

Rheological Study on the Adhesion Properties of the Blends of Ethylene Vinyl Acetate/Terpene Phenol Adhesives

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ABSTRACT: Measurements of the shear, tensile, peel, and creep strength of ethylene vinyl acetate (EVA)/CaCO₃/terpene phenol adhesive system at three different ratios [100/60/0 (EVA-O), 80/48/20 (EVA-20), and 60/36/40 (EVA-40) by weight, using wood and aluminum as adherends] were conducted. Over a wide range of temperatures and rates of deformation, adhesion shear, tensile, and peel strength results, as well as the creep response over a broad range of temperature and stresses, were found to yield a single master curve by means of the reduced-variable technique. It was observed that the peak of E'' representing T_g , shifted toward higher temperatures as the amount of terpene phenol in the blend was increased. The most obvious effect of increasing the tackifier resin was the shifting of the adhesion strength master curves to the direction of lower rates. The shift was associated with the rise in T_g as the blend ratio was increased. The influence of the tackifier resin in modifying the viscoelastic properties of the adhesive was further described in a comparison of the adhesion strength master curves with corresponding dynamic viscoelastic curves of the adhesive films. The master curves for the creep response of the adhesives showed that the stress-breaking time relationship shifts toward longer time for EVA-40 with high T_g . Thus, it was found that the strength of adhesion is due mainly to dynamic effects in the adhesive of a viscous nature in the same way to the cohesive strength of the viscoelastic materials. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 409–418, 1998

Key words: EVA; ethylene vinyl acetate copolymer; hot-melt adhesive; rheological study; time-temperature superposition

INTRODUCTION

Hot-melt adhesives are widely used for spreading over the substrates in the melting state, followed by solidifying after cooling. For the base polymers of the hot-melt adhesives, thermoplastics such as ethylene vinyl acetate copolymer (EVA), polyole-

fins, polyamides, and polyesters are often used. EVA has been chosen as the subject of investigation because it is the most widely used hot-melt adhesive in industry, including in wood. Tackifiers are generally formulated in EVA-based adhesives. Because they have a high glass transition temperature (T_g) and low molecular weight, compared with the EVA, the addition of tackifiers increases T_g and enhances tackiness of the adhesives, if the two components are miscible. The relationship between the viscoelastic and adhesion properties were investigated by us^{1–4} and other research groups.^{5,6} In this article, the adhesive properties (shear and tensile strength) of the

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blends of EVA/CaCO₃/terpene phenol system were measured both on wood and aluminum adherends over a wide range of test rates and temperatures. In addition, peel strength and creep responses were also measured only on wood adherend but over a broad range of experimental parameters. So far, earlier studies have not extended to a comprehensive investigation of the viscoelastic and adhesion properties of EVA/CaCO₃/terpene phenol blends over a wide range of temperature. The present study was undertaken to determine the possible relation between dynamic viscoelastic properties and adhesion strength properties of these blends over wide ranges of test rate and temperatures, as well as their creep response over a broad range of temperatures and stresses, and to compare the results of adhesion tests on wood adherend with that of aluminum adherend.

In the first part of this study, dynamic viscoelastic properties of the blends were measured, analyzed, and interpreted in terms of linear viscoelasticity. Then, experimental investigations of other strength properties follow to examine the behavior of the blends in both wood and aluminum adherends; and to examine the degree of correspondence between adhesion strength and viscoelastic behavior of the adhesives by a reduced-variable technique.

EXPERIMENTAL

Materials

Adhesives

The raw materials of the commercially available EVA/CaCO₃ mixture (Ultracen CE 710/Tosoh Corp., Mie, Japan) and terpene phenol resin (YS polystar T130/Yasuhara Chemical, Hiroshima, Japan) were mainly used. The ratio of EVA and CaCO₃ is 5 : 3 by weight, and EVA contains 27.7 mol % of vinyl acetate (VAc). EVAs without CaCO₃ were also used for confirmation of the miscibility with terpene phenol. The commercial names of the EVA were Evaflex EV310 (Du Pont Mitsui Polychemical Co., Ltd., Tokyo, Japan) and Ultracen UE750 (Tosoh Corp., Mie, Japan), which contained 25.0 and 32.0 mol % of VAc, respectively. For evaluation of miscibility, EVA without CaCO₃ and terpene phenol resin were blended at ratio of 90 : 10, 70 : 30, 50 : 50, 30 : 70, and 10 : 90, respectively in chlorobenzene, followed by casting on glass plate and drying *in vacuo*. Adhesives

were prepared by blending EVA/CaCO₃ and terpene phenol at ratios of 160 : 0, 128 : 20, and 96 : 40, by weight, so that the weight ratio of EVA and terpene phenol resins were 100 : 0 (EVA-O), 80 : 20 (EVA-20), and 60 : 40 (EVA-40), respectively. Blending was done in a melt stage at 180°C for ~ 20 min in a blender equipped with thermal and mixing speed controller. The films were prepared by spreading the polymer blends between Teflon sheets and hot-pressing at 180°C. The films were allowed to cool in air before removing out from Teflon sheets. Long-time cooling was avoided for EVA-40 as the films become brittle. A spacer was used to keep the polymer film thickness at ~ 0.3–0.35 mm. The films thus made were used for thermal analysis and adhesion tests.

Adherends

Kaba wood (*Betula Maximowicziana Regal*. 12.2% m.c.) was used for peel and creep tests. For shear and tensile tests, both wood (*Betula Maximowicziana Regal*. 12.2% m.c.) and aluminum blocks were used. Surfaces of aluminum blocks were polished smoothly with sandpaper and metal polisher, and thoroughly washed with acetone and trichloroethylene to remove greasy matters.

