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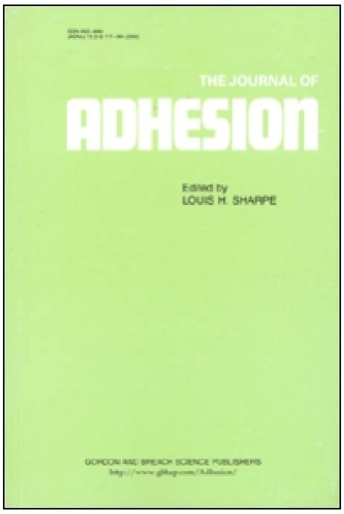

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Hot Melt Adhesive Model: Interfacial Adhesion and Polymer/Tackifier/Wax Interactions*

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This work continues our study of the hot melt adhesive (HMA) model published earlier [1]. This HMA model was developed based on the pressure sensitive adhesive (PSA) tack model established previously [2]:

$$P = P_0 BD \tag{1}$$

where P is the adhesive bond strength, P_0 is the interfacial (intrinsic) adhesion term, B is the bonding term and D is the debonding term. The previous paper [1] describes the B and D terms in detail. However, only a brief discussion of the P_0 term was given. The present paper will provide a more in-depth but still rather qualitative study of the P_0 term within the framework of the adhesion model described in Eq. (1). HMAs studied are ethylene/vinyl acetate copolymer (EVA)/tackifier/wax blends. Substrates studied are untreated and corona-discharge-treated polyolefins such as polypropylene (PP) and polyethylene (PE). First, it has been found that the tackifier surface tension could be roughly correlated with one of its thermodynamic parameters: the solubility parameter dispersion component. Secondly, except for EVA/tackifier binary blends, the compatibility of any two of these three components, the EVA polymer, the tackifier and the wax, in a HMA can be estimated from surface tension and X-ray photoelectron spectroscopy (XPS) measurements. Thirdly, based on the study of the EVA/mixed aliphatic-aromatic tackifier/wax model HMA system, it has been observed that the HMA/polyolefin substrate interfacial composition depends on the wax/substrate compatibility. The cause of an inferior peel strength of a HMA containing a high wax content to a polyolefin substrate is possibly due to the formation of a weak boundary layer (WBL) of wax at the interface and/or low dissipative properties of the HMA.

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Also, the relationship between EVA/tackifier/wax interactions and HMA peel strength will be discussed. A correlation between the EVA/tackifier compatibility measured by cloud point and viscoelastic experiments to the debonding term, D, in Eq. (1) has been found.

Keywords: Hot melt adhesive; tackifier; polyolefin; adhesion; compatibility; peel strength; surface tension; weak boundary layer; corona-discharge treatment; loss tangent; debonding frequency; wax

INTRODUCTION

HMAs are usually formulated from a semi-crystalline polymer such as an EVA, a tackifier and a wax. These three components are blended together and applied in the molten state at elevated temperatures. The resultant properties are obtained when the adhesive is cooled to a tough and flexible solid to form the bond between substrate surfaces [1].

Experimental studies using pendant drop, contact angle, XPS, stress-strain and viscoelastic measurements have been undertaken to understand the interfacial term, P_0, of the HMA. Surface tensions of the EVA polymer, a number of different tackifiers and the wax have been compared. Effects of the wax content and the substrate surface treatment on both the surface and interfacial composition of HMA/substrate interfaces, and the peel strength have been investigated. The substrates used are untreated and corona-discharge-treated (CDT) PP and PE surfaces.

The interfacial adhesion term, P_0, can be represented by [1]:

$$P_0 \sim \gamma_a + \gamma_s - \gamma_{as} \tag{2}$$

where γ_a = the surface tension of the adhesive, γ_s = the surface tension of the substrate and γ_{as} = the interfacial tension between the adhesive and the substrate. In this work, no attempt will be made to determine the P_0 term of the HMA/substrate system. Rather, surface tensions of various HMA components, surface properties of a number of model HMAs and the interfacial composition of several HMA/polyolefin substrate interfaces will be discussed.

Also, experimental studies using cloud point, stress-strain and viscoelastic measurements have been undertaken to understand the interactions of EVA, tackifier and wax with emphasis on component compatibility. The key criterion for a higher HMA bond strength is a better component (EVA, tackifier and wax) compatibility. Component compatibility results in an adhesive surface free of, or at least comprising a minimum quantity of, a WBL, and a bulk adhesive layer able to dissipate input mechanical energy in the industrial peel frequency range. A WBL-free surface is the first requirement for sufficient interfacial interactions between the adhesive and the substrate; otherwise, the interface cannot support any stress and no energy can then be dissipated in the bulk adhesive. Effects of the tackifier type and the wax content on the peel strength and the melt viscosity have been investigated. The major substrate used is the untreated PP surface. The main purpose is to relate EVA/tackifier/wax interactions to the adhesive bond strength within the framework of Eq. (1).

EXPERIMENTAL

Materials

One of the EVA polymers Escorene® 7750, the wax, and PP and PE substrates have been described previously [1], [3]. Both the PP and PE substrates contain only antioxidant(s), but have no processing aid, slip, anti-block or anti-static agent. For this work, another lower molecular weight EVA, Escorene 7710 polymer, was used only for the cloud point measurements. The comparison of these two polymers (both with a vinyl acetate content of 28 wt. %) is shown in Table I.

TABLE I Characterization of EVA polymers

Escorene	*MI*	M_n	M_w	M_w/M_n	M_z	*DSC* T_g, °C	*DSC* T_m, °C
7710	499	13 K	25 K	1.9	40 K	−34	68
7750	32	22 K	44 K	2.0	75 K	−31	72

where MI denotes the melt index, which was measured according to ASTM D1238, condition *E*, 190°C and 2.16 kg. GPC and DSC measurements of the polymers were described previously [3]. Tackifiers used in this work will be discussed below.

Tackifier Solubility Parameter Measurements

GPC

The solubility parameter dispersion component, δ_d, of the tackifier was determined from GPC measurements. The GPC used was a Waters 410 instrument having a five-column set with porosity ranging from 10^2 to 10^5 Å. The flow rate was 2.5 ml/min. The filtered solution of the tackifier in THF with a concentration of about 0.5% (w/v) at 30°C was used. Column calibrations were obtained with the use of polystyrene standards. The characteristics of each tackifier used in this work is shown in Table II. All the Escorez® tackifiers are products of Exxon Chemical Company. Wingtack® 95 tackifier is a product of Goodyear Chemical Division.

Notice that M_n and M_w/M_n values of some of these tackifiers are different from those reported before [1–2] because a different GPC instrument was used previously.

By running polymer standards such as polyisobutylene (L140; Exxon Chemical), polyisoprene [2], polybutadiene (Diene 35NF; Firestone) and polystyrene (GPC standard; peak molecular weight = 92,800) with known values of refractive index, n, and δ_d in the GPC, one can arrive at the following two equations:

$$n = 1.4032 + 2.471 \times 10^{-4} \, [(\text{GPC Peak Area})/(\text{GPC Solution Concentration})] \quad (R^2 = 0.99) \tag{3}$$

and

$$\delta_d = 13.22\,n - 11.87 \quad (R^2 = 0.95) \tag{4}$$

TABLE II Tackifier characterization

Tackifier	M_n	M_w/M_n	δ_d, $cal^{1/2}/cm^{3/2}$	*DSC* T_g, °C	*Aromatic Proton, %*
Escorez 5320	330	1.67	8.54	66	0
Escorez 7312	710	1.50	9.31	63	54.1
Escorez 6372	750	1.67	8.65	50	
Escorez 2393	760	1.88	8.81	45	25.1
Escorez 1310LC	900	1.56	8.23	46	0
Wingtack 95	1060	1.51	8.19	52	0
Escorez 2520	540	1.31	8.28	−16	

where the GPC peak area and the GPC solution concentration are expressed in mV·sec and mg/10 ml, respectively. Therefore, the tackifier was first run in the GPC and the *n* value was obtained from Eq. (3). The δ_d value was subsequently calculated from *n* according to Eq. (4).

