Explanation of Tackifier Effect on the Viscoelastic Properties of Polyolefin-based Pressure Sensitive Adhesives

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ABSTRACT: The effects of three tackifiers on the glass transition temperature, terminal relaxation time, plateau modulus, and steady shear viscosity of polyolefin-based pressure-sensitive adhesives (PSAs) were investigated. Free volume theory and the Gordon-Taylor equation are used to explain the special effects of tackifiers on the glass transition temperature of the PSA systems. The plateau modulus and zero shear viscosities were determined from which entanglements and monomeric friction coefficients were calculated. The terminal relaxation time (related to the whole molecular chain relaxations) was calculated from the plateau modulus and zero shear viscosity. Explanations were offered as to why tackifiers have "paradoxical" effects on the viscoelastic properties of the polyolefin-based PSA, such as increasing the glass transition temperature but decreasing the plateau modulus of the base polymer. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2408–2413, 2006

Key words: pressure sensitive adhesives; amorphous polyolefin; tackifiers; glass transition temperature; terminal relaxation time

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are unusual materials that are tacky at room temperature. They can be easily deformed and flowed into contact with a substrate under light pressure, yet they show appreciable resistance to be separated.

Tackifiers and base polymers are the most important components of PSAs. Many different tackifiers are added into the base polymers (natural rubber, styrenic block copolymers, and amorphous polyolefin) to improve their tack property. Tackifiers are special materials that have low molecular weight 500–2000 but high glass transition temperature. Previous research shows that tack property of PSAs is due to their surface and bulk properties.[1–26] Tackifiers improve the tack property of the base polymers by changing both their surface and bulk properties (viscoelastic properties).[2–4,6,10,18,20,21,24] Although the effects of tackifiers on the PSAs have been studied over the past four decades, a fundamental understanding of how tackifiers affect these properties is still incomplete.[3,4,14,18,24,25]

The relationship between the viscoelastic properties and the tack property has been investigated.[2,7,10,11,13,14,20,22,27–29] Tackifiers act by bringing the viscoelastic state of the adhesive to one more state suitable to bonding and unbonding.[2] Previous studies show that tackifiers increase the glass transition temperature but lower the plateau modulus of the base polymers.[2,4,6,18,21] This is very different from the effect of plasticizers or low molecular weight oils that decrease both the plateau modulus and the glass transition temperature of the systems. At the same time, tackifiers reduce the viscosity at low frequency rather than increase the viscosity as might be expected in the terminal zone[6] of the PSA systems. It seems like a paradox that tackifiers have different effects on the glass transition temperature, plateau modulus, and viscosity of PSA systems. No completely satisfactory explanation has been given to the special effects of tackifiers.

The aim of this paper is to study why tackifiers have different effects on glass transition temperature, plateau modulus, steady shear viscosity, and terminal relaxation time of polyolefin-based PSAs, and to give an explanation of how tackifiers affect the viscoelastic properties of PSA systems. Since terminal relaxation time, plateau modulus, and steady shear viscosity are closely related, a further study of the relationship among them should greatly help to improve our understanding of the effect of tackifiers on the base polymer.

In this paper, the glass transition temperature, the plateau modulus, steady shear viscosity and terminal relaxation time of amorphous polyolefin-based PSA systems are studied, and the terminal relaxation time of PSAs is calculated from plateau modulus and zero shear viscosity. The effect of tackifiers on the free volume of polyolefin-based PSA systems is investigated, and viscoelastic results in the terminal zone are used to explain why tackifiers have the special effects, *e.g.*, increasing glass transition temperature but decrease plateau modulus and zero shear viscosity of the PSAs.

EXPERIMENTAL

Materials

The base polymer used in this thesis is EASTOFLEX E1060 from Eastman Chemical, a copolymer of ethylene and propylene. Base polymer E1060 is a model base polymer to formulate PSAs and hot melt adhesives, according to the recommendation of Eastman.

