Thermal Properties and Adhesion Strength of Amorphous Poly(α-olefins)/Styrene–Ethylene–Butylene Copolymer/Terpene Hot-Melt Adhesive

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ABSTRACT: The thermal stability and adhesion properties, such as lap-shear strength of hot-melt adhesives were obtained from amorphous poly(α-olefins) and thermoplastic rubber [styrene–ethylene–butylene copolymer (SEBS)] blends. The addition of SEBS increased the toughness and viscosity and decreased the lap-shear strength of the hot-melt adhesive. Terpene tackifier resin offered enhanced lap-shear strength; this was more effective when combined tackifier resin was added on the hot-melt adhesive. Only a small amount of wax and antioxidant affected the thermal stability and lap-shear strength of the hot-melt adhesive. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3312–3319, 2012

Key words: adhesion; adhesives; polyolefins; toughness

INTRODUCTION

Hot-melt adhesives are, in general, solid at low temperatures and spread onto substrates at elevated temperatures; then, they rapidly set on cooling.[1,2] They are widely used in various fields of applications, including hygienics, woodworking, paper lamination, packaging, and structural adhesives.[3] A typical hot-melt adhesive is formulated with four main components: a polymer (20–50%), a tackifier resin (20%), wax (0–20%), and antioxidants (0.1–1%).[3,4] Thermoplastics, such as poly(ethylene-*co*-vinyl acetates) (EVA), polyolefins, polyamides, and polyesters, have been used in the formulation of hot-melt adhesives. Amorphous poly(α-olefins) (APAOs), produced by the copolymerization of α-olefins such as ethylene, propylene, and 1-butene with Ziegler–Natta catalysts,[5] are useful for the production of hot-melt adhesives for the manufacture of the baby diapers, feminine hygiene products, and incontinence products.[5] Previous studies have shown that APAOs and thermoplastic rubbers, such as styrene–ethylene–butylene copolymer (SEBS), have lower adhesion properties than EVA hot-melt adhesives but are known to have better thermal stabilities.[7–11]

Tackifier resins enhance not only the wetting and tack of hot-melt adhesives[6] but also increase the glass-transition temperature and act as a diluent to lower the plateau modulus of hot-melt adhesives.[6,7] Terpene resins, mainly used for tackifiers, are fairly stable, despite the double bond in the cyclohexyl rings.[12–15]

Various waxes have been used as additives to reduce the melt viscosity and increase the surface energy of polymers to improve their processability and tack with adherends and also to control the pot life of adhesives.[9] When added to the matrix polymer, wax can also negatively affect the adhesion properties because of the shrinkage of the adhesive.[9] The role of antioxidants in adhesives stabilizes the adhesive against oxidation and heat and light degradation. However, remaining residue can also deteriorate the tensile strength and stiffness of the polymer.[9] It is important to select suitable amounts of these additives to maximize the adhesion properties in applications.

The objective of our study was to formulate APAO/SEBS blends to prepare thermally stable and more processable hot-melt adhesives, which could be used as alternatives for current EVA hot-melt adhesives. The optimum composition of the APAO/SEBS for good adhesion properties and the effect of the antioxidant and wax on the adhesion properties of the hot-melt adhesives were also studied.

EXPERIMENTAL

Materials

APAO (Eastoflex E106PL, Eastman Chemical, Inc. Kingsport, Tennessee, USA) and SEBS (Kraton

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G1657, Kraton, Houston, Texas, USA) were used as polymers. The antioxidant (Anox20) was a phenolic resin purchased from Chemtura, Inc. Paraffin wax (LP350F) was supplied by Kukdong Oil and Chemical, Inc. Two terpene resins, including H-terpene (DERTOPHENE 1510, Yasuhara Chemical, Inc., Japan) and terpene phenolics (Daelim Industrial, Inc., Korea), were used as tackifiers. All materials were used without further purification. The properties of the materials are shown in Table I.

Preparation of the hot-melt adhesives

The blends, consisting of two polymers, antioxidants, and wax, were combined to give a total batch weight of 170 g. The mixture was heated to 170°C for 20 min, and then, the tackifier resin (polymer/tackifier = 50/50 wt %) was added with agitation for 6 h to obtain a homogeneous material. To obtain specimens for lap-shear tests, the melt blend was cast onto an aluminum plate with a thickness of 0.6 mm with a rubber roll. The press rate was 2 m/min.

