Mechanistic Studies in Tackified Acrylic Emulsion Pressure Sensitive Adhesives

SINGA D. TOBING,[1,2] ANDREW KLEIN[2]

[1] Avery Dennison, 7670 Auburn Road, Painesville, Ohio 44077, USA

[2] Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, USA

ABSTRACT: Twenty-three wt % aqueous tackifier dispersion based on glycerol ester abietic acid (T_g = 64°C, M_w = 940) was added to emulsion polymer 50/32/15/3 poly(2-ethyl hexyl acrylate-*co*-vinyl acetate-*co*-dioctyl maleate-*co*-acrylic acid) pressure sensitive adhesive (PSA). From these latices, 25 μm thick films were cast. The films were dried at 25°C for 24 h or at 121°C for 5 min. Dynamic mechanical analysis (DMA) of the films included measuring elastic modulus (G') and damping factor (tan δ). Under the above drying conditions, the films did not produce significant differences in their DMA and PSA properties as measured by loop tack, peel, and shear holding power. DMA of the tackified acrylic film showed thermodynamic miscibility between the tackifier and polymer regardless of the drying conditions. Microgels formed during emulsion polymerization of the acrylic PSA brought inherent weakness to the tackified film properties. In the neat acrylic PSA film, these discrete networks entangled with the uncrosslinked chains while in the tackified film, these networks could not form entanglements due to the increased molecular weight between entanglements for the uncrosslinked chains. This lack of network entanglements caused shear holding power of the tackified acrylic PSA film to be 4× lower than that of the neat acrylic PSA film. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1965–1976, 2000

Key words: PSA; emulsion; tackifier; acrylic; network

INTRODUCTION

Pressure Sensitive Adhesives (PSAs) are viscoelastic-elastomeric materials that can adhere strongly to solid surfaces upon application of light contact pressure and short contact time. Commercial use of PSA covers a broad range of label, tape, medical, and cosmetic products. PSAs are different from viscous liquids in that typical peel energy required to peel a PSA tape off a substrate could range from 1 to 10 lbs/in. whereas a tape coated with a viscous liquid such as honey or molasses would only take ≤0.1 lbs/in. (S. Tobing, unpublished results).

The PSA adhesive properties are a result of three processes. First, when PSA-coated tape or label is bonded onto a substrate, the adhesive flows instantly to form intimate contact with the substrate even under a few grams of contact force. In viscoelastic terms, this means that its 1 s creep compliance ≥ 10^{-6}cm²/dyne.[1,2] Second, adsorption must take place by intermolecular interactions such as van der Waal attraction, dipole interaction, hydrogen bonding, or rarely, chemical reaction. Third, when the PSA tape is peeled off, a substrate, large viscoelastic energy dissipation must take place to get high-peel energy.

Lower bound approximation relating peel energy with viscoelastic energy dissipation (V.E.D.) and work of adhesion (W_a) can be expressed as[3]

$$\text{Peel energy} \propto W_a[1 + \text{V.E.D.}] \qquad (1)$$

and

$$W_a = \gamma_S + \gamma_A - \gamma_{SA} \qquad (2)$$

where γ_S is the substrate's surface energy, γ_A is the adhesive's surface energy, and γ_{SA} is the substrate-adhesive's interfacial surface energy. W_a is much smaller in quantity than V.E.D. and therefore, the measured peel energy is largely attributed to the viscoelastic properties. Zosel[3] showed that when polyisobutylene PSA peel adhesion was tested against various substrates with critical surface tensions ranging from 20 to 50 dynes/cm, a strong dependence on the substrate was observed at very short contact time (0.015 s) with the substrate. When the contact time was increased to 100 s, there was a weak dependence observed in peel energy.

