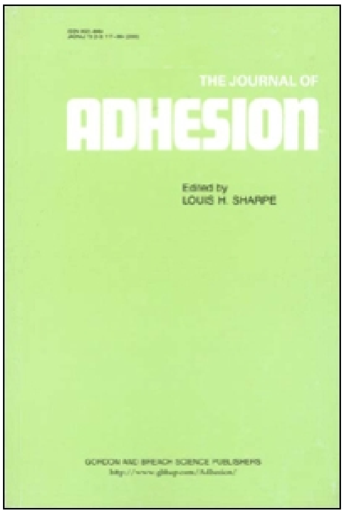

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Pressure Sensitive Adhesives Based on Vector^R SIS Polymers I. Rheological Model and Adhesive Design Pathways

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Pressure Sensitive Adhesives Based on Vector® SIS Polymers I. Rheological Model and Adhesive Design Pathways*

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Dexco Polymers (a Dow/Exxon partnership) has been manufacturing Vector® SIS polymers since 1990.[1] This paper describes experiments carried out to study Vector SIS polymers and model pressure sensitive adhesive (PSA) formulations based on Exxon Chemical's Escorez® 1310LC tackifier. The adhesive behavior of tackified polymers was quantitatively analyzed by applying the rheological principle of time-temperature superposition[2] and the mapping approach,[3,4] and the pressure sensitive rheological model[5] developed earlier. This model[5] was developed by expanding and modifying an equation [adhesive fracture strength = (intrinsic adhesion) × (bulk energy dissipation)] proposed by Gent *et al.*[6,7] and Andrews *et al.*[8,9] This study delivers two key results. The first is that the fracture strength of the PSA/steel bond is the multiplication of three terms: the intrinsic (or interfacial) adhesion, the bonding and the debonding terms (Fig. 1). The debonding term is correlated with the logarithm of the loss modulus at the PSA debonding frequency or with the logarithm of the monomeric friction coefficient of the block copolymer/tackifier system. Both the loss modulus and the monomeric friction coefficient measure the energy dissipation in the bulk adhesive. The second is that PSA design pathways can be established by a mapping approach in the rheological space of the plateau modulus *versus* the loss modulus peak position in the frequency scale (Fig. 2). Plateau modulus is the bonding parameter because it measures the wetting capability of the adhesive with the substrate surface. The loss modulus peak position is the debonding parameter because it corresponds approximately to the time scale (or the frequency scale) in which one deforms the adhesive to maximize energy dissipation. Therefore, the tackifier and oil combination lowers the plateau modulus, but increases the T_g of the polyisoprene phase of the SIS polymer. This increase in T_g is equivalent to the lowering of the rate of local rearrangement (frequency of segment jumps) of the polyisoprene chains of the block copolymer. An optimal "tackification pathway" in this rheological space is achieved by tailoring the tackifier type and T_g, and the amount of oil used in the PSA.

In brief, the PSA rheological model and mapping approach described in this work for Vector SIS polymers give a comprehensive understanding and adhesive design pathways. This concept and approach not only allow raw material suppliers to improve and design better tackifier and polymer products, but also provide PSA formulators a quantitative tool to achieve PSA end property results.

KEY WORDS: Pressure sensitive adhesive; block copolymer; tackifier; adhesion; tack; rheology; time-temperature superposition; storage modulus; loss modulus.

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INTRODUCTION

The design of adhesive systems has been practiced as an art rather than a science for many years. However, beginning a couple of decades ago, researchers[6-9] began their efforts to examine the factors contributing to the strength of an adhesive bond. It appears that the intrinsic adhesion (attractive forces at the interface: van der Waals, electrostatic, hydrogen bonding, acid-base, covalent chemical bonding, interfacial molecular complex structures and others) and the rheology of the bulk adhesive are two contributing factors. For organic adhesives on common polymeric substrates the intrinsic adhesion is typically of the order of 10^{-1} J/m^2 (6×10^{-4} lb/in). However, due to the rheological energy dissipation within the adhesive, most practical measures of joint strength yield detachment energies of 10^2–10^4 J/m^2 (0.6–60 lb/in), which are several orders of magnitude larger than the intrinsic adhesion. Therefore, the science of rheology is basic for the understanding of adhesives on a more scientific level. Unfortunately, previous researchers[6-9] did not disclose the exact functional form of the rheological contribution of the bulk adhesive. Also, this scientific understanding has not been rapidly translated into the purposeful design of adhesive systems. Many formulators still rely on past experience and accumulated knowledge in the practice of their art.

As a first step to attack the above problems, we have developed a comprehensive adhesion model which includes thermodynamic and rheological effects of PSAs.[5] This model describes the fracture strength, P, of an adhesive/substrate bond by the following equation (see Fig. 1):

$$P = P_0 B D \tag{1}$$

where P_0 is the intrinsic adhesion, B is the bonding term and D is the debonding term. The first application of this model has been to understand the tack phenomena of PSAs (blends of triblock copolymer of SIS with Exxon Chemical's Escorez 1310LC tackifier),

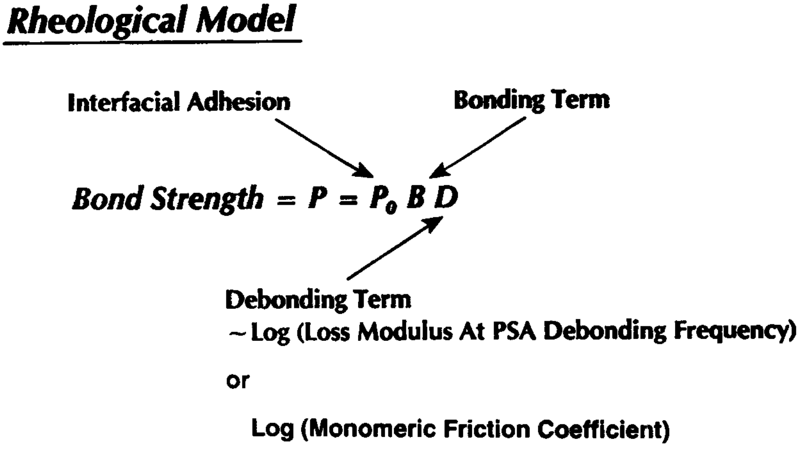


FIGURE 1 Key result I of this work.

with emphasis on the debonding term *D* (the rheological or energy dissipative contribution) of bulk adhesives.[5] A one-to-one correspondence between the energy dissipation measured viscoelastically and the debonding resistance measured by industry tests is obtained when the adhesives fulfill the Dahlquist criterion.[10] In essence, PSA performance in several industry tests is linearly correlated with the logarithm of loss modulus at the reduced frequency corresponding to the speed of the debonding test.

