

Water-Based Polymers As Pressure-Sensitive Adhesives—Viscoelastic Guidelines

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SYNOPSIS

Water-based polymers have been widely used as pressure-sensitive adhesives (PSAs). This article addresses the fundamental viscoelastic parameters that govern PSA performance. The viscoelastic behavior of polymers before and after resin tackification is investigated. Commercial acrylic, CSBR, natural rubber emulsion polymers, and low M_w petroleum-based hydrocarbon resins with various softening points are used to demonstrate the tackification effects. Basic guidelines for selecting the appropriate polymer/resin system to achieve the target performance are given. © 1995 John Wiley & Sons, Inc.

BACKGROUND

In the early 1970s, many authors¹⁻⁶ investigated the mechanism of adhesive failure by using model adhesive joints between a crosslinked amorphous rubber and rigid polymer substrates. They proposed an adhesive physical model that considered the adhesive failure energy as the sum of different energies involved. There were two primary energy components considered in the model: the intrinsic surface energy and the dissipated energy. The intrinsic surface energy arose from the thermodynamic interactions between the adhesive and the adherend at the interface. The dissipated energy was the energy lost during deformation due to the viscoelastic nature of the adhesive material. The experimental results supported the hypothesis that the dissipated energy is also proportional to the intrinsic surface energy. The dissipated energy was usually dominating and was a function of the peel rate and the peel temperature. However, by using a W-L-F shift factor, the authors were able to demonstrate that the rate-temperature dependence of the peel strength can be merged into a single master curve.

In their original proposed model, Andrews and Kinloch^{5,6} wrote the energy balance equations as:

$$P = I + D \quad (1)$$

$$D \propto I \quad (2)$$

where P is the peel failure energy, I is the intrinsic surface energy, and D is the dissipated energy.

What was not included in the above study was the effect of the bond establishment process on the peel failure energy. This process is especially important for PSA applications and can be related to the wetting behavior of the adhesive. Bond formation can be both physical and chemical. In the current study, we are primarily interested in physical bond formation and interfacial failure because it is very rare in PSA that covalent bonds are formed between adhesive and substrate.

Theoretical Considerations

Physical bond formation is both a thermodynamic and a kinetic process. From a thermodynamic point of view, we need to consider various forces involved that are responsible for intermolecular attractions between surface energy of a material, and their effects are included in the first term in the above Eq. (1). From a kinetic point of view, bond formation depends on the time, the temperature, and the pressure involved. It is also governed by the viscoelastic behavior of the adhesives. Prior to any bond formation through thermodynamic interactions, two materials (adhesive and adherend) must be brought into intimate contact. This "intimate contact" depends largely on the viscoelastic nature of the ad-

hesive. The viscoelastic nature of the adhesive governs the kinetics of the bond formation and necessitates the introduction of a third factor (A/A_o) into the above equations. Here, "A" represents the established contact area between the adhesive and the adherend and " A_o " is the total area available for the contact. Thus, we can rewrite Eq. (1) as:

$$P = (I + D) \times (A/A_o) \\ \cong D \times (A/A_o) \quad \text{since } D \text{ is orders} \\ \text{of magnitude greater than } I. \quad (3)$$

In the above equation, the dissipated energy includes the deformation energy lost to both the adhesive and the substrate (as in PE or OPP films). In the present study, only the adhesive energy loss is considered. Recently, it has been demonstrated⁷ that the energy dissipated during a peel test is proportional to the loss modulus in the linear viscoelastic measurement of the adhesive. We can, therefore, rewrite Eq. (2) as:

$$D \propto I \cdot G''(\omega_1) \quad (4)$$

where ω_1 is the frequency corresponding to the peel test.