There are three different types of PSAs used commercially today. They can be divided into solvent borne, water borne (emulsion), and hot melt (100% solid). Historically, the oldest PSA was made by blending natural rubber and rosin ester tackifier in toluene and heptane.[4] The PSA solution was coated onto paper and crepe to make masking tapes. To increase peel energy at high temperature and creep resistance (shear holding power), light crosslinking was done by adding a low level of sulfur. Hence, a higher performance product could be made by tailoring the network architecture and gel to sol ratio. Thermally initiated SBR emulsion was introduced during World War II that could be made into PSA by adding high level of rosin ester tackifier aqueous dispersion. Rosin ester dispersion was prepared by direct emulsification of molten resin in water. In the early 1960s, styrene-isoprene-styrene (SIS) block copolymer (Kraton®) was blended with high level of rosin ester and hydrocarbon tackifiers and napthenic oil to make hot melt (100% solid) PSAs using a heated sigma blade mixer. In the 1970s, both solution and emulsion polymerization of low glass transition temperature (T_g) acrylics such as poly(butyl acrylate) and poly(2-ethyl hexyl acrylate) gave inherently tacky PSAs without the need of adding tackifier. The absence of plasticizer and tackifier in acrylic PSAs made them an attractive choice when migration of low molecular weight components into a substrate was an issue. Another attractive feature of acrylic PSA in the label industry is that paper labels coated with acrylic PSA could be die cut at much faster web speed than those coated with SIS, SBR, or natural rubber based PSAs. Lower fracture toughness of acrylic polymers owing to their high entanglement molecular weights could be the cause. From the 1980s to today, strict VOC level reduction as required by the EPA Clean Air Act (Title 5) has made the use of solvent-borne PSAs unattractive. The high energy cost of the solvent recovery process and the limitation on the recovery rate and its impact on slowing down the coating web speed had reduced the consumption of solvent-borne PSAs.

Although both solvent- and water-borne acrylic PSAs are derived from the same monomers, the adhesive (peel and tack) and cohesive (shear holding power) properties of emulsion PSAs are much inferior to those of solvent PSAs. Early investigators believed that surfactant migration onto the PSA-substrate interface was the root cause of the problem, but later it was found that not all surfactants migrate onto the interface.[5–7] Delgado et al.[5,6] showed that post adding ammonium lauryl sulfate into crosslinked acrylic PSA caused a reduction in peel energy which improved after the PSA film was aged for 1 week at 72°F, 50% RH. On the contrary, nonyl phenol ethylene oxide[5,6] and hexadecyl pyridinium chloride[7] surfactants did not show reduction in peel energy when post added to as high as 8%. In short, surfactant migration can be minimized if the surfactant desorption rate is slow, its compatibility with the polymer film is high, and film forming characteristic of the latex is excellent.

Fundamentally, the major differences between emulsion and solvent PSA properties may be caused by the heterogeneous morphology and the distribution of discrete micro-networks in emulsion film. Charmeau et al[7] compared directly the peel energy of emulsion acrylic PSA film vs solvent cast PSA film made by dissolving the emulsion film into solvent. Solvent cast film showed higher peel energy than emulsion cast and the difference was significantly increased when structured latex with high T_g shell polymer or when high T_g PSA latex were used. Latex particles often have functional groups at the surface due to either the initiator persulfate or copolymerized acid groups. Based on the surface concentration of these groups, the particles may be considered

structured and film formation could be affected. Emulsion polymerization of low T_g acrylics carried out to complete conversion produced significant amount of microgels inside the particles due to chain transfer to polymer via hydrogen abstraction of tertiary vinyl carbons.[8] Discrete micro-networks were formed after film formation, in contrast to continuous network formed in solution acrylic PSA[9] when the film was crosslinked by either AlO_3 or TiO_4.

To increase the peel energy of emulsion acrylic PSAs, aqueous tackifier dispersion was added at 15–25 wt % into the base latex.[10−12] There are numerous problems created by this technology due to a lack of understanding of the emulsion film formation and the formation of the network morphology. Buildup on the die during the high speed rotary die cutting process was found as well as significantly lower shear holding power when compared with that of the neat emulsion. More surprisingly, peel energy from low surface energy substrates such as HDPE or LDPE showed little improvement when compared with that of the neat emulsion.

The purpose of this research is to seek fundamental understanding on the role of tackifier in water-borne acrylic PSAs by comparing it to high performance solvent-borne and hot melt PSAs. The mechanism of mixing aqueous dispersion tackifier with the neat acrylic emulsion will be derived from adhesion, viscoelastic, and morphological data. A molecular explanation will be presented to elucidate the mechanism of the problems inherent in the present system. Hot melt PSA based on tackified SIS block copolymer will be used as a comparative system in which the physical network is *continuous* throughout the film with the tackifier mainly bound to the polyisoprene block. Dynamic mechanical data (DMA) will be used to characterize PSA's T_g. Also, entanglement molecular weight will be compared for blends of *cis*-1,4 polyisoprene/tackifier vs *cis*-1,4 PI/oil.

