Adhesion and rheological properties of EVA-based hot-melt adhesives

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Abstract

Ethylene vinyl acetate (EVA) copolymers of various melt indexes were blended with aromatic hydrocarbon resin in the molten state, and the thermal and adhesion properties as hot-melt adhesives (HMAs) were investigated. The thermal properties for the EVA blends with aromatic hydrocarbon resin were studied using differential scanning calorimeter, Brookfield viscometer and dynamic mechanical thermal analyzer. Their adhesion strength was also obtained using single lap shear strength. The examination of thermal properties for the blend of EVA copolymers with aromatic hydrocarbon resin over a large temperature range showed that the glass transition temperature was independent of their melt index (MI), but that their heat of fusion decreased with increasing MI of EVA copolymers. Furthermore, the storage and loss moduli of the blends decreased with increasing temperature and MI of EVA copolymers, but the loss tangent (tan δ) of the blends increased. An increase in the MI of EVA copolymers decreased the adhesion strength of the blend at the same test condition.

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1. Introduction

Hot-melt adhesives (HMAs) are widely used in the packaging, bookbinding, footwear and wood industries. Their usage is increasing more and more because of their convenience and environmental characteristics. HMAs are 100% solid thermoplastic compounds that contain neither solvent nor an aqueous carrier for the active adhesive components. Most HMAs are based on thermoplastic polymers such as ethylene vinyl acetate copolymer (EVA), polyamide, polyurethane and polyester, etc. Among these polymers, EVA copolymers are the most commonly used in the HMA industry [1–3].

EVA has a wide range of melt indices (MIs) and good adhesion properties to various adherends, and it is not expensive. Therefore, EVA copolymer is the most popular thermoplastic polymer used in the HMA industry [4]. General EVA copolymers used in HMAs have 18–40 wt%

of vinyl acetate content and their MIs are 2–400 dg/min [5]. The properties of EVA copolymers are mainly determined by their vinyl acetate contents and their MI. In general, MI means the melt flow property of polymer materials at fixed pressure and temperature. Thus, high MI means superior injection molding property. The domain structure of EVA copolymers consists of stiff and partially crystalline polyethylene blocks, and flexible, soft and polar amorphous vinyl acetate blocks [6]. Tackifiers are commonly added to impart tack to HMA and pressure-sensitive adhesive based on EVA and styrenic block copolymers [7–9]. The 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 [10]. Therefore, the addition of tackifiers modifies viscosity, rheology and adhesion properties.

Miscibility, viscoelastic property and mechanical behavior of EVA-based HMAs have been studied by different researchers [10–15]. Takemoto et al. [11–12] studied the relationship between the miscibility and

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adhesion properties of EVA copolymers and different tackifiers using phase diagrams and peel strength. Shin et al. [13] reported the viscoelastic properties of EVA-based HMAs for the miscible and immiscible blends. They concluded that too high tackifier content decreases the mechanical properties of EVA-based HMAs and that the tackifier prevented the crystallization of EVA copolymers when the EVA-based HMAs cool down from molten state.

In our previous studies [10,15], viscoelastic and adhesion properties of EVA-based HMAs were studied when three aromatic hydrocarbon resins with different softening points were added to three EVA copolymers with different vinyl acetate contents (15–28 wt%) as a function of blend ratio. The miscibility of the EVA/aromatic hydrocarbon resin blends was inhibited with increasing softening point of the aromatic hydrocarbon resins, but was fostered with increasing vinyl acetate content as the result of the loss tangent (tan δ) peaks height.

In this study, to examine the role of MI in the EVA/ aromatic hydrocarbon resin blends, the thermal and viscoelastic properties of EVA-based HMAs were measured using differential scanning calorimeter (DSC) and dynamic mechanical thermal analyzer (DMTA). The single lap shear strengths of the EVA-based HMAs were examined at different temperatures and crosshead speeds using stainless steel as the adherend. Here, we will discuss the possible relationship between the thermal and viscoelastic properties, and the lap shear strength of EVA-based HMAs blended with EVA copolymers containing similar vinyl acetate contents.