As mentioned before, the kinetic term A/A_o in the above Eq. (3) is governed by the viscoelastic behavior of the adhesive. In PSA applications, the contact is established through deformation of the adhesive material under light pressure and within a short period of time, around 1 s. A/A_o is, therefore, related to the creep compliance, $J(t)$, of the adhesive material through following Eq. (5). Creep compliance is a measurement of how readily a material can deform when subjected to force.

$$A/A_o = 1 - e^{-J(t)} \\ \simeq J(t) \quad (5)$$

In the above relationship, the total area available for the contact, A_o , is defined as the contact area when $J(t)$ approaches an infinite large value. $J(t)$ is also related to the storage modulus, $G'(\omega)$, through the following equation⁸:

$$J(t) = \frac{1}{G'(\omega)} \times \frac{1}{[1 + \tan^2 \delta^2(\omega)]} \\ \cong \frac{1}{G'(\omega)} \quad \text{in case when } \tan \delta \ll 1 \quad (6)$$

Because in most cases, $\tan \delta \ll 1$ at the bonding region, we can combine Eq. (3) to (6) in a simplified form. This gives the peel energy as:

$$P \propto I \times G''(\omega_1)/G'(\omega_2) \quad (7)$$

Here, G'' is the loss modulus at the peel frequency, ω_1 (rad/s), and G' is the storage modulus at the bonding frequency, ω_2 (rad/s).

In order to demonstrate the validity of Eq. (7), a series of 13 copolymers based on methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate in various combinations were synthesized using an emulsion polymerization technique.

The copolymer latexes were coated over Mylar films and dried in a forced air oven at 110°C for 3 min. The dry film thickness was regulated at 0.038 mm. Films were aged for at least 24 h under controlled temperature and humidity before testing.

The surface tensions for these acrylic copolymer films were calculated from contact angle measurements. Contact angles with water (θ_1) and methylene iodide (θ_2) were measured for each of the dry films by using a telescope fitted with a goniometer eyepiece. Surface tensions were calculated by the harmonic-mean method⁹ by solving the following two simultaneous equations:

$$(1 + \cos \theta_1) \gamma_1 = 4 \left(\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} \right) \quad (8)$$

$$(1 + \cos \theta_2) \gamma_2 = 4 \left(\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right) \quad (9)$$

In the preceding two equations, the values for the surface tension of water, its dispersion, and polar components are $\gamma_1 = 72.8$, $\gamma_1^d = 22.1$, and $\gamma_1^p = 50.7$ dyne/cm, respectively. Similarly, $\gamma_2 = 50.8$, $\gamma_2^d = 44.1$, and $\gamma_2^p = 6.7$ dyne/cm are the corresponding values for methylene iodide. We found that for all acrylic samples, the surface tensions were in the range between 31 and 37 dyne/cm. Because the surface tension of the stainless steel is at 44 dyne/cm, we can expect good wetting to be achieved for all samples and the variation in the intrinsic surface energy to be small. In fact, the intrinsic surface energies calculated based on the following geometric-mean equation⁹ for all acrylic samples over stainless steel plate were between 74 and 78 Erg/cm².

$$I = 2(\gamma_s^d \gamma_{ss}^d)^{1/2} + 2(\gamma_s^p \gamma_{ss}^p)^{1/2} \quad (10)$$

In the above equation, $\gamma_{ss}^d = 29$ dyne/cm and $\gamma_{ss}^p = 15$ dyne/cm. These were the dispersion and

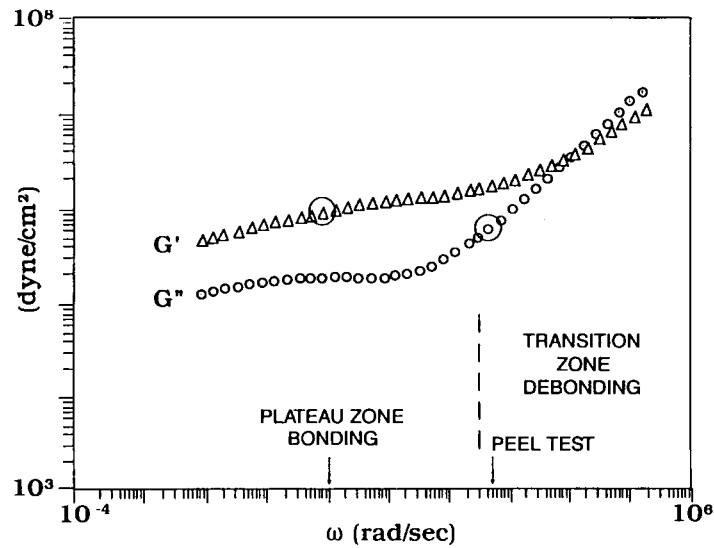


Figure 1 G' and G'' of poly(*n*-butyl acrylate).

the polar components of the stainless steel plate used in the peel test.

