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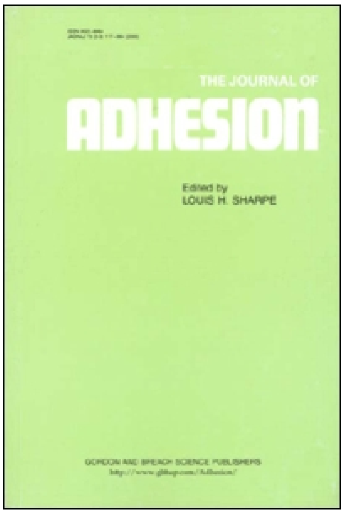

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Fundamental Understanding in Rolling Ball Tack of Tackified Block Copolymer Adhesives*

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In the pressure sensitive adhesive (PSA) industry, rolling ball tack is a very common tack test, which is simple, inexpensive and easy to operate. This work attempts to search for key parameter(s), which will affect the rolling ball tack of a PSA based on a blend of styrene-isoprene-styrene triblock copolymer (SIS) and hydrocarbon tackifier(s). We want to better understand whether this particular PSA performance is controlled by the surface or bulk properties of the adhesive.

Firstly, to test the contribution from the surface properties, we employ a model system of SIS/aliphatic tackifier in 1/1 wt. ratio as the control. Part of the tackifier in this PSA is then replaced by various amounts of low molecular weight diluents with different surface tensions. The idea is to vary the surface properties of the PSA because these low surface tension and low molecular weight diluents tend to migrate to the PSA surface. It is observed that the incorporation of a lower surface tension and a lower molecular weight diluent in the PSA tends to produce a larger increase in rolling ball tack compared with the unmodified PSA. On the other hand, the incorporation of a higher surface tension and a more compatible diluent tends to produce a larger increase in loop, peel and quick stick. Each diluent lowers the shear adhesion failure temperature (SAFT) of the diluent-modified PSA. These observations are explained in terms of tackifier molecular weight, and surface tension and compatibility of the various components (polyisoprene, tackifier, diluent and oil) in the adhesive formulation.

Secondly, to test the contribution from the bulk properties, we derive an equation for rolling ball tack in terms of the bulk viscoelastic behavior of the block copolymer PSA. However, experimental values of rolling ball tack do not follow this equation. Also, with increasing tackifier concentration in SIS, rolling ball tack has very different behavior compared with loop, peel, quick stick and probe tack. The latter set of performance

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criteria is known to be related to PSA bulk viscoelastic behavior. Therefore, these suggest that rolling ball tack is related more to the surface properties than to the bulk properties of the adhesive based on these results and those of the diluent-modified PSA systems.

Keywords: Pressure sensitive adhesive; tackifier; block copolymer; tack; adhesion; rolling ball tack; peel strength; loop tack; quick stick; probe tack; surface tension; viscoelasticity; loss tangent

INTRODUCTION

Researchers in the PSA industry routinely employ tests such as loop tack, 180° peel strength, 90° quick stick, probe tack, rolling ball tack and SAFT to characterize their product performance. Previous studies [1–3] have established a PSA model, which predicts loop tack, peel, quick stick, probe tack and SAFT by PSA bulk viscoelastic parameters such as plateau modulus, loss modulus (energy dissipation), polystyrene domain disruption temperature, etc. For example, loop, peel, quick stick and probe tack of Kraton® 1107 SIS blended with increasing amount of Escorez® 1310LC tackifier increase in rough accord not only with the logarithm of the loss modulus at PSA debonding frequency [2], but also with the logarithm of the monomeric friction coefficient of the adhesive blend (Fig. 1). Rolling ball tack has not been analyzed by this rheological approach because, when the ball rolls on the PSA, both the bonding and debonding frequencies, which are used to measure the storage and loss moduli, respectively, vary. Also, we have found that rolling ball tack behaves very differently from loop, peel, quick stick and probe tack with increasing Escorez 1310LC level in SIS (Fig. 2). It remains quite constant up to a certain tackifier level but drops drastically with a further increase in tackifier level. This may suggest that rolling ball tack is related to properties other than the bulk viscoelastic behavior of the adhesive. Therefore, the purpose of this work is an attempt to better understand and search for key parameter(s) that will affect the rolling ball tack of a block copolymer PSA.

Rolling ball tack is the oldest and the most commonly-used tack test in the PSA industry. This test only requires an inclined plane, several steel balls and a ruler to measure the tack performance of a PSA tape. A steel ball is rolled down from an inclined plane with a specific geometry. At the foot of the inclined plane is the PSA tape held

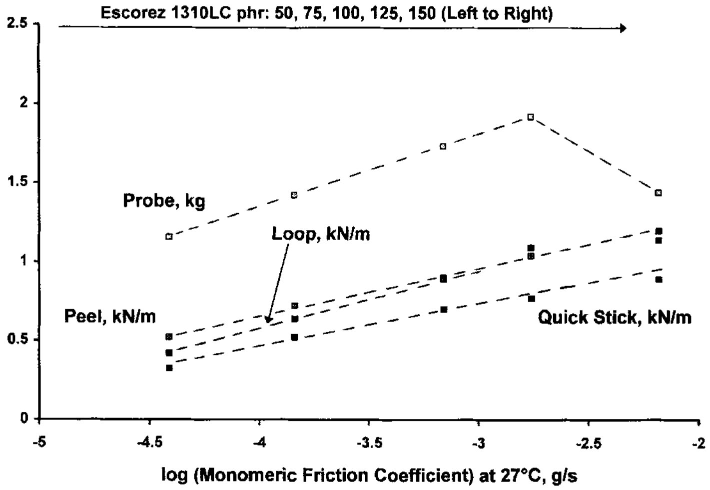

FIGURE 1 Loop, peel, quick stick and probe tack increase approximately with monomeric friction coefficients of block copolymer PSAs.