Tackifiers used in this paper include Eastotac H100R (Eastman, denoted as tackifier H) a partially hydrogenated oligomer of 1,4-pentadiene and Regalite R1090 and R1100 (Eastman, denoted as tackifier R1, R2) that are fully hydrogenated oligomers, using styrene-methylstyrene-indene feedstock.

Polyolefin-based PSA systems offer a number of advantages over well-known natural rubber, styrenic block copolymer or acrylic PSAs, such as thermal stability, hot-melt application, a wide range of PSA performance, thermal stability, hot-melt application, a wide range of PSA performance, low raw materials costs, low formula density, and efficient processing.

Techniques

Glass transition temperatures were measured by Differential Scanning Calorimetry (DSC), using DSC 2950 from TA Instruments at a ramp speed of 10°C/min with nitrogen purge. First run data were discarded and only the second heating scan collected. The T_g is taken as the midpoint of the inflection in the DSC curve.

Rheological measurements were performed using a Rheometrics Scientific RMS 650 rheometer under nitrogen environment. Dynamic and steady shear experiments were performed using 25-mm parallel plates. The master curves were prepared at the reference temperature of 40°C (313.15 K), using the frequency sweep data at temperatures of 40°C (313 K), 50°C (323 K), 60°C (333 K), 70C° (343 K), 80°C (353 K), 90°C (363 K), 100°C (373 K), 110°C (383 K), and 120°C (393 K). The steady shear experiment was performed at 40°C.

RESULTS AND DISCUSSIONS

Gordon-Taylor equation

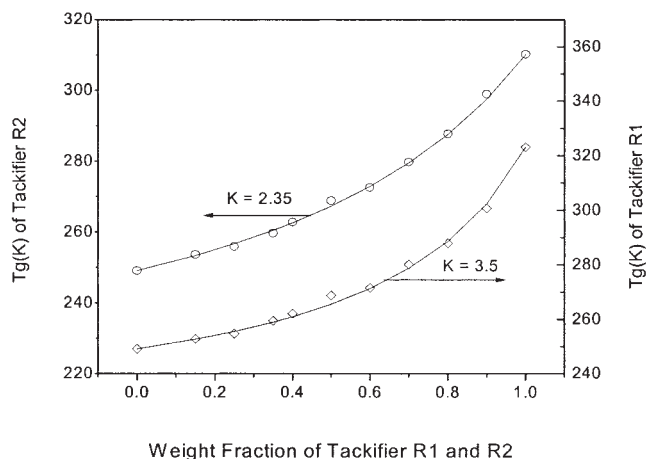The Gordon-Taylor equation is widely used to predict the glass transition temperature of polymer blends. It

Figure 1 T_g data fittings according to Gordon-Taylor equation for tackifier R1, R2 systems.

can be justified by the "free-volume models."[30] By assuming the ideal volume-mixing of the monomeric units in copolymers and the isofree volume fraction at $T_{g'}$

$$f(T, w_2) = (1 - w_2) f_1(T) + w_2 f_2(T) \qquad (1)$$

the following equation is obtained.

$$T_g = \frac{w_1 T_{g_1} + K w_2 T_{g_2}}{w_1 + K w_2} \qquad (2)$$

In the above equation, the coefficient $K = \frac{\alpha_{f,2}}{\alpha_{f,1}}$, where $\alpha_{f,2}$ and $\alpha_{f,2}$ are the expansion coefficients of the free volume of component 1 and component 2, respectively. Subsequently, it was found that the glass transition temperatures of polymer–diluent and polymer–polymer mixtures could also be represented by the Gordon-Taylor equation.

Effect of tackifiers on the glass transition temperature

All our adhesive samples show a single glass transition temperature for each specimen.