EXPERIMENTAL

Materials

The neat emulsion acrylic used in this study was based on 50/32/15/3 poly(2-ethyl hexyl acrylate-*co*-vinyl acetate-*co*-dioctyl maleate-*co*-acrylic acid) made by semicontinuous emulsion polymerization where the vinyl acetate was added earlier in the monomer feed delay. The intensity mean diameter of the particles was 214 ± 44 nm as determined by dynamic light scattering. The aqueous tackifier dispersion was based on glycerol ester abietic acid (M_w = 940, PDI = 1.1, T_g = 64°C). The mean particle diameter for the tackifier dispersion was 514 ± 202 nm. Less than 10% by weight of the tackifiers had particle diameters between 2–5 μm representing the tail end of the distribution. The tackified emulsion acrylic was made by blending 77% by weight of the neat acrylic with 23% tackifier dispersion at room temperature for 15 min using low shear agitator.

The hot melt PSA used as a comparison was based on a blend of SIS/SI and tackifying resins (rosin ester and hydrocarbon) and napthanic oil at 40/50/10 composition. The SIS/SI blend had 15% polystyrene content and 50% diblock and the GPC molecular weight (M_w = M_n) of the triblock was 200,000 g/mol and of the diblock was 100,000.

The solvent-borne PSA used to illustrate the utility of PSA viscoelastic models was based on a blend of *cis*-1,4 polyisoprene (NATSYN® 2210) (M_w = 700,000) and hydrocarbon tackifier (WINGTAC® 95) (M_w = 2000) at 40/60 polymer/tackifier ratio. For the comparative purpose, a blend of polymer and napthanic oil (SHELLFLEX® 371) at the same ratio was also used. All the blends were prepared in 50/50 toluene/THF solvent blend.

PSA Testing

Emulsion PSAs were coated using wire-rod die directly onto 50 μm PET (MYLAR®) to give a 25 μm dry film thickness. For hot melt PSA, a heated knife-over-roll die was used to give 25 μm film thickness. A standard drying temperature of 121°C for 5 min was used to dry the emulsion film, unless it was otherwise indicated. PSA testing was done at 23°C and 50% R.H. and the samples were climatized into this condition 24 h before testing.

For the loop tack test, 1 × 8 in. (2.54 × 20.32 cm) strips were die cut from the PSA-coated MYLAR film. The strips were folded to form loops where on each ends, 1 × 2 in. paper was used to cover 1 × 1 in. area. Hence, the total perimeter of each loop was 6 in. Stainless steel, or HDPE substrates of 1 × 6 in. was mounted on the lower grip of the tensile tester and the loop was mounted on the upper grip. The upper grip holding the loop was brought in contact with the substrate using 12 in/min downward crosshead speed until the distance between the grip and the substrate

reached 1 in. making contact area of 1×1 in. After 1 s contact, the upper grip would be brought upward at 12 in/min crosshead speed until detachment occurred. The maximum force of detachment was recorded as loop tack.

For the peel test, 1×6 in. strips were die cut. The strips were laminated against the substrates using 4 lbs. rubber roller. After 15 min dwell, 90° peel off the substrate was done at 12 in./min. The average force for 1 in. wide tape was recorded as peel energy.

For shear holding power, $1/2 \times 1/2$ in. strips were die cut. The strips were laminated against stainless steel using 4 lbs. rubber roller to make contact areas of $1/2 \times 1/2$ in. After 15 min dwell time, at the end of the strips, 500 g weights were placed. Automatic timers were placed below the weights to count the time of failure. Thus, shear holding power is measured as time to failure in minutes.

Viscoelastic Characterization

Rheometrics® RDA II was used to study the PSA film viscoelastic properties. Dynamic mechanical analysis (DMA) measurements were done by heating the samples at 3°C/min, and by oscillating at 10 rad/s. For PSA films, the geometry used was 8 mm diameter disc parallel plates with 1.5 mm sample thickness at the starting temperature (-80°C). PSA films were prepared by direct coating onto siliconized paper, drying them, and plying them up to build thickness. DMA measurements were also done on insoluble (gel) and soluble (sol) fraction of the adhesive film following 48 h Soxlet extraction in THF. Since tackifiers are low molecular weight species ($M_w << M_e$), determination of T_g via tan δ peak requires special test geometry because parallel plate geometry will not be able to resolve that peak. Glass fiber cloth (0.20 $\times$ 1.25 $\times$ 50 mm) was impregnated with tackifier dispersion and completely dried at room temperature for 3 days followed by 50°C for 8 h. The dried composite was then pressed at 125°C to a uniform thickness. DMA was done using Rheometrics RMS-800 torsion rectangular geometry at 10 rad/s frequency. Glass fiber cloth was chosen because it only exhibited glassy behavior throughout the test temperature range.