2. Experimental

2.1. Materials

Three EVA copolymers with MIs of 20, 150 and 400 were used in this study and were supplied by Hanwha Chemical Corp. and Hyundai Petrochemical Co. Ltd., Korea. Some characteristics of EVA copolymers, such as the vinyl acetate contents, MIs and molecular weights, are shown in Table 1. All EVA copolymers had similar vinyl acetate contents.

One type of aromatic hydrocarbon resin was used in this study and was supplied by Kolon Chemical Co., Ltd., Korea. Its softening point is 120 °C. Table 2 indicates the softening point and molecular weight of the tackifier.

To reduce the thermal degradation of the HMAs during the melt process to prepare adhesive samples, 0.25 parts by weight of a phenolic antioxidant, Irganox 1010 (Ciba Geigy), was used as a thermal stabilizer.

Pure EVA copolymers and blended adhesive samples were molded using an injection molder to prepare test samples with size of $24 \times 6 \times 1.7\,mm^3$ for viscoelastic properties.

Stainless steel plates (ASTM A 167–99, type 302) with dimensions of $101.6 \times 25.4\,mm^2$ were used to perform the single lap shear tests for the EVA-based HMAs. The thickness of the stainless steel adherend was 1.5 mm. The stainless steel plates were washed with acetone before adhesion.

2.2. Methods

2.2.1. Gel permission chromatography (GPC)
2.2.1.1. Polymers. The molecular weights and molecular weight distributions (M_w/M_n) of the EVA copolymers were measured using a Waters 150-CV (Shodex linear column, GPC HT-806M). EVA copolymer was maintained in an oven at 165 °C for 1 h and then filtered. The solvent used was 1,2,4-trichlorobenzene. An RI detector was used.

2.2.1.2. Tackifier. The molecular weight and molecular weight distribution (M_w/M_n) of the aromatic hydrocarbon resin were measured using a Waters Company GPC

Table 1
Melt index, VAc content and melting temperature of EVA copolymers

Code	Melt index (dg/min)[a]	VAc content (wt%)[b]	M_n	M_w	MWD	T_m[c]	Heat of fusion[c]	Commercial name
EVA20	20	20.0	19920	120150	6.03	78.1	81.9	EVA1156
EVA150	150	19.0	19760	75970	3.85	79.3	77.6	VA920
EVA400	400	19.0	13110	48680	3.71	75.6	60.4	VA930

[a]Melt index indicates the viscosity of the polymer and helps to estimate its molecular weight, ASTM D1238.
[b]Vinyl acetate, HCC method.
[c]Measured by DSC.

Table 2
Softening point and molecular weight of tackifier resin

Code	Softening point (°C)	M_n	M_w	MWD	T_g (°C)[a]	Commercial name
P120	120±5.0	694	1420	2.05	72.9	P-120

[a]Measured by DSC.

(Column: HR-1, HR-2, HR-3, HR-4). Tetrahydrofuran (THF) was used as the solvent. An RI detector was used. The calibration material was polystyrene with 14 different molecular weight values being used.

2.2.2. Blend of polymer and tackifier

EVA-20, EVA-150 and EVA-400 were mixed with tackifier P-120 in a 300 g internal mixer at 30 rpm with a machine temperature of 170 °C. First, the EVA copolymer and antioxidant were added. The quantity of antioxidant, Irganox 1010, was 0.25 parts per hundred of each of EVA and tackifier. When the EVA copolymer had become masticated and formed a homogeneous melt, the tackifier was slowly added until completion. The mixing time was about 20 min. The blend ratio of EVA and tackifier was 5:5. EVA-based HMA films were obtained by compression molding.

2.2.3. Thermal analysis

2.2.3.1. Differential scanning calorimeter.
The glass transition temperature was measured using a TA instrument Q-1000 DSC (TA Instrument) at a heating rate of 5 °C/min. The scanning circles consisted of heating from room temperature to 150 °C at 5 °C/min, cooling from 150 to −85 °C by electronic quenching, and heating to 150 °C again at a rate of 5 °C/min. The results of the second run were used for this study.

