Glycerol ester of hydrogenated rosin

^a Weight average molecular weight determined from GPC.

^b Number average molecular weight determined from GPC.

^c Glass transition temperature determined from GPC. Temperatures are in Celsius scale.

^d Temperature range of phase diagrams is 60–170°C.

^e Critical temperatures shown in phase diagram.

^f Not used in this study.

^g Product of Yasuhara Chemical Company, Ltd.

^h Product of Arakawa Chemical Industries Company, Ltd.

Evaluation of Miscibility

EVA and tackifier resin were individually dissolved in chlorobenzene, blended at ratios of 90 : 10, 70 : 30, 50 : 50, 30 : 70, and 10 : 90 by weight, and cast on a glass plate. The blends were dried in vacuo and kept at a desirable temperature for at least for 24 h and then visually observed as to whether or not they were uniform. We decided that the clear blends were miscible at a certain temperature. These procedures were repeated in the temperature range 60–180°C. To confirm the miscibility as just decided, blending was also done in a melt stage at 140°C for ~ 20 min 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 thus made were employed for microscopic observation and dynamic mechanical analysis (DMA).

Preparation of Test Specimens

PET films were used as adherends. Dimensions of PET films are shown in Figure 1. Test specimens for peel strength test were prepared with a 0.3–0.35-mm thick spacer according to the conditions presented in Figure 1. Adhesion temperature and pressure were 140°C and 80 kg f/cm² (7.87 MPa), respectively. These specimens were conditioned at 20°C (65% relative humidity) for ~ 1 week before testing to ensure adhesives were completely in the equilibrium state.

Measurement of Peel Strength

Measurement of peel strength was conducted with a Shimadzu Autograph with a cross-head speed of 200 mm/min, at the temperatures of 20,

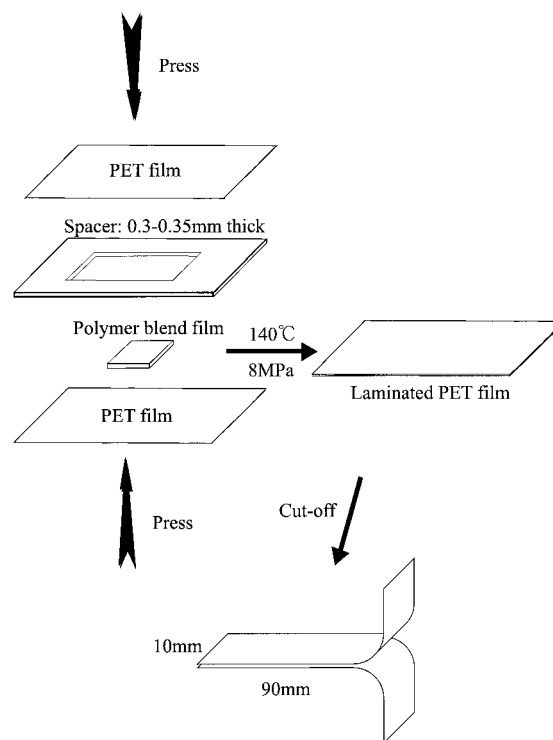


Figure 1 Dimensions of test specimen for peel strength test.

40, 60, 80, 100, 120, and 140°C. Test results are an average of five measurements under the same conditions.

Measurement of Viscoelasticity

Measurement of storage modulus and $\tan \delta$ for these blends was done by DMA with a Perkin-Elmer DMA5 dynamic mechanical analyzer. All samples were time-scanned in the three-point bending mode, with a heating rate of 3.0°C/min.

RESULTS AND DISCUSSION

Phase Diagrams

Phase diagrams of the EVA/Clearon K-4090 system are shown in Figures 2 and 3. Blends of EVA10/Clearon K-4090 are the UCST type, whereas those of EVA20/Clearon K-4090 are the miscible type. The critical temperature (T_c) for the EVA10/Clearon K-4090 system is 170°C. This fact implies that the miscible zone of these phase diagrams becomes wider as the VAc content in EVA increases. In other words, the EVA/Clearon K-4090 system is basically the UCST type and T_c becomes lower as VAc content in EVA increases. Accordingly, T_c must be $< 60^\circ\text{C}$ in EVA20/Cle-