Test Specimens

Test specimens for shear, creep, tensile, and peel tests were prepared accordingly as shown in Figure 1. Those for peel test were composed of wood (Kaba) adherend and aluminum backing. Adhesion temperature and pressure were 180°C and 0.98 MPa, respectively. The specimens were conditioned at 20°C (65% relative humidity) for 1 week before testing.

Methods

Evaluation of Miscibility

EVA without CaCO₃ (VAc content: 25 or 32 mol %) and terpene phenol resin were blended at ratio of 90 : 10, 70 : 30, 50 : 50, 30 : 70, and 10 : 90 by weight, respectively and cast on a glass plate. They were kept in a desirable temperature for at least 24 h and then visually observed whether they were uniform or not. We decided that the clear blends were miscible. These procedures were repeated in the temperature range from 60°C to 180°C.

Measurement of Thermal Properties of Adhesive Films

Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DSC7 at a heating

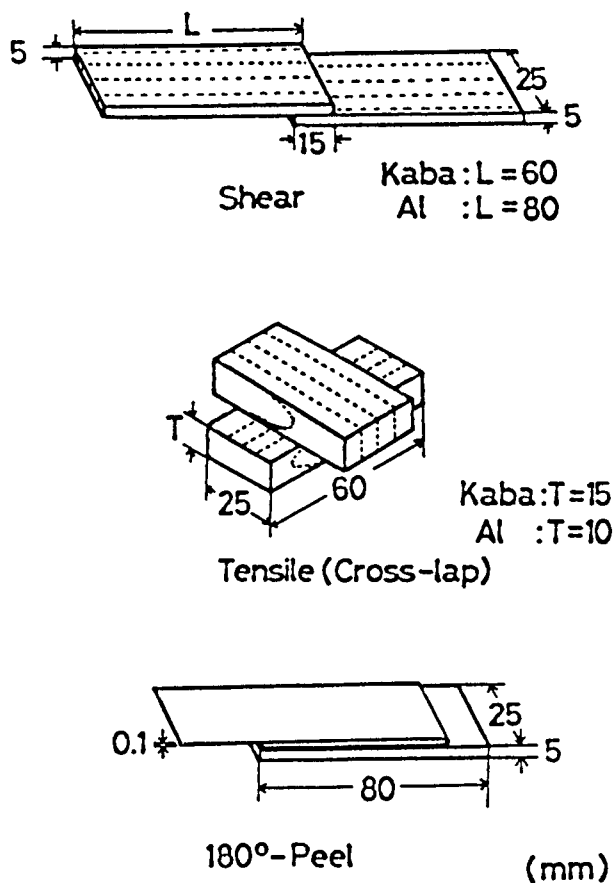


Figure 1 Dimensions of test specimens.

rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$ in helium. The measurement of the viscoelastic properties of the films were conducted using the Orientec Rheovibron DDV-II apparatus at 110 Hz in the temperature range from -80°C to 40°C at a heating rate of $2^{\circ}\text{C} \cdot \text{min}^{-1}$ in nitrogen.

Measurement of Adhesion Strength Properties

Shear and Tensile Strength Tests. Measurements of both adhesive strengths were conducted in the temperature range from -21°C to 48°C at cross-head speeds of 0.5, 5.0, and 50 mm min^{-1} with an Orientec Tensilon UCT-5T. Five specimens were tested for each condition.

Peel Strength Test. Using the same apparatus and crosshead speeds mentioned previously for tensile and shear tests, measurement of peel strength in the temperature range from -36°C to 50°C was conducted at a peel angle of 180° . Peel strength was calculated as the average failing load divided by the width of the bonded area.

Creep Test. This test was conducted using an Orientec Creep Testing Machine CP6-L-500 in the temperature range from 21°C to 60°C under constant stresses. The breaking time t_b was measured as a function of temperature T and stress σ .

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of Adhesive Films

Figure 2 shows the temperature dependences of the blends at a frequency of 110 Hz. As shown, the tensile storage modulus (E') of the adhesives varied drastically between -40°C to 40°C , and the tensile loss modulus (E'') of the polymers have peaks at -25°C , 10°C , and at 35°C for EVA-O, EVA-20, and EVA-40, respectively. Around 30°C , the E' of EVA-O showed a slight absorption peak or a shoulder, which is attributable to some molecular motion of some crystallites present in the polymer. These phenomena were confirmed by means of DSC. The DSC thermogram (not shown) of EVA-O showed a baseline shift at -30°C and an endothermic peak at 30°C . These were correspondent to glass transition temperature (T_g)

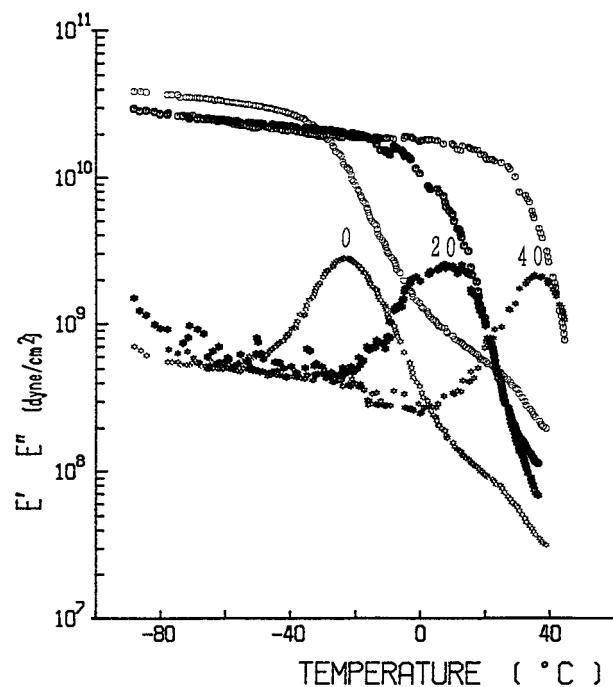


Figure 2 Unified plots of storage modulus (E') and loss modulus (E'') vs. temperature of the blends of EVA/ CaCO_3 /terpene phenol adhesive. Numbers 0, 20, and 40 represent the blend ratios for the terpene phenol resin (EVA-O, EVA-20, and EVA-40, respectively).

and melting point (T_m), respectively. T_g of terpene phenol resin was 107°C by DSC, which was too brittle to measure the viscoelastic properties. Figure 2 further shows that the value of E' for EVA-O is inversely higher, compared with the E' of EVA-20 above 30°C. This proves the fact that crystallites that behave as rigid fillers in an amorphous matrix have high moduli, compared with the rubbery amorphous. Thus, the modulus increased with the degree of crystallinity.⁷ The effect of crystallites in Figure 2 lasted up to temperature above 30°C.