From Figure 1 and 2, we can see that the glass transition temperature increases as tackifiers are added to the base polymer. But there are significant differences between H blends and R1, R2 blends. For the latter two tackifiers, the dependence of T_g on composition can be adequately represented over the entire ranges of compositions by the Gordon-Taylor equation with K values of 3.5 and 2.3, respectively (see Fig. 1). For the tackifier H systems, however, only the T_g values of the tackifier-rich compositions can be fitted by the Gordon-Taylor equation with a K value of 4.1 (see Fig. 2). For mixtures rich in base polymer, there is a systematic deviation of T_g values from the predic-
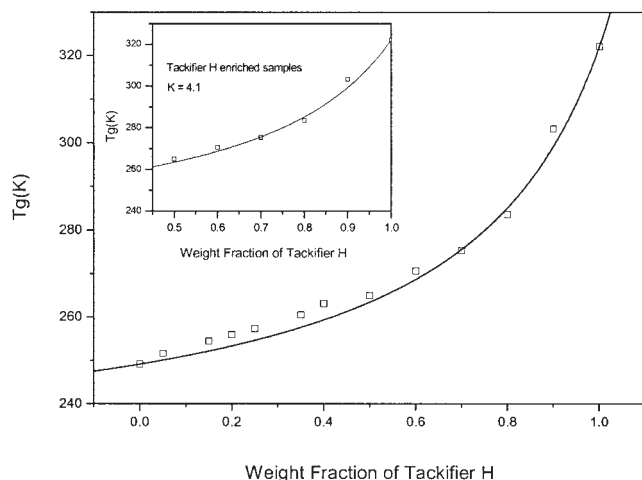
Figure 2 T_g data fitting according to Gordon-Taylor equation for tackifier H systems.

tions of the Gordon-Taylor equation (Fig. 2). The deviation seems to go hand in hand with tackifier content up to about 35%. At 35% and 50% tackifier H, the deviations become smaller and eventually the T_g data follow the Gordon-Taylor curve. We are not aware of the literature reports of similar T_g behavior and therefore propose an explanation in the following discussion.

In the context of the free volume treatment, the elevated T_g implies that the actual free volumes in these blends are less than that expected from the additive rule. We therefore add, *a priori*, a term p_1w_1 to eq. (1).

$$f(T, w_2) = (1 - w_2) f_1(T) + w_2 f_2(T) - p_1w_1 \quad (3)$$

After rearrangement of eq. (3), eq. (4) is obtained as follows:

$$T_g = \frac{w_1 T_{g_1} + Kw_2 T_{g_2} + AKw_1}{w_1 + Kw_2} \quad (4)$$

where $K = \dfrac{\alpha_{f,2}}{\alpha_{f,1}}$ has the same definition as it in the Gordon-Taylor equation and $A = p_1/\alpha_2$. The term $(-p_1)$ represents the effect of tackifier H on free volume (in the base polymer-rich compositions) apart from the additive rule, and is responsible for the higher-than-expected T_g values. With the inclusion of the new term, the T_g results in the base polymer-rich compositions that can be fitted nicely with a A value of 6.18 (Fig. 3). At $w_1 = 0.35$, the $-p_1w_1$ term causes a decrease of $\sim 1 \times 10^{-3}$ in the magnitude of free volume fraction that in turn contributes to a T_g increase of 3°C.

A possible scenario leading to eq. (4) is that some of the tackifier molecules nestle closely along the base polymer segments in the space within the coil or in the

region of coil overlap. The residence of tackifier molecules in these spaces causes a negative contribution to the expected free volume additivity. Needless to say, such a scenario is inapplicable to tackifier-rich blends, in which conventional rules prevail.

It is interesting to note that tackifier R1 and R2 blends do not show similar anomalies. A likely explanation is that their chemical structures are dissimilar to that of the base polymer; while they can act as diluents, they do not occupy spaces in the same way as tackifier H molecules, which have a similar chemical structure as the base polymer. We shall see later that the above explanation is relevant to the interpretation of the viscoelastic data.