Measurement

The viscosity of the materials was measured with a Brookfield DV-II+ viscometer (Middleboro, Massachusetts, USA) with increasing temperature. The lap-shear test was performed on a universal testing machine (Instron 4465, Instron, Inc.), and we confirmed the load of the sample to failure according to ASTM D 1002-05. The melted blend was applied to the region to be lapped. The bonded length and the thickness of the applied adhesive were 12.7 and 0.6 mm, respectively. The crosshead speed was fixed at 300 mm/min. The shear strength was taken as the average of five test results.

The discoloration of the adhesive due to thermal degradation was determined by the yellowness index (YI) according to ASTM D 1925-70. The specimen was coated on a slide glass 1.5 mm thick, and

then, the color was measured with a Minolta spectrophotometer (CM-2600d, Konica Minolta, Inc., Japan). The tests were executed at different conditions of storage time and temperature. The YI value was obtained by the following equation.[16]

$$YI = 100 \times (0.72a + 1.7ab)/L \quad \Delta YI = YI - YI^{\circ}$$

The three coordinates a, b, and L represent the lightness of the color in CIELAB color space model.

RESULTS AND DISCUSSION

### Effect of the blending ratio of the polymer

The viscosity values of the materials with a 160–200°C application temperature range are shown in Table II.

To clarify the effect of SEBS on the viscosity of the APAO/SEBS blends, the viscosity values of blends with different SEBS amounts with increasing temperature were measured, and the results are shown in Figure 1. Figure 1 shows that the addition of SEBS increased the blend viscosity, which negatively affected the mixing control of the blends, even at high temperatures.

The styrene–rubber block copolymer consists of a two immiscible blocks, where the styrene phase offers the hardness and tensile properties of the hot melt and the rubber phase tends to soften the hot melt.[17] The adhesion properties of a hot-melt adhesive depend on the styrene block content, which also affects the cohesion and thermal properties of the

TABLE II
Viscosity of the Materials

Temperature (°C)	160	170	180	190	200
Eastoflex E106PL (Pa s)	4.0	3.6	3.2	2.6	1.8
Clearon P125 (Pa s)	8.4	3.6	2.4	2.0	1.4
PB950 (Pa s)	0.4	0.35	—	—	—
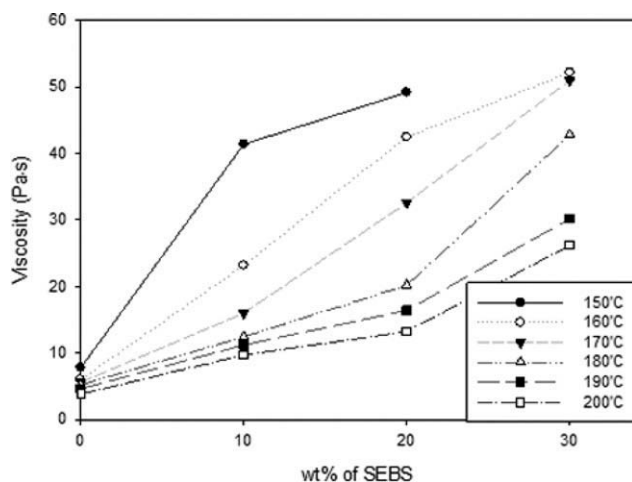
Figure 1 Influence of SEBS on the viscosity of the polymer blends.

hot melt.[18] However, an increase in the rubber phase results in a reduction of the viscosity and also in a high wettability and tack in the hot melt. As shown in Figure 1, the increase in the melt viscosity of the blend may have been due to the styrene content in SEBS.

Figures 2 and 3 show the stress–strain behavior and toughness, respectively, of the hot-melt adhesive as a function of the APAO/SEBS blending ratio. It was found that an increase in the SEBS content contributed to a high tensile strength in the hot melt. Moreover, SEBS addition also caused an increase in the melt viscosity of the hot melt; the blending ratio should be constrained to 90/10 and 80/20. It was assumed that the addition of SEBS decreased the tack properties, although it had a positive influence

on the toughness of hot-melt adhesive. The effect of the SEBS amount on the lap-shear strength of the hot melt is shown in Figure 4. Depending on the level of SEBS used, we observed that the lap-shear strength of the hot-melt decreased. One possible factor for this result may have been the high melt viscosity of the hot melt with SEBS addition.