It is also observed from this figure that the peak of E'' representing T_g is shifted toward higher temperatures as the amount of terpene phenol in the mixture is increased. This phenomena indicates that EVA and terpene phenol resin are miscible at least when the blend film is cast. In fact, the visual observation of the blend without CaCO_3 showed that they were miscible at a ratio of 90 : 10 to 10 : 90 in the temperature range from 60°C to 180°C. This result is not in the case of the Ultracene CE 710, of which viscoelastic property was measured. But, the molecular weight and composition are not so different from the tested EVA. We believe that the Ultracene CE 710 and YS polystar T130 are miscible in considerably wide ranges.

Rate and Temperature Dependence of the Strength of Adhesion

Shear and Tensile Strength

Wood Adherend. Figures 3 and 4 present the master curves of shear and tensile strengths, respectively, of the blend reduced to 20°C. Generally, the strength of polymer increases with increasing testing rate and decreasing temperature. This fact also holds true for the present adhesives, at which cohesive failure takes place, as shown in the figures. When adhesive failure or wood failure takes place at higher testing rate and lower temperature, the values of strength are slightly scattered. The most obvious effect of increasing the tackifier resin is the shifting of the master curves to the direction of lower rates. Figures 5 and 6 show the unified plots of the master curves for the mean values of shear and tensile strength, respectively. As shown in Figures 5 and 6, this shift is associated with the rise in T_g as the blend ratio is increased.

Aluminum Adherend. The results herein revealed a similar trend with wood adherend. At

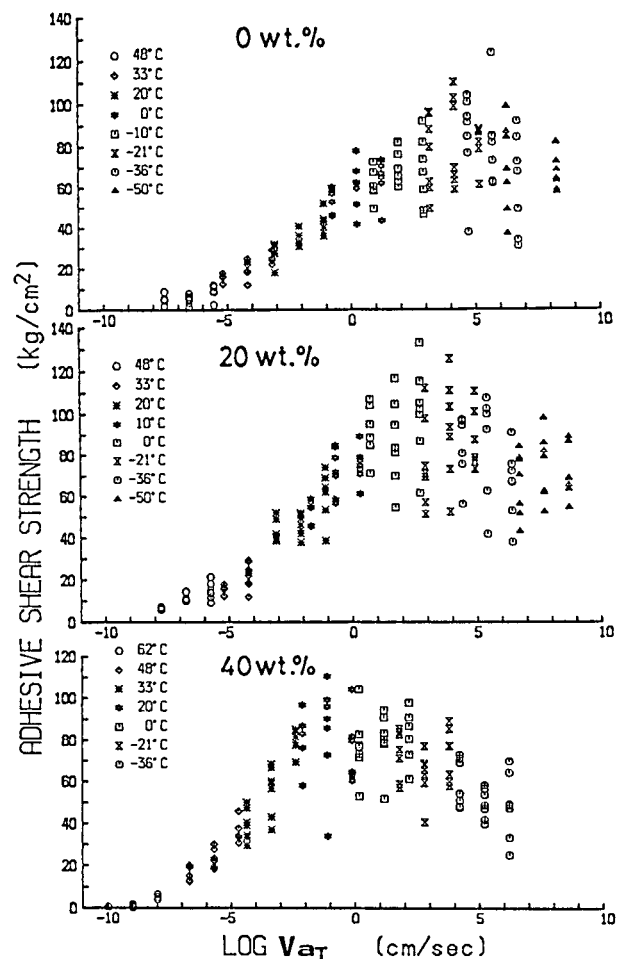


Figure 3 Master curves of adhesive shear strength for EVA-O, EVA-20, and EVA-40 reduced to 20°C for wood adherend.

high temperature and at low rate, both adhesive strength were low for the three blends. As the temperature was increased toward the T_g of the respective adhesives, the bond strength gradually rose to a maximum value at ~ 0 –30°C, 0°C, and 20°C for EVA-O, EVA-20, and EVA-40, respectively, for shear test, and ~ 20 °C, 20°C, and 32–46°C, respectively, for tensile test. Beyond these points, the adhesive strength fell at high rates and at lower temperatures. Cohesive fracture was predominant in almost all temperatures and type of test. Although significant differences in strength values could not be observed over the entire range of test rate and temperature, the average values of EVA-40 were quite lower than EVA-O and EVA-20 in shear strength test. However, a significant difference was observed for tensile strength test, wherein EVA-O obtained