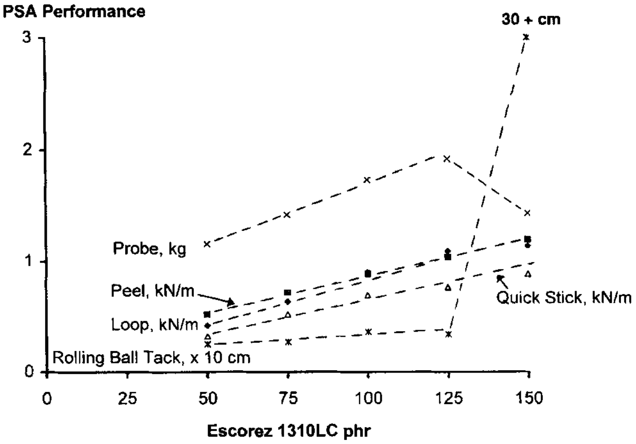

FIGURE 2 Rolling ball tack shows completely different behavior from loop, peel, quick stick and probe tack as a function of tackifier concentration for the Kraton® 1107/ Escorez® 1310LC system.

securely to a horizontal, rigid surface. Rolling ball tack is the roll-out distance of the steel ball on the tape. A shorter roll-out distance means a better rolling ball tack of the tape.

Rolling motion of a ball on a PSA tape mounted on an inclined surface was studied by the school of Mizumachi [4]. They concluded that it is more scientific to express the measured tack in terms of the rolling friction coefficient, which depends on the physical properties of the PSA. They [5] also studied the rolling motion of a ball on a PSA on a horizontal surface. Both the rolling distance *versus* time and the roll-out distance *versus* the height of the inclined plane were measured. The rolling distance and the roll-out distance were analyzed by a unified theory in which the rolling friction coefficient is a key parameter. In another report [6] they studied the theoretical and experimental aspects of peel strength and rolling cylinder tack on acrylic PSAs. The method of rolling cylinder was used so that they could pull the cylinder at different speeds on the PSA surface at room temperature. This will yield the rolling friction coefficient of the PSA as a function of the rolling speed. They claimed that PSA performance such as adhesion and tack described by the peel strength and the cylinder rolling friction coefficient, respectively, depends greatly on physical properties of PSAs, among which chemical structure, viscoelastic properties, and surface tensions of both the adhesive and the substrate are mostly important. For example, they observed that the rolling friction coefficient depends strongly on the surface tensions of both the PSA and the rolling cylinder, especially in the high-speed region. Also, the maxima of the curves of both peel strength *versus* log (peeling speed) and rolling friction coefficient *versus* log (rolling speed) at room temperature shift toward lower speeds as the relaxation time (or T_g) of the adhesive increases. Relaxation time can be considered as the time needed to accomplish a particular molecular rearrangement of the polymer chain in response to an applied stress and field. This time is usually longer for a longer chain length or a chain with more restricted motion. It has been found [2, 3] that the incorporation of an aliphatic tackifier in a low-styrene SIS polymer restricts the segmental motion of the polyisoprene chains, resulting in a higher monomeric friction coefficient (Fig. 1).

Work of Mizumachi *et al.* [4–6] triggers our interest to investigate if rolling ball tack is governed by the surface or the bulk properties of the block copolymer PSA. Different from the acrylic PSA, the block copolymer PSA contains many components with different surface tensions and molecular weights such as SIS, tackifier(s) and oil. The tackifier, usually a broad molecular weight distributed material, is formed by fractions with a wide range of molecular weight. Therefore, in the first part of this study, we employ one of the Escorez 1310LC tackifier fractions, three different liquid tackifiers and an oil as diluents of different surface tensions to modify the model PSA of SIS/Escorez 1310LC. The idea is to vary the PSA surface properties because these low surface tension and low molecular weight diluents tend to migrate to the PSA surface. The reasonably uncontaminated surface of a tackified SIS, studied by static secondary ion mass spectroscopy (SSIMS), is enriched about 40% in Escorez 1310LC compared with the bulk [7]. Also, we attempt to employ the difference in rolling ball tack, loop, peel, quick stick and SAFT to track qualitatively the partitioning of tackifier and diluent between the polystyrene, the polyisoprene, the surface and the bulk regions of the SIS polymer. In the second part of this study, we derive a relation between the roll-out distance and bulk viscoelastic parameters of the PSA using theories of mechanics and viscoelasticity. The idea is to use this relation to test the contribution of experimentally-determined PSA bulk properties to rolling ball tack.

EXPERIMENTAL

Materials

Vector® 4111, Vector® 4113 and Kraton® 1107 block copolymers, denoted by SIS-1, SIS-2 and SIS-3, respectively, and Escorez 1310LC and ECR-327 tackifiers have been described earlier [1–3], [8].

The fractionation of Escorez 1310LC was carried out in a large-scale fractionator. Cyclohexane was employed as the solvent and ethanol as the non-solvent. When the tackifier was completely dissolved (*ca.* 0.3 kg tackifier in 2 liters cyclohexane), the first portion of non-solvent was added (typically, enough to give a 50/50 v/v mixture of solvent/non-solvent). The first addition should result in 15–20% of the tackifier precipitating out of the solution. After the precipitate had settled out of solution, the solution was filtered off (the precipitate frequently came out as a sludge-like material; if the apparatus permitted, the solution may simply be decanted). The solution was set aside or stored in a holding flask, and the precipitate dissolved in solvent, removed and recovered by distillation/precipitation. The solution in the holding flask was returned to the fractionation flask, where a second portion of non-solvent was added (usually much smaller than the first addition; typically, subsequent additions were approximately 1/2 the first addition). Again, about 15–20% of the total tackifier should precipitate out of solution. The recovery and addition process was repeated until five or six cuts had been obtained. At this point, the remaining tackifier in solution should be recovered by distillation and precipitation. This procedure resulted in cuts of decreasing molecular weight; *i.e.*, the first cut had the highest molecular weight whereas the last cut had the lowest molecular weight.

Solubility Parameter and Proton NMR Measurements

The use of refractometry for determining solubility parameters, and proton NMR measurements of tackifiers were detailed elsewhere [9].

Rheological and Surface Tension Measurements

Rheological measurements of toluene-cast PSA samples [1–3], and surface tension measurements of tackifiers and polymers [8, 9] were described previously.

PSA Tests

Loop, peel, quick stick and SAFT measurements were described previously [2, 3]. The only difference is the drying process of the PSA tape specimens. To avoid heat-aging effects, we dried these specimens coated from toluene in a well-ventilated hood for 3 hours at room temperature. Rolling ball tack was measured according to test method of the Pressure Sensitive Tape Council PSTC-6.