Refractometry

Values of *n* of THF solutions of a tackifier at several concentrations were measured in a Bausch and Lomb refractometer. Figure 1 shows the data of two of the tackifiers in Table II. By extrapolating to 100 wt. % tackifier, the *n* value of the tackifier in the condensed state was obtained. The value of *n* of Escorez 2520, a liquid tackifier, was measured by using the extrapolation method and by the direct measurement of this liquid material in the refractometer. The extrapolation method and direct measurement gave *n* values of 1.522 and 1.524, respectively. After the determination of *n*, the δ_d value was then calculated according to Eq. (4). It was found that GPC and refractometry yield similar values of δ_d for the tackifier.

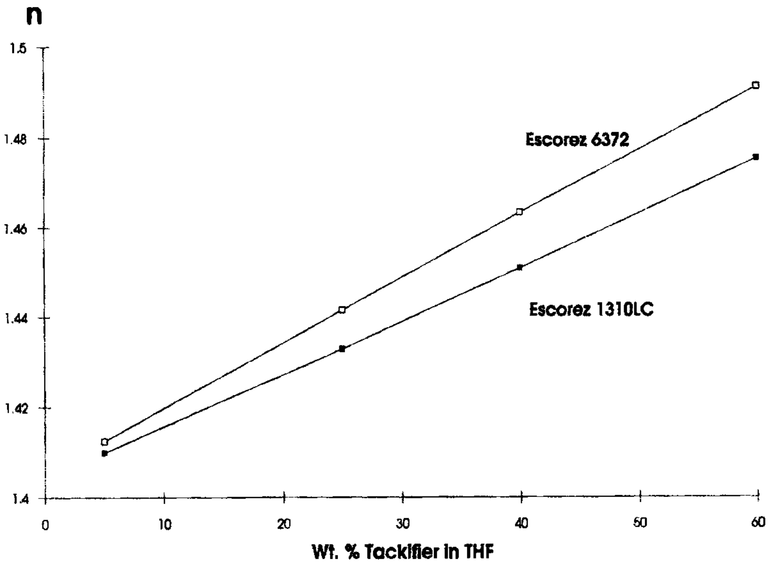


FIGURE 1 Refractive index data of tackifiers in THF.

Differential Scanning Calorimetry (DSC)

The glass transition temperature, T_g, of the tackifier in Table II was measured in a Du Pont 9900 DSC. A sample weighing approximately 10 mg was scanned from −50° to 150°C at a heating rate of 10°C/min. The T_g was determined from the mid-point of the thermal transition in the heating cycle.

Proton NMR Measurements

Proton NMR data was obtained in a Varian VXR 300 MHz spectrometer equipped with a 10 mm broadband probe. Samples were dissolved in deuterated chloroform at a concentration of 80 mg/ml and run at 50°C. Chemical shifts are given in ppm and are relative to tetramethylsilane (TMS) which has a reference at 0 ppm.

Due to the structural complexity of tackifiers, only generic proton asssignments were made. These assignments are useful in accessing differences between samples based on general proton categories. The different proton types were calculated by integrating the signal area in three spectral regions. The aliphatic region was defined as signals between 0–3.5 ppm, the olefinic as signals between 4.5–6.0 ppm and the aromatic as signals between 6.5–7.5 ppm. By summing the area of the three regions the percentage of each proton type was calculated by dividing total area into the signal intensity of each region. Values of % aromatic proton in various tackifiers are shown in Table II.

Contact Angle Measurements

Wu's harmonic-mean method [4] employing water and methylene iodide as the probing liquids was used to determine the surface tensions of the wax, the PP and PE surfaces. The contact angle drop size was about 7 μL. These probing liquids are nonsolvents for the wax, PP and PE. Wax specimens were prepared by preheating the material (at about 130°C) and pouring on a horizontal substrate to form a smooth surface. PP and PE specimens were extruded films. Liquid drops were then placed on these surfaces and contact angles were determined with an NRL C. A. Goniometer (Ramé-Hart, Inc.) It was observed that, in most cases, the measured contact angle had a variation of about ± 3°. This resulted in ~10% error in the calculated surface tension.

X-Ray Photoelectron Spectroscopy (XPS)

A Leybold XPS/Auger Spectrometer was used. X-rays were generated from a Mg anode.

Specimen Preparation

Hot melt compositions were prepared by melt blending the components together at an elevated temperature (150–180°C) under an inert gas blanket in a stainless steel vessel, which was equipped with a mechanical stirrer and heated using a heating mantle. The mixing time was about 30 minutes or longer until a homogeneous mix was obtained. After being cooled and solidified, a homogeneous mix was a reasonably strong and flexible slab without any portions which were mechanically weak and which appeared in a different color. In a 100 g HMA formulation, 0.5 g of Irganox® 1010 was always added as a stabilizer.

T-peel specimens were prepared in the following manner. The preheated adhesive (at about 130°C) was poured onto a release-coated paper and drawn to produce a thin adhesive film. Once cooled and allowed to set, the adhesive film had a smooth surface, and a uniform light-transmitting behavior when viewed through a light source, for a homogeneous polymer/tackifier/wax mix. The film was then trimmed to an appropriate size. Polyolefin (PP or PE) to polyolefin bonds were made by placing this adhesive film between two pieces of polyolefin substrate and heat-bonding (150°C and 120°C for PP and PE, respectively) in a positive pressure, Teflon-coated mold at 0.28 MPa (40 psi) for 10 sec. The adhesive thickness was controlled at 6 mils = 152 μm. The laminate was then cut into 1/2″ = 1.3 cm wide specimens for *T*-peel measurements.

Pendant Drop, Viscoelastic and *T*-Peel Measurements

Experimental procedures have been detailed elsewhere [1].

Cloud Point Measurements

Cloud point is the temperature at which the clear and molten EVA/tackifier blend (wt. ratio = 1:1) cools to give the first indication of a cloud or haze. It provides a qualitative measure of EVA/tackifier compatibility: the lower the cloud point, the more compatible is the

EVA polymer with the tackifier. As mentioned before, the lower molecular weight Escorene 7710 polymer was used in these cloud point measurements (Tab. I).

RESULTS AND DISCUSSION

Surface Tensions of HMA Components

Figure 2 shows the surface tension as a function of temperature for the various HMA components determined by the pendant drop method. Some of the results have been reported earlier [1]. Results for the wax are shown by two data points, which are the extrapolated values of the surface tension at room temperature (=27.0 mJ/m^2 determined by contact angle method) of this wax with the assumption of a slope of −0.05 [4]. This was done because experimental difficulties were encountered when the wax was measured in the pendant drop instrument. For treated or untreated capillaries, the molten wax still wetted the outer wall of the capillary, rendering inaccurate results.