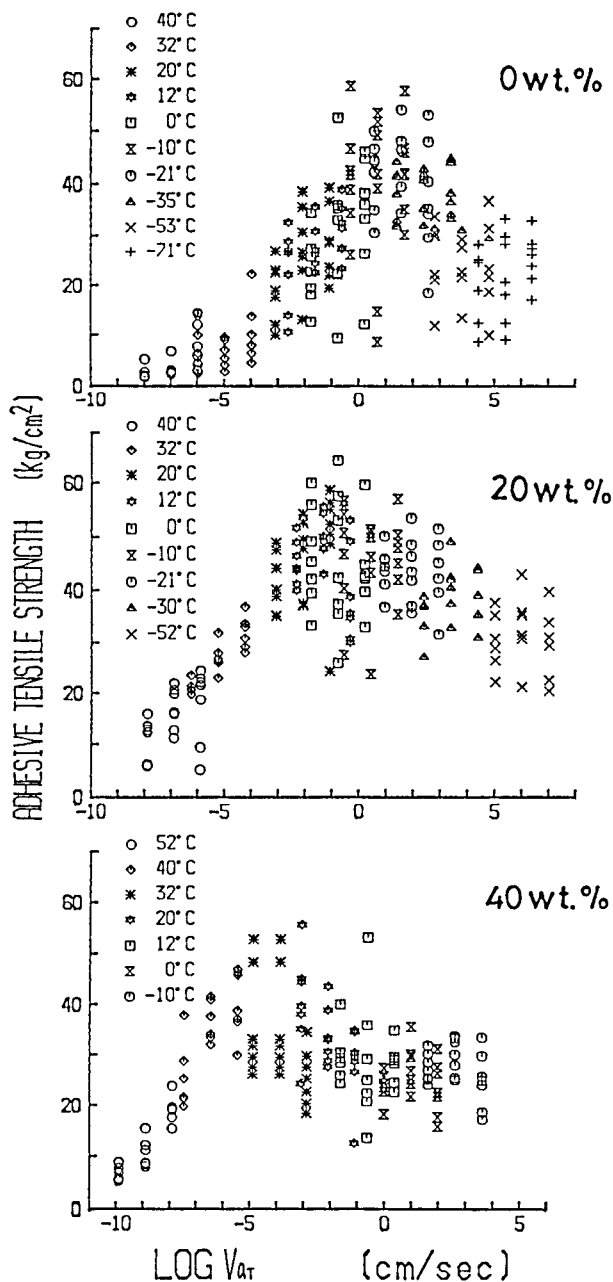


Figure 4 Master curves of adhesive tensile strength for EVA-O, EVA-20, and EVA-40 reduced to 20°C for wood adherend.

higher values, compared with the other two blends. The overall results of this study showed that the adhesive strength values with aluminum adherend were higher, compared with that of wood. This conforms the fact that strong adhesive forces are the natural property of metallic surfaces and other surfaces in the state of cleanliness.⁸ The presence of an oxide layer on the surface of aluminum is the most important factor to

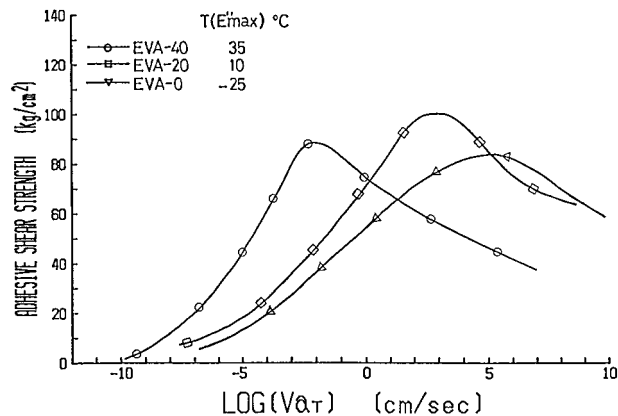


Figure 5 Unified plots of master curves of adhesive shear strength for EVA-O (Δ), EVA-20 (\square), and EVA-40, (\circ) reduced to 20°C for wood adherend.

be taken into account in making satisfactory joints, as pointed out by West.⁹ In other words, in the process of joining aluminum metals, the oxide film provides a useful base for adhesion.⁷ The master curves of the shear strength of the three blends reduced to reference temperature of 20°C are shown in Figures 7–9. These curves were constructed by shifting the shear strengths at various temperatures along the log scale of test rate so that they overlapped each other. The reduced-variable technique was found applicable to these types of adhesives, because a smooth superposition of shear strengths at various temperatures was observed. The master curves of the tensile strength of the adhesives at reference temperature of 20°C are shown in Figures 10–12. Since the master curves of the adhesives were obtained,

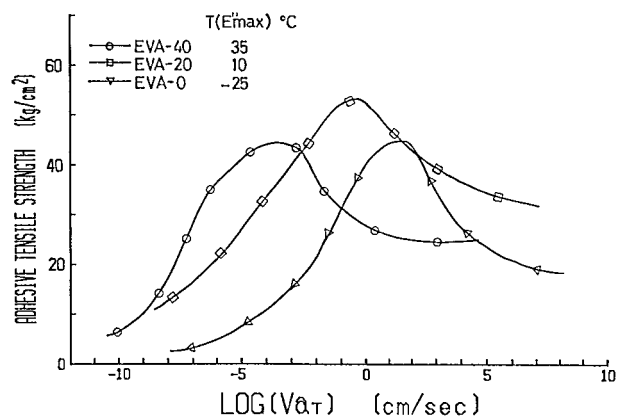


Figure 6 Unified plots of master curves of adhesive tensile strength for EVA-O (Δ), EVA-20 (\square), and EVA-40 (\circ) reduced to 20°C for wood adherend.