RESULTS AND DISCUSSION

Rolling Ball Tack of Diluent-modified PSA Systems

To test the contribution of PSA surface properties to rolling ball tack, we first study the PSA performance of the SIS-1/Escorez 1310LC system modified by one of the fractions of Escorez 1310LC, Escorez 1310LC-1 (Tab. I). Surface tensions of Escorez 1310LC and Escorez 1310LC-1 are compared with that of polyisoprene (the elastomeric block of SIS) in Figure 3. Surface tension *versus* temperature, T, of each of these materials obeys a linear relationship described by the following equation:

$$\gamma = -(d\gamma/dT)(T - 25^\circ\text{C}) + (\gamma \text{ at } 25^\circ\text{C}).$$

TABLE I Characterization of polyisoprene, tackifiers and oil

Material	n	δ_d	γ *at 25°C*	M_n	T_g, °C
Polyisoprene	1.5210	8.10	35.9	58,000	−60
Escorez 1310LC	1.5208	8.23	31.4	900	47
Escorez 1310LC-1	1.5164	8.17	30.5	510	13
Escorez 1310LC-3	1.5211	8.23	29.2	810	50
Escorez 1310LC-4	1.5240	8.27		1100	67
Escorez 1310LC-5	1.5244	8.27		1410	80
Escorez 1310LC-6	1.5257	8.29		2190	99
ECR-143H	1.4901	7.83	29.0	510	−26
Escorez 2520	1.5216	8.25	30.5	250	−16
ECR-327	1.5405	8.50	36.5	100	−13
Flexon 766 Oil	1.4843	7.75	29.2		

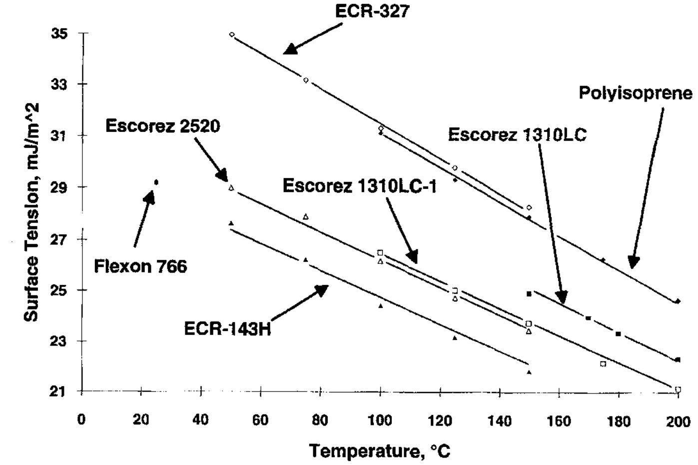

FIGURE 3 Surface tensions of low molecular weight diluents, polyisoprene, Escorez 1310LC and Escorez 1310LC fraction.

From this equation, we can estimate the surface tension of the material at room temperature, 25°C. Therefore, some properties of Escorez 1310LC and Escorez 1310LC-1 are shown in Table I, where n is the refractive index, δ_d is the solubility parameter dispersion component in $\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$ measured by refractometry, and γ at 25°C is the estimated surface tension in $\mathrm{mJ/m}^2$ at room temperature based on the last equation. For comparison, we also include four other diluents: ECR-143H, Escorez 2520, ECR-327 and Flexon® 766 oil in this study. Their properties are shown in Figure 3 and Table I. Escorez 1310LC-1 and ECR-143H have similar M_n values. However, their T_g's and δ_d's differ widely, indicating the structural difference of these two tackifiers.

Figure 4 plots both δ_d and the DSC T_g *versus* M_n for the Escorez 1310LC whole tackifier and its fractions. If δ_d is assumed as an indicator of the composition of these non-polar, hydrocarbon tackifiers, these fractions should be compositionally quite homogeneous for their small changes in δ_d with M_n. Based on temperature-volume considerations, Fox and Loshaek [10] derived the following equation relating T_g and M_n for polymers

$$T_{g,\infty} - T_g = C/M_n$$

where $T_{g,\infty}$ is the T_g at infinite M_n; C is about 2×10^5 for PS and PMMA, and 3.5×10^5 for atactic PαmS. In other words, T_g of an

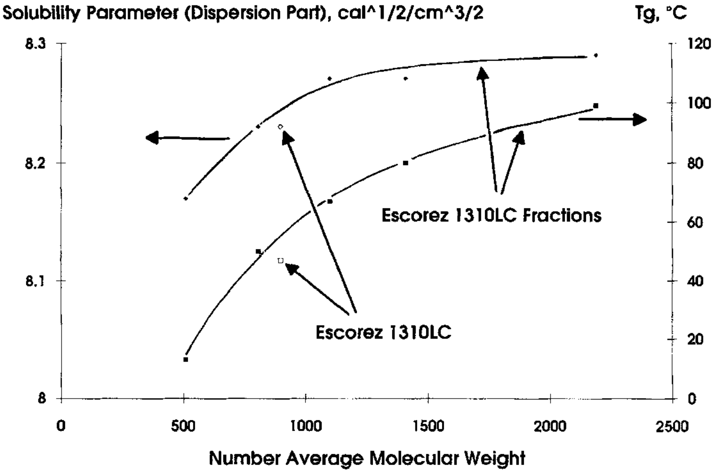

FIGURE 4 Characterization of Escorez 1310LC and its fractions.

oligomer is often lower than $T_{g,\infty}$ of a high polymer and the correction is scaled to $1/M_n$. According to data in Figure 4, the narrow molecular weight distributed Escorez 1310LC fractions obey the following equation:

$$121°\text{C} - T_g = 56,100/M_n \quad (R^2 = 0.99)$$

which gives further support for the compositional similarity of Escorez 1310LC and its fractions. We also use proton NMR to characterize Escorez 1310LC and its fractions. Figure 5 shows the proton NMR spectrum of Escorez 1310LC. Proton NMR spectra of all the Escorez 1310LC fractions (results not shown here) show very similar structural profiles to that in Figure 5, in agreement with data in Figure 4 that Escorez 1310LC and its fractions are compositionally homogeneous.