As a second step or a follow-up study[3,4] of the tack model, Equation (1), we have taken the above scientific understanding[5] and used it in a systematic approach to design PSAs (Fig. 2). The basic conclusion is that a target zone for adequate PSA performance can be established in the rheological space of the plateau modulus *versus* the loss modulus peak position in the frequency scale. Therefore, the performance of PSAs can be designed and adjusted, both effectively and economically, within this target zone through the use of polymer, tackifier and oil combinations. It is well known from the PSA literature that oil in PSA has the advantages of lowering the price and viscosity of the formulation. However, oil also has the disadvantage of lowering the PSA cohesive strength as discussed later.

The purpose of this work is to apply a similar analysis of block copolymer/Escorez 1310LC blends[3-5] to Vector 4113/Escorez 1310LC blends, where Vector 4113 is a triblock copolymer of SIS containing 18 wt.% diblocks (Table I).

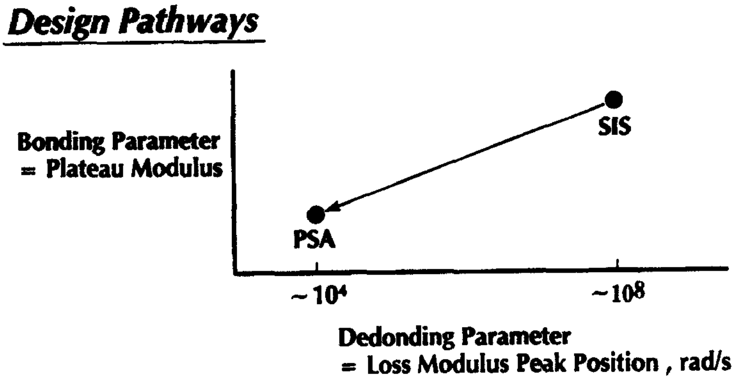


FIGURE 2 Key result II of this work.

TABLE I
Characterization of vector SIS polymers

Polymer	Vector 4111	Vector 4113	Vector 4114-D
Diblock, wt. %	0	18	42
Cis-1,4-Isoprene, mole %	60.8	63.1	62.7
Trans-1,4-Isoprene, mole %	18.9	19.0	18.9
3,4-Isoprene, mole %	7.1	7.6	7.8
Styrene			
mole %	13.2	10.3	10.6
wt. %	18	15	15

EXPERIMENTAL

GPC experiments on SIS polymers were performed by employing six ultra-Styragel columns with 10^2–10^5 Å porosity and THF solvent. Carbon^{13} NMR spectra of SIS polymers were acquired on a Varian VXR-300 NMR spectrometer. Each sample was dissolved in tetrachloroethane-d_2 at a concentration of 15 wt.%. The samples in solution were thermostated at 125°C during data acquisition.

Table I compares the characteristics of three Vector SIS polymers for PSA applications. Vector 4111 is a pure triblock, whereas Vector 4113 and Vector 4114-D are triblocks containing different levels of diblock. The microstructure in the polyisoprene center block and the styrene content of each block copolymer were characterized by NMR. Vector 4111 has 18 wt. % styrene, whereas the other two block copolymers have 15 wt. % styrene.

Figure 3 shows the morphology of Vector 4111, the pure triblock copolymer. Due to the incompatibility of the polystyrene and the polyisoprene, polystyrene endblocks will aggregate to form domains dispersed in the polyisoprene matrix. At temperatures well below T_g of the polystyrene, the two ends of a given polyisoprene chain are anchored at polystyrene domains. Therefore, any entanglements along the polyisoprene chain will be trapped within polystyrene domains with sizes ranging from 200 to 300 Å.

The tackifier used in this work was Escorez 1310 LC, a hydrocarbon tackifier. Hydrocarbon tackifiers are prepared by cationic or thermal polymerization from monomer feeds obtained from petroleum sources, wood and coal. They are amorphous materials. Escorez 1310LC is polymerized from petroleum streams containing C_5 olefins and diolefins. It has a GPC weight average molecular weight of 1460 (based on a four-column ultra-Styragel set with porosities of 100, 500, 10^3 and 10^4 Å; THF is the mobile phase), and a DSC T_g of 46°C.

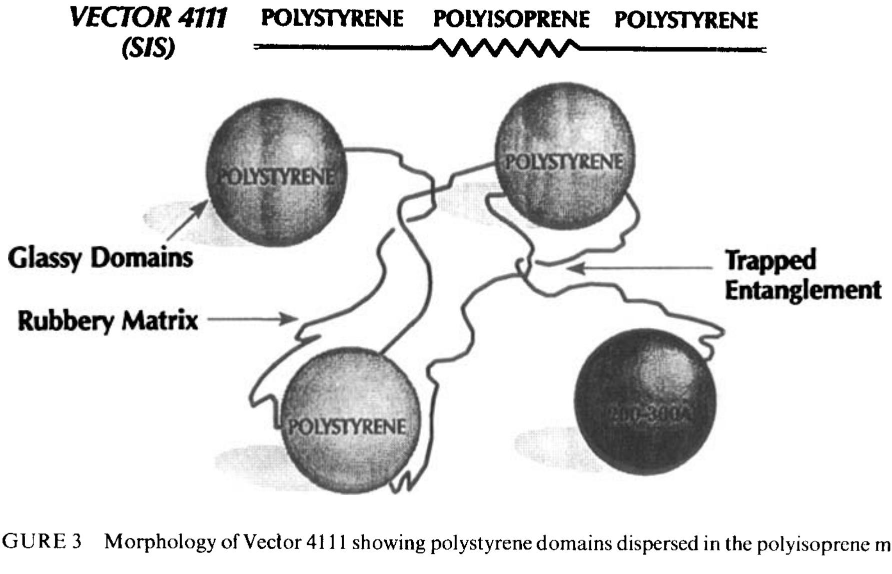


FIGURE 3 Morphology of Vector 4111 showing polystyrene domains dispersed in the polyisoprene matrix.

Experimental details of the sample preparation, rheological measurements and various PSA tests are described elsewhere.[5] The holding power, a measure of the room temperature shear strength of the PSA bond to stainless steel, was measured according to PSTC-7 (178° hold to stainless steel). The contact area was 2.5 × 2.5 cm (1″ × 1″), and the weight used was 2 kg.

RESULTS AND DISCUSSION

Time-Temperature Superposition and Master Curve

The frequency-scan curves of storage moduli at various temperatures of Vector 4113 are shown in Figure 4. A wide range of temperatures from − 50 to 160°C was covered. If the 27°C curve is chosen as the reference, and the curves at other temperatures are shifted according to the time-temperature superposition principle,[2] a master curve of the storage modulus over an extended frequency scale at 27°C can be constructed as shown in Figure 5. The icon in this figure signifies the storage modulus as a measure of the elastic behavior of polymers.