Effect of the tackifier resin

We estimated the viscosity values of the hot-melt adhesives with different tackifier resin contents: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100. Two tackifiers were used; one was terpene phenolic resin (DE 1510), and the other was hydrogenated terpene resin (Clearon P125). The mixing ratio of the polymer and tackifier resin was fixed at 50/50 w/w.[7] Figure 5 shows the viscosity of the hot-melt adhesives in the temperature range between 160 and 200°C. It could be seen that the tackifier resin decreased the viscosity of the hot-melt adhesives. Moreover, the contribution of DE 1510 to the viscosity of the hot melt was much clearer than that of P125, regardless of the polymer/tackifier resin ratio.

Figure 6 shows the effect of the tackifier resin on the toughness of the hot-melt adhesive. Because of the higher deformation ratio of the APAO/SEBS/terpene hot-melt adhesive, the crosshead speed of UTM (universal testing machine) preferred to increase at 400 mm/min. As shown by the results, as DE 1510 was added to the hot melt, it may have enhanced the tensile strength but deteriorated the tensile strain. Thus, the toughness of the hot melt changed little. On the other hand, the addition of P125 to the hot-melt adhesive increased the strain
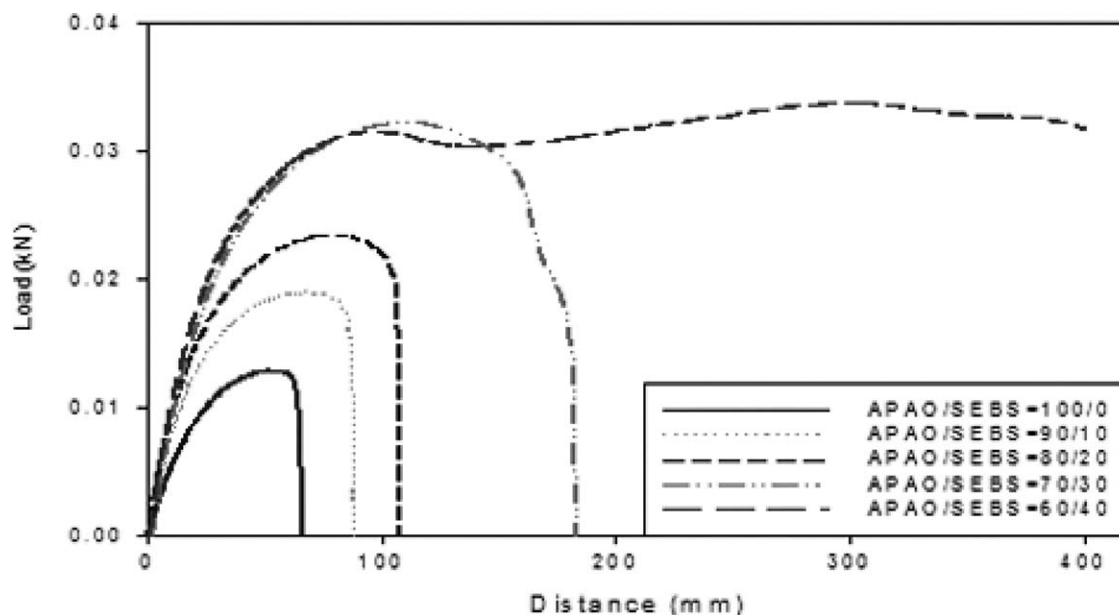
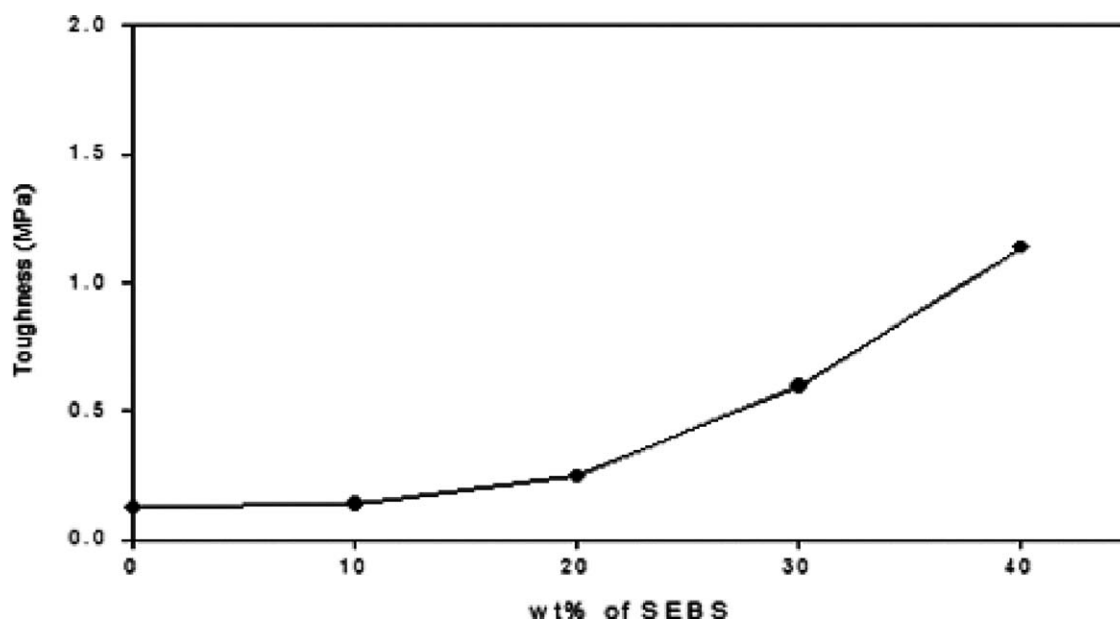**Figure 2** Influence of the SEBS amount on the tensile properties of the blend.