Four interesting observations are noted in Figure 2. Firstly, the magnitude of the surface tension in decreasing order is: Escorez 5320 > EVA > Escorez 7312 > Escorez 2393 ~ Escorez 6372 > Escorez 1310LC > Wingtack 95 > Escorez 2520 > wax. Therefore,

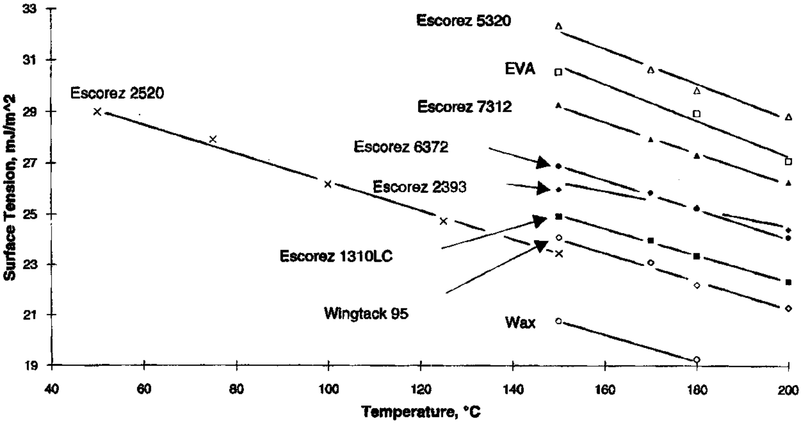


FIGURE 2 The surface tension of the HMA component depends on its structure.

when the wax or the tackifier (with the exception of Escorez 5320) is blended with the EVA polymer, according to thermodynamics the lower surface tension and lower molecular weight wax or tackifier should bloom to the EVA surface. The component enrichment on the blend surface will be discussed further in the next section. Secondly, the surface tension decreases with temperature and roughly obeys a linear relation. Thirdly, $-(d\gamma/dT)$ values of all the tackifiers are close to 0.05 mJ/m^2°C. This is similar to the behavior of EVA (Fig. 2) and other polymers [4]. On the other hand, surface tensions of small-molecule liquids also vary linearly with temperature but the $-(d\gamma/dT)$ values are higher, about 0.1 mJ/m^2°C [4]. For polymers, low values of $-(d\gamma/dT)$ are attributed to conformational restrictions of long-chain molecules because $-(d\gamma/dT)$ represents the surface entropy. For tackifiers, low values of $-(d\gamma/dT)$ may be attributed to conformational restrictions of these condensed, space-filling, cyclic molecules. Fourthly, based on data in Figure 2, the surface tension at 150°C as a function of δ_d of the tackifier can be plotted in Figure 3. It appears that, except for the hydrogenated cyclic Escorez 5320, the surface tension increases with increasing δ_d as expressed by the following equation:

$$\gamma = 4.3\ \delta_d - 11.0\ (R^2 = 0.96). \tag{5}$$

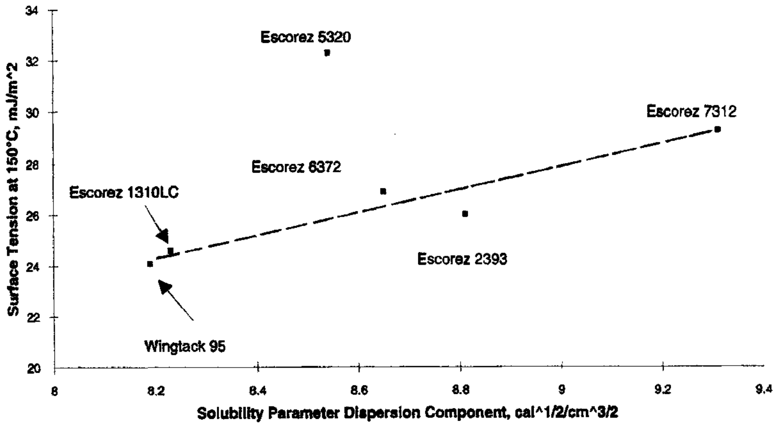


FIGURE 3 Except Escorez 5320, the tackifier surface tension increases with increasing tackifier solubility parameter dispersion component.

In terms of tackifier bulk properties, a compatible tackifier for the EVA should have δ_d, δ_p and δ_h values (solubility parameter components due to dispersion force, dipole forces and hydrogen bonding, respectively) closely matched to those of the EVA polymer. On the other hand, in terms of tackifier surface properties, a compatible tackifier for EVA should have a surface tension, γ, (also consisted of contributions from dispersion force, dipole forces and hydrogen bonding) similar to that of EVA so that, at thermodynamic equilibrium, there is a minimal interfacial tension between the tackifier component and the EVA component in the HMA. Therefore, if there is a relationship between γ and δ for tackifiers or polymers (as shown by Eq. (5) for γ and δ_d), it is not necessary to perform two different experiments to measure both these quantities, which are used as a guideline for estimating the polymer/tackifier compatibility. Also, this relationship provides the information about the difference between the properties of a tackifier or a polymer in the bulk (condensed phase) and in the surface layer. This difference has a fundamental significance in polymer adhesion. The behavior of tackifiers shown in Figure 3 is different from that of solvent [5]. At room temperature, solvents obey the following empirical equation:

$$\delta^2 = 13.8\,\gamma/V_m^{1/3}$$

where δ = total solubility parameter and V_m = molar volume.

XPS Studies of Individual HMA Components

Due to its high surface sensitivity, XPS is a good tool for observing the segregation of a component to the air-cooled hot melt blend surface or on the HMA surface debonded from the substrate if that component has a characteristic functional group or heteroatom (tag). For example, Figure 4a shows the XPS spectrum of the intensity *versus* the binding energy of the EVA polymer. This polymer exhibits a distinct oxygenated carbon peak in addition to the aliphatic carbon peak. Areas under these two peaks determine the oxygen-to-carbon ratio on the EVA surface. The mixed aliphatic-aromatic tackifier (Escorez 2393) in Figure 4b exhibits a unique aromatic satellite which is 6.5 eV higher in binding energy than the aliphatic carbon peak.

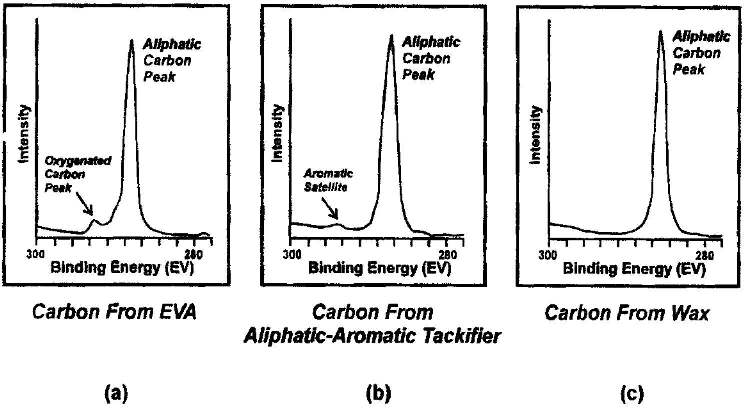


FIGURE 4 The XPS peak shape, intensity and position of the EVA polymer, the mixed aliphatic-aromatic tackifier (Escorez 2393) and the wax provide chemical composition information.

The paraffin wax only shows a single sharp and narrow aliphatic peak (Fig. 4c). These spectral signatures (the oxygenated carbon peak and the aromatic satellite), along with the peak shape, the intensity and the position provide the chemical composition information on the air cooled hot melt blend surface or on the HMA surface debonded from the substrate as discussed below.

HMA Component Compatibility

The compatibility of any two of the three components, the EVA polymer, the tackifier and the wax, in a HMA has been studied by surface tension and XPS measurements. The experimental approach for this HMA component compatibility study is described as follows. By performing surface tension measurements of each individual HMA component as described in a previous section and analysing XPS spectrum of the binary blend of the tackifier and the wax, or the EVA and the wax, one could estimate whether the blend is compatible or incompatible with a single component appearing preferentially on the surface.