The low frequencies on the left end in Figure 5 correspond to time periods measured in hundreds of years. The high frequencies on the right end correspond to time periods measured in nanoseconds. According to Figure 4, 0.1 and 200 rad/s are the lower and upper limits, respectively, of the frequency range measured by a regular rheological experiment. However, the use of high and low temperatures, and the time-temperature superposition principle, allow one to generate this master curve without waiting for

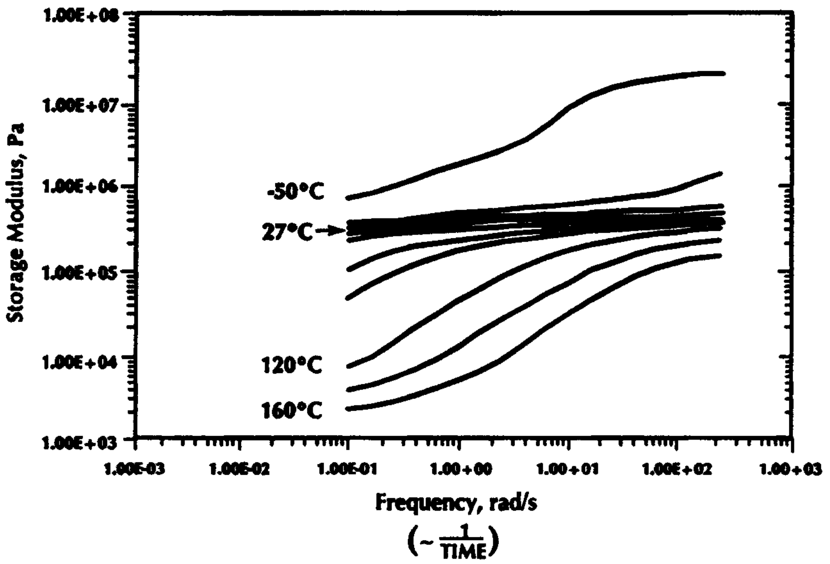


FIGURE 4 Frequency scan curves at various temperatures for Vector 4113.

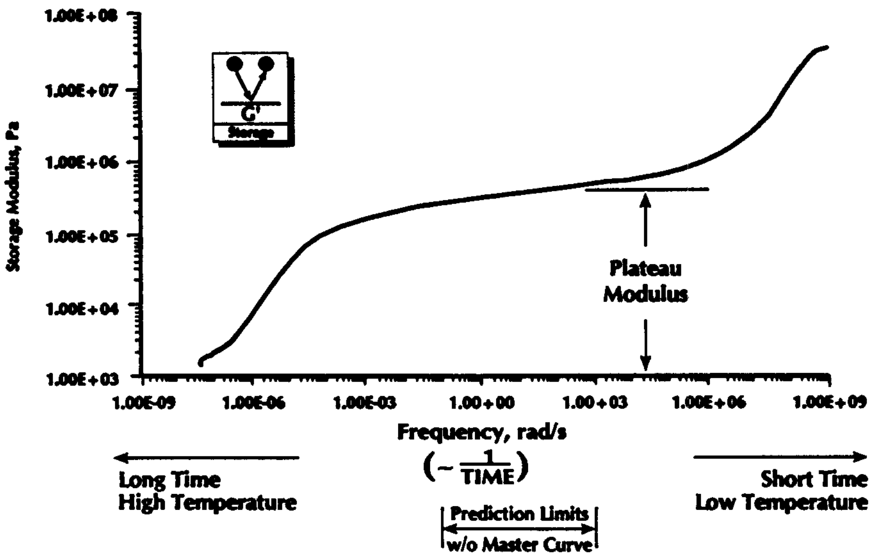


FIGURE 5 The time (or frequency)–temperature superposition principle gives the storage modulus master curve of Vector 4113 over an extended frequency scale at 27°C.

centuries at low frequencies and without using expensive equipment to measure nanosecond processes at high frequencies.

The above shifting procedure of the storage modulus, G', can also be used to generate master curves of the loss modulus, G'', and the loss tangent, tan δ. It is worth pointing out that the master curve of G' in Figure 5 has been smoothed. Actually, for each polymeric system, there is less superposition for both loss moduli and loss tangents between the plateau and terminal regions. Similar behavior was observed for the other block copolymer/Escorez 1310LC system.[5] Overall, the superposition does not work as well when the diblock content in the SIS polymer increases. An example is shown in Figures 6–7 for Vector 4113 and 4114-D containing 18 and 42 wt.% diblock, respectively. Polystyrene domains behave as an inert filler at low temperatures, but they become softened with increasing temperature. The degree of softening will be higher for the higher diblock-containing polymer, thus contributing more to the total modulus of the block copolymer.

The average storage modulus value of the plateau zone in the mid-frequency region of Figure 5, determined by some modifications of a method from Kraus *et al.*,[11] is known as the plateau modulus. It is a very important bonding parameter for PSAs as discussed later.

PSA Rheological Model

As stated above, several researchers[6–9] proposed that the fracture strength for the interface of a crosslinked rubbery adhesive and a rigid substrate is expressed by the following equation:

$$P = P_0 F,$$

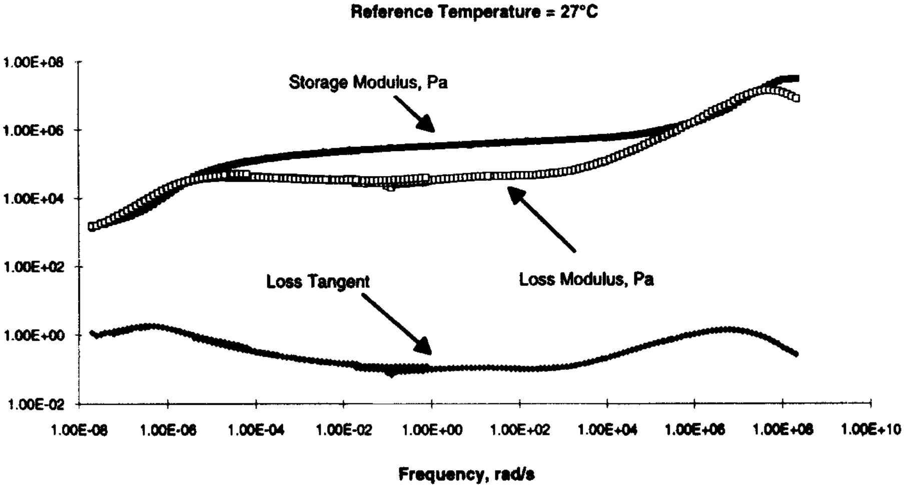


FIGURE 6 Master curves of viscoelastic functions of Vector 4113, which contains 18 wt. % diblock.