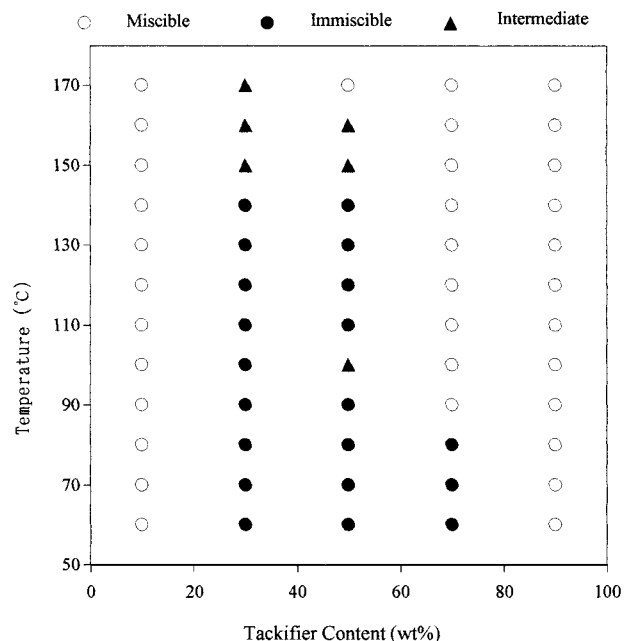


Figure 2 Phase diagram for EVA10/Clearon K-4090 system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

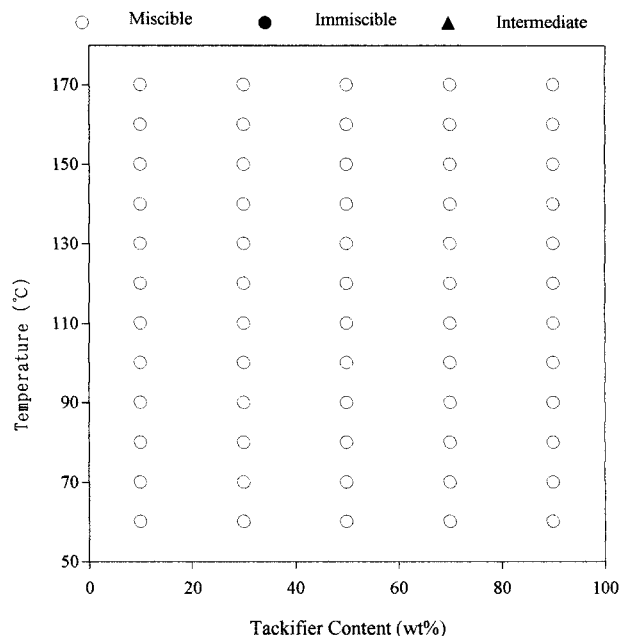


Figure 3 Phase diagram for EVA20/Clearon K-4090 system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

aron K-4090. We must recognize that the temperature range of phase diagrams in this study is limited to 60–170°C.

In contrast with the EVA/Clearon K-4090 system, the EVA/YS Polystar T130 and EVA/Estergum H systems have basically LCST type phase diagrams. Phase diagrams of EVA/YS Polystar T130 are shown in Figures 4 and 5. Blends of EVA10/YS Polystar T130 are the LCST type (T_c , 150°C) and that of EVA20/YS Polystar T130 is the miscible type. In this case, these phase diagrams suggest that EVA/YS Polystar T130 is basically the LCST type and LCST becomes higher as VAc content in EVA increases. The T_c must be $> 170^\circ\text{C}$.

Phase diagrams of EVA/Estergum H system are shown in Figures 6–9. 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. The T_c for EVA20 and EVA25/Estergum H systems are 110 and 140°C, respectively. This fact implies that the miscible zone of these phase diagrams becomes wider and wider as VAc content in EVA increases. In other words, the EVA/Estergum H system is basically the LCST type, and T_c becomes gradually higher as VAc content in EVA increases. Therefore, T_c must be $< 60^\circ\text{C}$ in the

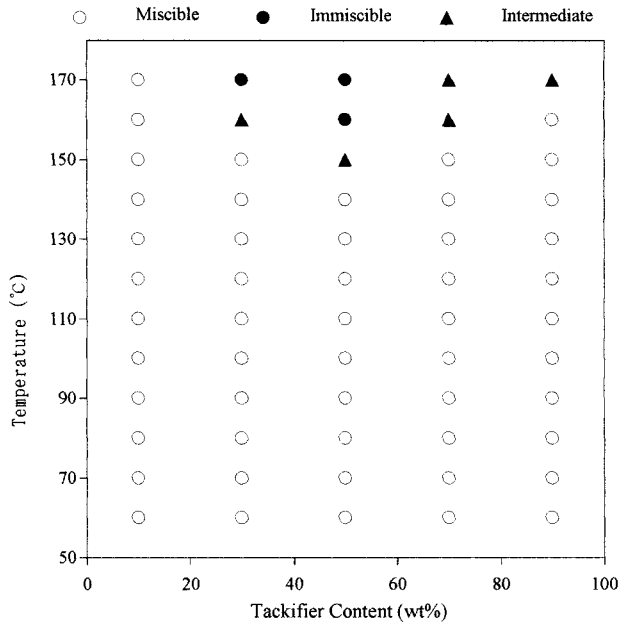


Figure 4 Phase diagram for EVA10/YS Polystar T130 system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