2.2.3.2. Dynamic mechanical thermal analyzer.
The viscoelastic properties of the HMAs were measured using a DMTA MARK IV (Rheometric Scientific) at a frequency of 1 Hz. The testing temperatures were in the range of −80–70 °C with a heating rate 3 °C/min under liquid nitrogen.

2.2.3.3. Melt index.
The melt index of the pure EVA copolymers and the blends were measured based on ASTM D1238.

2.2.4. Single lap shear test

The adhesive joint was then obtained by pressing the film between two stainless steel plates at a temperature of 180 °C for 5 min. The bondline thickness was maintained at 0.1 mm. Single lap shear strength was measured using a Zwick Universal Testing Machine Z101 at crosshead speeds of 10, 50, 100, 300, 500 and 1000 mm/min and temperatures of 25, 40, 55 and 70 °C.

3. Results and discussion

3.1. Differential scanning calorimeter

In general, T_g measured by DSC is widely used for determining the miscibility of polymer blends. It has usually been associated with the onset of segmental mobility in the amorphous phase of an amorphous or semicrystalline polymer [4,15].
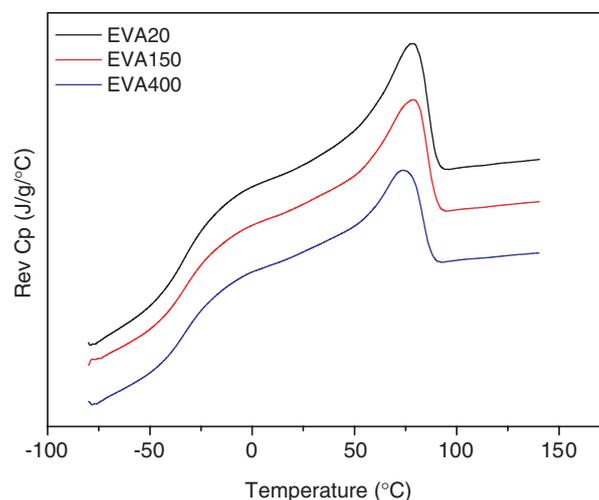
Fig. 1. DSC thermograms of pure EVA copolymers and aromatic hydrocarbon resin, P120.

Table 3
Melting temperature and heat of fusion for the blend of EVA copolymers with 50 wt% of aromatic hydrocarbon resin

Code	T_m[a]	Heat of fusion[a]	Melt index[b]
EVA20: P120	75.2	38.1	169.54
EVA150: P120	75.8	34.6	448.40
EVA400: P120	74.8	24.6	756.70

[a]Measured by DSC.
[b]ASTM D1238.

The thermal properties of the EVA copolymers and aromatic hydrocarbon resin were determined using modulated DSC. The thermograms in Fig. 1 show T_g and the melting temperature (T_m) of EVA copolymers. All the EVA copolymers displayed T_g at about −30 °C and a large endothermic peak in the thermogram, while the aromatic hydrocarbon resin showed T_g at about 70 °C (not shown) [15]. Values of T_m, heat of fusion (ΔH) and MI of the blends are given in Table 3. In general, T_m of EVA copolymers was affected by vinyl acetate contents of EVA copolymers, but less affected by MI of EVA copolymers [16]. Although T_m of EVA copolymers are somewhat similar, their heat of fusion decreased with increasing MI of EVA copolymers, a result which seems to be related their melt viscosity. Although T_g and T_m of EVA copolymers are similar, the heat of fusion and melt viscosity decreased with increasing MI because less energy was required for flow or mobility.