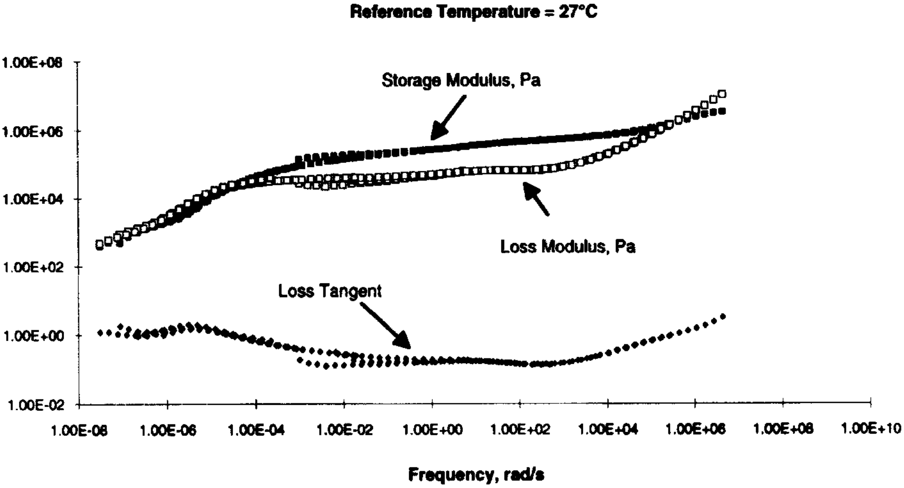


FIGURE 7 Master curves of viscoelastic functions of Vector 4114-D, which contains 42 wt. % diblock.

where P_0 is the intrinsic adhesion between the adhesive and the substrate, and F is a rheological loss function depending on rate and temperature. A modified equation has been proposed:[5]

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

In Equation (1), P_0 is the intrinsic (or interfacial) adhesion term. It is the surface debonding energy to overcome the surface anchoring and/or interfacial bonding at the adhesive/substrate interface. The B term characterizes the bonding process. It depends on the bonding time and the bonding pressure of a particular PSA test, and also on the plateau modulus of the adhesive. If the plateau modulus is below a certain level, as described by Dahlquist criterion,[10] the PSA is less elastic, and thus has a sufficient amount of viscous or flow characteristics to conform and to wet the substrate surface (Fig. 8). The D term is the rheological contribution in the debonding process. It represents the energy loss or energy dissipation in the adhesive. Energy dissipation is the amount of energy absorbed by the bulk adhesive to keep the input mechanical energy from being transferred to the interface to break the interfacial bonds (Fig. 8). Under conditions of constant P_0 and B, the higher the amount of the input energy dissipated by the bulk adhesive, the higher is the strength of adhesion of the adhesive bond. In other words, the D term functions like a shock absorber or an energy sink. Therefore, some connection between this debonding term and the loss modulus of the adhesive should exist because the loss modulus is a measure of energy dissipation.

From surface energy measurements of PSA surfaces by contact angle,[12] the intrinsic adhesion, P_0, in Equation (1) is estimated to be very small, and it remains quite constant as the tackifier concentration varies. (As an example, for organic adhesives on common polymeric substrates, P_0 is typically of the order of 0.1 to 0.001% of P.) If the plateau modulus of the adhesive fulfills the Dahlquist criterion, B in Equation (1) is also constant for a given PSA test because the same bonding time and bonding pressure are used. Then, as shown in Figure 8, the adhesive fracture strength or tack, P, should be proportional to D only:

$$P = (\text{Constant})D. \tag{2}$$

Therefore, the performance of these model adhesive compositions (Vector 4113 tackified by different contents of Escorez 1310LC) as PSAs for bonding to clean, smooth stainless steel substrate surfaces was studied to test Equation (2). All the plateau moduli of tackified Vector 4113 are below the Dahlquist criterion (data not shown here).

Before the quantification of the debonding function D, it has been recognized that each PSA test has its own characteristic debonding frequency as shown in Table II.[5] This is due to the fact that different PSA tests have different kinds of test geometry and

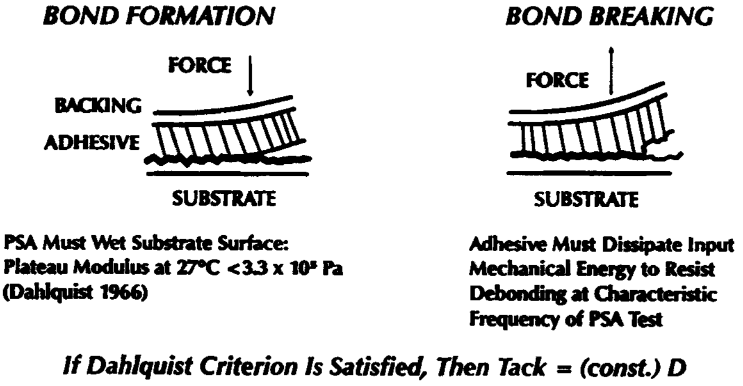


FIGURE 8 PSA bonding and debonding processes, and the model hypothesis.

TABLE II
PSA Debonding Frequencies

Standard PSA Test	Test Frequency = 2π(Bond Rupture Speed)/(Bond Thickness), rad/s
Loop	140
Peel	435
Quick-Stick	870

different bond rupture speeds. For example, both peel and quick-stick experiments were done at an Instron cross-head speed of 12.5 in/min. However, the peel experiment was done at a peel angle of 180° but the quick-stick experiment was done at a peel angle of 90°. This difference in test geometry (or peel angle) made the test frequency of peel half that of quick-stick. All the samples used for PSA tests were adhesive formulations coated from toluene onto 38.1 μm Mylar with an adhesive thickness of 38.1 μm.

Figure 9 shows master curves of the loss modulus for the model Vector 4113 PSA system. The icon in this figure signifies the loss modulus as a measure of the loss behavior or energy dissipation of polymers. Because of this, two major conclusions then follow. For each of these model adhesives, different PSA tests correspond to different loss modulus values or different degrees of energy dissipation. On the other hand, for a given PSA test, for example, loop tack, SIS containing a higher loading of tackifier has a higher loss modulus or a higher degree of energy dissipation than SIS containing a lower loading of tackifier.