Figure 3 Influence of the SEBS amount on the toughness of the blend.

slightly. The toughness of the hot melt with P125 was higher than that with DE 1510, even at high amounts.

The influence of the tackifier resin on the adhesion properties of the hot-melt adhesive is shown in Figure 7. It seems that a higher lap-shear strength in the hot melt with tackifier resin was due to the enhanced molecular motion from the lower molecular weight tackifier resin. This reinforcing effect of the tackifier resin was distinct for the combined tackifier resin, DE 1510/P125 at a 50/50 mixing ratio. At this mixing ratio of hot-melt adhesives, we

also observed that the viscosity range of the hot-melt adhesive was suitable for wetting the surface of the adherend.

Effect of the wax

Considering the previous test results, we prepared hot-melt adhesives with 90/10 APAO/SEBS and 50/50 DE 1510/P125 mixing ratios. After several amounts of wax (5, 10, and 15 wt %) were introduced into the hot melt, the viscosity change, toughness, and lap-shear strength of the hot-melt adhesive
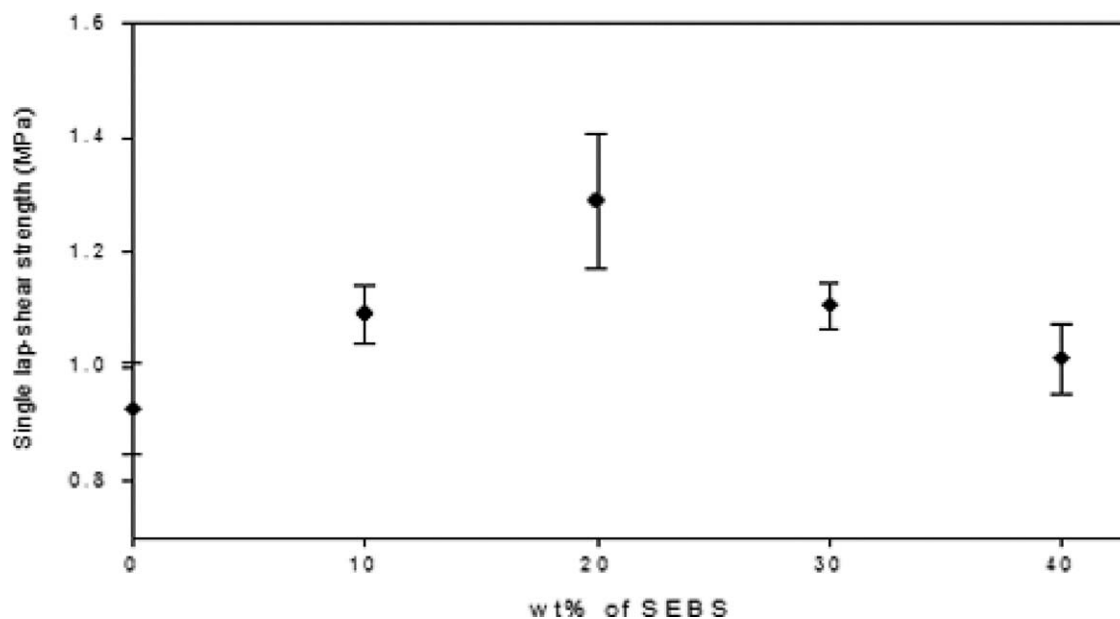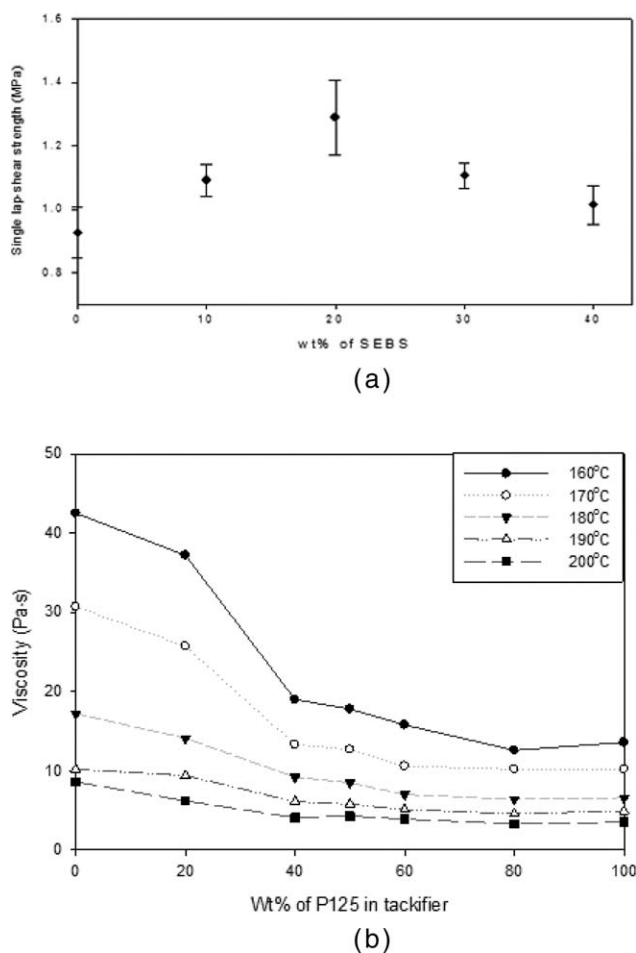

Figure 4 Influence of the SEBS amount on the lap-shear strength of the polymer blends.

Figure 5 Viscosity of the APAOs/SEBS hot-melt adhesive with tackifiers: polymer/tackifier = (a) 50/50 and (b) 60/40.

were measured; they are shown in Figures 8–10, respectively. It is generally accepted that wax is used as an additive to improve the processability of a hot-melt adhesive by controlling the viscosity. Figure 8 indicates that the viscosity of the hot melt obviously decreased at 160°C with 5 wt % wax, but no significant change in the viscosity was observed, even with 15 wt % wax addition. Similar results were also obtained for the toughness of the hot-melt adhesive. We suggest that the toughness of the hot-melt adhesive was strongly dependent on that of the polymer itself, not on that of the additives. From the results, we assumed that the addition of wax was limited to 5 wt % for good adhesion properties.

Effect of the antioxidant

The influence of the antioxidant on the viscosity of the hot-melt adhesive was studied, and the results are shown in Figure 11. Increasing the concentration of antioxidant had no effect on the viscosity, even at high temperature. It is well known that antioxidants support the rather efficient inhibiting radical chain reaction after polymer chain scission.[19] Possibly, the constraint for thermal degradation of the hot melt is favored by a small amount of antioxidant. It is also suggested that only the addition of 0.1 wt % antioxidant was surely useful to constrain the thermal degradation of the hot-melt adhesive.