M_n of the oil is not available in Table I. It has a lower δ_d than the other materials. Based on Figure 3 and Table I, the surface tension (γ) is found to be: oil ≅ ECR-143H < Escorez 2520 < Escorez 1310LC-1 < polyisoprene < ECR-327. Therefore, when each of these tackifiers

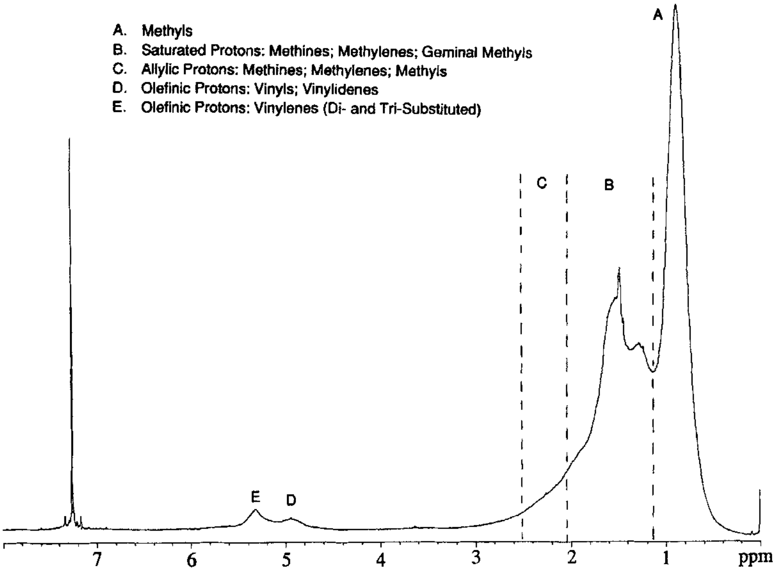

FIGURE 5 Proton NMR spectrum of Escorez 1310LC.

(with the exception of ECR-327) or oil is blended with the SIS, the lower surface tension material should segregate on the SIS surface according to thermodynamics. Of course, the polystyrene phase of SIS should always stay in the bulk of the PSA because it has the highest surface tension ($40+\mathrm{mJ/m^2}$) [11] among all these materials.

As described above, the system of SIS-1/Escorez 1310LC in 1/1 wt. ratio is the control in this study. We then replace part of Escorez 1310LC by various amounts of each diluent: Escorez 1310LC-1, ECR-143H, Escorez 2520, ECR-327 or oil, study the PSA performance of these diluent-modified PSA systems, and compare with the control.

Figure 6 shows the rolling ball tack behavior. Overall, relative to the control, the addition of a higher surface tension diluent such as Escorez 1310LC-1, Escorez 2520 or ECR-327 in the PSA lowers the ball tack, whereas the addition of a lower surface tension diluent such as ECR-143H or oil enhances the ball tack. However, at a given level of Escorez 1310LC replacement, oil is more effective than ECR-143H in improving ball tack possibly due to the lower molecular weight of oil.

At this point, there may be two possible explanations for the above rolling ball tack behavior: the T_g depression (the bulk effect) and/or the migration of the low surface tension and low molecular weight

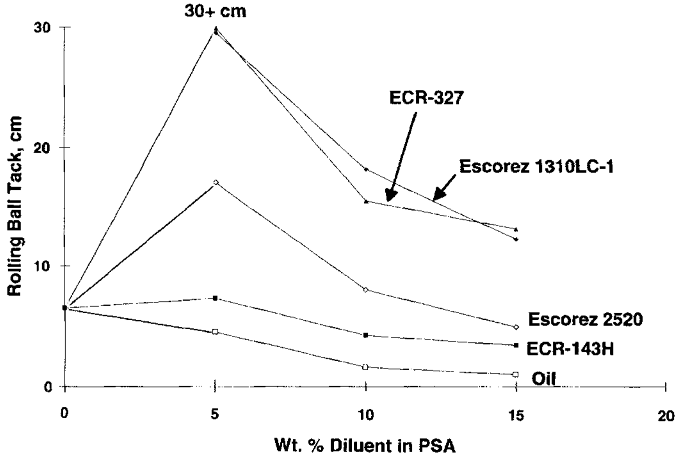

FIGURE 6 Effects of low molecular weight diluents on rolling ball tack of SIS-1/Escorez 1310LC.

diluent to the PSA surface (the surface effect). The diluent T_g is found to be: ECR-143H < Escorez 2520 < ECR-327 < Escorez 1310LC-1. If we further assume that the oil has the lowest freezing point (or, on a less scientific ground, the lowest T_g), a lower T_g diluent seems to result in a higher rolling ball tack of the PSA according to Figure 6. Of course, the T_g effect is related to viscoelasticity, of which we do not have a clear picture because both the bonding and debonding frequencies vary in the ball-rolling process as described before. Also, rolling ball tack behaves very differently from loop, peel, quick stick and probe tack with increasing Escorez 1310LC level in SIS (Fig. 2). The latter set of performance criteria, as noted before, is known to be related to the PSA's bulk viscoelastic behavior [1–3]. Therefore, for rolling ball tack, surface properties may predominate over bulk properties. Furthermore, subsequent results of this paper show that rolling ball tack cannot be predicted from a theoretical equation derived from theories of mechanics and bulk viscoelastic properties of the PSA.

For the second explanation, diluent migration to the surface results in a weak boundary layer (WBL) so that the ball is subsequently coated by the diluent (cohesive failure). This may stop the ball at a shorter roll-out distance. The degree of diluent migration depends on the surface tension of the diluent. According to Figure 3, the lower surface tension Escorez 1310LC-1 or Escorez 2520 has a higher tendency to migrate to the surface of SIS than the higher surface tension ECR-327. Oil and ECR-143H have similar surface tensions. However, it is believed that the oil, due to its lower molecular weight, has a greater chance to migrate to the PSA surface than ECR-143H. This description appears to be consistent with the rolling ball tack results in Figure 6.

Some more data supporting the surface segregation explanation are illustrated in Table II, which compares the PSA performance of SIS-1 blended with 100 phr of Escorez 1310LC ($T_g = 47°C$) and SIS-1 blended with 100 phr of the narrow molecular weight distributed middle fraction, Escorez 1310LC-3 ($T_g = 50°C$). The PSA formulated from Escorez 1310LC has similar loop, peel, quick stick, SAFT, but a much higher ball tack compared with the PSA formulated from Escorez 1310LC-3 with a similar T_g. The surface segregation effect seems to be more important than the T_g effect.

TABLE II PSA Performance of SIS-1/Escorez 1310LC and SIS-1/Escorez 1310LC-3

Formulation in phr		
SIS-1	100	100
Escorez 1310LC	100	–
Escroez 1310LC-3	–	100
PSA Performance		
Loop, kN/m	0.5	0.5
Peel, kN/m	0.7	0.7
Quick stick, kN/m	0.3	0.2
SAFT, °C	107	101
Rolling ball tack, cm	6.4	30+

Figure 7 shows the rolling ball tack of SIS-1 blended with 100 phr of each of Escorez 1310LC and its various fractions. Rolling ball tack of SIS-1 blended with Escorez 1310LC-1 is higher than that of SIS-1 blended with the Escorez 1310LC whole tackifier. However, SIS-1 blended with the other higher molecular weight fraction has rolling ball tack above 30 cm. Therefore, the low surface tension and low molecular weight species of Escorez 1310LC may play an important role in rolling ball tack because it tends to migrate to the block copolymer PSA surface and stop the ball at a shorter roll-out distance.