Effect of the tackifiers on the viscoelastic properties in the terminal zone

Effect of tackifier H

From above discussion, we can see that the tackifiers increased the glass transition temperature by decreasing the free volume of the base polymer, since tackifiers contain less free volume than that of the base polymer. From Figure 4, it can be seen that addition of tackifier H to the system decreases the storage modulus at higher temperature. Similar effects of tackifiers on the glass transition temperature and modulus have been previously reported for other PSAs, such as natural rubber[2,21] and SBS-based systems.[31] But no fully satisfactory explanation of these effects of tackifiers has been given by previous researchers.

From Figure 5, we can see that the plateau modulus G_N decreases as the concentration of tackifier H increases at lower frequency. G_N was determined by taking the value of the onset of transition from segmental to terminal mode. This can be used to explain why the addition of the tackifier is good for PSAs[2]: in the bonding process (lower frequency), the modulus is
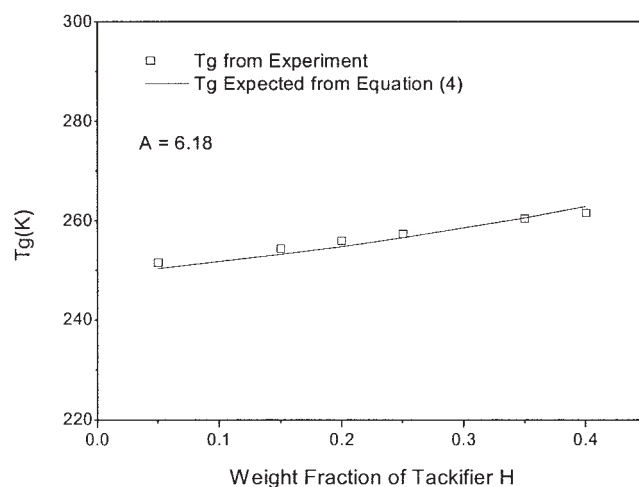

Figure 3 T_g fitting according to the eq. (4) for tackifier H enriched samples.
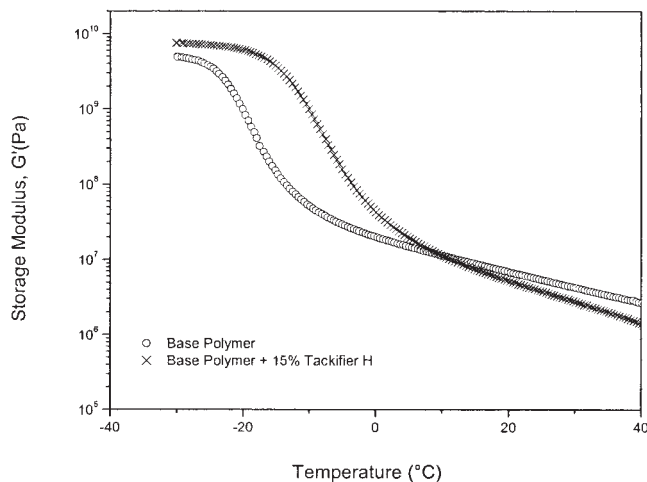
Figure 4 Effect of tackifier H on the storage modulus of the base polymer.

Figure 6 Effect of tackifier H on the steady shear viscosity of base polymer.

low, which means if we press on the PSAs for a longer time (low frequency), we can deform the PSAs and they can make a good contact with the surface of the adherend. In the debonding process (higher frequency), the modulus is high, which means we need more effort to peel a PSA off the surface of an adherend quickly. We also note that the onset of modulus plateau moves to a lower frequency as tackifier concentration increases.