Polymer latexes were carefully dried to obtain a solid disk-like sample for viscoelastic measurements. The measurements were carried out using a Rheometric System-4 rheometer over a range of temperatures and frequencies. Master curves of the storage modulus, G' , and the loss modulus, G'' , at room temperature can be constructed from these measurements by using a shifting technique. A typical plot of G' and G'' vs. frequency is displayed in Figure 1.

At a peel rate of 30 cm/min and a film thickness of 0.038 mm, the peeling frequency was calculated

to be 435 rad/s. The bonding was done at much lower frequency, typically at around 1 rad/s during PSA sample preparation.

The peel strength values were obtained according to the Pressure-Sensitive Tape Council PSTC-1 test procedures. The plot of (peel strength) vs. G''/G' for all samples is shown in Figure 2. A near linear relationship is, indeed, obtained. The Y intercept of the plot gives the intrinsic surface energy between acrylic copolymer and the stainless steel substrate. The magnitude is small compared to that obtained from energy dissipation. This result is consistent with the conclusion drawn earlier by Kinloch, et al.

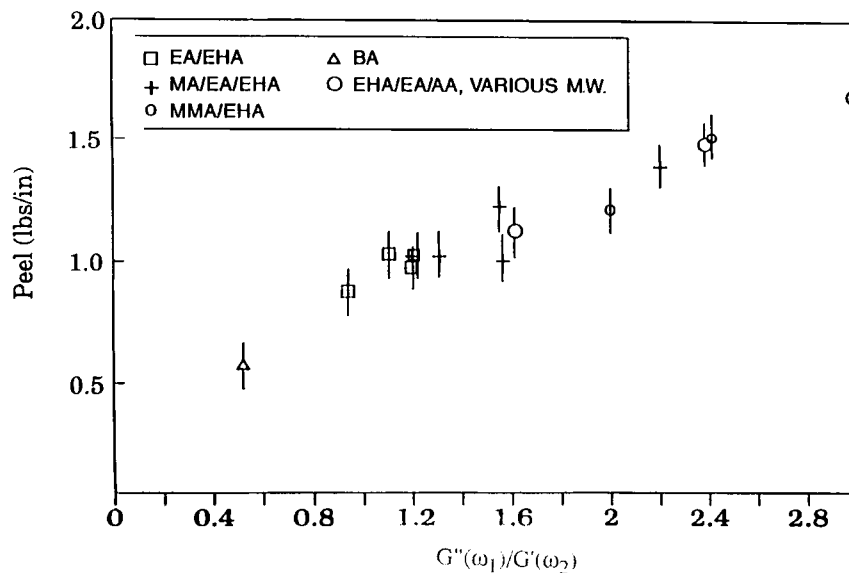


Figure 2 Dependence of peel strength on G''/G' .

They found that the contribution from energy dissipation can be orders of magnitude greater than that of the surface energy.

Equation (7) indicates that in order to improve the peel strength, one needs to lower the storage modulus, G' , at the bonding frequency and increase the loss modulus, G'' , at the debonding frequency.

Applying the Viscoelastic Model to PSA System Design

There are many ways to affect G' and G'' of a given polymer. One can find from the literature that a formulator may blend various types of copolymers together in order to manipulate the viscoelastic behavior of the final product. Plasticizers and cross-linking agents are frequently used. These approaches, however, will affect both G' and G'' in the same direction. As mentioned before, to increase the peel strength, one needs to increase G'' while simultaneously decreasing G' . Blending a compatible low MW resin into a PSA polymer is a typical approach. A compatible resin/polymer blend can be regarded as a concentrated polymer solution with resin as the solvent. From viscoelastic theory, if the concentrated solution is ideal (namely zero excluded volume effect), the plateau modulus will decrease according to the following equation:¹⁰

$$G'_n = \frac{\rho RT}{Me} \cdot V_p^2 \quad (11)$$

where V_p is the volume fraction of the polymer in the polymer/resin blend, Me is the entanglement MW of the polymer, ρ is the density of the blend, and T is the measurement temperature.

