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To cite this article: Young-Jun Park , Hyun-Joong Kim , Miriam Rafailovich & Jonathan Sokolov (2003) Viscoelastic properties and lap shear strength of EVA/aromatic hydrocarbon resins as hot-melt adhesives , Journal of Adhesion Science and Technology, 17:13, 1831-1845, DOI: [10.1163/156856103322538714](https://doi.org/10.1163/156856103322538714)

To link to this article: <https://doi.org/10.1163/156856103322538714>



Published online: 02 Apr 2012.



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Viscoelastic properties and lap shear strength of EVA/aromatic hydrocarbon resins as hot-melt adhesives

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Received in final form 31 July 2003

Abstract—A series of ethylene vinyl acetate (EVA) copolymers were blended with aromatic hydrocarbon resins in the molten state in various ratios and possible relations between viscoelastic and adhesion properties as hot-melt adhesives (HMAs) were investigated. When the softening point of aromatic hydrocarbon resin was high and the concentration of aromatic hydrocarbon resin was low, the $\tan \delta$ peak height decreased and broadened. This result corresponds to the miscibility of the blend. The single lap shear strength increased with increasing softening point of the aromatic hydrocarbon resin and it reached a maximum value with increasing temperature. A large scatter was observed in lap shear strength values, which were higher at higher test rates and lower temperatures, and under these conditions interfacial failure occurred.

Keywords: EVA; aromatic hydrocarbon resin; hot-melt adhesives; lap shear strength; interfacial failure.

1. INTRODUCTION

Hot-melt adhesives are gaining importance in all areas of adhesive usage because of their superior application properties and due to environmental concerns about solvent based adhesives [1]. Hot-melt adhesives containing synthetic polymers, natural waxes, rosins, pitch and other naturally occurring substances have been used, either alone or in mixtures, to produce sealing compounds for a variety of applications [2]. Hot-melt adhesives are 100% solid thermoplastic compounds that contain neither a solvent nor an aqueous carrier for the active adhesive

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components [3]. Hot-melt adhesives are widely used for applying in the molten state over the substrate, followed by solidification after cooling [4], and require quick and strong bonding in manufacturing processes. These adhesives are solids at room temperature, but they liquefy when heated to the temperature at which they are applied.

Hot-melt adhesives are used for cartons, boxes, trays, aluminum foil, cans, bookbinding, disposable diapers and sanitary products [2]. They are also widely used to manufacture inner/outer panels in architecture, automobiles, electronic products, product assembly, shoes, tapes, labels and laminates.

Hot-melts are commonly made of some combinations of polymers, tackifying resins and waxes. Polymers provide the body of the adhesive formulations, the tackifying resins provide the requisite tackiness and waxes are commonly added to modify the viscosity.

Various kinds of elastomers have been used for hot-melt adhesives. However, an elastomer alone cannot provide the desired properties. Thus, low molecular weight hydrocarbon resins, known as tackifiers, for example, aliphatic resins, aromatic resins, and rosin derivatives, are added to an elastomer in order to improve its adhesive properties [5]. A tackifier must be reasonably compatible with the base polymer, have a very low molecular weight relative to the base elastomer, and have a glass transition temperature (T_g) that is higher than that of the base elastomer. Here, EVAs with different vinyl acetate contents were chosen as the subject of this investigation because they are the most widely used in the hot-melt adhesive industry. Also, the aromatic hydrocarbon resins with different softening points are used.

The final test for any adhesive is that it should produce joints, which are strong and durable. The shear strength is a measure of the force or energy needed to break such a joint. In general, adhesives display their highest strength when loaded in shear. The standard test method for evaluating the shear strength of adhesive bonds is described in ASTM D1002. This test method is one of the most common and most studied test methods for the evaluation of adhesive bonds [6].

In this study, the viscoelastic properties of EVA-based hot-melt adhesives were measured using dynamic mechanical analysis (DMA). The single lap shear strengths of the EVA-based hot-melt adhesives were examined at different temperatures and crosshead speeds using stainless steel as the adherend. We discuss here possible relations between the viscoelastic properties and the lap shear strength of the EVA-based hot-melt adhesives. The failure modes were classified as interfacial, interfacial-cohesive, or cohesive failure, based on the results of scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1. Materials

2.1.1. Polymers. EVAs were supplied by Hanwha Chemical (South Korea). Table 1 shows the vinyl acetate contents, melt indices and molecular weights of EVAs.

2.1.2. Tackifiers. Aromatic hydrocarbon resins with different softening points were supplied by Kolon Chemical (South Korea). Table 2 presents the softening points and molecular weights of the aromatic hydrocarbon resins used in this study.