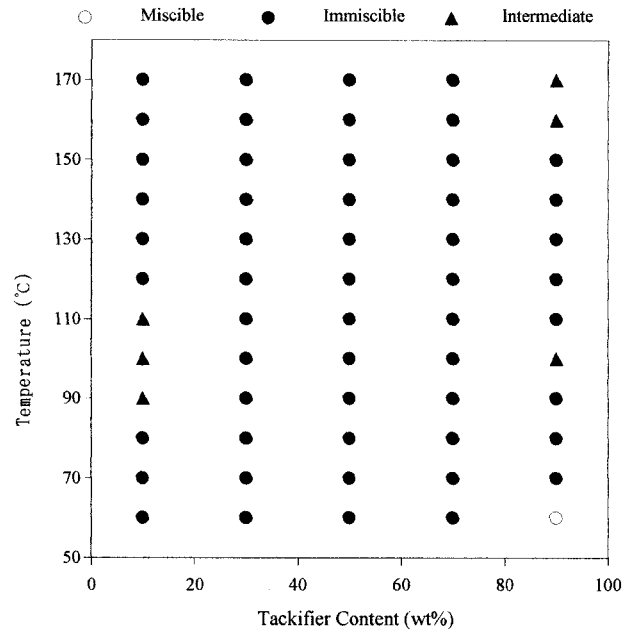


Figure 6 Phase diagram for EVA10/Estergum H system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

EVA10/Estergum H, but > 170°C in the EVA32/Estergum H system.

Miscible zones of phase diagrams for the EVA/Clearon K-4090 system and the EVA/YS Polystar

T130 system are relatively larger than those of the EVA/Estergum H system, especially as for the EVA10 and EVA20 blends. This fact has to be investigated further in detail with spectroscopes in a future study.

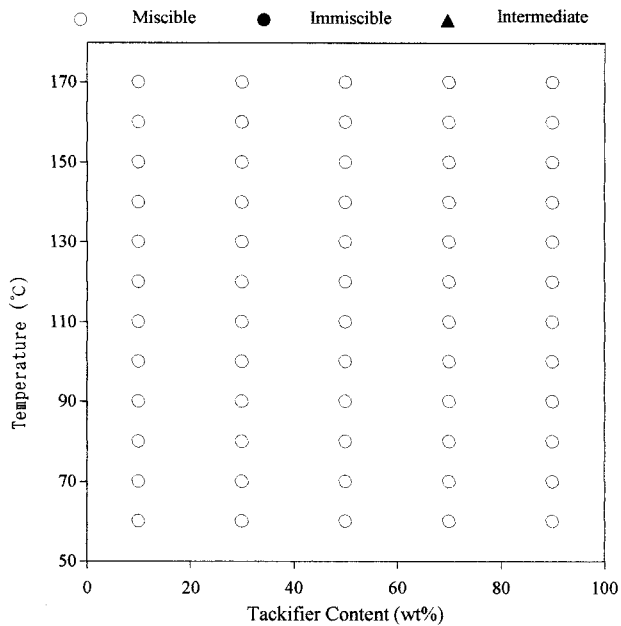


Figure 5 Phase diagram for EVA20/YS Polystar T130 system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