Therefore, for each PSA test shown in Figure 9, there are three different loss modulus values, which correspond to three different concentrations of Escorez 1310LC. The correlation of these loss modulus values with the measured tack for each PSA test is shown in Figure 10 for the loop, peel and quick-stick. Hence, with the exception of quick-stick results for Vector 4113 containing 150 parts Escorez 1310LC, for each PSA test, the measured tack is linearly related to the logarithm of the loss modulus expressed by the following equation:

$$\text{Tack} = (\text{Constant})D = K_1 \log G''(\omega_{\text{debond}}) + K_2 \qquad (3)$$

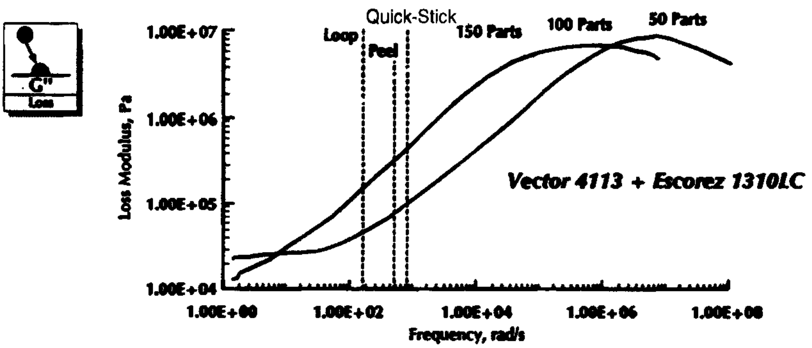


FIGURE 9 The location of the debonding frequency of the PSA test on the loss modulus master curve.

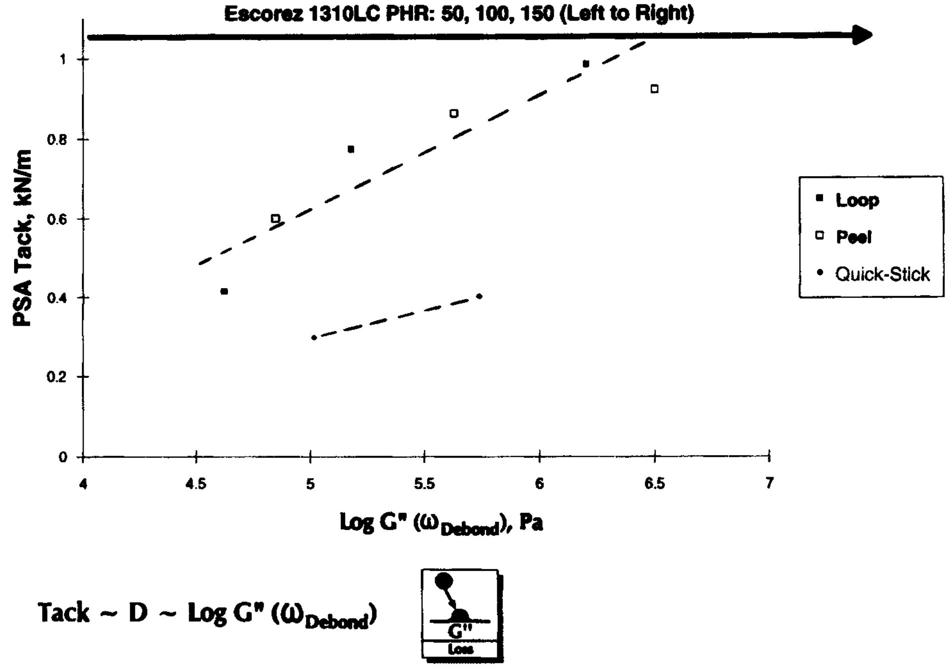


FIGURE 10 The measured tack is consistent with the debonding hypothesis.

where K_1 and K_2 are constants expressed in N/m, and ω_{debond} is the PSA characteristic debonding frequency for a given PSA test as shown in Table II. Values of K_1 and K_2, and correlation coefficients of these linear relations, are listed as follows:

Test	K_1	K_2	Correlation Coefficient
Loop	341	− 1090	0.9489
Peel	193	− 294	0.9284

The drop in quick-stick at the highest concentration of Escorez 1310LC appears to be similar to the probe tack results of what Wetzel[13] and one of the authors[5] observed for natural rubber/tackifier blends and SIS/Escorez 1310LC blends, respectively. Wetzel[13] considered a two-phase character of natural rubber/tackifier blends and attributed the maximum value to a possible phase inversion with increasing tackifier concentration. On the other hand, we speculate that this is a rheological effect. There is a formation of a polyisoprene-rich and tackifier-rich phase (corresponding to transition temperatures of T_{g1} and T'_1, respectively; $T_{g1} < T'_1$) in SIS/tackifier blends.[5] Both the quick-stick and probe tack impart a high debonding frequency to the PSA (the probe tack debonding frequency = 1650 rad/sec[5]) during the PSA debonding process. At such a high debonding frequency, which corresponds to a temperature approaching the T'_1 of the PSA, the PSA may have a low energy dissipative response. The result is a drop in the quick-stick or probe tack.

In general, based on loop and peel measurements, the PSA tack of the Vector block copolymer/tackifier system increases with increasing tackifier concentration (Fig. 10). Therefore, if the adhesive has a plateau modulus fulfilling the Dahlquist criterion, the measured tack is only proportional to the debonding term, D, for a given PSA test. D could be expressed in terms of the logarithm of the loss modulus at the PSA debonding frequency as described by Equation (3). At this point, one may wonder why the PSA tack is proportional to $\log G''(\omega_{\mathrm{debond}})$ rather than to $G''(\omega_{\mathrm{debond}})$. A satisfactory answer is not available. Possibly due to the reason that the block copolymeric PSA is non-polar, whereas the steel substrate is polar, the P_0 term (or the interfacial interaction) is low. This low interfacial interaction cannot support a sufficient amount of stress at the PSA/steel interface. Therefore, all the energy dissipative capacity of the bulk adhesive cannot be fully consumed in the debonding process.

Another interesting feature revealed by Figure 9 is that loss moduli of different tackified Vector 4113 formulations maximize at different frequencies. The higher the concentration of Escorez 1310LC tackifier in the SIS, the lower is the loss modulus peak position in the frequency scale, suggesting a lower rate of local rearrangement (a lower frequency of segment jumps or a longer relaxation time) of polyisoprene chains. This loss modulus peak position will be chosen as the PSA debonding parameter in the discussion of PSA design pathways.