Enhanced thermal stability through the addition of a small amount of antioxidant was also observed from YI as a function of time. It was shown that use of antioxidant resulted in reduced yellowing of the hot-melt adhesive at 200°C for 4 h of testing, as shown in Figure 11.
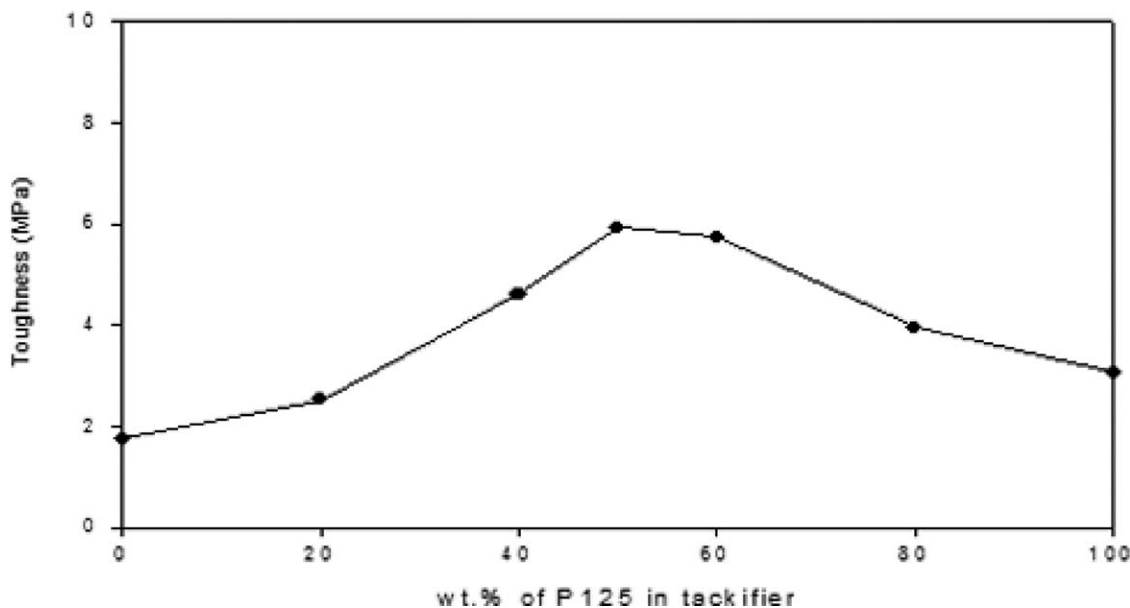
Figure 6 Effect of the mixing ratio of the combined tackifier resin on the toughness of the hot-melt adhesives.
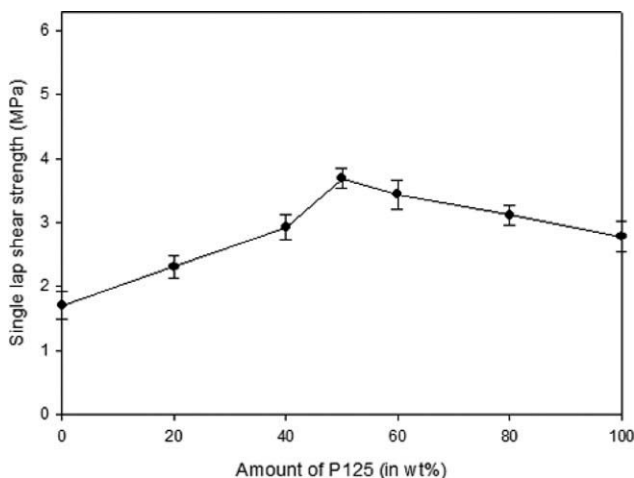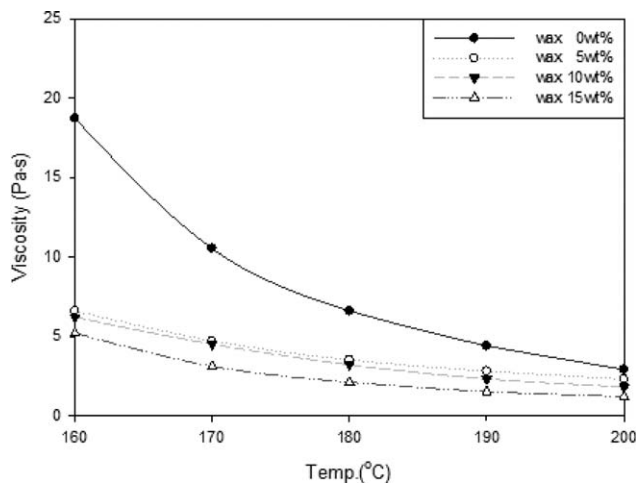
Figure 7 Effect of the mixing ratio of the combined tackifier resin on the lap-shear strength of the hot-melt adhesives (APAOs/SEBS = 90/10, polymer/tackifier = 50/50).