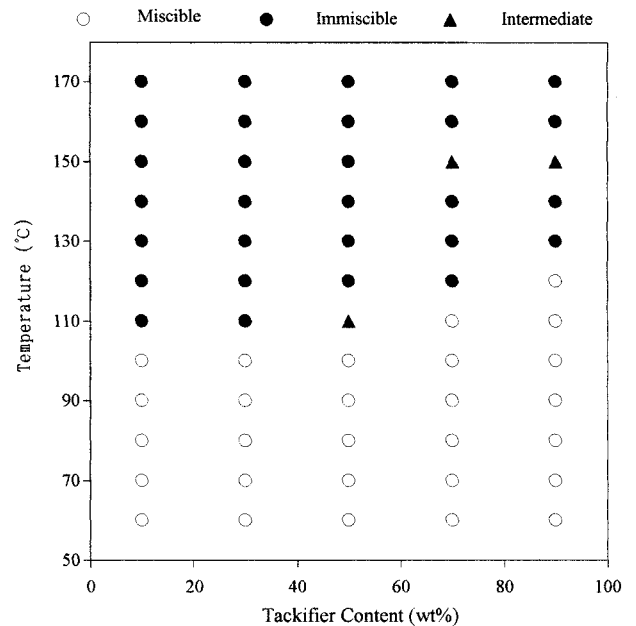


Figure 7 Phase diagram for EVA20/Estergum H system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

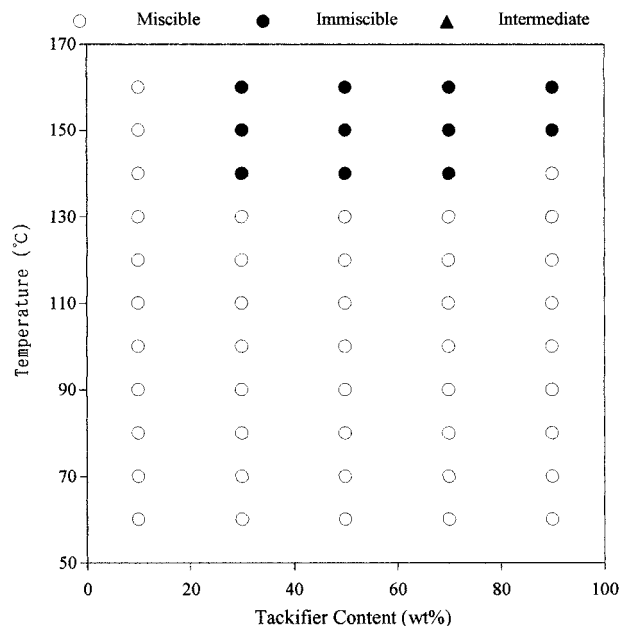


Figure 8 Phase diagram for EVA25/Estergum H system. Key: (○) miscible; (●) immiscible; (▲) intermediate.

Peel Strengths for EVA/Clearon K-4090 Blends

The temperature dependence of peel strength for EVA10 and EVA20/Clearon K-4090 blends are shown in Figures 10 and 11, respectively. In the case of the EVA20/Clearon K-4090 blends, whose

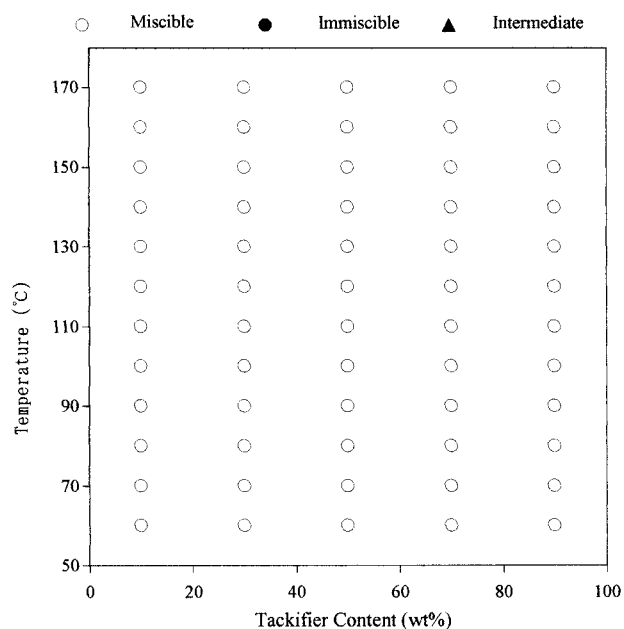


Figure 9 Phase diagram for EVA32/Estergum H system. (○) miscible; (●) immiscible; (▲) intermediate.