Dependence of Peel on Rate and Temperature

One question that arises is whether the shape of the G'' *versus* frequency curve is similar to the shape of the peel *versus* peel rate curve. Figures 11–12 show master curves of the

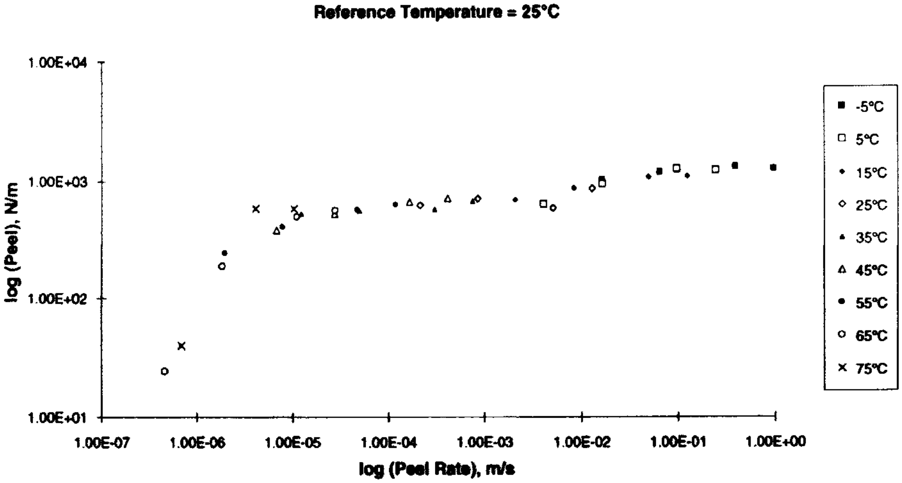


FIGURE 11 Peel strength *versus* peel rate curves at different temperatures of Vector 4113 containing 100 parts Escorez 1310LC bonded to steel are superimposed to a master curve by a horizontal shift along the rate scale.

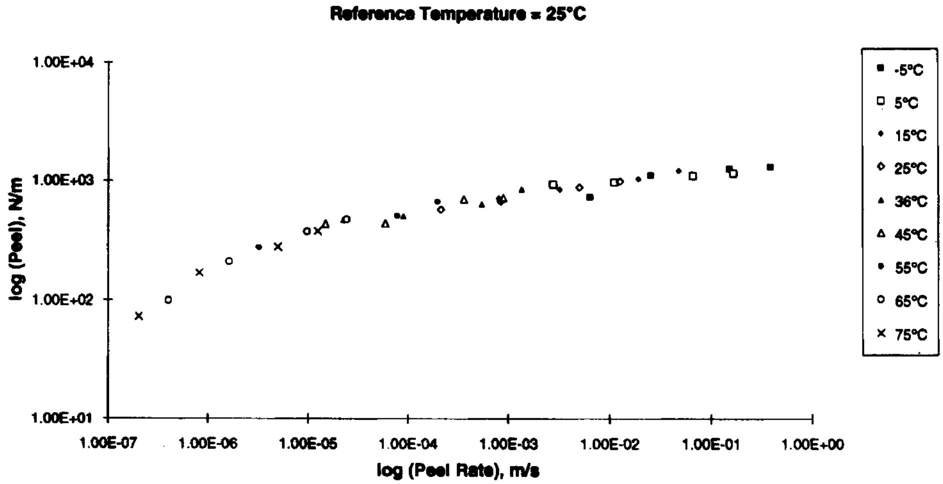


FIGURE 12 Peel strength *versus* peel rate curves at different temperatures of Vector 4111 containing 100 parts Escorez 1310LC bonded to steel are superimposed to a master curve by a horizontal shift along the rate scale.

180° peel to steel *versus* peel rate of Vector 4113 containing 100 parts Escorez 1310LC and Vector 4111 containing 100 parts Escorez 1310LC, respectively, at a reference temperature of 25°C. Both PSA joints failed interfacially at all the rates and temperatures shown. The peel strength, which increases with increasing peel rate, does not show a maximum up to the highest peel rate used in this study. However, it is believed that, above a certain peel rate, the peel strength should drop with increasing peel rate, similar to what Gent and Petrich[14] observed for un-crosslinked and crosslinked SBR elastomer model adhesives adhering to Mylar. A similar discussion of the peel adhesion of a model hot melt adhesive as a function of rate and temperature is described elsewhere.[15]

Master curves of the peel *versus* peel rate for these two PSA joints are compared in Figure 13. Peel strengths at high peel rates of these two joints are quite similar. However, possibly due to the presence of the diblock copolymers in Vector 4113, the PSA joint of the Vector 4113/Escorez 1310LC blend shows lower peel strengths than that of the Vector 4111/Escorez 1310LC blend in the low peel rate region.

Molecular Picture of Energy Dissipation

Similar to the loss modulus at the debonding frequency, the monomeric friction coefficient, ζ_0, of the polyisoprene chain segment in the tackifier environment[5] could be used to describe energy dissipative effects, on a molecular basis, of the tackified polymer. Figure 14 shows loop, peel and quick-stick test results as a function of ζ_0. Therefore, as expected, the measured tack increases with ζ_0 with the exception of Vector 4113 containing 150 parts Escorez 1310LC. This behavior is very similar to that of Figure 10 with the difference that the dependent variable in Figure 10 is the loss modulus at the debonding frequency at 27°C, whereas that in Figure 14 is ζ_0 at 27°C.

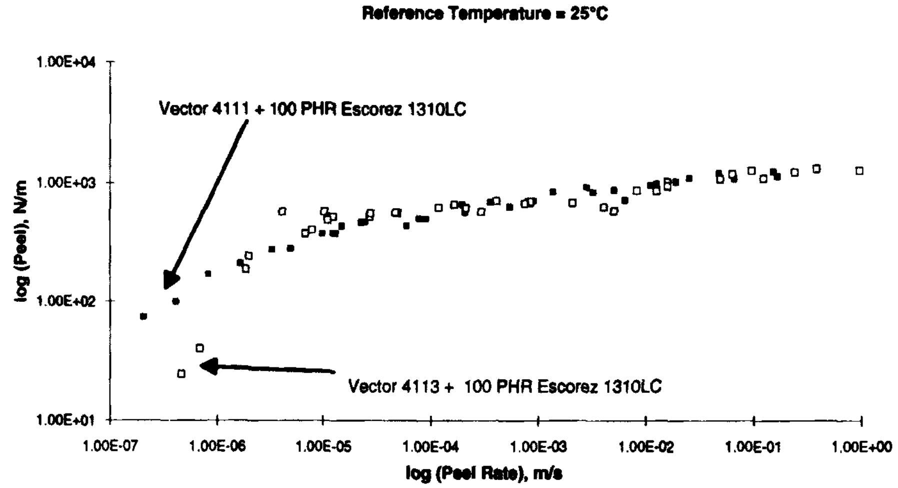


FIGURE 13 The peel strength deviates at low peel rates for the Vector 4113/Escorez 1310LC and Vector 4111/Escorez 1310LC blends shown in Figures 11–12.

