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Viscoelastic and adhesion properties of EVA/tackifier/wax ternary blend systems as hot-melt adhesives

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Abstract—Two types of wax were added to a ethylene vinyl acetate (EVA) copolymer/aromatic hydrocarbon resin (tackifier) blend in the molten state and the miscibility, viscoelastic and adhesion properties of ternary blends as hot-melt adhesives (HMAs) were investigated. Miscibility and viscoelastic properties were studied using differential scanning calorimetry (DSC), Brookfield viscometry and dynamic mechanical thermal analysis (DMTA), and their adhesion strength was determined in terms of single lap shear strength. DSC thermograms of both types of waxes showed their melting peaks in a similar region to that of EVA/tackifier blend. It was difficult to evaluate the miscibility of ternary blends using DSC because the melting peaks of the waxes overlapped with those of the EVA/tackifier blend, although the glass transition temperature (T_g) of the ternary blend systems slightly increased with increasing wax concentration. However, their storage modulus (E') increased slightly and loss tangent ($\tan \delta$) showed different peaks when two types of wax were added to the EVA/tackifier blend. Therefore, the miscibility of EVA/tackifier blend altered with addition of waxes. In addition, their melt viscosity decreased with increasing wax concentration. Furthermore, the adhesion strength of the ternary blends decreased with increasing wax concentration, despite the increment of storage modulus. These results suggested that the ternary blends of EVA/tackifier/wax were heterogeneous.

Keywords: EVA; aromatic hydrocarbon resin; wax; hot-melt adhesive.

1. INTRODUCTION

Hot-melt adhesives (HMAs) generally contain various combinations of polymers, tackifier resins, waxes and antioxidants. In general, polymers provide the main

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constituent of the adhesive formulations and the tackifier resins are generally added to impart tack to HMA formulations. Waxes are commonly included for several reasons, two of which are to modify the melt viscosity and to reduce cost, while antioxidants reduce thermal degradation during processing [1, 2].

Most of the HMAs are based on thermoplastic polymers such as ethylene vinyl acetate (EVA) copolymer, polyamide, polyurethane or polyester [3, 4]. Among these polymers, EVA copolymers are the most widely used raw materials for HMAs because of their wide range of melt index values and vinyl acetate contents, good adhesion to a variety of materials, and their low price. HMAs are widely used in packaging, bookbinding, footwear and wood industries and their usage continues to increase because of their convenience and environmentally friendly characteristics.

The miscibility, viscoelastic property and mechanical behavior of EVA-based HMAs have been studied by many researchers [5–11]. Shin and Hamed [7] have reported the viscoelastic properties of EVA-based HMAs for both miscible and immiscible blends. Takemoto *et al.* [8, 9] have studied the relationship between the miscibility and adhesion properties of EVA copolymers and different tackifiers using phase diagrams and peel strength measurements. Ramirez-Guillem *et al.* [12] reported on the role of two types of wax, paraffin wax and Fisher–Tropsch wax, in EVA/tackifier/wax blends. In addition, Gibert *et al.* [13] reported the relationship between peel behavior and rheological properties of hot-melt adhesives with the same basic formulation before and after crystallization.

In our previous studies [5, 6], 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 decreased with increasing softening point of the aromatic hydrocarbon resin but increased with increasing vinyl acetate content as determined by the peak of the loss tangent ($\tan \delta$). We also investigated the adhesion properties of EVA-based HMAs as a function of the melt index of EVA copolymer [11]. The adhesion strength of EVA-based HMAs generally decreased with increasing melt index of EVA copolymer. Shin and Hamed [7] have reported on the influence of wax on the adhesion strength of both miscible and immiscible EVA/rosin blends by measuring viscoelastic properties and the failure mode. However, not many researchers have considered the effect of wax on the adhesion performance of HMAs.

Therefore, in this study, to evaluate the role of wax in the EVA/tackifier/wax ternary blends, the thermal and viscoelastic properties of EVA-based HMAs were measured using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Single lap shear strengths of the EVA-based HMAs were examined at different temperatures and crosshead speeds using stainless steel plates as adherends. In addition, we discuss a possible relationship between the thermal and viscoelastic properties and the lap shear strength of EVA-based HMAs composed of EVA copolymers containing similar vinyl acetate contents.