Figure 8 Effect of the wax on the viscosity of the hot-melt adhesive.

Activation energy

The activation energy of the hot melt can be written as

$$\eta = \eta_0 \exp(E_n/RT)$$

where η is the viscosity, η_0 is absolute viscosity, E_n is the activation energy of the polymer, R is the ideal gas constant, and T is the temperature.[20] As the viscosity of the polymer decreases with temperature, it can be assumed that the change in polymer viscosity is closely related to the activation energy of the polymer.[5] Figure 12 shows that the activation energy of the hot-melt adhesive increased at concentrations of P125 between 20 and 60 wt %, but the value was independent of the tackifier resin at the initial and

final stage of P125 loading. Similar transitions were also observed for different polymers and tackifier resin concentrations. It may be that this change in activation energy was associated with the compatibility between the polymer and tackifier resin.

CONCLUSIONS

Hot-melt adhesives based on APAO/SEBS polymer blends were prepared, and the effects of the tackifier resin, wax, and antioxidant on the properties of the adhesives were studied:

1. When SEBS was added to the system, the toughness of the hot-melt adhesive was enhanced, and the viscosity was also increased. The lap-shear strength was reduced at over 20
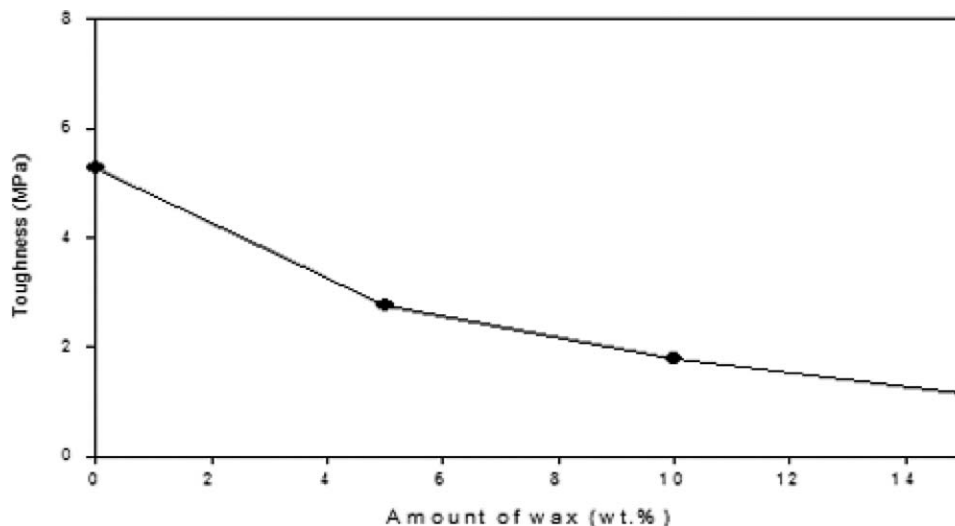
Figure 9 Effect of the wax on the toughness of the hot-melt adhesive.
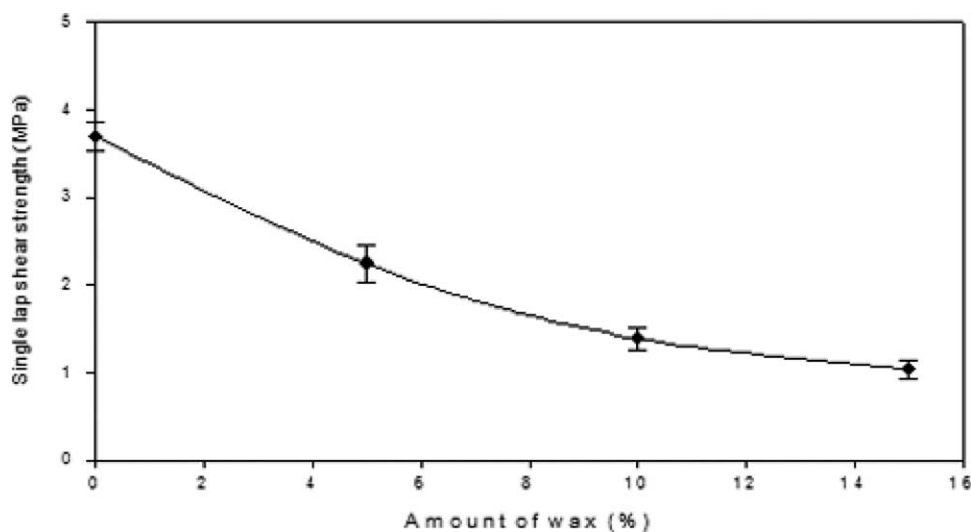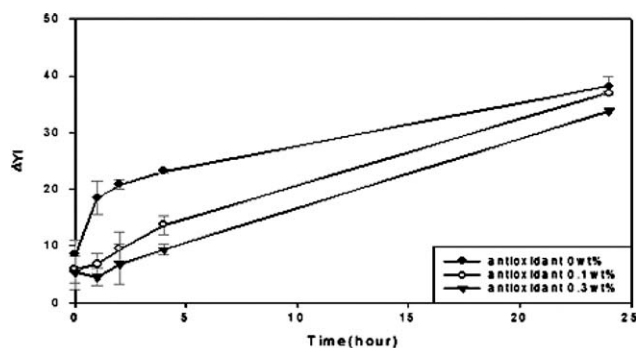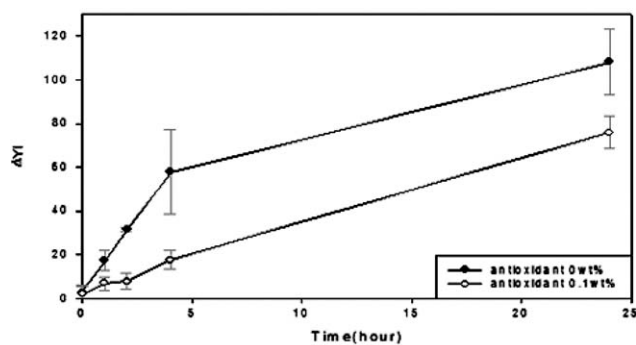
Figure 10 Effect of the wax on the lap-shear strength of the hot-melt adhesive.