Fig. 2 shows the thermograms of EVA copolymer blends with 50 wt% of aromatic hydrocarbon resin. It is difficult to confirm the miscibility between EVA copolymers and aromatic hydrocarbon resin because T_m of EVA copolymer and T_g of aromatic hydrocarbon resin were shown at a similar temperature region. However, T_m of the blend very slightly decreased with increasing MI of EVA copolymers.
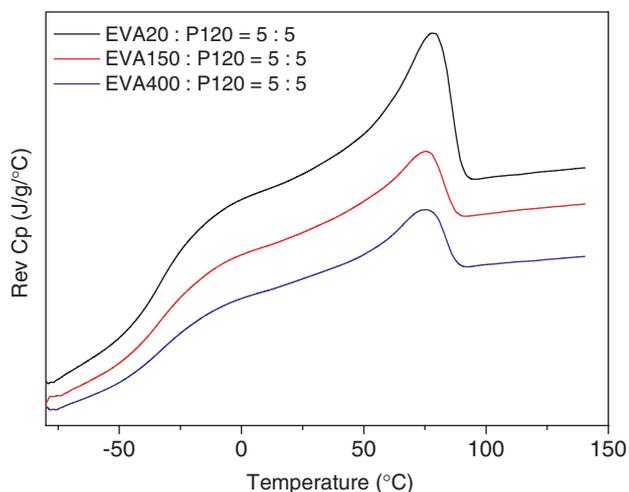
Fig. 2. DSC thermograms for the blends of EVA20, EVA150 and EVA400 with 50 wt% of aromatic hydrocarbon resin.
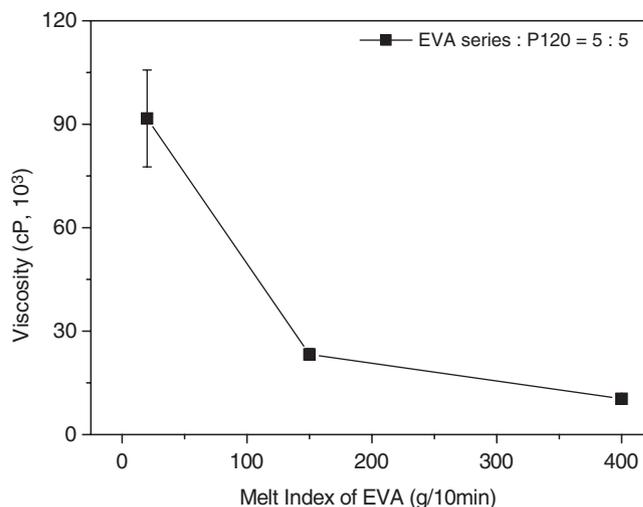
Fig. 3. Melt viscosity for the blends of EVA copolymers with 50 wt% of aromatic hydrocarbon resin.

Values of T_m and heats of fusion of the blends are given in Table 3. When EVA copolymers were blended with aromatic hydrocarbon resin, their T_m slightly decreased and their heat of fusion decreased marginally by over half a percent because of the low molecular weight of aromatic hydrocarbon resin comparing to that of EVA copolymers. Therefore, we can predict the adhesion strength of the blend with these DSC thermograms. For instance, EVA400 blend with 50 wt% of aromatic hydrocarbon resin can flow with less energy than EVA20 blend with 50 wt% of aromatic hydrocarbon resin at the same condition.

3.2. Viscoelastic properties

The melt viscosity for the blend of EVA copolymers with 50 wt% of aromatic hydrocarbon resin was obtained using a Brookfield viscometer at 180 °C. Fig. 3 displays the melt viscosity of the blends. In the same blend ratio, melt viscosity drastically decreased with increasing MI of EVA copolymers.