2.1.3. Antioxidant. To reduce the thermal degradation of the hot-melt adhesives, 0.25 parts by weight of a phenolic antioxidant, Irganox 1010 (Ciba Geigy), was used as an antioxidant.

2.1.4. Adherends used for measuring single lap shear strength. Stainless steel plates (ASTM A 167-99, type 302) with dimensions $101.6 \times 25.4 \text{ mm}^2$ were used for the single lap shear test on the EVA-based hot-melt adhesives. The thickness of the stainless steel adherend was 1.5 mm. The stainless steel plates were washed with acetone before bonding.

Table 1.

Vinyl acetate content, melt index and molecular weight of EVAs

Code	VAc. content (wt%) ^a	Melt Index (deg/min) ^b	T_g^c (°C)	M_n^d	M_w^d	MWD ^d	Commercial name
EVA-15	15.0	10.0	-29	19207	161214	8.39	EVA1152
EVA-20	20.0	20.0	-28	17863	95191	5.33	EVA1156
EVA-28	28.0	18.0	-27	19053	84777	4.45	EVA1159

^a Vinyl acetate, measured by elemental analysis and FT-IR spectroscopy.

^b ASTM D1238.

^c Measured by DSC.

^d Measured by GPC.

Table 2.

Softening point and molecular weight of aromatic hydrocarbon resins

Code	Softening point (°C)	T_g^a (°C)	M_n^b	M_w^b	MWD ^b
P-90	95 ± 5.0	46	446	760	1.70
P-120	120 ± 5.0	74	694	1421	2.05
P-140	145 ± 5.0	106	993	2254	2.27

^a Measured by DSC.

^b Measured by GPC.

2.2. Methods

2.2.1. Gel permeation chromatography (GPC).

2.2.1.1. Polymers. The molecular weights and molecular weight distributions (M_w/M_n) of the ethylene vinyl acetate copolymers were measured using a Waters 150-CV equipment (Column: GPC HT-806M). EVAs were maintained in an oven at 165°C for 1 h and then filtered. The solvent used was 1,2,4-trichlorobenzene and a refractive index detector was used.

2.2.1.2. Tackifiers. The molecular weights and molecular weight distributions (M_w/M_n) of the aromatic hydrocarbon resins were measured using a Waters GPC equipment (columns: HR-1, HR-2, HR-3, HR-4). The solvent used was THF (tetrahydrofuran) and a refractive index detector was used. Polystyrenes with different molecular weights were used for calibration.

2.2.2. Blends of polymers and tackifiers. EVA-15, EVA-20 and EVA-28 were mixed with tackifiers P-90, P-120 and P-140 in a 300-g internal mixer at 30 rpm with a blend temperature of 180°C. First, the tackifier and antioxidant were mixed. The quantity of antioxidant, Irganox 1010, was 0.25 parts. When the tackifier became masticated and formed a homogeneous melt, the EVA was slowly added until completely melted. The mixing time was about 20 min. EVA and tackifier were blended in various ratios, 7 : 3, 6 : 4, 5 : 5, 4 : 6 and 3 : 7. EVA-based hot-melt adhesive films were obtained by compression molding.

2.2.3. Dynamic mechanical analysis (DMA). The viscoelastic properties of the hot-melt adhesives were measured on a TA Instruments DMA 2980. Samples of dimensions $400 \times 10 \times 2 \text{ mm}^3$ were used for this study. The experiments were carried out at a frequency of 10 Hz over a temperature range of -100 to 75°C with a heating rate of $5^\circ\text{C}/\text{min}$ under liquid nitrogen in a dual cantilever mode. The $\tan \delta$ and storage modulus were measured for each sample in this temperature range.

2.2.4. Single lap shear test. The adhesive joint was obtained by pressing the hot-melt adhesive film between two stainless steel plates at a temperature of 180°C for 5 min. The bondline thickness was maintained at 0.1 mm. After the lap joints assembly, these were conditioned for 24 h in a temperature and humidity chamber in which a relative humidity of 50% at 30°C was maintained. Single lap shear strength was measured using a Zwick Universal Testing Machine Z101 (at NICEM, Seoul National University) at crosshead speeds of 10, 50, 100, 300, 500 and 1000 mm/min and temperatures of 25, 40, 55 and 70°C . For certain experiments, single lap shear strength was also measured at a crosshead speed of 300 mm/min and at temperatures of -35 , -20 , -5 and 10°C . Failure modes were noted as being interfacial, cohesive-interfacial, and cohesive failures by visual method with SEM. We defined an interfacial failure when stainless steel adherend

was seen in the micrograph, and cohesive failure was defined when stainless steel adherend was not seen.