Effect of Resin Tackification on G'

Figure 3 illustrates the change of the storage modulus, G' , as hydrocarbon resin Escorez[®]9271 (Escorez[®] is the trademark of Exxon Chemical) is blended into a prototype acrylic A copolymer. The storage modulus in the bonding region continuously decreases as more resin is blended into the polymer. The lower storage modulus favors bonding by increasing the efficiency of contact between the adhesive and the adherend.

Effect of Resin Tackification on G''

The effect of resin addition on the polymer loss modulus, G'' , is illustrated in Figure 4. We found that the loss modulus at the debonding region continuously increases as more resin is blended with the polymer. This occurs because the resin T_g is higher than the T_g of the polymer and the peak of the loss modulus is related to the glass transition temperature. As a result of blending resin into polymer, the T_g of the blend increases. However, this trend may reverse if the debonding test is carried out at a rate beyond the the peak of G'' .

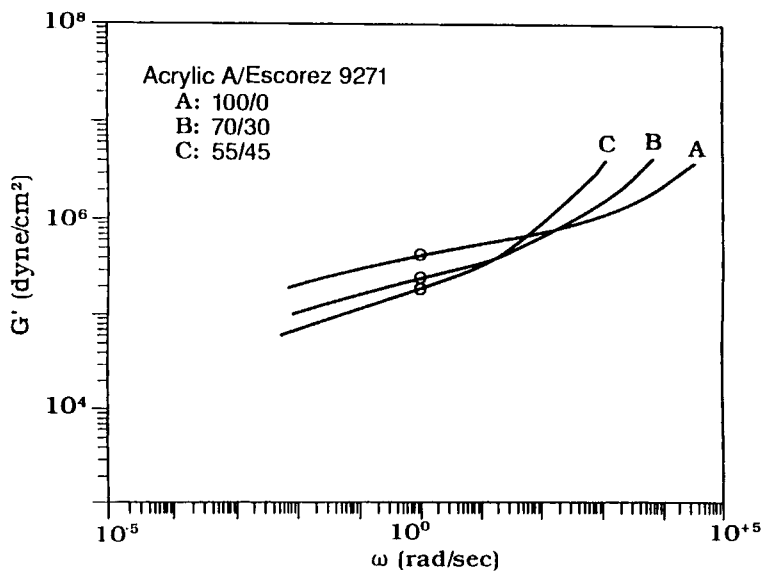


Figure 3 Resin tackification lowers G' at bonding region.

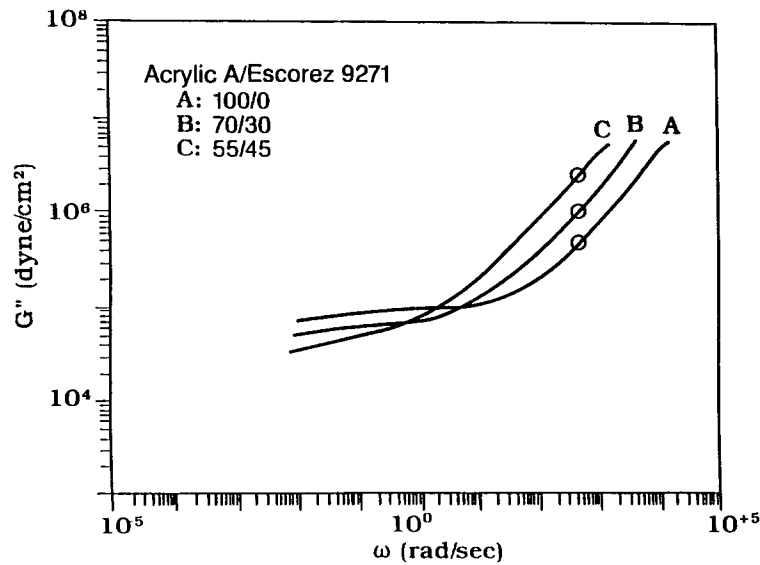


Figure 4 Resin tackification increases G'' at debonding region.

Peel Strength Is Proportional to G''/G'

The results of the peel test show that a significant increase in peel strength is obtained in the resin tackified acrylics. Figure 5 shows the plot of peel strength vs. G''/G' . A near linear relationship is obtained.