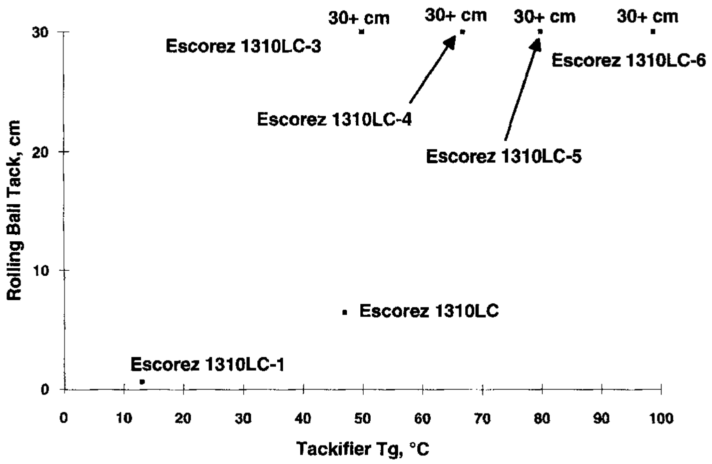

FIGURE 7 Low molecular weight species of Escorez 1310LC may play an important role in rolling ball tack.

Other Performance of Diluent-modified PSA Systems

Figure 8 shows the loop tack behavior of the SIS-1/Escorez 1310LC system modified by various diluents. For the wt.% diluent shown, all the liquid tackifiers and the tackifier fraction enhance the loop tack relative to the control. On the other hand, except at 5 wt.%, the oil diminishes the loop tack relative to the control. Approximately, the enhancement in loop tack seems to be higher for the diluent with a higher surface tension at a low diluent loading. The more compatible diluent such as Escorez 1310LC-1 with a δ_d closer to that of polyisoprene usually maintains a better level of loop tack enhancement at a higher diluent loading. Overall, compared with the control, the higher surface tension and/or the more compatible diluent seems to improve loop tack more effectively.

Figure 9 shows the peel behavior of the diluent-modified SIS-1/Escorez 1310LC systems. Only Escorez 1310LC-1, ECR-327, and 5 wt.% ECR-143H and Escorez 2520 enhance the peel relative to the control. On the other hand, oil, and 10 and 15 wt.% of ECR-143H and Escorez 2520 all diminish the peel relative to the control. Again, the surface tension and the compatibility of the diluent play a similar role in both the peel performance and the loop tack performance described in the previous paragraph.

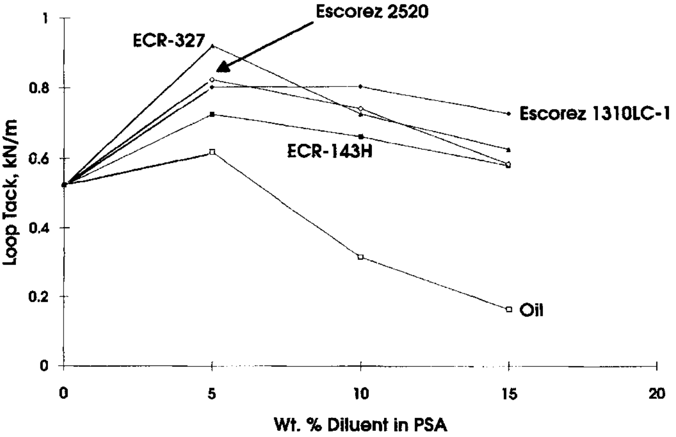

FIGURE 8 Effects of low molecular weight diluents on loop tack of SIS-1/Escorez 1310LC.

Figure 10 shows the quick stick behavior. Except for 15 wt.% oil, all the other diluents enhance the quick stick with respect to the control. Again, surface tension and compatibility of the diluent play a role in this performance similar to the loop and peel performance described in the previous two paragraphs.

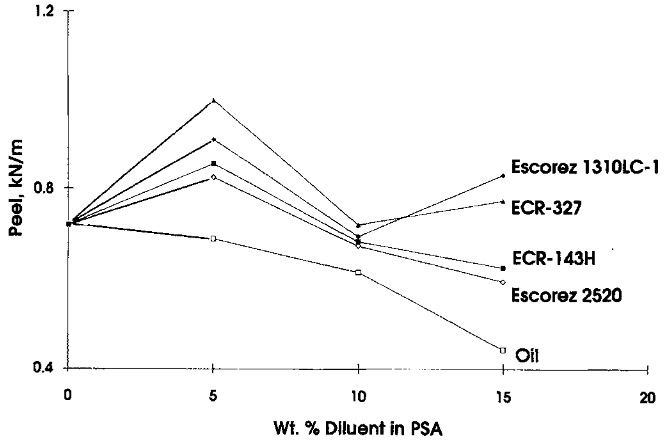

FIGURE 9 Effects of low molecular weight diluents on peel of SIS-1/Escorez 1310LC.

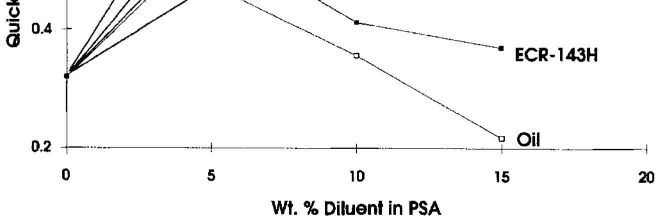

FIGURE 10 Effects of low molecular weight diluents on quick stick of SIS-1/Escorez 1310LC.

Figure 11 shows the SAFT behavior of SIS-1/Escorez 1310LC modified by three of the diluents: Escorez 1310LC-1, ECR-143H and oil. All diluents lower the SAFT relative to the control. Both Escorez 1310LC-1 and ECR-143H depress SAFT of the SIS-1/Escorez 1310LC system slightly. However, oil results in a drastic drop in SAFT possibly due to a relatively high amount of this diluent intruding into the polystyrene phase of SIS. Simply put, the low surface tension and low molecular weight oil may have higher concentrations both at the PSA surface and in the polystyrene domains of the PSA compared with Escorez 1310LC-1 and ECR-143H (Fig. 12), producing the highest rolling ball tack but the lowest SAFT. Therefore, we can qualitatively predict the distribution of tackifier, diluent or oil in the polystyrene and polyisoprene phases, and in the bulk and surface regions of SIS based on the tackifier molecular weight, and the surface tension and the compatibility of the various components (polyisoprene, tackifier, diluent and oil) in the PSA.