Table III shows results of this study. The EVA polymer is polar with a high surface tension (Fig. 2) and high XPS oxygen-to-carbon ratio

TABLE III HMA component compatibility deduced from XPS

System	*XPS O/C Ratio, %*	*Remarks*
EVA	11.0	Polar
Wax	0	Non-polar
Tackifier	0–0.2	High surface tension possibly due to cyclic structure/condensed space-filling molecules
Tackifier/Wax	0–0.2	Incompatible; wax-rich surface
EVA/Wax	0–10.0	Wax blooms to surface; wax has no effects on EVA T_g and T_m
EVA/Tackifier (1/1)	0–2.4	Partially compatible; dependent on tackifier structure

(XPS *O/C* ratio). Aristowax 165, a paraffin wax, is non-polar with a low surface tension (Fig. 2) and a vanishing amount of % *O/C* signal. Various Escorez tackifiers show different surface tensions due to their structural differences (Fig. 2). However, they are all non-polar according to XPS *O/C* ratios.

Figure 5 shows XPS spectra of Escorez 2393/wax blends at two different wax concentrations. The blend surface was made up completely of a wax layer even at 10% wax. Therefore, the wax should be incompatible with the Escorez 2393 tackifier and the blend

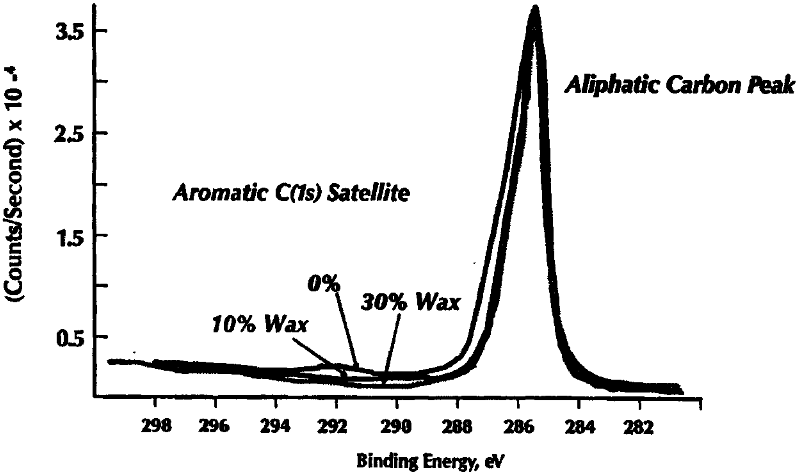


FIGURE 5 XPS results (carbon 1 s region) indicate the incompatibility of Escorez 2393/wax blends.

has a wax-rich surface. This agrees with the observation that the wax has a lower surface tension than Escorez 2393 (Fig. 2).

Figure 6 shows XPS spectra of EVA/wax blends. The oxygen-containing acetate peak at 290+eV decreases with the wax content in the EVA/wax blend. At 30% wax concentration, almost no oxygen is detected. This points to the possibility that the wax blooms to the EVA surface, in agreement with the lower surface tension of the wax compared with the EVA polymer (Fig. 2). This observation is also consistent with DSC measurements that the wax has no effects on the EVA T_g and melting point, T_m (DSC thermograms not shown). Therefore, the EVA polymer and the wax should be quite incompatible.

As shown in Table III, EVA/tackifier blends (1/1 wt. ratio) show low O/C ratios. The EVA/tackifier compatibility will be described later by cloud point and viscoelastic measurements in this paper. Overall, based on the results there, the EVA polymer and the tackifier are usually partially compatible. The degree of compatibility is highly dependent on the tackifier structure.

Composition of HMA/Substrate Interface

Most commerical HMA formulations contain a high wax level for improving hot melt processability. Therefore, effects of wax content on

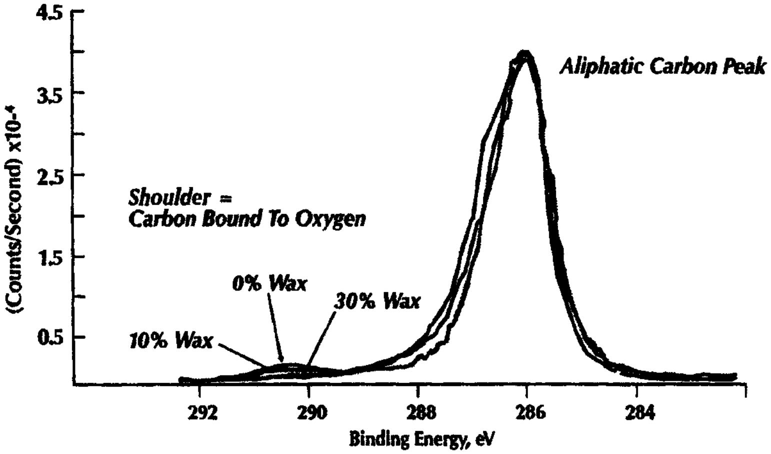


FIGURE 6 XPS results (carbon 1 s region) indicate the decrease in intensity of the oxygen-containing acetate peak with the wax in EVA/wax blends.

the EVA/Escorez 2393 hot melt system are studied in Figures 7–8. The EVA polymer used is Escorene 7750 (Tab. I). The EVA/tackifier wt. ratio is always kept at 1:1, with the wax in these EVA/Escorez 2393 HMAs varied from 0–50 wt. %.

Figure 7 shows XPS results of air-cooled HMA surfaces. Surface *O/C* values were determined from XPS measurements. Bulk *O/C* values were calculated from the wt. % wax in the HMA as shown by the number next to each data point. The surface *O/C* is always lower than the corresponding bulk *O/C* value, with a relatively sharp drop beyond 5–10 wt. % wax concentration. The diagonal line in Figure 7 represents the complete homogeneity throughout the HMA bulk and surface regions. Therefore, it appears that the wax in the HMA tends to migrate preferentially to the HMA/air interface. Again, this agrees with the surface tension data in Figure 2: EVA > Escorez 2393 > wax.

Next, these HMAs are bonded to the untreated PP substrate and *T*-peel strengths are measured. Interestingly, a sharp drop in the peel strength also occurs beyond 10 wt. % wax (Fig. 8). At this point, one is tempted to explain the detrimental effect of a high wax content on the HMA peel strength in Figure 8 by hypothesizing that the wax migrates to the adhesive surface so that a weak boundary layer (WBL) of wax is formed at the HMA/PP interface. However, as described below, XPS

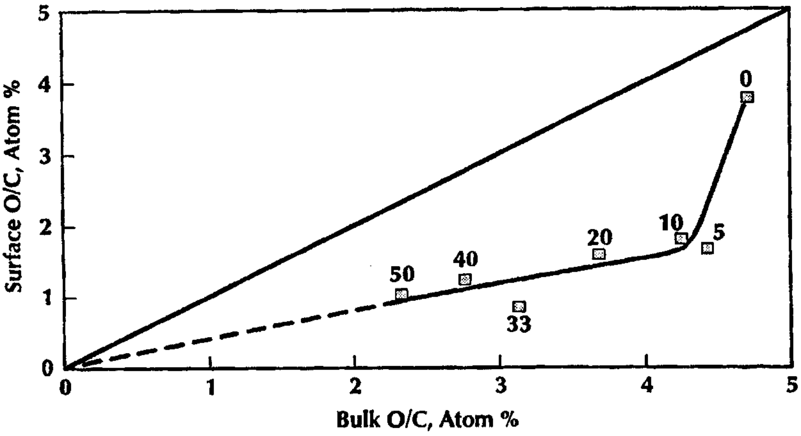


FIGURE 7 The surface oxygen-to-carbon ratio is always lower than the bulk oxygen-to-carbon ratio for the EVA/Escorez 2393/wax system containing different wax levels (EVA/tackifier wt. ratio = 1), indicating wax enrichment on the air-cooled HMA surface.