2.2.5. Scanning electron microscopy (SEM). After single lap shear tests, the morphology of each sample was determined using a Hitachi Scanning Electron Microscope S-2700. All samples were gold coated.

3. RESULTS AND DISCUSSION

3.1. DMA

The viscoelastic properties of the polymers are highly dependent on their structure. The storage modulus of the all blends varied significantly between 0 and 25°C as shown in Figs 1 and 2. In Fig. 1, the $\tan \delta$ of the P-90 blend shows a sharp peak at 63°C, whereas that of the other blends show indistinct peaks because these peaks are very broad. Around 70°C, the storage modulus (E') of the EVA-20 shows a slight absorption peak, which is attributable to some molecular motion of crystallites present in the polymer. Also, the damping increases as the softening point of the aromatic hydrocarbon resin in the blend increases. These properties are related to the miscibility of the blend and volume fraction of the aromatic hydrocarbon resin. The P-90 is miscible with EVA-20; therefore, it shows a sharp single peak, but P-120 and P-140 blends show partially miscible or immiscible states with increasing

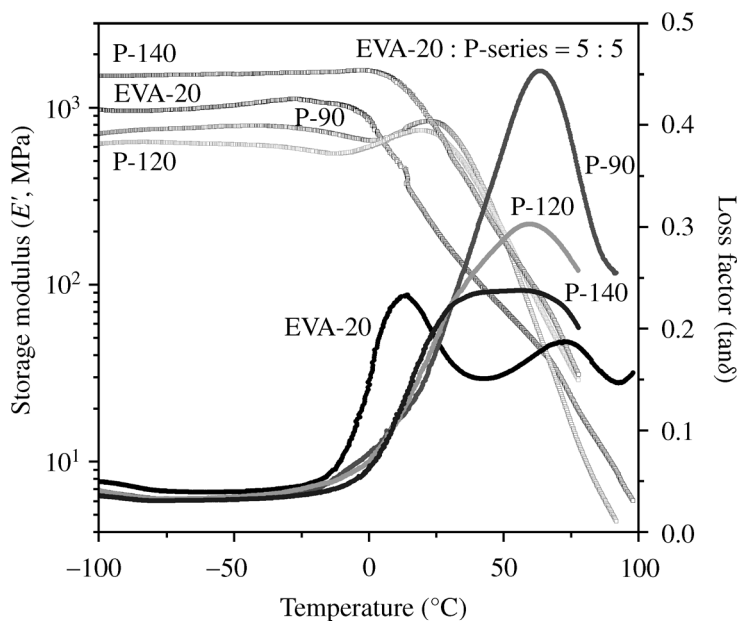


Figure 1. Storage modulus (E') and loss factor ($\tan \delta$) vs. temperature for blends of EVA-20 with 50 wt% of P-90, P-120, and P-140.

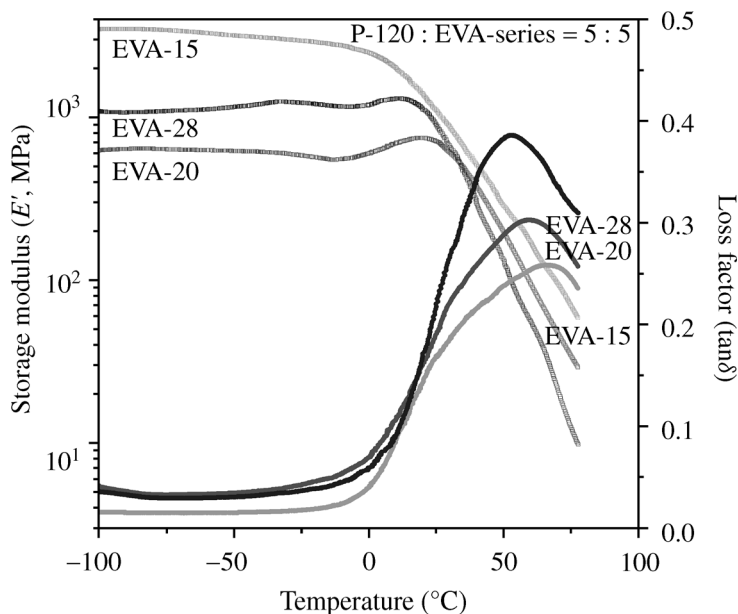


Figure 2. Storage modulus (E') and loss factor ($\tan \delta$) vs. temperature for blends of 50 wt% P-120 with EVA-15, EVA-20, and EVA-28.

softening point of aromatic hydrocarbon resin. These results agree with those found by Varghese *et al.* in their studies concerning Acrylonitrile Butadiene Rubber/EVA blends [7]. The glass transition temperatures of the above-mentioned aromatic hydrocarbon resins occurred at about 46, 74 and 106°C, respectively, as measured by DSC (not shown), but were too brittle to measure their viscoelastic properties. As shown in Fig. 2, the $\tan \delta$ values of P-120 blends with EVAs having different vinyl acetate contents show peaks at 67, 60 and 53°C for EVA-15, EVA-20 and EVA-28, respectively. The blend of EVA-28 with 50 wt% P-120 shows a sharp $\tan \delta$ peak, but it becomes slightly broader as the vinyl acetate content in the blend decreases because of viscoelastic properties (not shown) of pure EVAs.