2. EXPERIMENTAL

2.1. Materials

The EVA copolymer used in the study contained 20 wt% vinyl acetate with a melt flow index of 20 g/10 min and was supplied by Hanwha Chemical (South Korea) (Table 1). The aromatic hydrocarbon tackifier resin (P120) used was supplied by Kolon Chemical (South Korea) with a softening point and glass transition temperature (T_g) of about 120°C and 73°C, respectively. Molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the tackifier were 1420 and 2.06, as measured by GPC. The two synthetic Fischer–Tropsch waxes used, SX70 and SX100, were supplied by Shell MDS and their relevant properties are given in Table 2.

To reduce the thermal degradation of the HMAs, 0.25 parts by weight of a phenolic antioxidant, Irganox 1010 (Ciba Geigy), was used as a thermal stabilizer. Stainless steel plates (ASTM A 167-99, type 302) with dimensions of about $101 \times 25 \text{ mm}^2$ were used to perform the single lap shear tests for the EVA-based HMAs. The thickness of the stainless steel adherends was 1.5 mm. The stainless steel plates were cleaned with acetone before preparing the lap shear test specimens.

Table 1.

Some properties of the EVA copolymer used

Code	Melt index (dg/min) ^a	VAc. content (wt%) ^b	M_n	M_w	MWD	T_m (°C) ^c	Heat of fusion (J/g) ^c	Commercial name
EVA20	20	20.0	17860	95190	5.33	77.3	71.6	EVA1156

^a ASTM D1238.

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

^c Measured by DSC.

Table 2.

Properties of the waxes used (from technical report of Shell MDS)

Code	Drop melting point (°C) ^a	Cloud point (°C) ^b	Kinematic viscosity (mm ² /s) ^c	T_g (°C) ^d	Heat of fusion (J/g) ^d	Commercial name
SX70	73	85–93	5–8	–24.7	202.0	SX-70
SX100	108	106	12.8	–23.2	176.7	SX-100

^a ASTM D127.

^b ASTM D2500.

^c ASTM D445.

^d Measured by DSC.

2.2. Methods

2.2.1. Gel permeation chromatography (GPC).

2.2.1.1. *Polymer.* The molecular weight and molecular weight distribution (M_w/M_n) of the EVA copolymer were measured using a Waters 150-CV equipment (column: GPC HT-806M). EVA copolymer was kept in an oven at 165°C for 1 h and then filtered. The solvent used was 1,2,4-trichlorobenzene. A refractive index 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 Waters GPC equipment (columns: HR-1, HR-2, HR-3, HR-4). Tetrahydrofuran (THF) was used as solvent. A refractive index detector was used. The calibration material used was polystyrene with 14 different molecular weight values.

2.2.2. *Blend of polymer, tackifier and wax.* EVA20 and P120 were mixed with wax in a 300 g internal mixer at 30 rpm at a temperature of 170°C. First, the EVA copolymer and antioxidant were mixed. The quantity of antioxidant, Irganox 1010, was 0.25 parts per hundred of the sum of EVA and tackifier. When the EVA copolymer had been masticated, the tackifier was slowly added, after which wax was added until the blend formed a homogeneous melt. The mixing time was about 20 min. The blend ratio of EVA and tackifier was 5:5 and the wax contents were 15 and 30 wt%. EVA-based HMA films were obtained by compression molding.

2.2.3. *Differential scanning calorimetry (DSC).* The T_g was measured using a TA Instruments Q-1000 DSC at a heating rate of 5°C/min. A scanning cycle consisted of heating from room temperature to 150°C at 5°C/min, cooling from 150 to -85°C by electronic quenching, and then heating again to 150°C at a rate of 5°C/min to remove thermal history of the blends. The results of the second run were used for this study.

2.2.4. *Melt viscosity.* Melt viscosity was measured using a Brookfield Viscometer Model DV-II+ with a Brookfield Thermosel system. An SC4-28 spindle was used to measure the viscosity in the range of 250 to 5 000 000 cP at 180°C.