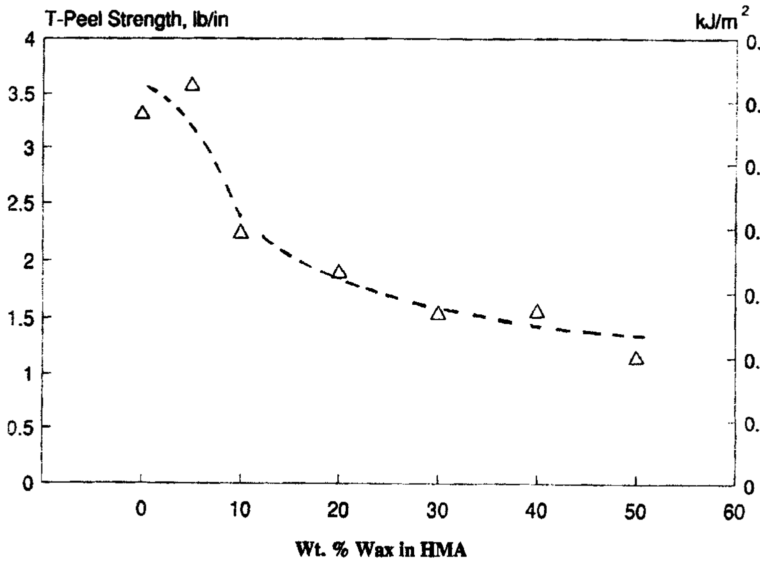


FIGURE 8 The peel strength of the EVA/Escorez 2393/wax system (EVA/tackifier wt. ratio = 1) to untreated PP drops with increasing wax level.

analysis of debonded surfaces of a HMA containing 33 wt. % wax (HMA: EVA/Escorez 2393/wax = 33/33/33 wt. ratio) from untreated and CDT PPs and PEs do not support this. A different behavior has been observed at the HMP/PP or the HMP/PE interface when compared to the HMA/air interface.

Besides the untreated PP and the CDT PP, the untreated PE and the CDT PE were studied for the following reason. CDT tends to crosslink surface regions of PE and other unsaturated polymeric substrates [6]. On the other hand, these plasmas of air and other excitation species during the surface treating process tend to degrade the surface regions of PP and poly (ethylene terephthalate), PET [7–9]. Principal adhesion mechanisms were investigated in depth for PE and PET, and attributed to an increased oxidation at the surface region. This leads to the possibility of an enhanced interfacial contact and a higher adhesion. However, it appears that the reorientation of the surface oxidation is pronounced with the CDT PET and CDT PP, and surface polar groups redistribute to form internal hydrogen bonds, thereby reducing its subsequent bond strength with adhesives.

On the other hand, crosslinking in the CDT PE surface region may hinder surface group reorganization, hence retaining the polar nature of the substrate surface.

XPS and bonding results for PP, CDT PP, PE and CDT PE substrate surfaces are summarized in Table IV. Surfaces exposed after the bond detachment in *T*-peel experiments show a slip-stick, apparent interfacial failure mode. As shown in Figure 9, where *F* denotes the force of separation, one surface appears to be a single substrate layer by a visual inspection and is referred as the substrate side (Tab. IV). The side of the ruptured bond with the bulk of the HMA on top of the polyolefin substrate is referred as the HMA side.

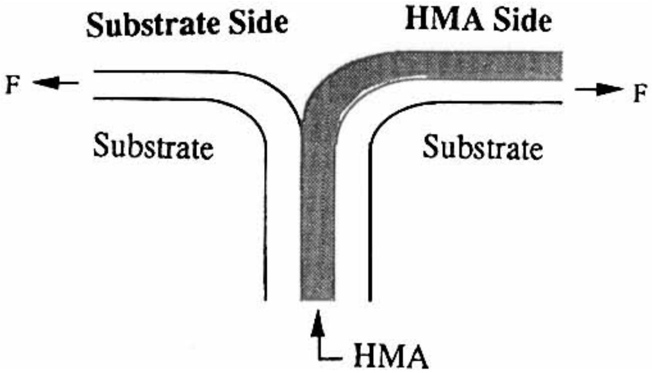
For bonding to untreated PP and CDT PP surfaces, the HMA shows similar failure surface characteristics (from XPS *O*/*C* data) and similar peel strengths. This could suggest two possibilities: either a WBL of wax has formed at the HMA/PP interface or surface polar groups on the CDT PP redistribute inwards to the bulk after the HMA bonding process. The second possibility is more likely to occur due to results of the following experiments.

Surface tensions of CDT PP and CDT PE substrates (one side treated only) were measured by the contact angle method. Results are shown in Table V, where γ^p, γ^d and γ represent the polar component, the dispersion component and the total surface tension expressed in $\mathrm{mJ/m^2}$, respectively. These treated PP and PE substrates were then

TABLE IV XPS results of various materials, and debonded HMA/polyolefin interfaces after *T*-peel (HMA:EVA/Escorez 2393/wax = 33/33/33 wt. ratio)

Material	*XPS O/C Ratio, %*
Untreated PP	0.1
Treated PP	5.9
Untreated PE	0.1
Treated PE	9.2
HMA	0.3
HMA (w/o Wax)	2.4

	XPS O/C Ratio, %		*T-Peel Strength*	
HMA/Substrate	*Substrate Side*	*HMA Side*	*kJ/m²*	*lb/in*
HMA/Untreated PP	0.3	1.4	0.10	0.60
HMA/Treated PP	0.4	1.5	0.10	0.60
HMA/Untreated PE	0.2	4.3	0.04	0.21
HMA/Treated PE	9.1	1.4	0.05	0.26



- **CDT PP: surface degradation ⇒ polar groups redistribute during bonding.**
- **CDT PE: surface crosslinking ⇒ polar groups remain on surface during bonding.**

FIGURE 9 A *T*-peel specimen showing the HMA side and the substrate side after bond rupture.

subjected to heat and applied pressure conditions (Tab. VI), and their surface tensions were re-measured. No pressure is applied to each CDT polyolefin substrate during the heating process in Thermomechanical Treatment (i) in Table VI. On the other hand, two pieces of the treated polyolefin film (a 10 cm × 10 cm square) are pressed together under 0.28 MPa (40 psi) and then separated after 10 s by hand at a normal speed before contact angle experiments in Thermomechanical Treatments (ii) and (iii).

Therefore, after being heated at 130°C for 10 s, with or without applied pressure, γ^p of the treated side of PP drops to a large degree. This may mean that the oxidized PP surface reorganizes at 130°C, even for a short period of 10 s. This result agrees with the literature [7–9]

TABLE V Surface tensions of untreated and treated polyolefin substrates

		γ^p	γ^d	γ
	PP	4.2	29.2	33.4
Untreated Side	PE	2.4	35.7	38.1
Polyolefin Substrate				
Treated Side	PP	11.7	28.2	39.9
	PE	18.1	30.7	48.8

TABLE VI Surface tensions of CDT substrates after thermomechanical treatments

		γ^p	γ^d	γ
i. Treatment: 0 MPa, 10 s and 130°C for PP (120°C for PE)				
	PP	3.3	31.0	34.3
Untreated Side	PE	4.1	34.3	38.4
Polyolefin Substrate				
Treated Side	PP	5.7	30.1	35.8
	PE	19.1	29.3	48.4
ii. Treatment: 0.28 MPa, 10 s and 130°C for PP (120°C for PE)				
Untreated Side				
Polyolefin Substrate	PP	1.2	34.7	35.9
Treated Side	PE	20.0	28.4	48.4
Untreated Side	PP	4.0	30.9	34.9
Polyolefin Substrate	PE	5.5	30.9	36.4
Treated Side				
iii. Treatment: 0.28 MPa, 10 s and 130°C for PP (120°C for PE)				
Untreated Side				
Polyolefin Substrate	PP	3.8	28.9	32.7
Treated Side	PE	18.8	30.1	48.9
Treated Side	PP	4.9	31.1	36.0
Polyolefin Substrate	PE	19.2	28.9	48.1
Untreated Side				

and can account for the low XPS *O/C* ratio on the substrate sides of the HMA/untreated PP and the HMA/treated PP systems in Table IV. On the other hand, the polar component of the surface tension of the CDT PE remains fairly constant after all these brief thermomechanical exposures. This agrees with the literature [6] that the crosslinking in CDT PE surface regions hinders the surface group reorientation.