Correspondingly, the $\tan \delta$ values of the blends in Fig. 3 show two small peaks or a broad peak at about 66, 57 and 60°C for blend ratios of 7 : 3, 6 : 4 and 5 : 5, respectively. On the other hand, the other blends, blend ratios 4 : 6 and 3 : 7, show single peaks at 64 and 66°C. This means that increasing of the aromatic hydrocarbon resin concentration in this blend has relation with miscibility.

3.2. Single lap shear strength

Figure 4 shows stress–strain curves of EVA-20 with 50 wt% P-120 at a crosshead speed of 300 mm/min at 25, 40, 55 and 70°C. The elongation-at-break increases with increasing temperature. Based on the viscoelastic properties in Figs 1–3 and stress–strain curves in Fig. 4, hot-melt adhesives manufacturers can design for using conditions such as strength or applicable temperature of hot-melt adhesives.

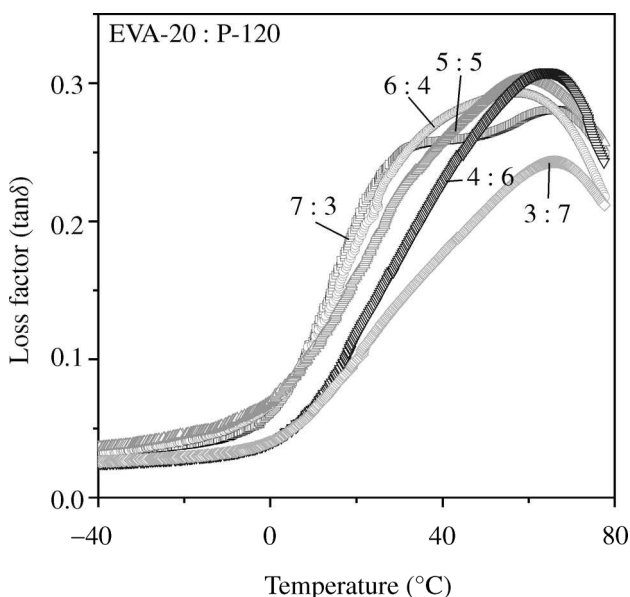


Figure 3. Loss factor ($\tan \delta$) vs. temperature of blends of EVA-20 with P-120 as a function of blend ratio.

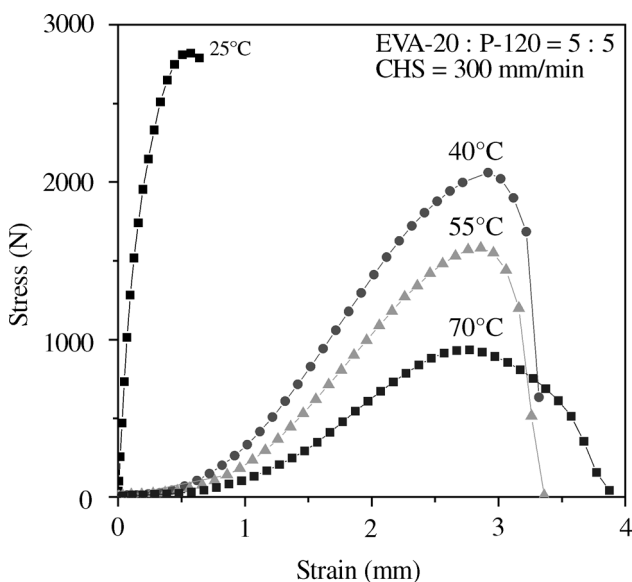


Figure 4. Stress-strain curves of EVA-20 blend with 50 wt% of P-120 at 25, 40, 55 and 70°C. (CHS = crosshead speed.)