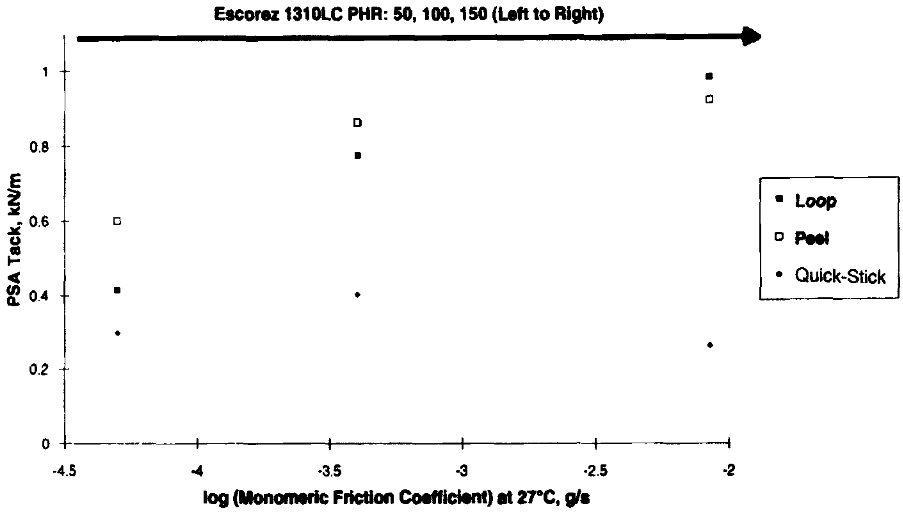


FIGURE 14 Overall, the measured tack also increases with increasing monomeric friction coefficient of the polyisoprene chain segment in the tackifier environment.

PSA Design Pathways

Thus far, we control the PSA tack by monitoring the loss modulus (Equation (3)). However, it is desired to generalize this rheological model by establishing PSA design pathways from certain bonding and debonding criteria. As shown in Figure 15, the plateau modulus is chosen as the bonding parameter because the plateau modulus measures how readily the adhesive conforms and wets the substrate surface. The

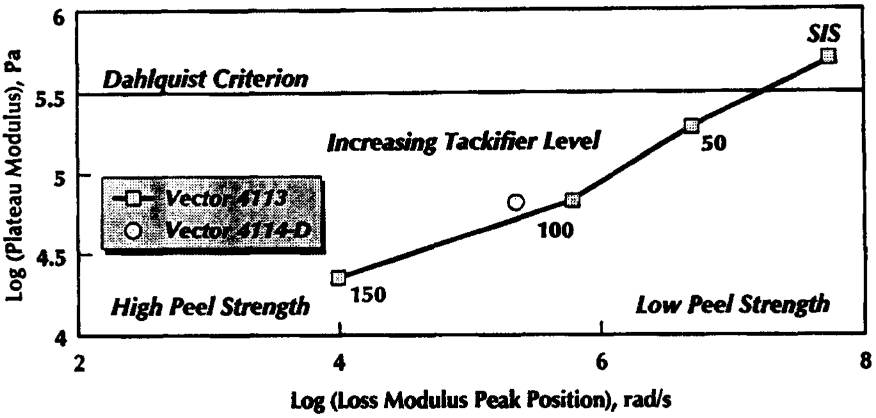


FIGURE 15 The adhesion model gives adhesive design pathways.

frequency at which the loss modulus master curve at 27°C maximizes is chosen as the debonding parameter, because this loss modulus peak position represents approximately the time or rate scale in which one deforms the adhesive to achieve a maximum energy dissipation.

Results of some model PSAs are shown in Figure 15. Vector 4113, the SIS polymer, is outside the PSA target region because, in the vertical direction, it is above the Dahlquist criterion so that the bonding requirement is not fulfilled. Increasing tackifier level from 50 parts to 100 parts and to 150 parts moves this SIS into the PSA region with a higher and higher peel strength, as described in Figure 10. "Tackification pathway" denotes the solid line connecting the data points in Figure 15 for the sake of discussion below. Figure 15 also shows the data point of Vector 4114-D (triblock containing 42 wt.% diblock) tackified by 100 parts Escorez 1310LC.

Based on previous studies[3,4] of Kraton 1107 blended with Escorez 1310LC, increasing the oil level in Kraton 1107 containing a certain level of tackifier, for example, 100 parts, lowers the plateau modulus, but also decreases the peel strength, because one pushes this system back towards the behavior of the neat polymer along the horizontal direction (Fig. 16). This is due to the fact that the incorporation of the oil, a low molecular weight material, into the SIS/tackifier blend will increase the rate of local rearrangement of polyisoprene chains. This is opposite to the requirement of the debonding criterion. The oil used was Tufflo 6056 (a fully hydrogenated paraffinic oil, obtained from Lyondell Petrochemical Company, Houston, TX, USA). Of course, the oil is less expensive than the tackifier which is, in turn, less expensive than the block copolymer. Therefore, there is an economic incentive to optimize the system for a particular performance target through the use of oil and tackifier combinations. Performance targets can vary from non-removable labels (high peel strength) to removable tapes (low peel strength), as shown in Figures 15–16. This is what PSA design pathways mean.

However, the presence of the oil in PSAs will affect its SAFT, shear adhesion failure temperature,[5] and holding power. Figure 17 shows the behavior of both the SAFT and

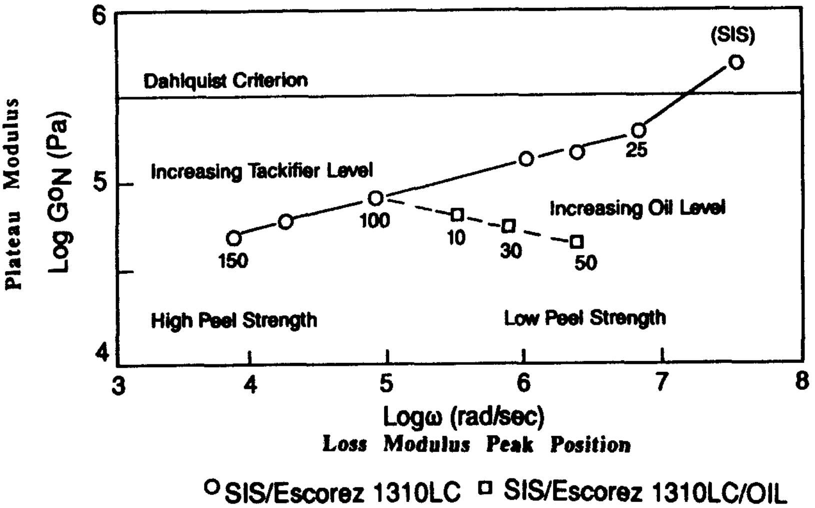


FIGURE 16 Oil effects on PSA design pathways.