The viscoelastic and rheological properties for pure EVA copolymers and the blend of EVA copolymers with 50 wt% of aromatic hydrocarbon resin were obtained using DMTA. Fig. 4 shows the storage modulus (E') and loss modulus (E'') as a function of the temperature for the blends of EVA20, EVA150 and EVA400 containing 50 wt% of aromatic hydrocarbon resin, P120. The storage modulus curves for all the blends have three of the following obvious regions: glassy, transition and rubbery. In the glassy region, all the blends show a high modulus values. Storage modulus is always decreased with increasing temperature and at about −30 °C, the decrease rate becomes more drastic. These modulus values correspond to the state of the materials [17]. Therefore, below the inflection temperature the solid-like behavior of EVA-aromatic hydrocarbon resin blends is dominant over the liquid-like behavior, but in the higher temperature region
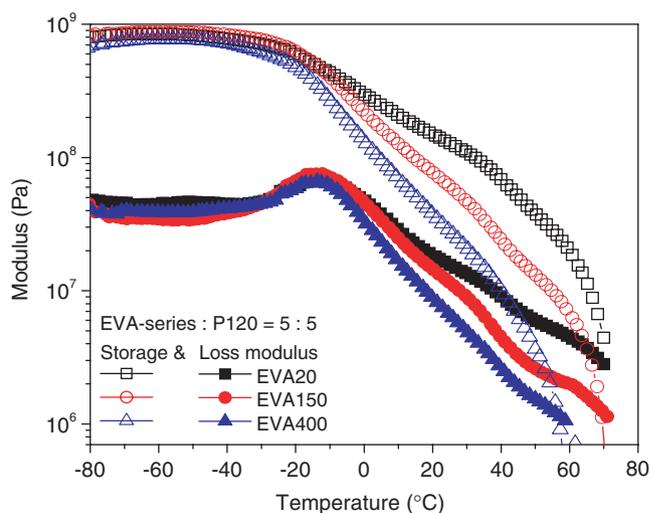
Fig. 4. Storage modulus (E') and loss modulus (E'') as a function of the temperature for the blends of EVA20, EVA150 and EVA400 containing 50 wt% of P-120.

than the inflection, liquid-like behavior is dominant. These modulus behaviors of the HMAs are very important due to the application of the HMAs for the end user. Chang [18] reported that general pressure-sensitive adhesives must have 10^6–10^3 Pa of E' at room temperature on the concept of performance windows. However, in general, a typical value of bookbinding HMAs at 23 °C is 10^8 and 10^7 Pa [19].

The tan δ values of the EVA-aromatic hydrocarbon resin blends as a function of temperature are shown in Fig. 5. T_g of pure EVA copolymers, EVA20, EVA150 and EVA400, was about −30 °C by DSC. In the case of the blends, there was a single transition at about −5 °C. There was no significant change in T_g value by increasing the MI of EVA copolymers. Miscibility cannot be judged from tan δ peak by DMTA because the blends began to be melted at above 40 °C. The damping properties of the blends increase with
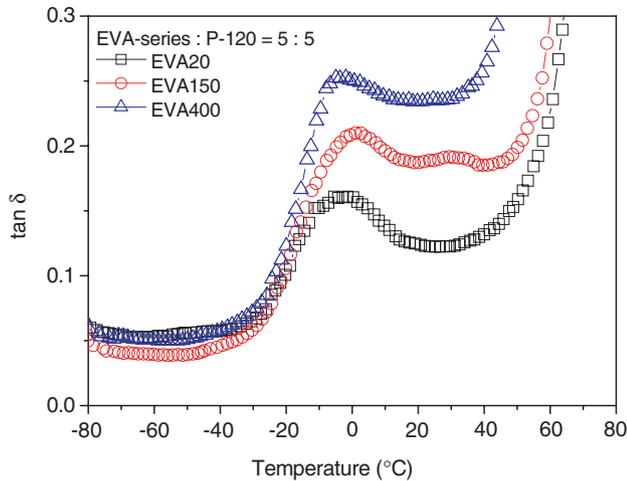
Fig. 5. Loss tangent (tan δ) as a function of temperature for the blends of EVA-20, EVA-150 and EVA-400 containing 50 wt% of P-120.

Fig. 6. Master curves of single lap shear strength of EVA-20, EVA-150 and EVA-400 blends with 50 wt% of P-120 (V is crosshead speed and a_T is shift factor).

an increasing MI of the EVA copolymers. However, an increase in the MI of the EVA copolymers produces higher maximum value of the tan δ due to lower E' or higher E'' in equation of tan $\delta = E''/E'$.

The MI values of the pure EVA copolymers and the blends are shown in Tables 1 and 3. In general, MI of the polymer can be measured very simple, which is determined by its viscosity and molecular weight. Therefore, MI of EVA copolymers increased with decreasing their molecular weight and also, although be added aromatic hydrocarbon resin with low molecular weight, that of the blends show same tendency.