Also included in this figure are data obtained for a commercial Acrylic B. This product, when tackified with Escorez[™]9271, shows a good balance of peel

and shear properties suitable for permanent paper label applications, as shown in Table I.

Effect of Resin T_g on G' and G''

In this example, we demonstrated the effect of the resin T_g on the polymer viscoelastic behavior and PSA properties. Acrylic C, a high cohesion acrylic for packaging tapes, was used for demonstration. Three resins were used: Escorez[™]9271 (T_g

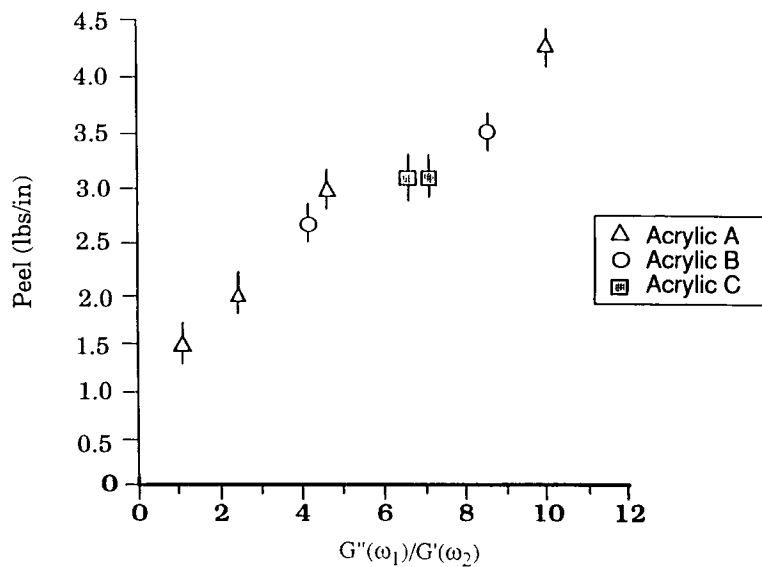


Figure 5 Peel strength is proportional to G''/G' .

Table I Acrylic B Tackified with Escorez™ 9271

Resin Content, Wt %	0	30	40
180° Peel, lbs/in			
Glass	2.5	2.9	3.4
PE	0.9	1.6	2.9
Loop Tack, lbs/in			
Glass	2.7	2.9	2.7
PE	1.1	2.2	1.9
Shear, Hours			
SS (1 × 1 × 1 kg)	160+	26	28

Data based on Mylar substrate at 20 g/m² coating weight.

= 25°C); Escorez™9251 ($T_g = 5^\circ\text{C}$); and Escorez™9241 ($T_g = -5^\circ\text{C}$). The blending ratio was kept at 70/30 acrylic/resin. Figure 6 showed that higher T_g resins result in blends with higher G' at the bonding region. The same results were obtained with G'' at the debonding region (Fig. 7). Both figures illustrated that viscoelastic responses were shifted toward lower frequencies as resin T_g increases. Thus, debonding properties were improved while sacrificing bonding properties.

In this example, the ratio G''/G' was only slightly increased with increasing resin T_g ; thus, the magnitude of the peel strength improvement was also small. The data was also demonstrated in Figure 5.

Natural Rubber Tackified by Escorez™9191

The above examples show that G'' and G' values of a polymer can be manipulated by the choice of com-

ponents in a polymer-resin system and by altering the level of tackification in this system. The resin chosen should be fully compatible with the polymer to be tackified. A compatible system would have maximum effect in lowering the G' according to Eq. (11), thus improving the bonding between the adhesive and the adherend. For example, while Escorez™9271 is an excellent tackifying resin for acrylics, it is not an ideal tackifying resin for natural rubber because of compatibility considerations.

To tackify natural rubber, Escorez™9191 was chosen. The results are shown in Figure 8. Escorez™9191 is fully compatible with polymers with low polarity. Significant increases in peel and loop tack values over poly(ethylene) and stainless steel substrates can be obtained.