For bonding to untreated PE and CDT PE surfaces, after bond rupture, the substrate side shows almost the same *O/C* ratio as the substrate before bonding. Initially, a puzzling data point is the surprisingly high *O/C* ratio observed on the HMA side of HMA/untreated PE system. This measurement was repeated twice and similar results were obtained.

Without direct evidence, an explanation is put forward in Figure 10, which shows the composition at the HMA/polyolefin substrate interface. In the preparation of *T*-peel specimens, the HMA film was cooled in air before bonding with the PP or PE surface. Therefore,

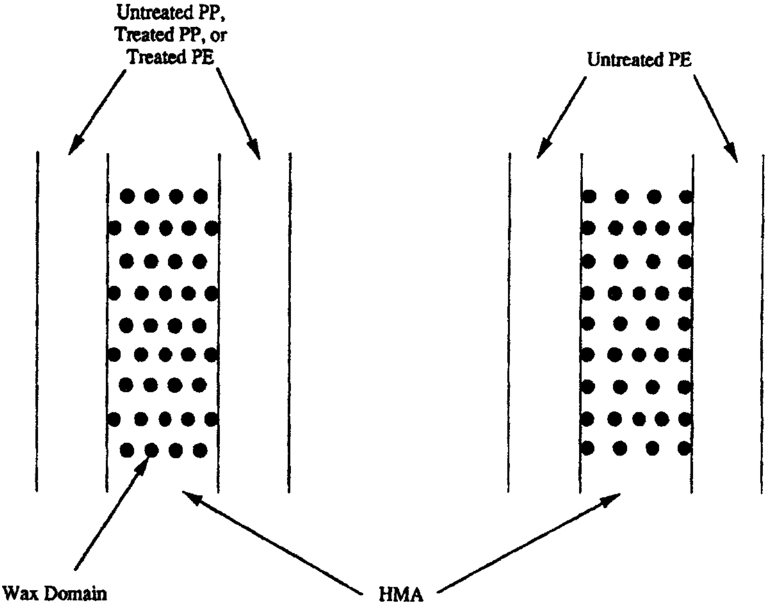


FIGURE 10 The wax could stay at the HMA/untreated PE interface possibly due to a better wax/untreated PE compatibility.

before bonding, the HMA film should have its wax domains, represented by black dots, more populated on the HMA surfaces, as shown by the simple drawing on the right hand side of Figure 10. This is due to the fact that the wax is not only incompatible with both the EVA polymer and the tackifier, but it also has the lowest surface tension (Fig. 2).

For systems on the left hand side of Figure 10, during and after the hot melt bonding process, the wax in a HMA would migrate back to the bulk of the HMA possibly due to incompatibility between the wax and the untreated PP, treated PP or treated PE substrate. On the other hand, for the system on the right hand side of Figure 10, the wax could stay at the interface, possibly due to a better wax/untreated PE compatibility. ^{13}C NMR measurements indicated that the wax is a linear alkane containing no detectable amount of unsaturation or isolated short chain branching. Therefore, it should have a structure very similar to a low molecular weight PE. If a weak boundary layer (WBL) of wax was at the interface of this HMA/substrate joint, after bond rupture, this WBL, or at least most of it, would be left on the PE side. This would give a high *O*/*C* signal on the HMA side due to the wax depletion on the surface of the adhesive. This is what one observes for the HMA/untreated PE system shown in Table IV.

At this point, one question will arise: why does a high wax content in HMA produce a detrimental effect on the peel strength to PP as described in Figure 8? The answer for this could be found in Figures 11–12. In Figure 11, f_a represents the hypothetical interfacial stress between the HMA and the PP substrate [10]. The wax increases the HMA yield stress. Therefore, a high yield stress ($>f_a$) of the tackified polymer cannot effect any crack tip plastic deformation to dissipate input mechanical energy. The peel strength increases with the deformation energy of the bulk adhesive which is the area under the stress-strain curve at the f_a value. The wax also decreases the loss tangent at the *T*-peel debonding frequency [1] of the bulk adhesive (Fig. 12). This and the yield stress enhancement by the wax will decrease the adhesive energy dissipation in both the small and large deformation regimes, hence lowering the adhesion to PP substrate. A more quantitative discussion of the influence of tensile and loss tangent properties on adhesive strength has been described previously [1].

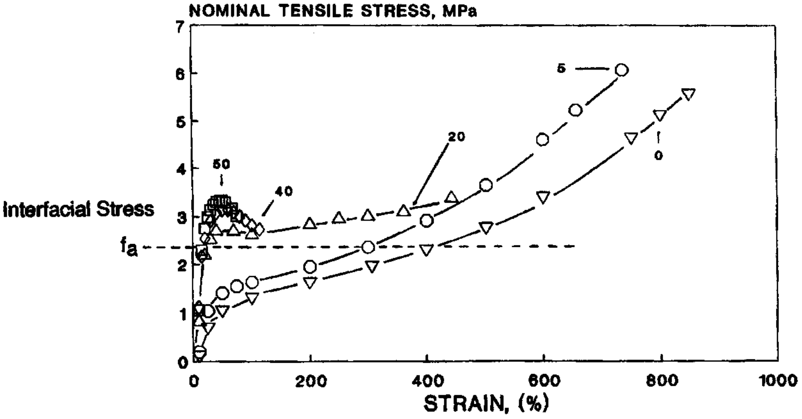


FIGURE 11 The wax increases the yield stress of the EVA/Escorez 2393/wax system (EVA/tackifier wt. ratio = 1), producing a lower adhesive deformation energy at a given interfacial stress.

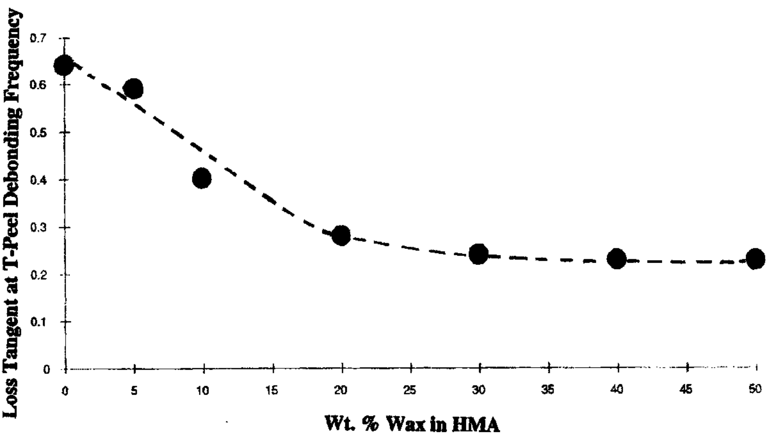


FIGURE 12 The wax decreases the loss tangent of the EVA/Escorez 2393/wax system (EVA/tackifier wt. ratio = 1) at the *T*-peel debonding frequency, producing a lower degree of energy dissipation or a lower *D* term in Eq. (1).