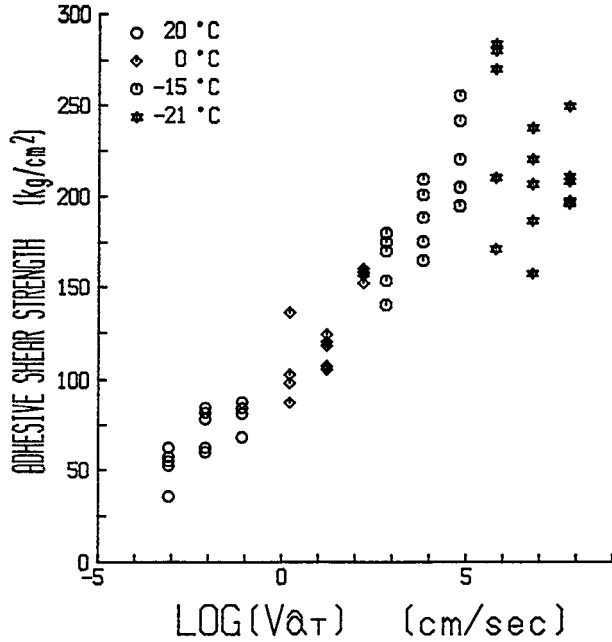


Figure 7 Master curves of adhesive shear strength for EVA-O reduced to 20°C for aluminum adherend.

the superposition principle of rate and temperature is therefore applicable to tensile strength of the adhesives. Figures 13 and 14 show the unified plots of the master curves of shear and tensile strengths of the blends, respectively. Figure 13

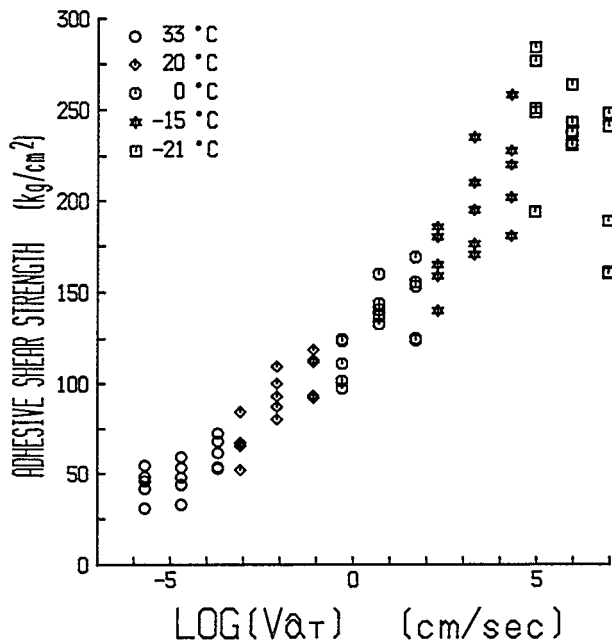


Figure 8 Master curves of adhesive shear strength for EVA-20 reduced to 20°C for aluminum adherend.

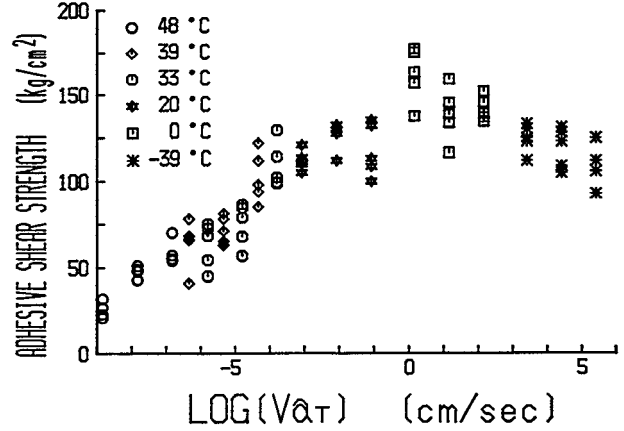


Figure 9 Master curves of adhesive shear strength for EVA-40 reduced to 20°C for aluminum adherend.

followed the same trend as that of wood adherend in all factors considered. However, the unified plots of the master curves of tensile strength showed an unusual trend similar to that of the peel strength, where EVA-O shifted to a lower rate, compared with EVA-20.

Peel Strength. Figures 15 and 16 are the master curves of peel strength of the blends with wood as adherend and aluminum as backing at the same reference temperature, as the previously de-

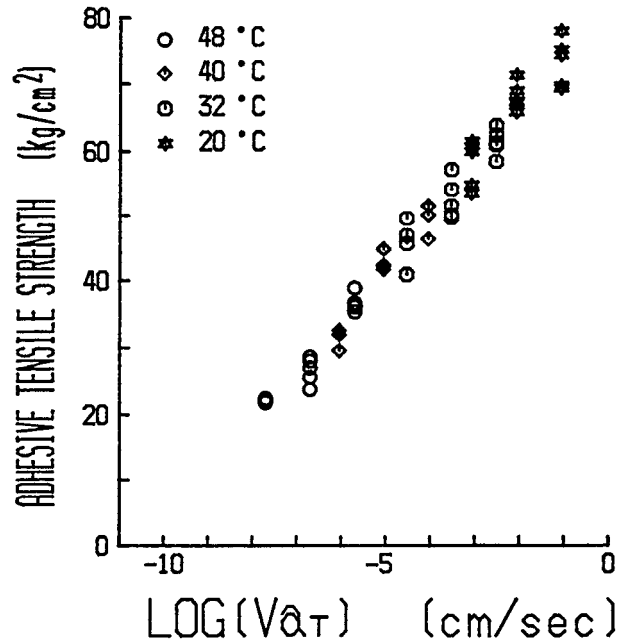


Figure 10 Master curves of adhesive tensile strength for EVA-O reduced to 20°C for aluminum adherend.