Tackification of CSBR

For CSBR, Escorez™9271, Escorez™9251, and Escorez™9241 can be used. The choice depends largely on the composition of the particular CSBR to be tackified. Figure 9 illustrates the use of Escorez™9241 to tackify a commercial CSBR sample with a T_g equal to -32°C . All adhesive properties are improved with this particular resin. In general, low T_g CSBR products would require a higher T_g resin as a tackifier in order to achieve the best improvements in adhesive properties. Table II summarizes the softening point and T_g of the neat resin for the present study. Various polymers including natural rubber, CSBR, and acrylics can be tackified with these resins. This table, in conjunction with

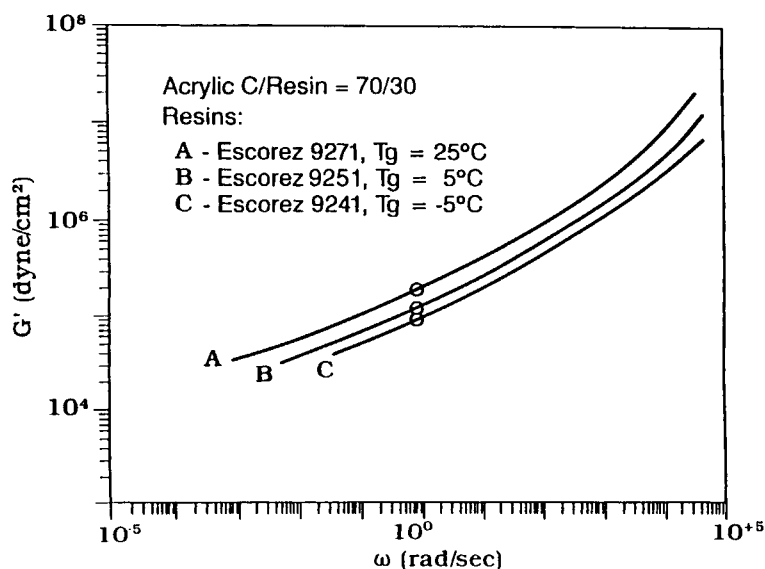


Figure 6 Effect of resin T_g on G' at bonding region.

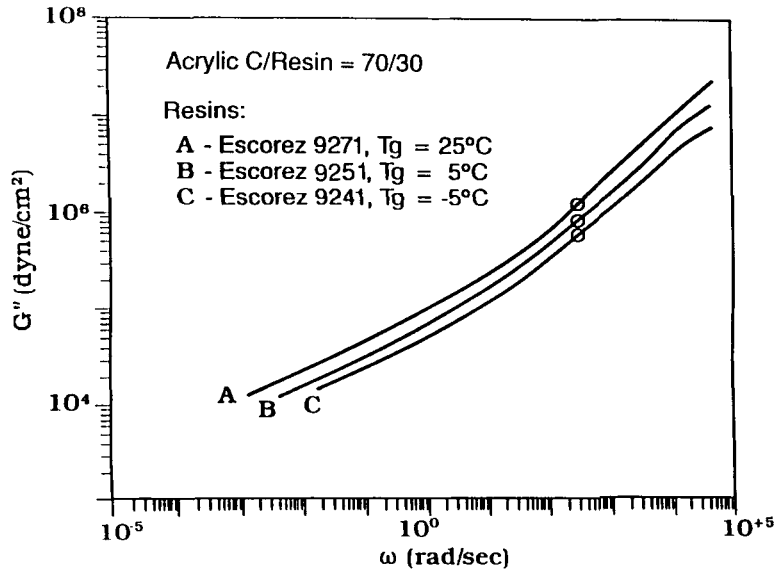


Figure 7 Effect of resin T_g on G'' at debonding region.

the viscoelastic model described in this article, provides a good guideline for tackifying water based polymers for PSA applications.

CONCLUSIONS

A physical model that relates fundamental polymer parameters to PSA peel adhesion properties is developed. This model is developed by investigating the linear viscoelastic behavior of the polymers and

the energy involved during peeling for systems that exhibit adhesive failure. We found that, in cases where variation in surface energy is small, the peel strength was proportional to the ratio of G''/G' , where G'' is the loss modulus measured at the frequency corresponding to the peel test. G' is the storage modulus measured at the bonding frequency, typically at 1 rad/s.