Theory of Rolling Ball Tack

To test the contribution of PSA bulk properties to rolling ball tack, we believe that a theoretical derivation of the motion of the steel ball on the inclined plane and on the PSA surface will help us visualize the

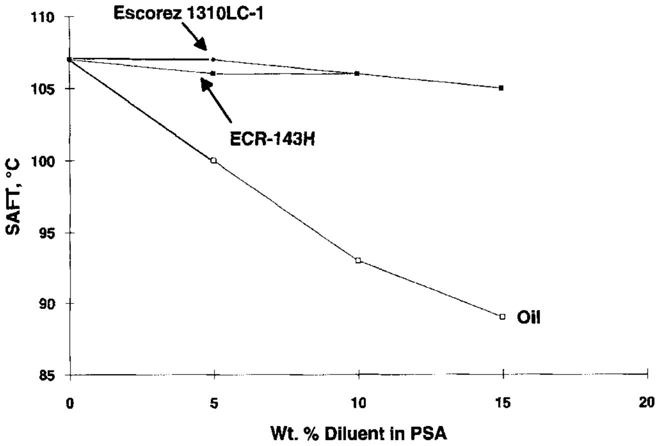

FIGURE 11 Effects of low molecular weight diluents on SAFT of SIS-1/Escorez 1310LC.

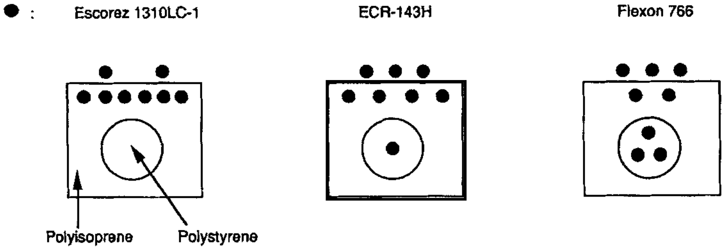

FIGURE 12 Distribution of low molecular weight diluents in the polystyrene/polyisoprene phase and the bulk/surface region in SIS.

underlying mechanisms which stop the rolling ball on the PSA surface. This derived relation can then be used to compare with the experimental values of rolling ball tack.

Motion of the Rolling Ball on the Inclined Plane

The rolling ball tack experiment is shown in Figure 13. It involves the motion of a uniform spherical ball of mass, *M*, and radius, *R*, rolling down an inclined plane with length, *L*, and angle of inclination, θ. We assume that on the inclined plane the force of friction, *f*, between the ball and the plane is large enough to cause the ball to roll without sliding. The problem is to find the velocity of the ball at the bottom of the plane, *v*. According to the conservation of energy:

$$1/2[M(dX/dt)^2] + 1/2[Mk^2(d\theta/dt)^2] - MgX\sin\theta = 0$$

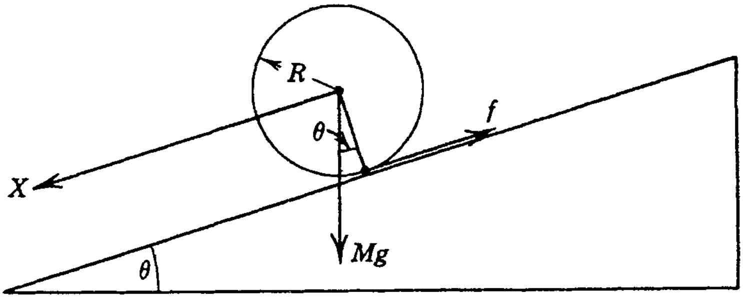

FIGURE 13 The stainless steel ball rolling down an inclined plane.

where X is the distance along the inclined plane, t is the time, k is the radius of gyration of the ball about its center of mass, and g is the gravitational constant. For rolling without sliding, $d\theta/dt = (dX/dt)/R$. Then the last equation becomes

$$(dX/dt)^2 = 2gX\sin\theta/[1 + (k/R)^2] = (10gX\sin\theta)/7$$

because $k^2 = 2R^2/5$ in this case. Therefore, the velocity of the ball at the end of the inclined plane is

$$v = [(10gL\sin\theta)/7]^{1/2} = 92\ \mathrm{cm/s}$$

because $L = 16.5$ cm and $\theta = 21.5°$ according to test method of PSTC-6.

Motion of the Rolling Ball on the PSA Surface

As shown in Figure 14, we assume the coefficient of friction between the ball and the PSA surface is μ. Then the equations of motion of the ball are:

$$Md^2s/dt^2 = F = \mu Mg \qquad (1)$$

$$(2/5)MR^2 d\Omega/dt = -RF = -R\mu Mg \qquad (2)$$

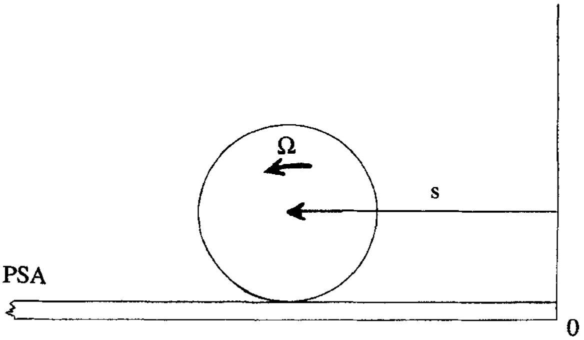

FIGURE 14 The stainless steel ball rolling on the PSA sample.

where s is the roll-out distance of the ball on the PSA surface at time t, F is the friction force between the ball and the PSA, and Ω is the angular velocity of the ball at time t. The initial conditions ($t = 0$) are: $ds/dt = 0$, $\Omega = v/R$ and $s = 0$. By solving Eq. (1), we have

$$s = (1/2)\mu g t^2 \tag{3}$$

By solving Eq. (2), we have

$$R\Omega = -(5/2)\mu g t + v \tag{4}$$

Rolling ceases after a time t' when $\Omega = 0$. Therefore, we have

$$t' = 2v/5\mu g.$$

If we substitute this t' value into Eq. (3), we obtain the rolling ball tack s' (the distance the ball travels before it stops on the PSA surface):

$$s' = 2v^2/25\mu g.$$

By substituting $v = 92\,\text{cm/s}$ in this last equation, we have

$$s' = 0.691/\mu \tag{5}$$

where s' is expressed in cm. In other words, we can estimate rolling ball tack if we know the coefficient of friction between the steel ball and the PSA surface. We attempt to relate μ to PSA viscoelasticity in the next section.