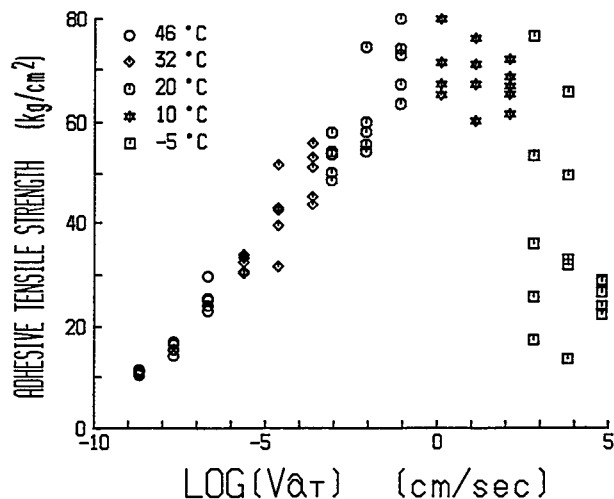


Figure 11 Master curves of adhesive tensile strength for EVA-20 reduced to 20°C for aluminum adherend.

scribed tests. Again, smooth curves were obtained that prove the applicability of the reduced-variable technique. The overall pattern of peeling behavior are similar to each other, except that the curve of EVA-O shifted to the lower rate with a very prominent peak around $\log Va_T$, -5, as shown in Figure 17. This unusual response of the adhesive could be due to the presence of crystallites in the sample. Crystallization generally increases the strength of polymers.⁷ The ability of the chains to be ordered into crystallites is a function of temperature. The deviation of the resulting values of EVA-O from the general trend is in agreement with previous observations with the dynamic viscoelastic curve. The curve of EVA-40

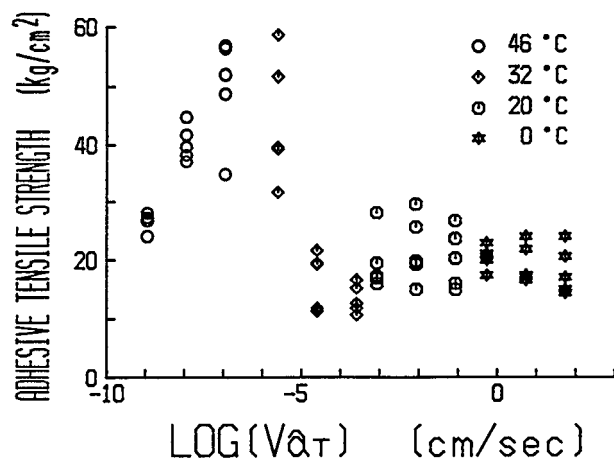


Figure 12 Master curves of adhesive tensile strength for EVA-40 reduced to 20°C for aluminum adherend.

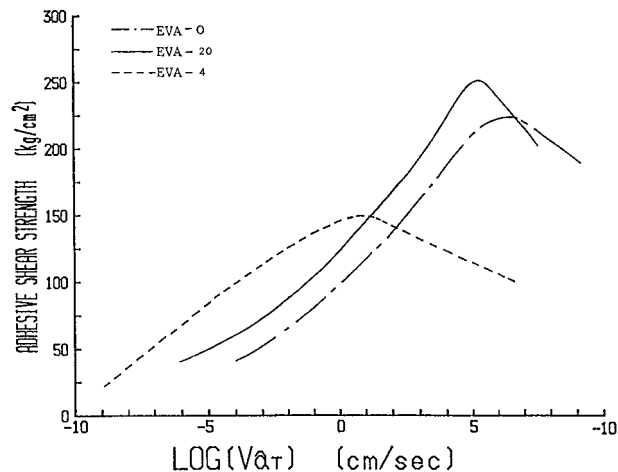


Figure 13 Unified plots of master curves of adhesive shear strength for EVA-O (- · -), EVA-20 (—), and EVA-40 (· · ·) reduced to 20°C for aluminum adherend.

shifted more to the left along the abscissa. This shift reflects the difference in T_g of the polymer. Although there is no significant difference in peel strength values of EVA-20 and EVA-40, it is clear that the dramatic change is the lateral shift due to the change in bulk properties of the adhesives in altering its basic chemical composition. Thus, addition of tackifier resin maybe important because it broadens the range of conditions from which a more desirable rubbery mode of peeling is observed. It is apparent from the preceding figures that the peel forces becomes very low at low rates or high temperatures. As test rates are re-

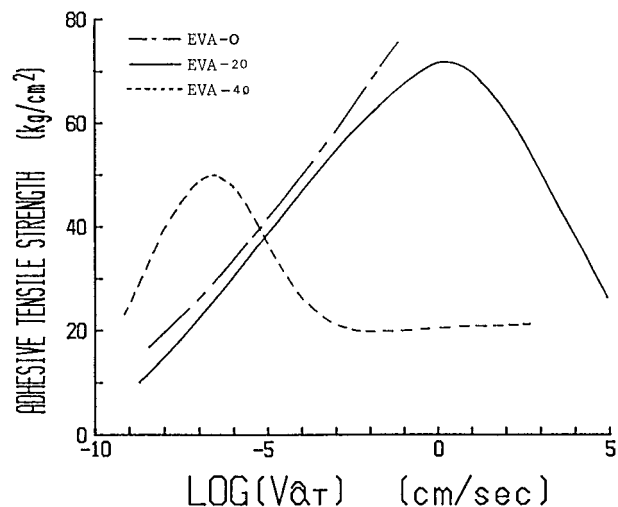


Figure 14 Unified plots of master curves of adhesive tensile strength for EVA-O (- · -), EVA-20 (—), and EVA-40 (· · ·) reduced to 20°C for aluminum adherend.