The proposed physical model is being applied to PSA system design. Examples are given to demonstrate the tackification effect on peel strength for

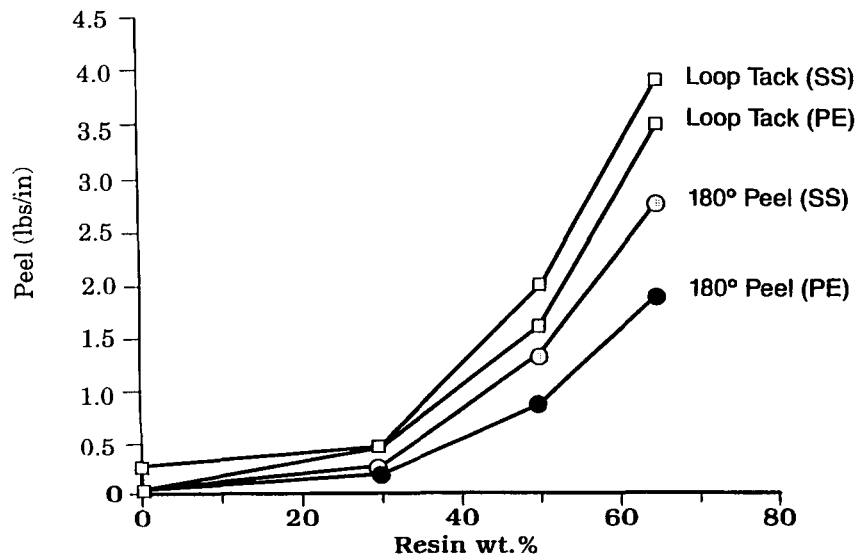


Figure 8 Natural rubber tackified by EscorezTM9191.

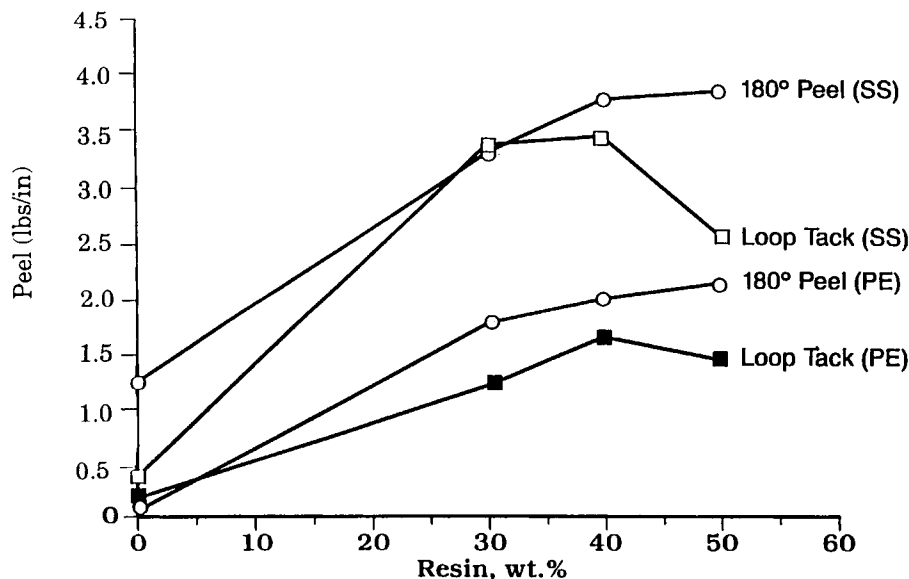


Figure 9 CSBR tackified by Escorez[®]9241.

acrylics with various compositions. Commercial hydrocarbon resins with various softening points are found to be useful in improving the peel strength and tackiness for a wide variety of water based polymers.

The current conclusions are based on studies of water-based acrylics, CSBR, and natural rubber. These are random copolymers and their plateau moduli after tackification are lower than 1×10^6 dyne/cm. Extension of this model to other polymer systems has yet to be studied.

Table II Tackification Matrix for Water-Based Polymers

Escorez TM Emulsions	Neat Resins		Water-based Polymers		
	Softening Point (°C)	T_g (°C)	NR	CSBR	Acrylics
Escorez TM 9191	93	40	O		
Escorez TM 9241	40	-5		O	O
Escorez TM 9251	50	5		O	O
Escorez TM 9271	70	25		O	O

O indicates good tackification effect.

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