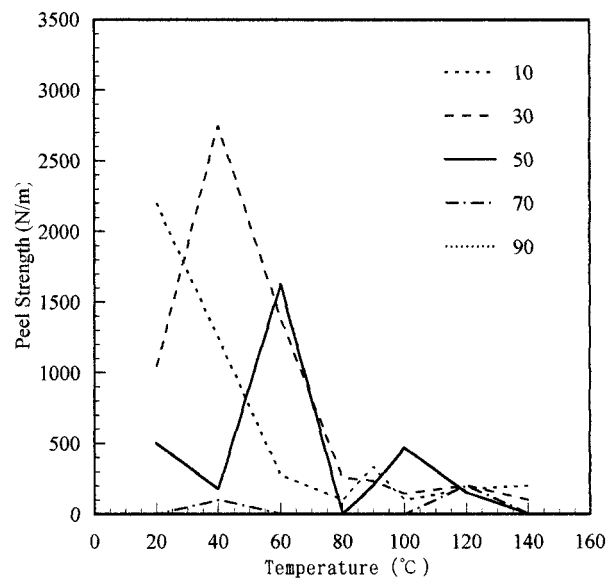


Figure 10 Temperature dependence of adhesive tensile strength for EVA10/Clearon K-4090 system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

phase diagrams are the miscible type (miscible at all testing temperatures), the temperature at which the maximum value of peel 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 of the

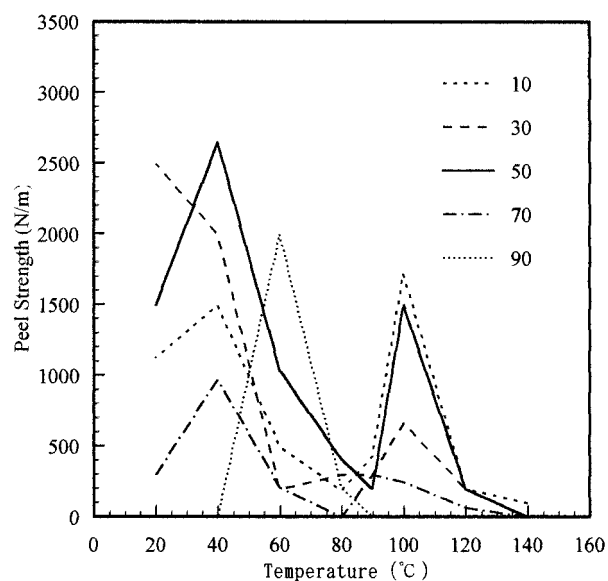


Figure 11 Temperature dependence of adhesive tensile strength for EVA20/Clearon K-4090 system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

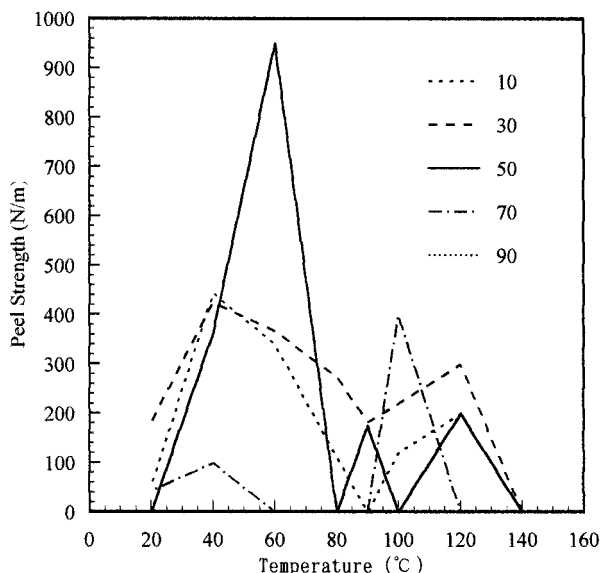


Figure 12 Temperature dependence of adhesive tensile strength for EVA10/YS Polystar T130 system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

blends became higher as tackifier content of blends increased, as measured by differential scanning calorimetry (DSC; reported in our previous study⁸) and DMA. These general tendencies of peel strengths are essentially same for adhesive tensile strengths, which are reported in our paper that we have submitted already. As for EVA10/Clearon K-4090 blends, whose phase diagram is the UCST type (immiscible at testing temperatures), less clear but substantially the same tendencies of peel strength in terms of tackifier content as with EVA20/Clearon blends were observed. The value of peel strength showed a maximum at 20–60°C, especially at 40°C, then became weak at > 80°C. Very little peel strengths were observed when tackifier content of the blends was > 70%.

It was characteristic of peel strengths for all the blends that were investigated in this study to have second peaks at ~ 100°C in these peel strength curves that were not evident for adhesive tensile strengths for the blends. The values of these second peaks, however were much less than those of the first peaks, which are referred to as the “maximum value.” In general, the second peaks were about one third or half those of the first peaks. These second peaks tended to stay at 100°C because temperatures above this were much higher than the T_g values of these blends or the blend components; this result was similar to the tendency of the first peaks.