2.2.5. *Dynamic mechanical thermal analysis (DMTA).* The viscoelastic properties of the HMAs were measured using a DMTA MARK IV equipment (Rheometric Scientific) at a frequency of 1 Hz. Samples of dimensions 400 × 10 × 2 mm³ were used for this study. The test temperatures were in the range of -80 to 70°C with a heating rate of 3°C/min under liquid nitrogen in a dual cantilever mode. The tan δ and storage modulus were measured for each sample in this temperature range.

2.2.6. *Single lap shear test.* The adhesive joint was obtained by pressing the blend film between two stainless steel plates at a temperature of 180°C for 5 min.

The dimensions of the stainless steel plates were $25 \times 100 \times 1.5 \text{ mm}^3$. The bondline thickness and area were maintained at 0.1 mm and $2.5 \times 1.25 \text{ cm}^2$, respectively. 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 calorimetry (DSC)

The T_g measured using 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 [6, 14].

The thermal properties of the EVA copolymer, aromatic hydrocarbon resin, and two types of wax were determined using modulated-temperature DSC. The reversible DSC thermograms in Figures 1 and 2 show the T_g , melting temperature (T_m) and heat of fusion of pure waxes and the ternary blends EVA20/P120/SX70, respectively. In our previous studies, we presented the thermograms of pure EVA copolymer, tackifier and their blends [5, 6, 11]. The EVA20 copolymer showed its T_g at about -30°C and a large endothermic peak in the thermogram, while the aromatic hydrocarbon resin showed the T_g at about 70°C (not shown). The physical properties of EVA copolymer and waxes are given in Tables 1 and 2, respectively.

Although the T_g values of both types of waxes showed somewhat similar values, their T_m and heat of fusion are different as shown in Fig. 1 and Table 2. SX70 showed lower T_m and higher heat of fusion than SX100. When these two types of waxes were blended with EVA/tackifier blend, their T_g increased very slightly because of the higher T_g of the wax than of the blend. In the case of SX70, the T_g and heat of fusion were increased with increasing wax content, though their T_m presented somewhat similar values, as shown in Fig. 2 and Table 3. In the case of

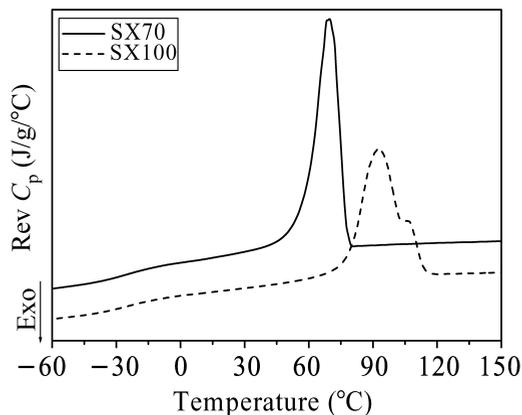


Figure 1. Modulated-temperature DSC thermograms of two types of pure waxes (C_p is heat capacity).

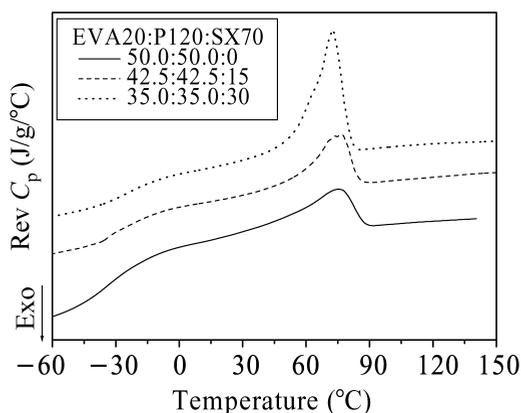


Figure 2. Modulated-temperature DSC thermograms of EVA20/P120/SX70 ternary blends for different wax contents (C_p is heat capacity).

Table 3.