Figure 5 presents the master curves of single lap shear strengths of the blend. Generally, the strength of a polymer increases with increasing test rate and decreasing temperature. This is shown in Fig. 5. The shear strength values are slightly scat-

tered at higher test rates and lower temperatures and interfacial failure takes place in this region. The most obvious result of increasing the concentration of aromatic

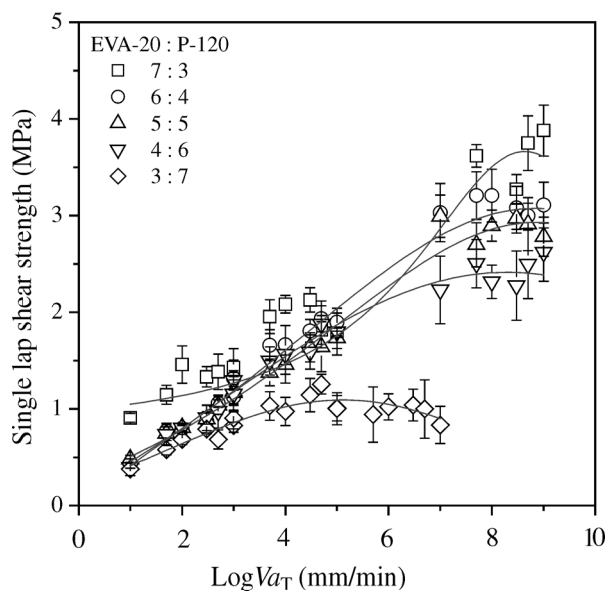


Figure 5. Master curves of single lap shear strengths of EVA-20 blend with P-120 as a function of blend ratio (V is crosshead speed and a_T is shift factor).

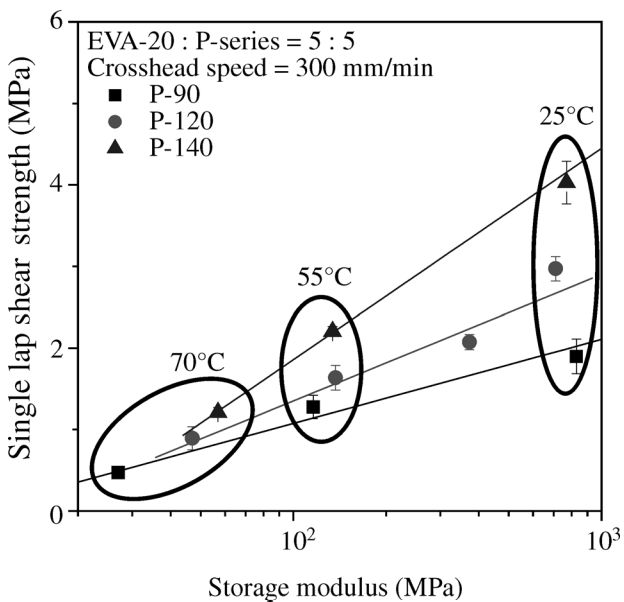


Figure 6. Single lap shear strength vs. storage modulus for blends of EVA-20 with 50 wt% of P-90, P-120 and P-140 at different temperatures.

hydrocarbon resin is a slight decrease of the values of shear strength up to 60 wt% of the aromatic hydrocarbon resin, and then, the values of shear strength drastically decrease above 70 wt%.

The adhesion properties are correlated with the viscoelastic properties. Figure 6 shows the correlation between the single lap shear strength and storage modulus of the blends of EVA-20 with 50 wt% of P-90, P-120 and P-140 at a crosshead speed of 300 mm/min and at different temperatures. The single lap shear strength increases with increasing storage modulus. At the same temperature, the higher the modulus, the higher the adhesion strength. Therefore, we can predict the value of shear strength by measuring viscoelastic properties of this blend. Hot-melt adhesives are polymeric materials with a viscoelastic behavior. A part of the energy is dissipated by the movements of chains (viscous flow) when a stress is applied to the polymer. These viscous losses are time (or speed) and temperature dependent [8].

Figure 7 shows the master curves of the single lap shear strengths of EVA-20 with P-90, P-120 and P-140. Similar to Fig. 5, the shear strength values are slightly scattered when interfacial failure takes place at higher test rates and lower temperatures. Figure 8 shows the single lap shear strength of the blends of EVA-20 with 50 wt% P-90, P-120 and P-140 as a function of temperature. Interfacial failure occurred at lower temperatures, while cohesive failure occurred at higher temperatures, for all blends. As the temperature was increased, the single lap shear strength increased up to about 25 °C for each blend. The peak for maximum single lap shear strength displayed a slight tendency to move toward a lower temperature. This move to lower temperatures reflects shift of $\tan \delta$ peaks of the blend, which