In Figure 6, it can be seen that the viscosities at low frequencies are decreased by the addition of tackifier H, but the viscosities at higher frequencies are essentially unchanged. Thus, the zero shear viscosity η_0, which is controlled almost completely by the terminal relaxation process because relaxation at long times is more or less isolated from the more rapid process, decreases with increasing amount of tackifier H. The two experimental quantities η_0 and G_N combine to
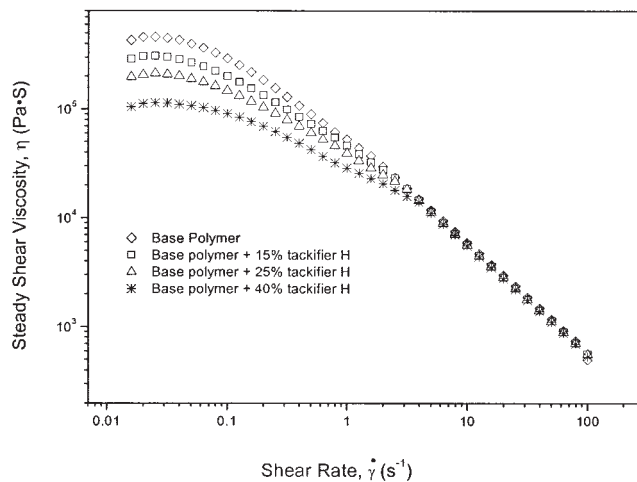
give the average relaxation time in the terminal region by eq. (5).[32]

$$\tau_N = \frac{\eta_0}{G_N} \tag{5}$$

From Figure 7, we can see that after adding tackifier H to the base polymer, both zero shear viscosity and plateau modulus of the PSAs decrease. But the plateau modulus decreases more markedly than the zero shear viscosity, and the combined effect of η_0 and G_N is that the addition of tackifier H makes the τ_N longer. From eq. (5), we can get the terminal relaxation time of the systems shown in Table I. The terminal relaxation time becomes longer as the concentration of tackifier H increases, which means the whole molecular chain has more difficulty to relax when the tackifier H has been added to the base polymer.
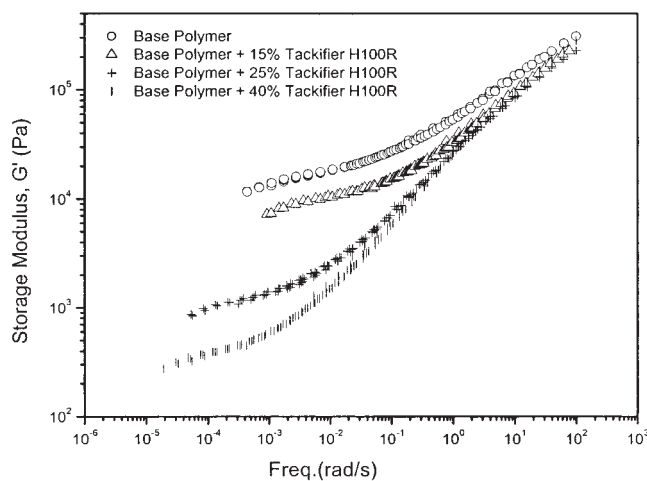

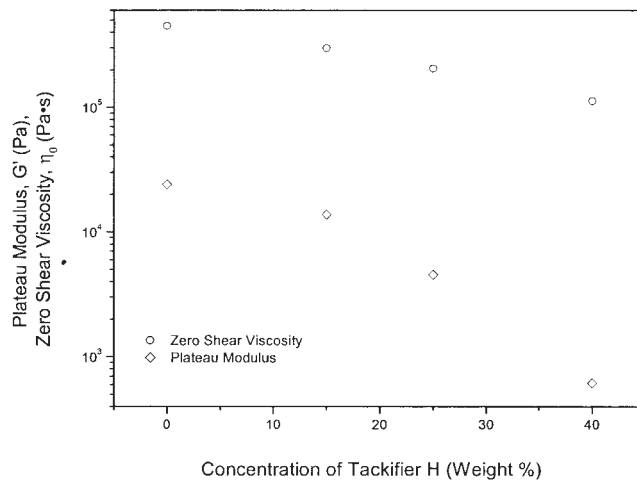**Figure 5** Effect of tackifier H on the storage modulus in the frequency domain.