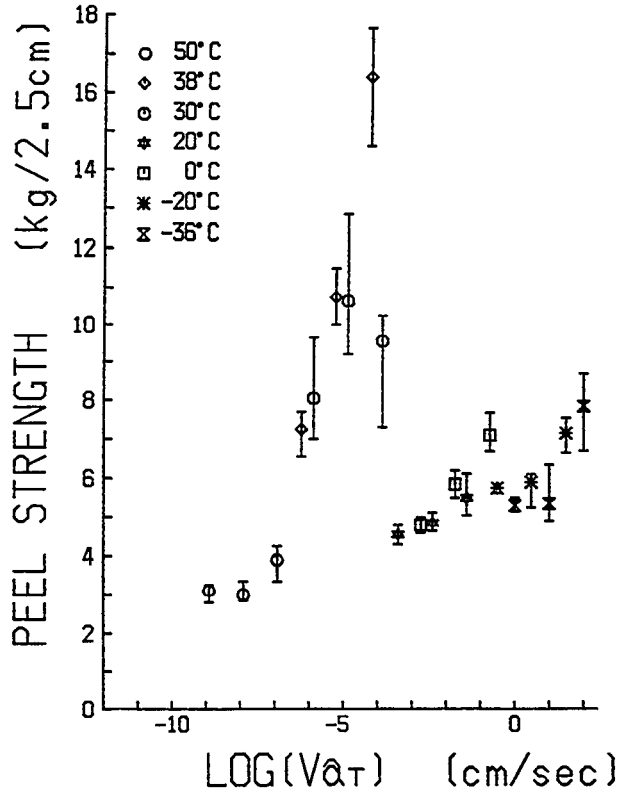


Figure 15 Master curves of peel strength for EVA-O reduced to 20°C for wood adherend with aluminum backing.

duced, the peeling force approaches that required for interfacial separation, because viscoelastic dissipation processes disappear. The mode of fail-

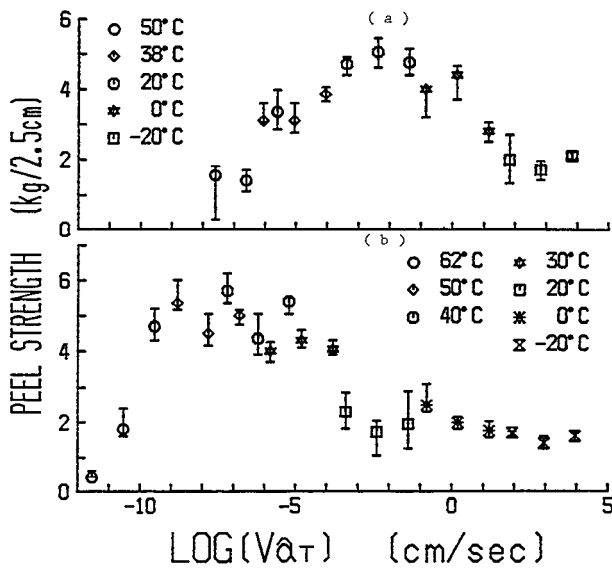


Figure 16 Master curves of peel strength for EVA-20 (a) and EVA-40 (b) reduced to 20°C for wood adherend with aluminum backing.

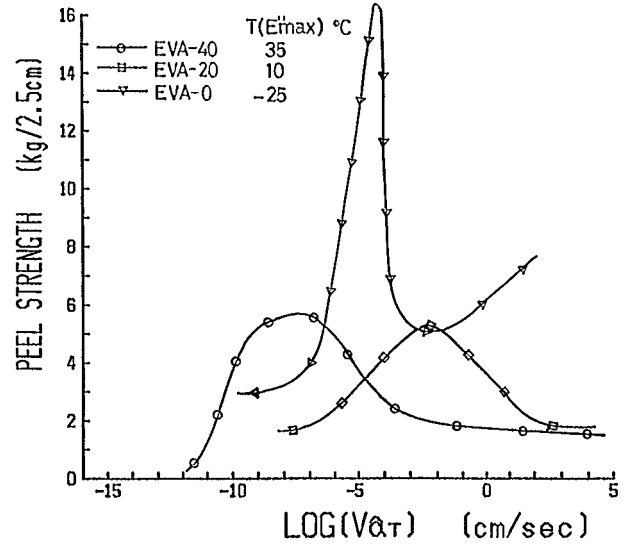


Figure 17 Unified plots of master curves of peel strength for EVA-O (∇), EVA-20 (\square), and EVA-40 (\circ) reduced to 20°C for wood adherend with aluminum backing.

ure changed from cohesive failure of the polymer to clean failure at the interface between the adhesive and the aluminum backing. When the failure was cohesive, adhesive surfaces were rough especially in the case with EVA-O.

Creep Response. The experiment on creep was limited to a temperature range not lower than 20°C. Figures 18–20 show the dependence of breaking time on the applied stress for the adhesives at several temperatures. Within the range of breaking time in this study, the relation be-

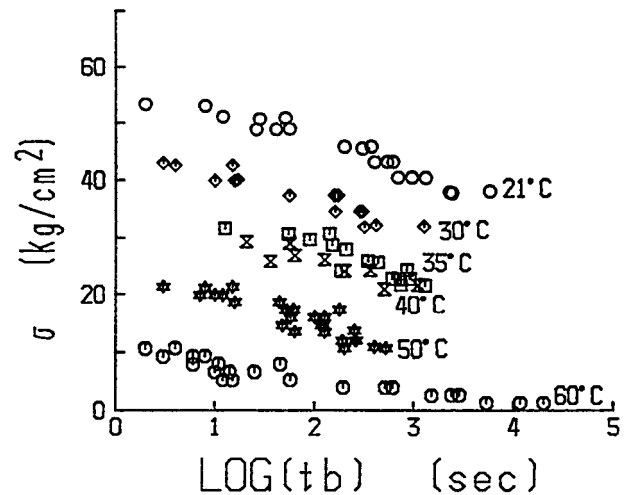


Figure 18 Dependence of breaking time, t_b , on the applied stress for EVA-O/wood adherend.