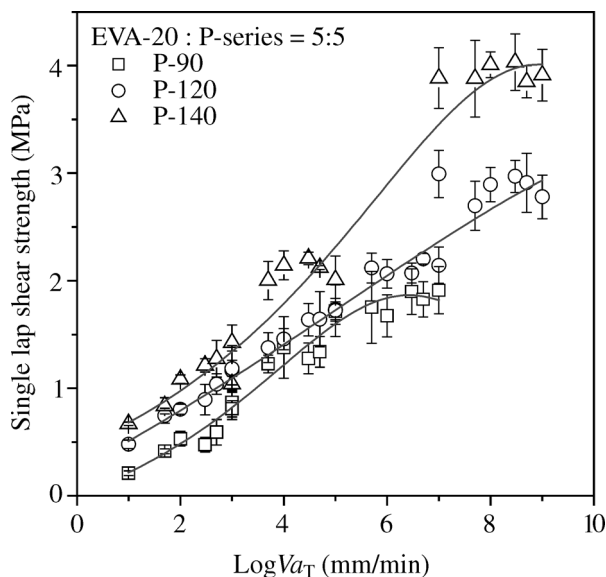


Figure 7. Master curves of single lap shear strengths of EVA-20 blends with 50 wt% of P-90, P-120 and P-140 (V is crosshead speed and a_T is shift factor).

is due to the increase in the softening point of the aromatic hydrocarbon resin. Turreda *et al.* [4] and Fujita *et al.* [9] have reported a similar behavior in the

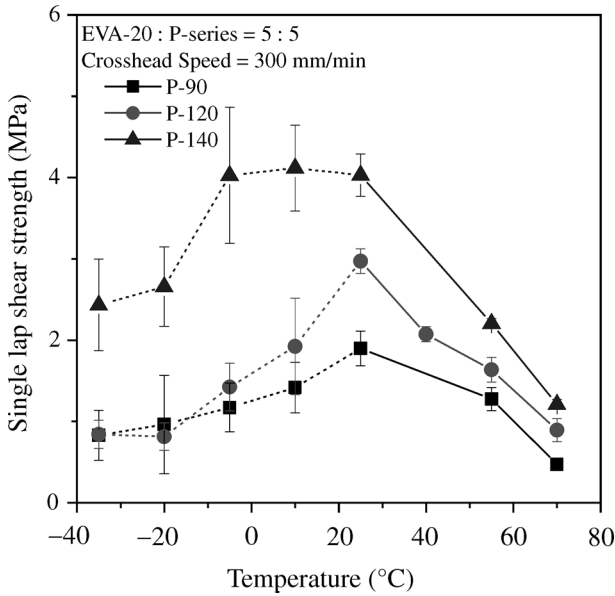


Figure 8. Single lap shear strengths of EVA-20 blends with 50 wt% of P-90, P-120 and P-140 as a function of temperature (dotted curve, interfacial failure; solid curve, cohesive failure).

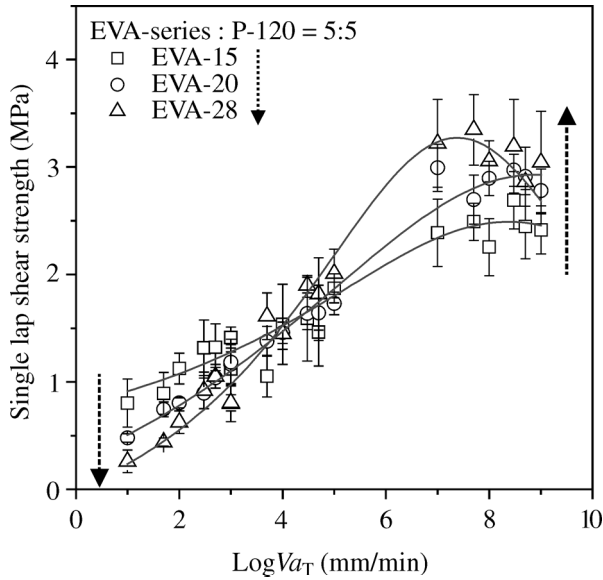


Figure 9. Master curves of single lap shear strengths of P-120 blends with 50 wt% of EVA-15, EVA-20 and EVA-28 (V is crosshead speed and a_T is shift factor).

case of EVA/terpene phenol adhesives and natural-rubber based pressure sensitive adhesives (PSAs).

Figure 9 shows the master curves of P-120 blends with 50 wt% of EVA-15, EVA-20 and EVA-28. The shear strength values, similar to Figs 5 and 7, are slightly scattered at higher test rates and interfacial failure occurred in this region. However, we should consider the transition point at about 4.0 (Va_T , mm/min) between low and high rates. We think that there are different mechanisms for shear strengths between low and high rates. Also, it is generally reported that the shear strength somewhat tends to increase with increasing vinyl acetate content [10]. Although we did not fully understand these mechanisms yet, our result shows different aspects of shear strength at high and low rates. Thus, we will investigate this aspect in a later study.