Figure 7 Effect of tackifier H on the plateau modulus and zero shear viscosity of the base polymer.

TABLE I
Effect of Tackifier H, R1, and R2 on the Viscoelastic Properties of Pressure Sensitive Adhesives

Samples	G_N (Pa)	η_0 (Pa/s)	τ_N (s)	ν (mol/cm^3)	$A\xi_0$
Base polymer	2.40×10^4	4.49×10^5	18.7	9.24×10^{-6}	2.41×10^{-5}
Base polymer + 15% tackifier H	1.38×10^4	2.98×10^5	21.6	5.32×10^{-6}	2.71×10^{-5}
Base polymer + 25% tackifier H	4.54×10^3	2.05×10^5	45.3	1.74×10^{-6}	1.78×10^{-5}
Base polymer + 40% tackifier H	616	1.13×10^5	182.9	2.37×10^{-7}	2.85×10^{-5}
Base polymer + 15% tackifier R1	1.01×10^4	2.12×10^5	20.1	5.00×10^{-6}	1.93×10^{-5}
Base polymer + 40% tackifier R1	329	7.20×10^4	218.6	1.26×10^{-7}	1.82×10^{-5}
Base polymer + 15% tackifier R2	832	2.12×10^5	255.4	3.20×10^{-7}	1.93×10^{-5}

The value of plateau modulus, which is the pseudo-equilibrium modulus of the entanglement network, could be related to v, the network density (the moles of network strands per cubic centimeter).[33] The relationship between plateau modulus and network density, v, is given by eq. (6).

$$G_N = g_N v R T \qquad (6)$$

In eq. (6), v is the moles of network strands per cubic centimeter, g_N is a numerical factor, ρ is the density (concentration of the polymers), and R is the gas constant; g_N has been simply taken as unity.

The v values of tackifier H systems are listed in Table I. It is apparent from the table that v decreases as the concentration of tackifier increases. This means the tackifier H made entanglement of the molecules of base polymer weaker, and the tackifier is essentially acting as a solvent of low molecular weight.

The effect of dilution on plateau modulus was given by Ferry[33] as $G_N \propto v_b^2$, where v_b is the volume fraction of polymer in the mixture. A plot of the plateau modulus as a function of volume fraction square of base polymer is shown in Figure 8. The data follow approximately Ferry's relationship.
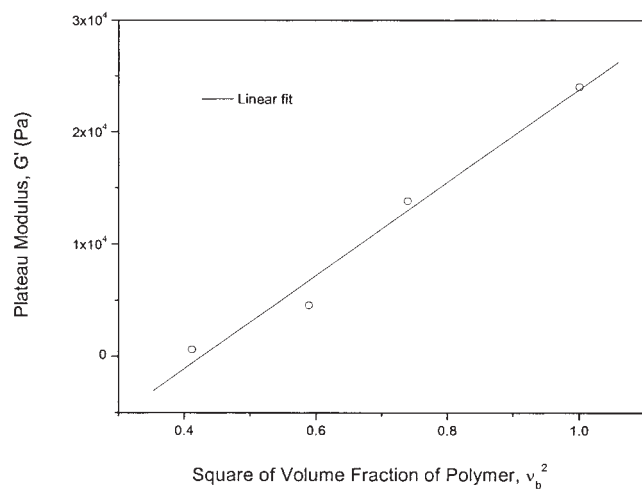

Figure 8 Dilution effect of tackifier H on the plateau modulus of the base polymer.

Zero shear viscosity is related to the entanglement and friction of the segments.[32] In the condensed form, η_0 is related to monomeric friction coefficient ξ_0 by eq. (7).

$$\eta_0 = A\xi_0 c^{3.5} \qquad (7)$$

Here, c is the volume concentration of the base polymer and A is a constant that relates to the molecular parameter of the base polymer. The relationship between η_0 and entanglement is hidden in the relationship between η_0 and c. Equation (8) was used to calculate the effect of tackifier on the monomeric friction coefficient.

$$A\xi_0 = \frac{\eta_0}{c^{3.5}} \qquad (8)$$

The values of $A\xi_0$ so obtained are also given in Table I.