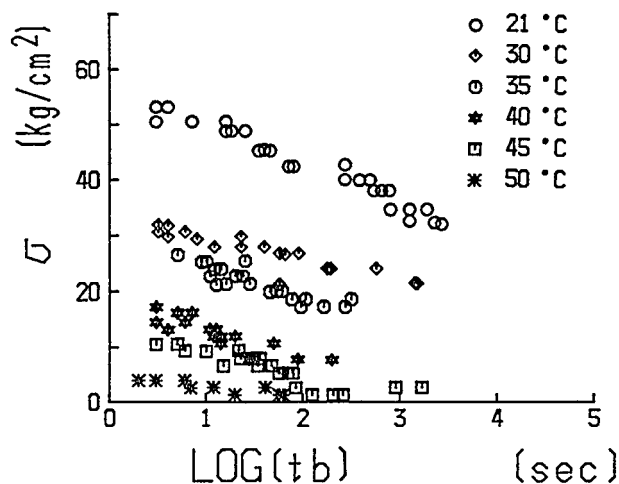


Figure 19 Dependence of breaking time, t_b , on the applied stress for EVA-20/wood adherend.

tween the stress and breaking time were relatively linear at 21°C and 30°C for EVA-O and EVA-20, and at 40°C for EVA-40, respectively. At highest temperatures, the plots showed a slight concave curvature. The EVA-40 maintained higher values for a long time, especially at 21°C, which is below its T_g and above the T_g of the other two blends. The strengths are approximately the same for both EVA-O and EVA-20 adhesives at 21°C. By means of the time-temperature superposition principle, these data were

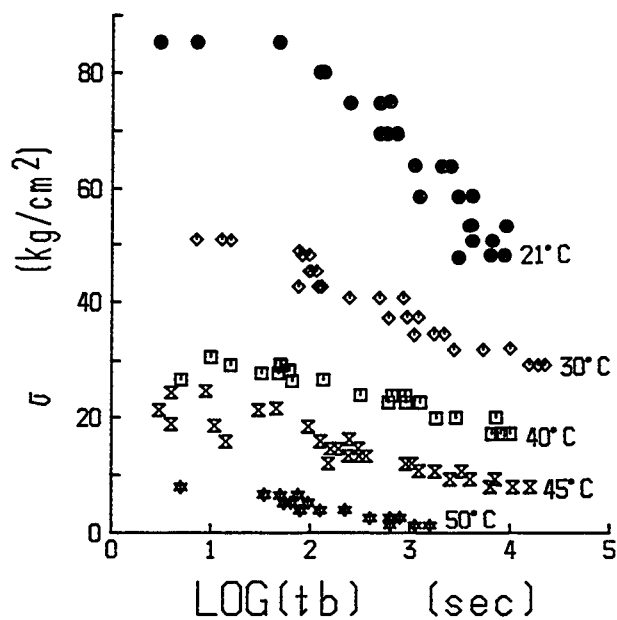


Figure 20 Dependence of breaking time, t_b , on the applied stress for EVA-40/wood adherend.

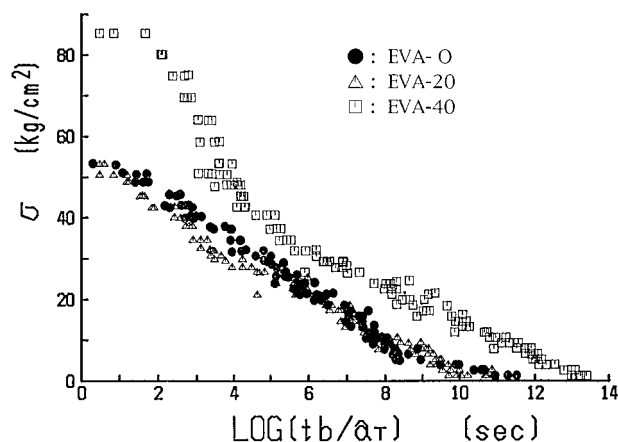


Figure 21 Unified plots of creep response for EVA-O (●), EVA-20 (△), and EVA-40 (□) wood adherend.

shifted to produce master curves reduced to 21°C. When the master curves of the blends were compared as shown in Figure 21, the $stress-t_b$ relationship shifts toward longer times for EVA-40 adhesive with high T_g . However, the general trend of shifting the curve to shorter times for polymers of lower T_g did not hold true for EVA-O adhesive. This result could be attributed to the presence of crystallites as described in the preceding section.

The temperature dependence of shift factor a_T was analyzed by the Arrhenius treatment. A careful analysis of the plots for shear, tensile, peel, and creep strengths reveal that the plots are divided into two segments with different slopes around T_g . This fact of having different activation energy implies that two mechanisms are involved in the debonding process.

CONCLUSIONS

The EVA (of which VAc content is 25–32 mol %) and the terpene phenol resin (YS polystar T130) are miscible in considerably wide ranges. The effect of temperature and rate on the adhesion of EVA/ $CaCO_3$ /terpene phenol miscible adhesives under the conditions studied was complex, but could be understood with reference to the bulk properties of the system. The shear, tensile, and peel strength behavior of the blends as shown in their respective curves are characterized by three regions corresponding to viscous, rubbery, and glassy adhesive response. Oscillatory response or stick-slip phenomena in peel-

ing did not occur in this system. It was shown that master curves were influenced by an increase in terpene phenol resin. The master curves of both shear and tensile strength of EVA-40 were displaced toward the lower test rate, which reflects the effect of increasing T_g of the adhesive as a result of increasing the terpene phenol resin concentration. These changes in both shear and tensile master curves correspond to the changes in the storage moduli (E') master curves. This illustrates that the function of terpene phenol as tackifier resin is primarily to modify the viscoelastic properties of the adhesives. The overall pattern of peeling behavior are similar to each other, except that the master curve of EVA-O shifted to the lower rate with a very prominent peak. This result could mean that addition of tackifier reduces the cohesive strength of the adhesive. For the creep test result, the $stress-t_b$ relationship shifted toward longer times for EVA-40 adhesive with high transition temperature. However, the general trend of shifting the curve to shorter time for polymer of lower T_g did not hold true for EVA-O adhesive. The master curves of adhesion strengths in wood were similar in pattern with that of aluminum adherend, but their positions on the rate axis differed. The strength values with aluminum adherend were

high, and peaks of the master curves shifted to higher rates of deformation.

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