3.3. Failure modes

Failure modes following single lap shear tests were divided into interfacial, interfacial-cohesive and cohesive failure. Interfacial failure signifies failure at the adherend/bond interface. Interfacial-cohesive failure (or mixed failure) signifies both interfacial failure and cohesive failure. Cohesive failure occurs when the adhesive remains on both adherends [6, 11].

Figure 10 shows optical pictures of the failure surface of EVA-20 with 50 wt% P-120. Failure modes as a function of the softening point of the aromatic hydrocarbon resins are given in Table 3. In all cases, there was an increasing tendency for cohesive failure to occur with both increasing temperature and crosshead speed. This tendency for cohesive failure to occur also increased as the softening point of aromatic hydrocarbon resin increased. Based on these results, Fig. 11 presents a

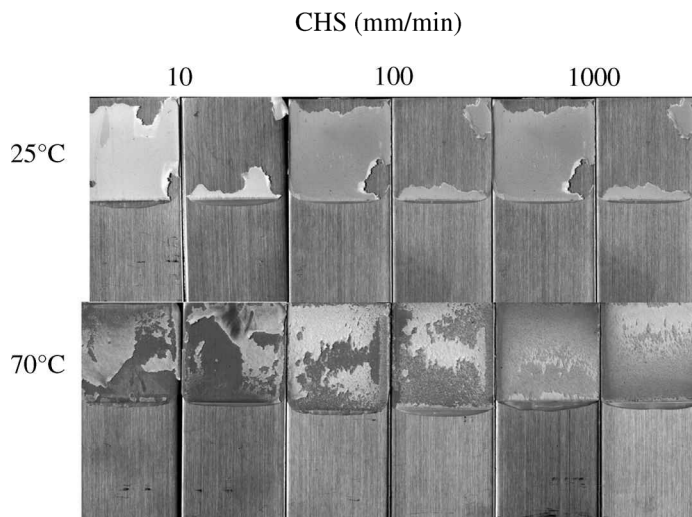


Figure 10. Optical pictures of the failure surface of EVA-20 blend with 50 wt% P-120 for two temperatures and three crosshead speeds (CHS).

scheme of failure modes observed in single lap shear tests. When the temperature was low, interfacial failure occurred at all crosshead speeds in this study. But, if the temperature or crosshead speed was increased, the interfacial failure turned to cohesive failure.

Table 3.
Failure modes for blends of EVA-20 with (a) P-90 = 50 wt%, (b) P-120 = 50 wt% and (c) P-140 = 50 wt%

Temperature (°C)	CHS (mm/min)					
	10	50	100	300	500	1000
EVA-20: P-90 = 5 : 5						
25	I	I	I	I	I	I
55	I	I	I	IC	IC	C
70	I	I	I	IC	IC	C
EVA-20: P-120 = 5 : 5						
25	I	I	I	I	I	I
40	I	I	I	IC	IC	IC
55	IC	IC	IC	C	C	C
70	IC	C	C	C	C	C
EVA-20: P-140 = 5 : 5						
25	I	I	I	I	I	I
55	C	C	C	C	C	C
70	C	C	C	C	C	C

I = interfacial failure, IC = interfacial-cohesive failure (or mixed failure), C = cohesive failure, CHS = crosshead speed.

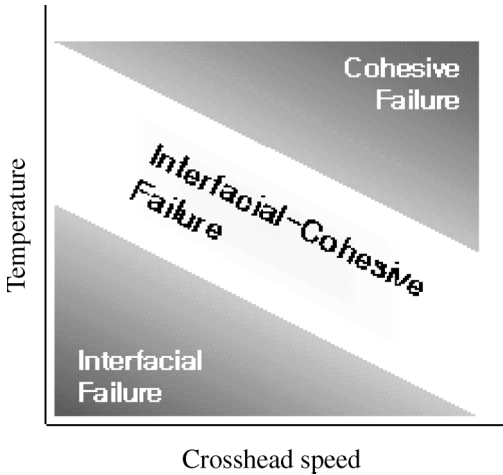


Figure 11. Scheme of failure modes.

3.4. SEM

The study of fracture surfaces is important with all classes of materials because of two reasons. First, by examining specimens broken in the laboratory under carefully controlled conditions, it may be possible to deduce the fundamental fracture mechanisms. And the second reason is that a microscopic examination of a field failure may indicate why a component had failed [12].