A distinct change of failure mode was also characteristic of peel strength for every blend that was investigated in this study. This change took place at ~ 100°C, from interface failure to cohesion failure. The former are the failures that occurred at the interface between an adherend (PET film) and solidified adhesive layer, which means neither adherends nor adhesive layer break. On the other hand, the latter are the failures that occurred within solidified adhesive layer, which means solidified adhesive layer itself breaks.

Peel Strengths for EVA/YS Polystar T130 Blends

The temperature dependence of peel strength for EVA10 and EVA20/YS Polystar T130 blends are shown in Figures 12 and 13. Phase diagrams of these blends are LCST type and miscible type, respectively, which mean all blends are miscible at all testing temperatures in the study. The temperature at which the maximum value of peel strength was recorded tended to move toward higher temperature as tackifier content of blends increased, and this result also corresponds to the fact that the T_g s of the blends became higher as tackifier content of blends increased. When tackifier content was < 50%, values of peel strength showed maxima at 40–60°C, especially at 60°C, then became weak at > 80°C. Peel strength

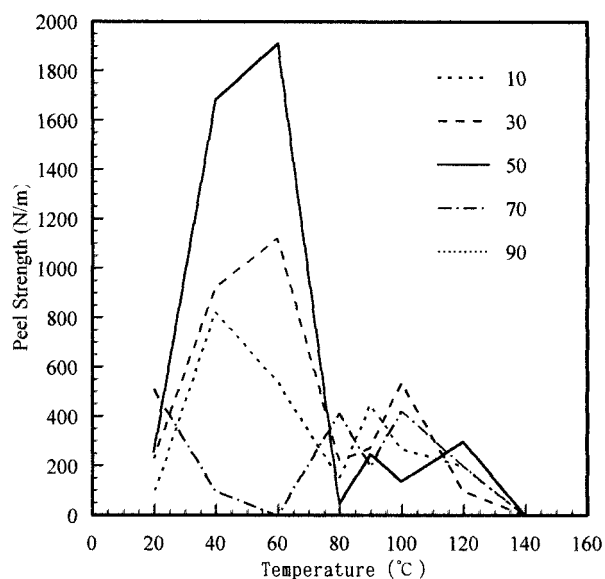


Figure 13 Temperature dependence of adhesive tensile strength for EVA20/YS Polystar T130 system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

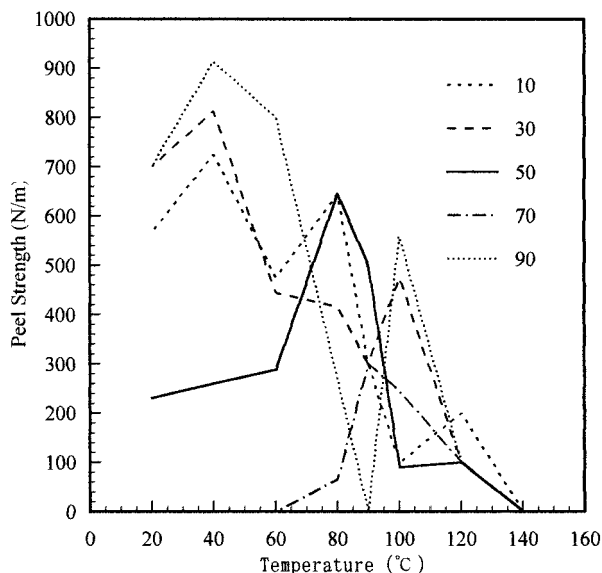


Figure 14 Temperature dependence of adhesive tensile strength for EVA10/Estergum H system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

curves for this system also had second peaks whose tendencies are similar to those for the EVA/Clearon K-4090 system.

Peel Strengths for EVA/Estergum H Blends

The temperature dependence of peel strengths for EVA10, EVA20, EVA25, and EVA32/Estergum H blends, are shown in Figures 14–17, respectively. In the case of EVA20, EVA25, and EVA32/Estergum H blends whose phase diagrams are 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. Again, this result corresponds to the fact that T_g s of the blends became higher as tackifier content of blends increased when blend components were miscible. These results also correspond to the curves of storage modulus of blends that moved toward higher temperature when tackifier ratio of these blends increased, and this is in common for all the miscible blends. We show storage modulus and $\tan \delta$ for EVA20/Estergum H, for example, in Figures 18 and 19. Peaks of $\tan \delta$ also moved toward higher temperature as the tackifier content of the blends increased. This tendency is essentially similar to those of storage modulus. The peaks of these peel strength were at $\sim 40^\circ\text{C}$ except EVA25/Estergum