We can see that the addition of tackifier H to the base polymer increases the monomeric friction coefficient. This surprising conclusion can be rationalized by the explanation proposed earlier in the section on T_g that some of the tackifier H molecules are situated in close proximity to base polymer segments, and thus make the segmental movement more difficult and increase the monomeric friction coefficient.

Effect of tackifier R1 and R2

The results for tackifier R1 and R2 are summarized in Table I. In comparing the three tackifiers, all three additives decrease the zero shear viscosity and plateau modulus of the base polymer. R2 causes a large drop in G_N (and hence v) and a large increase in τ_N. This may be due to the lower molecular weight of the tackifier R2. Only tackifier H induces an increase in monomeric friction coefficient; the other two cause a minor decrease. The effect of tackifier R1 and R2 on the plateau modulus and monomeric friction coefficient of base polymer is essentially that of a diluent.

Tackifiers and plasticizers

Three tackifiers all have the retarding effect on both segmental and terminal relaxations of the base poly-

mer. Tackifier H also increased the monomeric friction coefficient of the base polymer. Similar effect is also found for terpene resin tackified natural rubber systems.[6] But with increasing proportion of plasticizers (diluents), the monomeric friction coefficient ξ_0 is normally diminished and all relaxation times are reduced.[33] The plasticizers are traditionally composed of molecules smaller than the polymer. Each molecule brings with it a greater free volume per total volume of materials.[34] On the other hand tackifiers contain less free volume and tackifier H decreases free volume of the system expected by the additive rule. Similar to the effect of plasticizers, the three tackifiers all decrease the entanglement of the base polymer. Similar results are also found for natural rubber PSAs, but Aubrey and Sherriff reached a result that as resin concentration increases, there is a shift in the onset of the terminal zone to higher frequencies,[6] which is different from our result that the three tackifier all increase terminal relaxation time of the base polymer. Just because of the different effects of tackifiers and plasticizers on the viscoelastic properties of the base polymer, the tackifiers can bring the viscoelastic state of the adhesive to one more state suitable to bonding and unbonding.[2]

CONCLUSIONS

The two types of tackifiers show different effect on the glass transition temperature, free volume, and monomeric friction coefficient of the base polymer.

Tackifier H that has a structure similar to that of the base polymer: tackifier molecules nestle closely along the base polymer segments in the space within the coil or in the region of coil overlap. The residence of tackifier molecules in these spaces causes a negative contribution to the expected free volume additivity. Tackifier H decreases the entanglement, but increases the monomeric friction coefficient of the polyolefin-based PSA systems. For tackifier-enriched samples, the glass transition temperatures of the blends can be calculated by the equation:

$$T_g = \frac{w_1 T_{g_1} + K w_2 T_{g_2} + A K w_1}{w_1 + K w_2}$$

with $K = 4.1$ and $A = 6.18$. For base polymer-enriched samples, the glass transition temperatures of the blends follow Gordon-Taylor equation.

Tackifier R1 and R2 that are hydrogenated aromatic tackifiers: ideal mixing with the base polymer. Glass transition temperature follows Gordon-Taylor equation with $K = 3.5$ and 2.35, respectively. They decrease the entanglement and decrease monomeric friction coefficient of the systems. Their effects on plateau modulus and monomeric friction coefficient are only dilution.

The special effects of tackifiers on the properties (free volume, monomeric friction coefficient, segmen-

tal relaxation, and terminal relaxation) of PSA systems are very different from those of the plasticizers, and tackifiers bring less free volume than plasticizers to the base polymer. So tackifiers can improve the tack property efficiently but plasticizers cannot.

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