In summary, despite the observation that the air-cooled HMA surface is wax-rich, the wax in a HMA appears not to migrate preferentially to the HMA/untreated PP, treated PP or treated PE interface during the hot melt bonding process. On the other hand, the wax may stay at the HMA/untreated PE interface possibly due to a better wax/untreated PE compatibility.

Cloud Points of EVA/Tackifier Blends

Figures 13 and 14 show the cloud point data of EVA/tackifier blends (wt. ratio = 1:1), where the EVA polymer used is Escorene 7710. Escorez 2203 and 4401, which are both mixed aliphatic-aromatic tackifiers, have % aromatic proton of 1.3 and 25.3, respectively. They have molecular weights similar to those of Escorez 1310 LC, 2393 and 7312. One slightly higher molecular weight aromatic tackifier, Kristalex® F100 (DSC $T_g = 56°C$; Hercules), was also studied.

The DSC melting temperature, T_m, is used to characterize the nature of the cloud point in Figure 13. We can determine whether the observed cloud point is due to a liquid-liquid phase separation or a liquid-solid phase separation as explained later. Structures of the various tackifiers are characterized by their δ_d or % aromatic proton

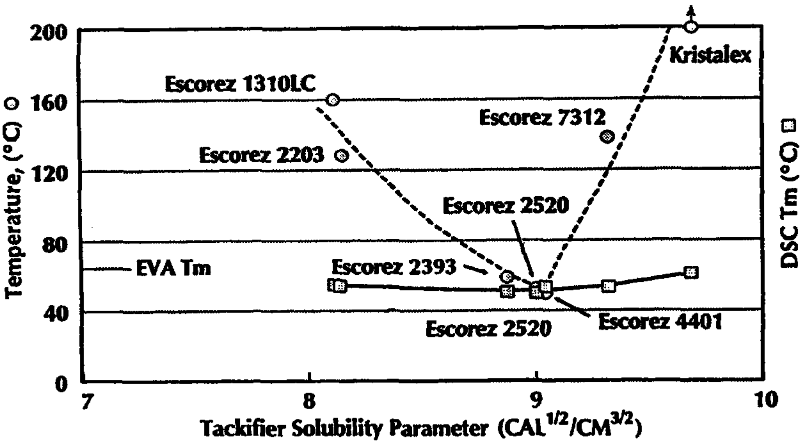


FIGURE 13 EVA is more compatible with tackifiers having intermediate δ_d values.

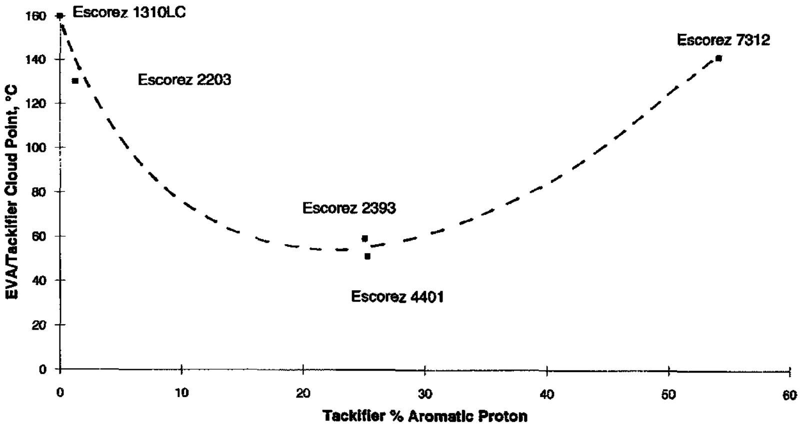


FIGURE 14 EVA is more compatible with tackifiers having intermediate levels of aromaticity.

values, as shown in Figures 13 and 14, respectively. Therefore, the upper dotted curve in Figure 13 is the cloud point curve and the lower solid curve is the melting point curve of the various EVA/tackifier blends. The arrow placed above the cloud point data point of the EVA/Kristalex blend indicates that the cloud point of this blend exceeds 200°C. The cloud point curve undergoes a minimum at δ_d values where mixed aliphatic-aromatic tackifiers such as Escorez 2393, Escorez 2520 and Escorez 4401 locate. This means that this group of tackifiers is more compatible with the EVA polymer. On the other hand, the purely aliphatic tackifier, Escorez 1310LC, and the purely aromatic tackifier, Escorez 7312, are less compatible with EVA due to their much higher cloud points. Therefore, both Figures 13 and 14 indicate that the cloud point of the EVA/tackifier blend depends strongly on tackifier structure.

The EVA polymer studied has a T_m of 68°C (Tab. I). According to the rather flat melting point curve in Figure 13, each tackifier with a different structure depresses the T_m of the EVA to a similar degree. However, cloud points of highly-incompatible EVA/tackifier blends such as EVA/Escorez 1310LC and EVA/Escorez 7312 possibly originate from the liquid-liquid phase separation. On the other hand, cloud points of more compatible EVA/tackifier blends such as EVA/Escorez 2393, EVA/Escorez 2520 and EVA/Escorez 4401 possibly originate from the liquid-solid phase demixing because the cloud point and the crystalline melting temperature, T_m, of each of these blends are close in magnitude to each other.

Relation of HMA Bond Strength to EVA/Tackifier Cloud Point and HMA Failure Surface

Table VII shows melt viscosities and *T*-peel strengths of HMAs containing 10% wax based on the same set of tackifiers studied in the cloud point measurements. The EVA polymer used is Escorene 7750. The EVA/tackifier wt. ratio is always kept at 1:1 in these HMAs because 1) the EVA/tackifier/wax system in 45/45/10 wt. ratio is widely used as a book-binding HMA; and 2) the cloud point results based on EVA/tackifier blends in 1:1 wt. ratio described in the previous section

TABLE VII Effect of tackifier structure on peel strength of EVA/tackifier/wax system (45/45/10 wt. ratio) to PP

Escorez	*150°C*	*T-Peel*		*HMA Loss Tangent*	*EVA/Tackifier*
	Viscosity, Pa·s	*kJ/m²*	*lb/in*	*At Debond. Freq.*	*Cloud Point, °C*
4401	35	0.44	2.5	0.34	51
2393	50	0.30	1.7	0.32	59
7312	40	0.04	0.2	0.28	141
1310 LC	27	0	0	0.20	160

↑ Increasing Compatibility

*All HMA/PP bonds failed iterfacially.

can be used. These adhesives are model HMA systems with similar melt viscosities at a bonding temperature of 150°C to the untreated PP substrate. One will notice that a better EVA/tackifier compatibility, *i.e.*, a lower EVA/tackifier blend cloud point (Figs. 13–14) and a smaller difference in the transition temperatures [3] of the EVA-rich phase and the tackifier-rich phase (Fig. 15), leads to an increase in the HMA loss tangent at the *T*-peel debonding frequency [1] and, consequently, a higher *T*-peel adhesion (Tab. VII). Therefore, we have:

A better EVA/tackifier compatibility → a lower EVA/tackifier cloud point → a higher HMA loss tangent at *T*-peel debonding frequency → a higher *T*-peel strength.

As described previously [1], the *T*-peel strength or the debonding term, *D*, increases with the loss tangent at the *T*-peel debonding frequency for various HMA/PP bonds which exhibit an apparent interfacial failure mode. Therefore, EVA/tackifier compatibility is one of the key criteria for a high HMA peel strength.