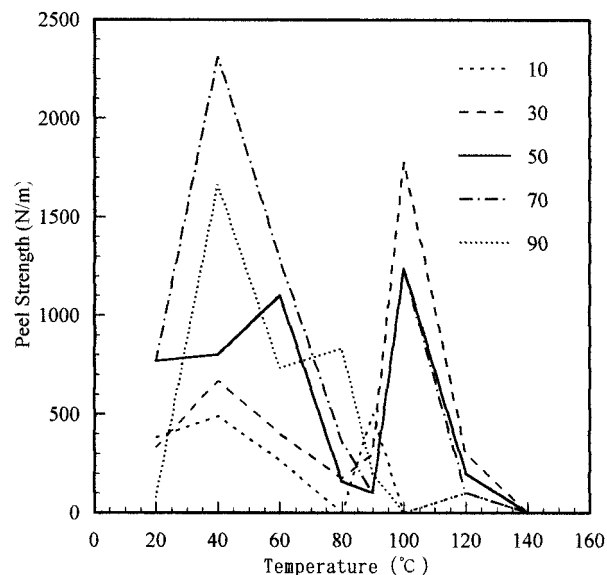


Figure 15 Temperature dependence of adhesive tensile strength for EVA20/Estergum H system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

H system whose peaks of peel strengths were at 20°C . This difference is supposed to be affected by much lower molecular weight of EVA25 than the others (see melt flow rates on Table I). These peel strengths became weak at $> 60^\circ\text{C}$ for the EVA25 and EVA32/Estergum H systems, but not neces-

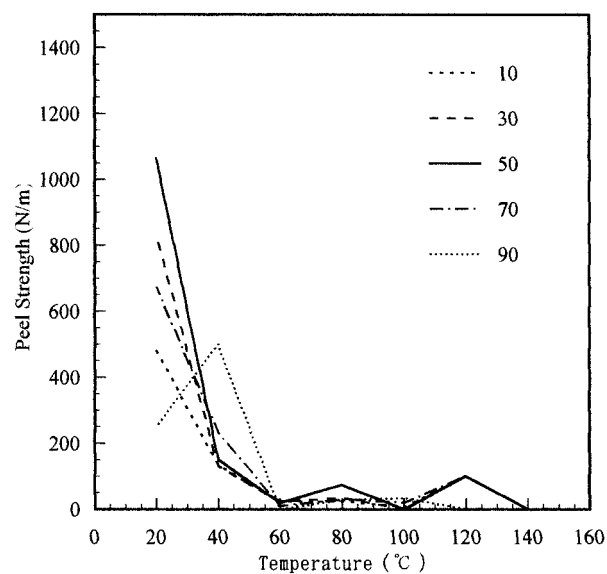


Figure 16 Temperature dependence of adhesive tensile strength for EVA25/Estergum H system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

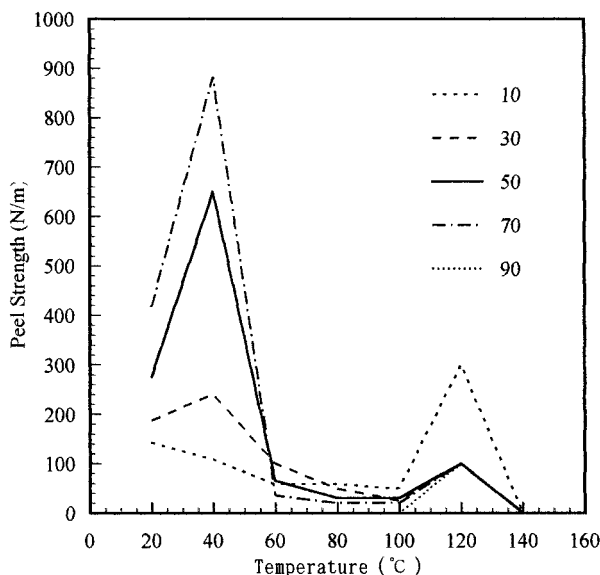


Figure 17 Temperature dependence of adhesive tensile strength for EVA32/Estergum H system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (▽) 70 wt %; (×) 90 wt %.

sarily for the EVA20/Estergum H system. The narrower miscibility for the EVA20/Estergum H system than for the EVA25, 32/Estergum H system may cause this difference. Only with the EVA20/Estergum H system did the peel strength remain much higher even when the tackifier content of the blends was 70%. The narrower miscibility for the EVA20/Estergum H system than the