wt % SEBS; this suggested that the viscosity of the hot melt governed mostly the adhesion properties and toughness of the hot-melt adhesives.

2. Terpene resin as a tackifier reduced the viscosity and enhanced the toughness of the hot-melt adhesives; this provided evidence for the
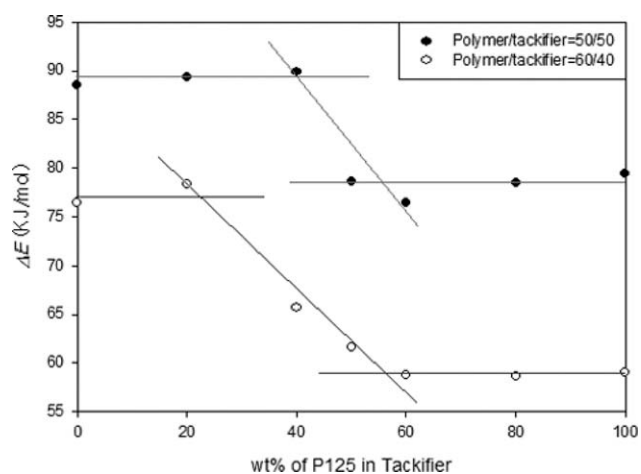

Figure 12 Activation energy (E) of the hot-melt adhesive as a function of P125 content.

improved lap-shear strength of the hot-melt adhesive. The synergic effect of the combined tackifier resin was also observed in the adhesion properties.

3. It could be seen that small amounts of wax and antioxidant had an effect on the physical properties of the hot-melt adhesive. Antioxidant in the amount of 0.12 wt % efficiently acted as an inhibitor for polymer chain scission at high temperatures and resulted in enhanced thermal stability.

(a)

(b)

Figure 11 Effect of the antioxidant on the thermal stability of the hot-melt adhesive as a function of time at (a) 200 and (b) 250°C.

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