Figure 16 shows scanning electron micrographs for the debonded HMA surfaces from the PP substrate for two of the HMAs described in Table VII. The light-color bar at the bottom of each micrograph represents a length scale of 10 μm. Both adhesives fail near the HMA/

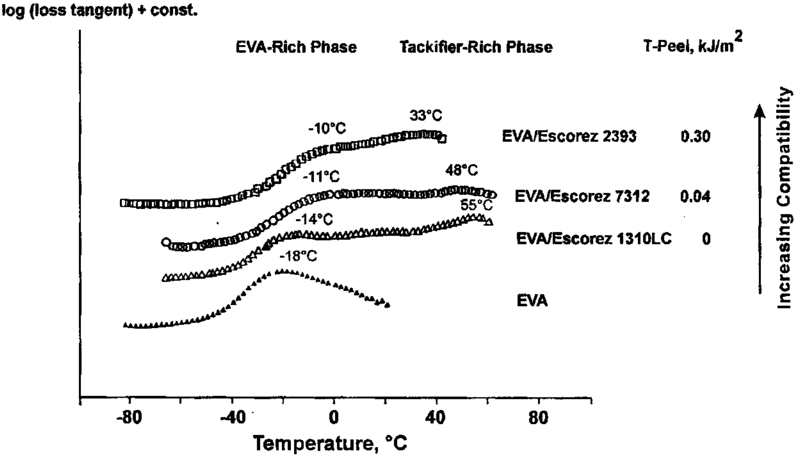


FIGURE 15 Loss tangent *versus* temperature (frequency = 10 rad/s) for EVA and different EVA/tackifier/wax systems obtained from a Rheometric Scientific RDS-7700 dynamic spectrometer using the torsion rectangle fixture.

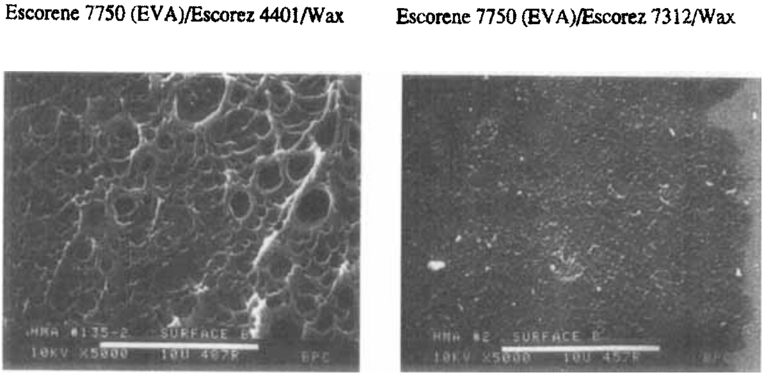


FIGURE 16 Scanning electron micrographs of debonded HMA surfaces from the PP substrate.

PP interface. However, the EVA/Escorez 4401/wax HMA shows a significant drawing of the adhesive after bond rupture. On the other hand, the failure of the EVA/Escorez 7312/wax HMA only involves a minor amount of plastic deformation in the adhesive. Stress-strain curves of these two HMAs are compared in Figure 17. The EVA/

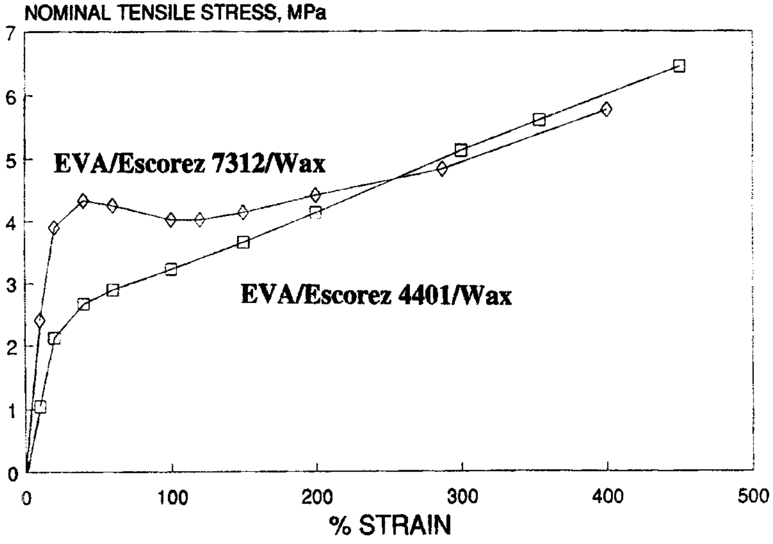


FIGURE 17 The adhesive with a lower yield stress and a larger strain at break dissipates more energy upon deformation.

Escorez 4401/wax HMA has a lower yield stress and a larger strain at break than the EVA/Escorez 7312/wax HMA. Therefore, observations in Figures 16 – 17 and Table VII agree qualitatively with each other that a higher HMA adhesion is the result of a larger amount of work (a larger degree of energy dissipation or a higher loss tangent) being expended in detaching the more ductile HMA from the substrate.

CONCLUSIONS

This work represents a further development of the adhesion model described by Eq. (1) for HMAs. Our major effort is to provide a more detailed discussion of the interfacial adhesion term, P_0. Up to this point, only a qualitative description of P_0 is available. Also, one other effort in this study is to correlate the EVA/tackifier compatiblity measured by cloud point and viscoelastic experiments to the debonding term, D, in Eq. (1). Overall, conclusions of this work are summarized as follows:

1. The interfacial adhesion term, P_0, is governed by the surface tension of each HMA component [1]. Surface tensions of HMA components, measured by pendant drop and contact angle methods, are in the following decreasing order:

   hydrogenated cyclic tackifier > EVA > aromatic tackifier > mixed aliphatic-aromatic tackifier > aliphatic tackifier > liquid mixed aliphatic-aromatic tackifier > wax

   The lower surface tension and lower molecular weight component (wax) tends to bloom to other material's surface when the contacting medium is air. The wax is incompatible with the tackifier and the EVA polymer due to its low surface tension.
2. The tackifier's surface tension can be roughly correlated to the solubility parameter dispersion component of the tackifier.
3. After a brief thermomechanical exposure (10 s at 120 – 130°C and 0 – 0.28 MPa), which simulates a typical HMA bonding process, surface polar groups of the corona-discharge-treated PP reorganize, whereas those of the corona-discharge-treated PE remain intact. This observation agrees with the literature [6 – 9].

4. The wax in a HMA migrates preferentially to the HMA/air interface, but distributes in various degrees at the HMA/polyolefin interface. For a HMA containing a high wax level (33 wt. %) bonded to various polyolefin surfaces, the HMA/substrate interfacial composition depends on the wax/substrate compatibility. No WBL of wax appears to exist at the HMA/untreated PP, HMA/treated PP or HMA/treated PE interface. However, the wax could stay or even migrate in a certain degree to the HMA/untreated PE interface possibly due to a better wax/untreated PE compatibility. Therefore, wax distribution in a HMA depends on the chemical nature of the bonded substrate.
5. The presence of a wax in a HMA decreases the HMA loss tangent at the *T*-peel debonding frequency, but increases the HMA yield stress.
6. According to cloud point and viscoelastic measurements of EVA/tackifier blends, mixed aliphatic-aromatic tackifiers are more compatible with EVA than the aliphatic or aromatic tackifier alone.
7. When the HMA bond exhibits an apparent interfacial failure mode, a better EVA/tackifier compatibility (indicated by a lower cloud point of the EVA/tackifier blend and a smaller difference in the transition temperatures of the EVA-rich phase and the tackifier-rich phase) results in a higher HMA loss tangent at the *T*-peel debonding frequency (*i.e.*, a higher energy dissipation in the bulk adhesive), hence a higher HMA peel strength.

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