Relation of Coefficient of Friction to PSA Viscoelasticity

According to Gent and Henry [12], for a rigid ball rolling over a soft viscoelastic substrate, the coefficient of friction, μ, between the rigid ball and the soft viscoelastic substrate can be related to tan δ and shear modulus, G (expressed in dynes/cm^2), of the substrate by the following equation:

$$\mu = 0.52 \tan\delta (Mg/3GR^2)^{1/3} = 9.36\ \tan\ \delta/G^{1/3} \tag{6}$$

because $M = 5.5955\,\text{gm}$ and $R = 0.56\,\text{cm}$ according to PSTC-6. By combining Eqs. (5) and (6), we have the final result:

$$s' = (0.074\ G^{1/3})/(\tan\delta) \tag{7}$$

Therefore, by measuring the bulk viscoelastic behavior of the PSA material such as G and $\tan\delta$, we could estimate rolling ball tack from Eq. (7). The validity of Eq. (7) will be tested in the next section.

Effects of Tackifier Concentration on Rolling Ball Tack

Figure 2 shows that loop, peel, quick stick and probe tack of the SIS-3/Escorez 1310LC blends increase in rough accord with increasing tackifier concentration (50 – 150 phr) [1 – 3]. These result from changes in bulk viscoelastic properties of SIS with the incorporation of different levels of Escorez 1310LC. However, rolling ball tack of these adhesive systems exhibits different behavior. It seems that, once the surface region and/or the near-surface region of the SIS polymer is changed or modified due to the incorporation of tackifier, ball tack remains quite constant no matter whether the Escorez 1310LC concentration is 50 or 125 phr. Beyond 125 phr Escorez 1310LC, ball tack drops drastically possibly due to the reason that some other undesirable tackifier component(s) begins to migrate to the surface region. Therefore, results in Figure 2 seem to provide indirect evidence that ball tack of tackified SIS does not depend on PSA bulk viscoelastic properties. A more quantitative comparison of the calculated values from Eq. (7) with the experimental values of rolling ball tack is shown in the next paragraph.

According to Eq. (7), we can estimate the rolling ball tack of the PSA if its viscoelastic behavior is known. To do this, we simply assume that G is the plateau modulus and $\tan\delta$ is the average loss tangent value at frequencies between 0 and 160 rad/s. We choose this frequency range because the deformation frequency experienced by the PSA is $v/R = (92\,\text{cm/s})/(0.56\,\text{cm}) \sim 160\,\text{rad/s}$ when the ball first hits the PSA at the foot of the inclined plane, and 0 rad/s when the ball stops on the PSA surface. The s' values, calculated from viscoelastic parameters determined previously [2], are compared with the experimental values in Table III.

TABLE III Calculated and measured ball tack values

phr Escorez 1310*LC*	*Plateau modulus* × 10^{-6}, *dynes/cm*^{2}	*Average tan* δ	s', *cm*	*Ball tack, cm*
0	5.21	0.051	250	
25	2.09	0.083	110	
50	1.54	0.097	88	2.5
75	1.42	0.157	53	2.7
100	0.88	0.319	22	3.6
125	0.62	1.32	4.8	3.4
150	0.50	1.72	3.4	30+

The calculated s' drops with increasing tackifier concentration. On the other hand, except at 150 phr Escorez 1310LC, the experimental values remain quite constant with various Escorez 1310LC concentrations. This disagreement could be explained as follows: (1) the procedure and assumptions used to derive Eq. (7) are wrong; and (2) rolling ball tack may depend more on the surface properties than the bulk viscoelastic behavior of the PSA. In the next section, we show some more data to support the second explanation.

One point worth mentioning about the data in Table III is that a higher tackifier concentration decreases the plateau modulus but increases the average tan δ value of the SIS/tackifier system. This agrees with our PSA model that a lower plateau modulus improves the bonding term, B, whereas a higher loss tangent enhances the energy dissipation or the debonding term, D [1–3].

Experimental Escorez 1310LC Tackifiers

Two experimental Escorez 1310LC tackifiers are described in Table IV. They have similar structural profiles (NMR spectra not shown here), T_g and δ_d compared with Escorez 1310LC. There are some minor differences in the various molecular weights of these two tackifiers. M_n, M_w and M_z of Tackifier A are slightly higher than those of Tackifier B. PSA test results based on SIS-2 of these tackifiers (150 phr tackifier and 10 phr Flexon 766 oil) are also shown in Table IV.

These formulations have similar loop, peel and SAFT, but different ball tack. They also have similar bulk viscoelastic behavior (Figs. 15 and 16). This will imply that the D term in the adhesion model [1–3]:

TABLE IV Experimental Escorez 1310LC tackifiers

Tackifier	*A*	*B*
T_g, °C	43	45
δ_d, cal$^{1/2}$cm$^{-3/2}$	8.22	8.24
M_n	700	640
M_w	1480	1190
M_w/M_n	2.11	1.86
M_z	2930	2160
PSA Performance		
Loop, kN/m	0.9	0.8
Peel, kN/m	1.3	1.2
SAFT, °C	86	87
Rolling ball tack, cm	30+	21

$P = P_o\, BD$, should be similar for these PSAs. Therefore, the variation in rolling ball tack is related more to the interfacial adhesion term, P_o, and the bonding term, B. As mentioned earlier, it is very difficult to quantify B because the bonding frequency varies as the ball rolls on the PSA surface. However, all the above results give further support for the dependence of ball tack on PSA surface properties. These results are also consistent with the conclusion of Mizumachi *et al.* [6] that the friction coefficient of rolling cylinder tack depends strongly on

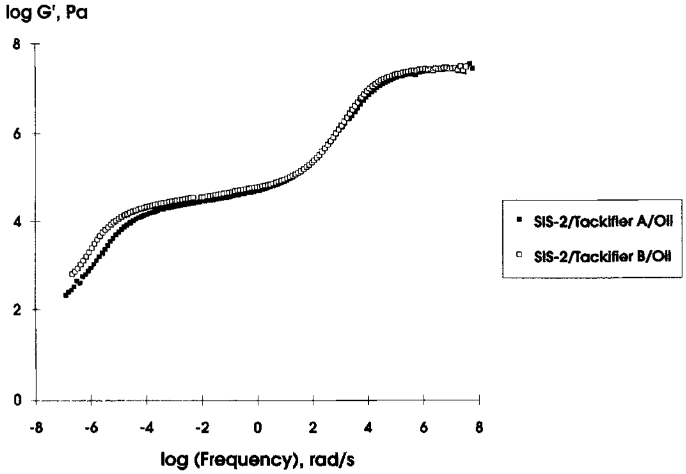

FIGURE 15 Comparison of master curves of storage modulus, G′, of PSAs based on experimental Escorez 1310LC tackifiers; reference temperature = 27°C.