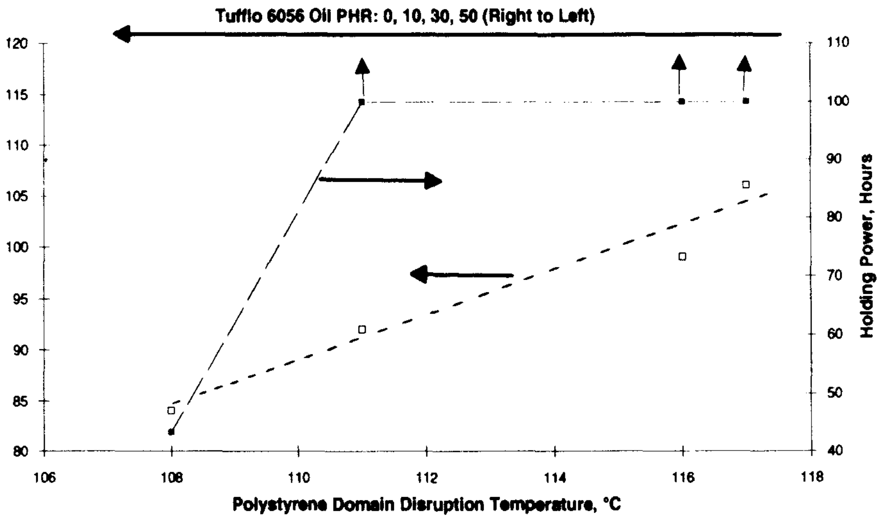
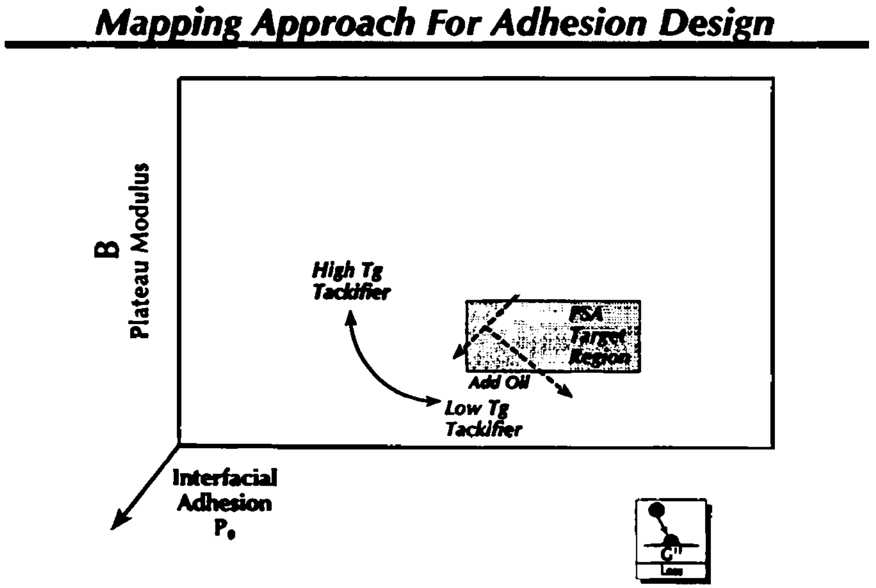


FIGURE 17 Overall, the oil decreases the shear performance of the tackified SIS polymer.

holding power with respect to T_{dd}, the domain disruption temperature,[5] of the SIS/Escorez 1310LC/oil system (100 parts Escorez 1310LC). The data points with arrows at the top for the holding power means that the holding power exceeds 100 hours. The T_{dd} represents the temperature at which polystyrene domains begin to intermix with the other components, the polyisoprene, Escorez 1310LC and the oil, in the PSA. Adding oil to the PSA will lower the T_{dd} of the adhesive. Overall, the lower the T_{dd} of the PSA (due to the oil addition), the lower is the shear performance, SAFT and holding power, of the PSA. Therefore, a poor shear performance is possibly due to the disruption/intrusion of the oil into polystyrene domains.

Based on the above discussions, rheology can be used for the design of adhesives in a scientific and systematic fashion. The first step is to obtain the rheological master curves G' and G'' at 27°C from the time-temperature superposition principle for the polymer of choice. The plateau modulus and the loss modulus peak position are estimated from the G' and G'' master curves, respectively. From these, the location of this polymer in the rheological space of Figure 18 can then be determined. The second step is to identify a compatible tackifier for the polymer based on thermodynamic considerations. The third step is to characterize the polymer rheologically in combination with the tackifier and other additive such as the oil. The plateau modulus and the loss modulus peak position of each of these formulations are determined to establish the "tackification pathway". Of course, the orientation of this "tackification pathway" will depend on the T_g (or the softening point) of the tackifier and the amount of oil used in the PSA formulations. By following these steps, the formulation to achieve appropriate rheological parameters which, in turn, control the adhesive performance can be designed. Therefore, this mapping approach of adhesive design will help one move the polymer into the PSA target region both effectively and economically.

Finally, for the completeness of this adhesion model, another axis corresponding to the interfacial (intrinsic) adhesion term, P_0, can be added to Figure 18 so that the resulting three dimensional space can describe P_0, B and D terms of the adhesive system. Of course, the next phase of this work should address further quantification of the adhesion model which includes study of the interfacial adhesion contribution in addition to the bonding and debonding criteria.



CONCLUSIONS

In summary, the adhesion model and mapping approach described give a comprehensive understanding and design pathways of PSAs. The major findings of this work are listed as follows. Firstly, for a given PSA test, the measured tack is correlated either with the logarithm of the loss modulus (a measure of energy dissipation in the bulk adhesive) at the PSA characteristic test frequency, or with the logarithm of the monomeric friction coefficient of the polyisoprene chain in the tackifier environment when the adhesive fulfills the Dahlquist criterion. Secondly, a target PSA region is established in the rheological space of the plateau modulus (bonding parameter) *versus* the loss modulus peak position in the frequency scale (debonding parameter). Thirdly, an optimal "tackification pathway" is achieved by tailoring the tackifier type and T_g, and the amount of oil used in PSAs. Also, the mapping approach in the three-dimensional space of P_0, B and D is useful for the scientific design of PSAs.

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