T_g , T_m and heat of fusion for ternary blends of EVA20/P120/wax as a function of wax type and content, as measured by DSC

Type of wax	Content of wax (wt%)	T_g (°C)	T_m (°C)	Heat of fusion (J/g)
SX-70	0	-30.7	75.2	34.3
	15	-26.9	76.2	34.9
	30	-23.7	72.6	62.9
SX-100	0	-30.7	75.2	34.3
	15	-24.2	87.2	45.5
	30	-24.6	89.6	80.6

SX100, the addition of wax increased the T_g of the ternary blend, but it was not affected by its concentration. Also, the T_m and heat of fusion of the ternary blends increased with increasing wax content because the T_m and heat of fusion of pure wax are higher than that of EVA/tackifier blend, although DSC thermograms for SX100 blends with EVA/tackifier are not shown. That is, this result suggests that the blends of SX100 with EVA/tackifier were heterogeneous.

When the waxes are added in the EVA/tackifier blend system, one can expect that the resulting ternary blends would need more energy to melt because of their increased heat of fusion. Also, Cantor [15] reported that the adhesion strength strongly depended on the T_g of the blend.

3.2. Melt viscosity and viscoelastic properties

The melt viscosity for the ternary blends having different wax concentrations was obtained using a Brookfield viscometer at 180°C. Figure 3 shows the melt viscosity of the ternary blends. With increasing wax content, the melt viscosity of the blends decreased, and that of SX100 blend was higher than that of SX70 blend at the same

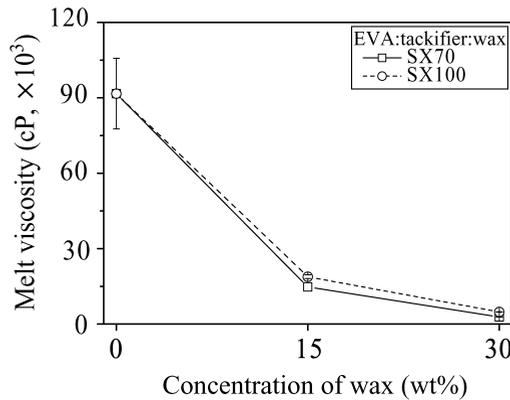


Figure 3. Melt viscosity of EVA/tackifier/wax ternary blend system at 180°C.

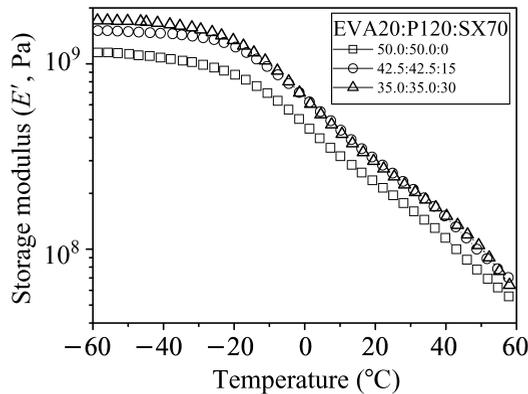


Figure 4. Storage modulus of EVA20/P120/SX70 ternary blends for different wax contents.

wax concentration. However, the wax type exerted only a slight effect because of phase separation. The viscoelastic properties for the ternary blends of EVA, tackifier, and 0, 15 and 30 wt% of wax were obtained using DMTA. Figures 4 and 5 show the storage modulus (E') and loss factor ($\tan \delta$) values, respectively, as a function of temperature for the blends using SX70 as the wax. The E' values were slightly higher with increased wax concentration. The E' curves for all the blends featured the following three obvious regions: glassy, glass transition and rubbery. In the glassy region, all the blends show a high modulus value. The E' value always decreased with increasing temperature, with a more drastic decrease at about -30°C . At temperatures below the inflection temperature the solid-like behavior of the blends was dominant over the liquid-like behavior, but in the higher temperature region, liquid-like behavior was dominant. General PSAs must have E' value of 10^6 to 10^3 Pa at ambient temperature according to the concept of viscoelastic window [16]. However, Bamborough and Dunckley [17] reported that a typical value of E' for bookbinding HMAs at 23°C was 10^8 to 10^7 Pa.