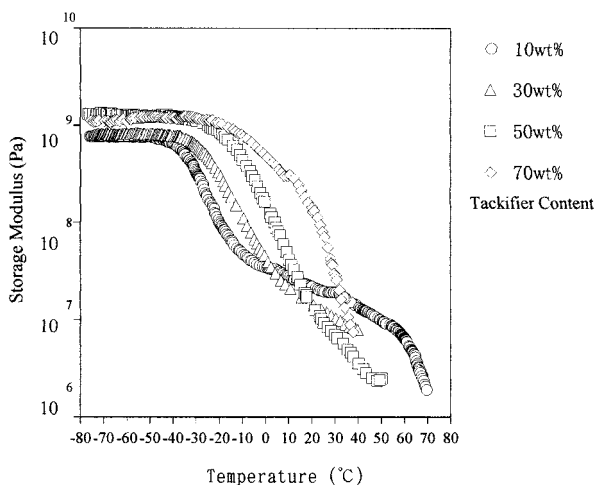


Figure 18 Storage modulus for EVA20/Estergum H system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (◇) 70 wt %. Time scan in three-point bending mode with a heating rate of 3.0°C/min.

other EVA/Estergum H systems may cause this difference again. Further study will be needed on this point. In addition, the temperature dependence of the peel strength for EVA25/Estergum H system suggests that there is a large spread at much lower temperatures.

As for EVA10/Estergum H blends, whose phase diagram is immiscible type (immiscible at testing temperatures), unclear and rather confusing tendencies of peel strengths in terms of tackifier content compared with the other EVA/Estergum H blends were observed. Miscibility might cause this difference between the EVA10/Estergum H blend and the other EVA/Estergum H systems. But, peel strength also showed maxima also at ~ 40°C and became very weak at > 80–90°C, like the other EVA/Estergum H blends.

Peel strength curves had second peaks for all EVA/Estergum H systems, as did the other systems that were investigated in this study.

Miscibility and Peel Strengths

Miscibility must have great influences on phase structure and, as a result, affect physical properties of the blends, including storage modulus. Complex modulus had great influences on peel strengths of the blends, as just reported. Thus, by deductive logic, we expect that there exists a certain relationship between miscibility and peel strengths. However, any significant tendencies caused by the miscibility of blend components were observed for all blends. Therefore, as far as

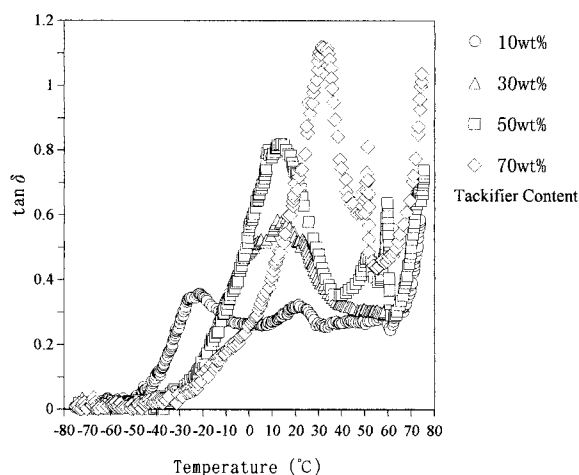


Figure 19 The $\tan \delta$ for EVA20/Estergum H system. Tackifier content: (○) 10 wt %; (△) 30 wt %; (□) 50 wt %; (◇) 70 wt %. Time scan in three-point bending mode with a heating rate of 3.0°C/min.

this study is concerned, we conclude that miscibility affects peel strengths of the blends indirectly, not directly. Other facts that directly cause differences in peel strengths have to be investigated.

CONCLUSIONS

Measurements of peel strength for EVA/tackifier resin systems were conducted. When a system was miscible at testing temperatures, the temperature at which the maximum value of peel strength was recorded tended to move toward higher temperature as tackifier content of blends increased. These results are supposed to correspond to the storage modulus of the blends whose curves tended to move toward higher temperature as tackifier content of blends increased when blend components were miscible, as well as their maximum values of $\tan \delta$ or T_g . Second peaks of peel strength curves at higher temperatures were evident. These peaks were a clearly distinguishable tendency from adhesive tensile strengths for these blends. As for absolute values of peel strength, any clear tendencies due to the difference of miscibility of the blends were not observed. When tackifier contents were ~ 30 – 50% , blends showed mostly high peel strength at

$< 60^\circ\text{C}$. Otherwise, at $> 80^\circ\text{C}$, most blends showed little peel strength because of the low T_g of the tackifiers.

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

REFERENCES

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