3.3. Single lap shear strength

Fig. 6 presents the master curves of single lap shear strengths of the blends. Generally, the strength of the polymer materials increased with increasing test rate and decreasing test temperature. The lap shear strength values were slightly scattered at higher test rates and in the lower temperature regions, and interfacial failure took place in this region. In addition, the lap shear strength values were decreased with increasing MI of EVA copolymers at higher temperature regions. The adhesion properties were correlated with the viscoelastic properties. In our previous paper, we demonstrated that the single lap shear strength increases with increasing E' [10]. Similarly, E' of the blend at over 40 °C decreased with decreasing single lap shear strength in Figs. 4 and 6. Thus, the higher the modulus, the higher the adhesion strength at the range 40–70 °C. From this result, therefore, we can predict the values of lap shear strength by measuring viscoelastic properties at the higher temperature region.

At 25 °C, the low temperature region, the single lap shear strength for the blend of EVA20 and P120 started to decrease from the fitting curve. However, the single lap shear strength for the blend of P120 with EVA150 and EVA400 were continuously increased. Although we could
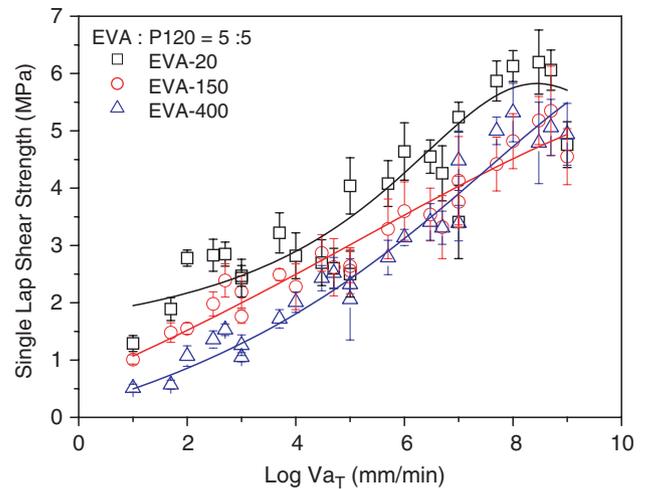
not measure at higher crosshead speeds because of the measuring limit of the Universal Testing Machine, we can predict that the peak of the single lap shear strength slightly shifted to a higher crosshead speed region from slopes of the fitting curves in master curves. We can estimate the adhesion strength values at low temperatures below 25 °C using these maximum peaks of single lap shear strength values and HMA makers can apply various formulations using many materials to produce the desired performance.

It is difficult to determine the miscibility of the blend from the DSC and DMTA results. The miscibility of the blend was determined from the overlapping of the melting peak of EVA copolymers and T_g of the aromatic hydrocarbon resin. It showed a very similar temperature. However, the single lap shear strength of the blends decreased with increasing MI of EVA copolymers. With increasing MI of EVA copolymers, their modulus and viscosity were decreased, indicating that EVA copolymers become soft with increasing MI. Therefore, the adhesion strength of the blend began to decrease with increasing MI of EVA copolymers, as shown by Takemoto et al. [11]. They showed the adhesion tensile strength of the blend of EVA and the tackifier, Estergum H. The EVA copolymers they used had MI of 20 and 400 g/10 min, respectively, but had similar vinyl acetate contents of 20 and 25 mol%, respectively. Over the full test temperature range of adhesion tensile strength, the blends were miscible. However, the adhesion tensile strength of the blend decreased in the overall blend ratio as MI increased from 20 to 400 g/10 min.

4. Conclusions

Miscibility and viscoelastic properties of the blends were obtained from DSC, Brookfield viscosity and DMTA. It was difficult to define the miscibility of the blends with glass transition temperature and tan δ peak because the

melting peaks of EVA copolymers and glass transition temperature of aromatic hydrocarbon resin presented in a similar temperature region. Nevertheless, an increase of melt index of EVA copolymers produced marked variation in DSC; with increasing melt index, both the heat of fusion and the melt viscosity of the blend decreased. Furthermore, an increase of melt index decreased storage and loss modulus, but increased the height of $\tan\delta$ peaks. As a result, the adhesion strength of the blends decreased with increasing melt index of EVA copolymers and test temperature, but the maximum adhesion strength values in the fitting curves of the master curves slightly shifted to the faster test speed region.

Acknowledgment

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