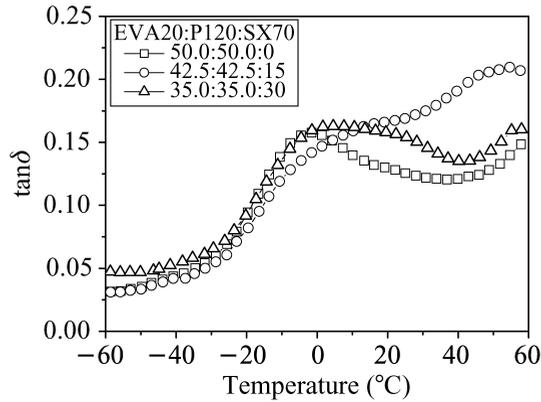


Figure 5. Loss factor ($\tan \delta$) of EVA20/P120/SX70 ternary blends for different wax contents.

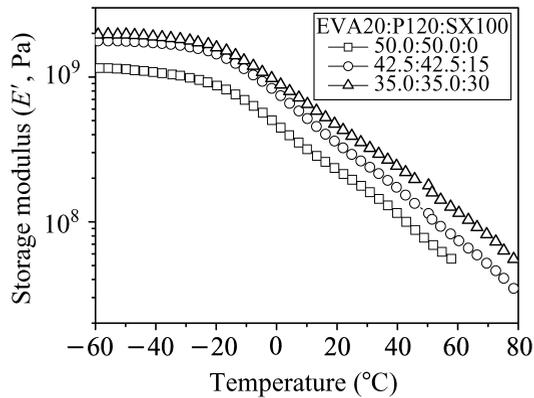


Figure 6. Storage modulus of EVA20/P120/SX100 ternary blends for different wax contents.

The $\tan \delta$ values of the ternary blends as a function of temperature are shown in Fig. 5. $\tan \delta$ of EVA/tackifier blend showed a single transition peak, but the addition of wax changed the EVA/tackifier miscibility. This effect was clearer when the wax added to EVA/tackifier blend. $\tan \delta$ curves showed two significant peaks, although the peak height of the $\tan \delta$ curve was not changed. Ramirez-Guillem *et al.* [12] reported that the addition of paraffin wax in EVA/tackifier blends increased their compatibility because the compatibility of pure EVA and the paraffin wax is enhanced. Also, Shin and Hamed [1] reported that the shape of loss tangent curve in immiscible blends of EVA/rosin/wax continuously changed. Therefore, the EVA/tackifier blend in this study changed to a immiscible system with increasing wax concentration, although paraffin wax was compatible with EVA as shown by Ramirez-Guillem *et al.* [12].

Similarly, Figs 6 and 7 show the E' and $\tan \delta$ values, respectively, as a function of the temperature for the blends using SX100 wax. Similar to the SX70 blends, the addition of SX100 wax shifted the melting of the blend to a higher temperature, and this shift was greater for higher wax concentration in the ternary blend (Fig. 6).

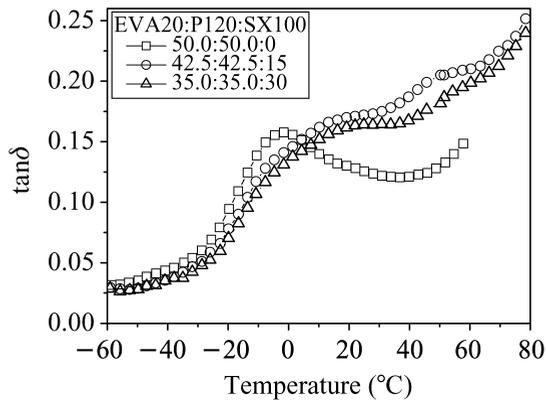


Figure 7. Loss factor ($\tan \delta$) of EVA20/P120/SX100 ternary blends for different wax contents.

However, their miscibility cannot be ascertained from their viscoelastic properties because SX100 showed two types of domains and higher melting peaks in DSC thermograms, as shown in Fig. 1.