Figure 12 shows scanning electron micrographs for the fracture surfaces of the EVA-20 blend with 50 wt% P-120 at a crosshead speed of 10 mm/min and temperatures of 25, 40, 55 and 70°C. Micrographs (a) and (b) show interfacial failure, and (c), and (d) show cohesive failure. In those cases where interfacial failure took place, parts of stainless steel adherend were observed, but in the SEM micrographs corresponding to the cases of cohesive failure, stainless steel adherend was not seen. Also, the same results were obtained at a crosshead speed of 1000 mm/min and the same temperatures (not shown). As mentioned in the above discussion on Fig. 11 and Table 3, cohesive failure increasingly occurs as the

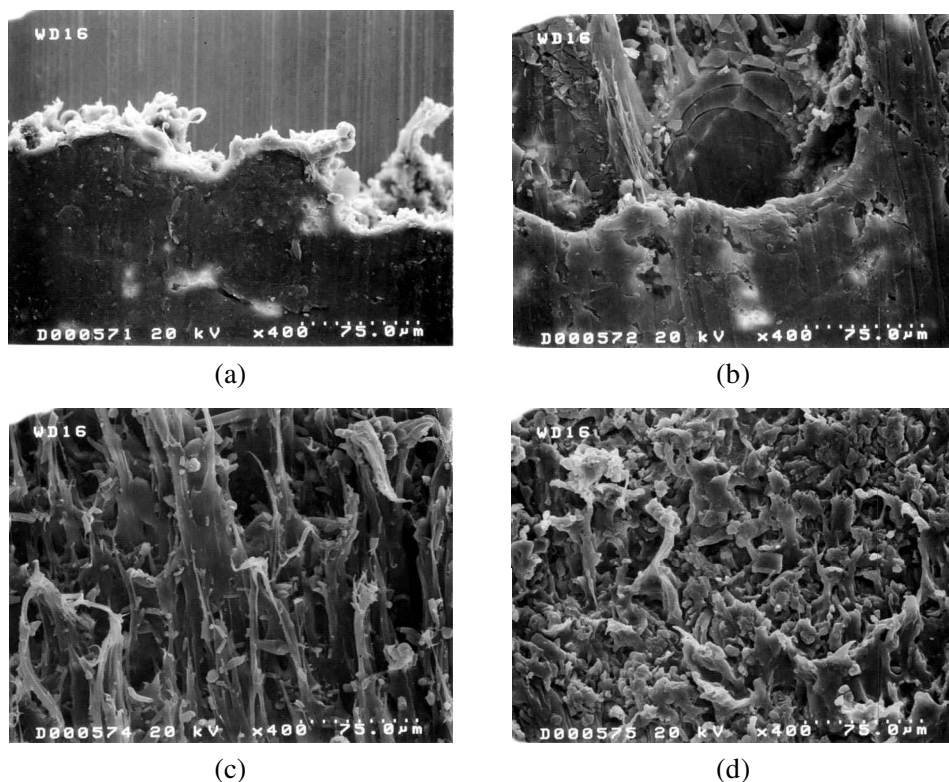


Figure 12. Scanning electron micrographs of the fracture surface of EVA-20 blend with 50 wt% of P-120 at a crosshead speed (CHS) of 10 mm/min as a function of temperature. (a) 25°C; (b) 40°C; (c) 55°C; (d) 70°C.

temperature increases. Also, for the same temperature, cohesive failure increasingly occurs as the crosshead speed increases.

4. CONCLUSIONS

Ethylene vinyl acetate copolymers constitute an important class of polymers used for hot-melt adhesives. The storage modulus of all EVA/aromatic hydrocarbon resin blends varied considerably between 0 and 25°C and the damping decreased and broadened as the softening point of the aromatic hydrocarbon resin in the blend increased and as the concentration of aromatic hydrocarbon resin decreased. This is related to the miscibility of the blend. In this system, an immiscible state occurred with increasing softening point. Also, the volume fraction of the aromatic hydrocarbon resin correlates with miscibility.

The shear strength increased as the storage modulus of the blend increased. The shear strength values are slightly scattered when interfacial failure takes place at higher test rates and lower temperatures. The shear strength increased with increasing softening point of the aromatic hydrocarbon resin and the maximum shear strength value slightly shifted to lower test temperature as the softening point of aromatic hydrocarbon resin increased. The shear strength decreased with increasing concentration of aromatic hydrocarbon resin because of the rigidity of the blend.

From failure modes and SEM micrographs, when the temperature was low, interfacial failure occurred at all crosshead speeds in this study. However, if the temperature or the crosshead speed is increased, the interfacial failure turns to a cohesive failure.

Acknowledgements

This work was supported, in part, by the Brain Korea 21 Project in 2003 and by the NSF-MRSEC program.

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