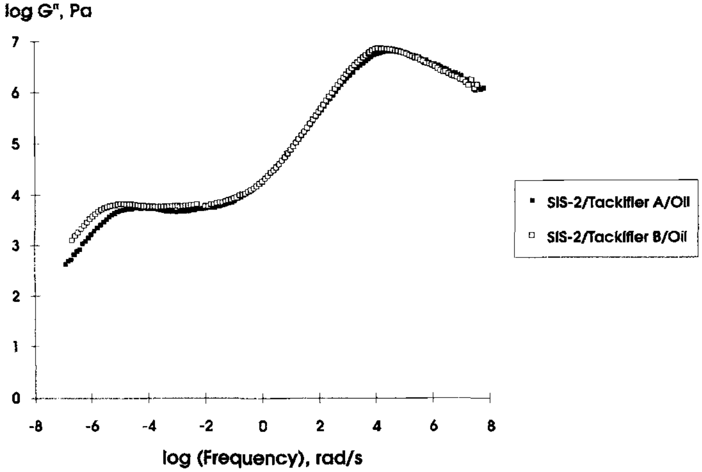

FIGURE 16 Comparison of master curves of loss modulus, G", of PSAs based on experimental Escorez 1310LC tackifiers; reference temperature = 27°C.

the surface tensions of both the PSA and rolling cylinder in similar rolling speed regions.

Final Comment

In our derivation of the mathematical expression for rolling ball tack, we believe that, up to Eq. (5):

$$s' = 0.691/\mu \tag{5}$$

our procedure should be correct and exact. Instead of using Eq. (6) from Gent and Henry [12], we can propose that

$$\mu = \text{Function } (P_o, B) = \text{ Function } (\gamma_a, \gamma_s, \gamma_{as}, B)$$

because $P_o \sim \gamma_a + \gamma_s - \gamma_{as}$ [8]. In the last equation, γ_a is the surface tension of the PSA, γ_s is the surface tension of the steel ball, and γ_{as} is the interfacial tension between the PSA and the steel surface. Another concern about applying Eq. (6) to PSAs has been addressed by Mizumachi [13]. He pointed out that μ of a PSA should consist of two terms: one term caused by the compressive deformation of the PSA as described by, for example, Eq. (6), and another term caused by the adhesion or extensional deformation of the PSA. Therefore, future work should be done along these directions to derive an exact equation describing rolling ball tack of tackified block copolymer adhesives.

Next, spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS) and SSIMS should be used to characterize surfaces of model PSA systems for a better understanding of the relationship between surface structure and ball tack. This will also help us confirm the distribution of the tackifier or the diluent in the polystyrene and polyisoprene phases, and in the bulk and surface regions of the SIS polymer.

CONCLUSIONS

- Overall, the modification of a block copolymer PSA by a lower surface tension and a lower molecular weight diluent tends to produce a larger increase in rolling ball tack. It is speculated that this diluent segregates on the PSA surface, forming a weak boundary layer (WBL). The ball will subsequently be coated by the diluent (cohesive failure) because of the much higher surface energy of the steel ball and stopped at a shorter roll-out distance on the PSA surface.
- Overall, the modification of a block copolymer PSA by a higher surface tension and/or a more compatible diluent tends to produce a larger increase in loop, peel and quick stick. This type of diluent should reside in the polyisoprene matrix of SIS. The result is a lower plateau modulus, but a higher energy dissipation at the PSA debonding frequency [2], producing higher loop, peel and quick stick.
- Overall, the modification of a block copolymer PSA by a lower surface tension and a lower molecular weight diluent decreases SAFT. Part of the diluent possibly intrudes into the polystyrene domains of SIS, impairing domain integrity and high temperature shear performance [3].
- Experimental values of rolling ball tack do not follow an equation derived from mechanics and PSA bulk viscoelastic behavior. Also, with increasing tackifier level in SIS, they show very different behavior compared with loop, peel, quick stick and probe tack.

These suggest ball tack, different from other PSA performance, is related more to surface properties than to bulk properties of the adhesive.

Two PSAs based on SIS and experimental Escorez 1310LC tackifiers exhibit similar loop, peel, SAFT and viscoelastic behavior, but different rolling ball tack. A similar viscoelastic behavior should mean a similar debonding term, D. Therefore, ball tack differs for different P_o and B terms. In other words, in the model [1–3]: $P = P_oBD$, ball tack may depend more on the interfacial adhesion term, P_o, and the bonding term, B, whereas loop, peel, and probe tack may depend more on the debonding term, D.

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References

[1] Tse, M. F. and McElrath, K. O., *Adhes. Age* **31**(10), 32 (1988).

[2] Tse, M. F., *J. Adhesion Sci. Technol.* **3**(7), 551 (1989).

[3] Tse, M. F. and Jacob, L., *J. Adhesion* **56**, 79 (1996).

[4] Urushizaki, F., Yamaguchi, H. and Mizumachi, H., *J. Adhesion Soc. Japan* **20**, 295 (1984).

[5] Mizumachi, H. and Saito, T., *J. Adhesion* **20**, 83 (1986).

[6] Tsukatani, T., Hata, T., Hatano, Y., Mizumachi, H. and Ramharack, R., *Eurocoat Conference* '91 Nice, France, September, 1991 and references therein.

[7] Brant, P., Private Communications (1993).

[8] Tse, M. F., *J. Adhesion* **48**, 149 (1995).

[9] Tse, M. F., *J. Adhesion* **66**, 61 (1998).

[10] Fox, T. G. and Loshaek, S., *J. Polym. Sci.* **15**, 371 (1955).

[11] Wu, S., *Polymer Interface and Adhesion* (Marcel Dekker, New York, 1982).

[12] Gent, A. N. and Henry, R. L., *Trans. Soc. Rheol.* **13:2**, 255 (1969).

[13] Mizumachi, H., *J. Appl. Polym. Sci.* **30**, 2675 (1985).