Ramirez-Guillem *et al.* [12] reported similar results that the addition of paraffin wax to EVA increased the E' value because of the increased crystallinity of the paraffin wax and decreased $\tan \delta$ value; however, the addition of the Fisher–Tropsch wax in EVA decreased the $\tan \delta$ value of EVA to a greater extent than paraffin wax did. Therefore, they concluded that paraffin wax was more miscible with EVA than the Fisher–Tropsch wax. Furthermore, when the two types of wax were added to the miscible EVA/tackifier blend, the T_g values of the paraffin wax blends did not change because of the miscibility between paraffin wax and EVA.

Therefore, we can conclude that the addition of the waxes used in this study altered the miscibility of the EVA/tackifier/wax ternary blends and increased the elasticity of the blends.

3.3. Single lap shear strength

Figure 8 shows master curves of single lap shear strengths of the ternary blends with SX70 wax. In general, the strength of a polymer material is affected by test conditions such as temperature and test speed. The lap shear strength values were highly scattered at higher test rate and in the lower temperature region, and interfacial failure (not shown) occurred in this region. The failure mode was determined visually. Gibert *et al.* [13] reported that interfacial failure mode occurred in the rubbery state and cohesive failure occurred at the terminal domain. Similarly, cohesive failure was observed at the lower peel rates. However, lap shear strength values decreased with increasing wax concentration over the whole peel rate range, although their E' values increased with increasing wax concentration. The adhesion properties of HMAs were correlated with the viscoelastic properties. In our previous papers [5, 11], we showed that the single lap shear strength increased with increasing E' , but Fig. 8 showed different tendency. Therefore, although DSC

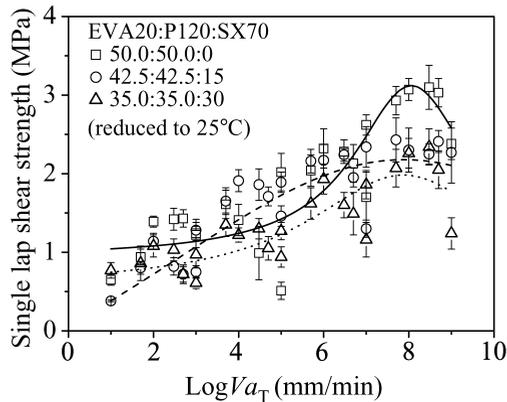


Figure 8. Master curves of single lap shear strength of EVA-20/P120/SX70 ternary blends for different wax contents (V is cross-head speed and a_T is shift factor).

thermogram and viscoelastic properties do not show their miscibility, the tendency of adhesion strength suggested that the ternary blends were immiscible.

The fitting curves in Fig. 8 show peaks in the regions of low temperature and higher speed. However, these peaks were neither shifted nor their height reduced, due to the immiscibility of these blends. Takemoto *et al.* [9] and Turreda *et al.* [10] reported similar results for the correlation between adhesion strength and PSA miscibility using master curves. In miscible blend systems, the maximum values of adhesion strength are shifted to the higher speed region, whereas in immiscible blend systems this shift does not occur and lower adhesion strength values are shown than for miscible systems. Also, in the case of the ternary blend using SX100 wax, although the lap shear strength was slightly higher than that for the SX70 blend system, similar trends of lap shear strength values were observed (not shown). This fact was correlated with their viscoelastic properties and miscibility. With increasing wax concentration, their modulus increased, melt viscosity decreased and miscibility changed to immiscibility. This indicates that the ternary blends become hard with increasing wax concentration.

4. CONCLUSIONS

The viscoelastic and adhesion properties of the EVA/tackifier/wax ternary blend systems were obtained by DSC, Brookfield viscometry, DMTA and lap shear strength measurements. It was difficult to determine the miscibility of the blends from the T_g and loss factor curves because the melting peaks of the EVA/tackifier blends and the wax appeared in a similar temperature region. Single lap shear strength values were measured to evaluate their adhesion properties as HMAs. The adhesion strength of the ternary blends decreased with increasing wax concentration because the addition of wax altered the miscibility of binary blend of EVA and tackifier. Therefore, although DSC thermogram and viscoelastic measurement did

not clearly show their miscibility, the trend of adhesion strength showed that the ternary blends became immiscible with increasing wax concentration.

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