Morphological Characterization

Tackified acrylic emulsion film was cast on microscopic glass slides by sliding a few drops of the emulsion between two glass surfaces. The emulsion was dried at 121°C for 5 min, or at room temperature. The dried films were stained by Os O_4 water vapor for transmission optical microscopy (TOM) and backscattered scanning electron microscopy (SEM). For transmission electron microscopy (TEM), the adhesive was cryomicrotomed to 0.1 μm sections before being stained.

Solvent Extraction and Swelling

Extraction of PSA films was done using a Soxhlet apparatus and hot THF as a solvent for 48 h. The gel fraction was determined gravimetrically. The gel also was used for DMA study. The soluble fraction was cast into film which was dried at 170°C for 10 min to be used for DMA study.

The gel fraction was compression molded between two release liners at 4000 psi and at 25°C to yield a film thickness of 25 μm. These films were then immersed in toluene at 25°C to measure swelling. The Flory-Rehner equation was used to calculate the average molecular weight between crosslink points (M_c).[13]

$$M_c = \frac{V_1 \rho [\phi^{1/3} - \phi/2]}{-[\ln(1 - \phi) + \phi + \chi\phi^2]} \quad (3)$$

where V_1 is molar volume of toluene (106.3 cm^3/mol), ϕ is the polymer volume fraction in solvent, and χ is polymer-solvent interaction parameter. If χ is not known, it can be estimated as follows[14]:

$$\chi = 0.34 + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (4)$$

where δ_1 is the solubility parameter of the polymer and δ_2 is the solubility parameter of toluene.

Molecular Weight Characterization

Wet emulsion, 0.2 g, was added into 10 mL THF and tumbled end-over-end for 2–4 h. Filtering was done by using a 0.45-μm TEFLON membrane syringe filter to separate the gel from the sol. GPC set up with 3 columns using 5-μm polystyrene particles was used to separate the molecular weights. The apparatus (Water Alliance 2690) was equipped with refractive index detector (Water 410) and data system (Water Millennium 32).

RESULTS AND DISCUSSION

Theory of PSA Viscoelasticity

T_g and entanglement molecular weight (M_e) are significant molecular parameters affecting PSA

adhesive properties.[2] While T_g relates to the onset of viscoelastic energy dissipation, M_e influences the elastic modulus. The T_g, on the other hand, is strongly dependent on the miscibility of the components in the PSA. For crosslinked PSAs, it is believed that molecular weight between crosslink points (M_c), gel and sol contents, molecular weight of the sol (uncrosslinked) fraction, and the network morphology are equally important parameters influencing PSA performance.

To evaluate the contribution of the viscoelastic theory to explain PSA performance, DMA measurements were done on *cis*-1,4 polyisoprene, on a 40/60 blend with hydrocarbon tackifier and a 40/60 blend with oil. Figure 1(a and b) shows G' (elastic modulus) vs temperature and tan δ (damping factor) vs temperature of the three samples. The T_gs of the blends follow those predicted by the Fox equation and hence they are all miscible (see Table I)

$$\frac{1}{T_g} = \frac{W_{\text{polymer}}}{T_{g,\text{polymer}}} + \frac{W_{\text{resin}}}{T_{g,\text{resin}}} \quad (5)$$

where w_i are the weight fractions and T_gs are in absolute temperature. For the rubber/oil blend, a single sharp T_g was observed whereas for the rubber/tackifier blend, a single but broad T_g signifies micro-heterogeneous microstructure. This is expected in lieu of the many different isomeric components that make up the tackifier composition (*cis*, trans 1,4 isoprene, vinyl isoprene, piperylene) with each having different T_gs and degree of miscibility with the polymer. Nonetheless, when eq. (5) was used to predict T_g of the blend from the known values of the T_g of the rubber (218°K) and the *average* T_g of the tackifier (347°K), the number agreed with the experimental data as determined by DMA.

Table I shows a summary of the important viscoelastic data taken from Figure 1. Whereas the rubber/tackifier blend is a PSA exhibiting high peel energy, the rubber/oil blend is not, as shown in Table I. At 25°C, the G' of both rubber/tackifier and rubber/oil blends was $<10^6$ dyne/cm^2, which gave rise to the same degree of contact with a substrate if the interfacial energies were similar. When peeled off a substrate, the rubber/oil blend did not impart high viscoelastic energy dissipation. Under large deformation, the adhesive filaments did not have high cohesive strength

(a)

(b)
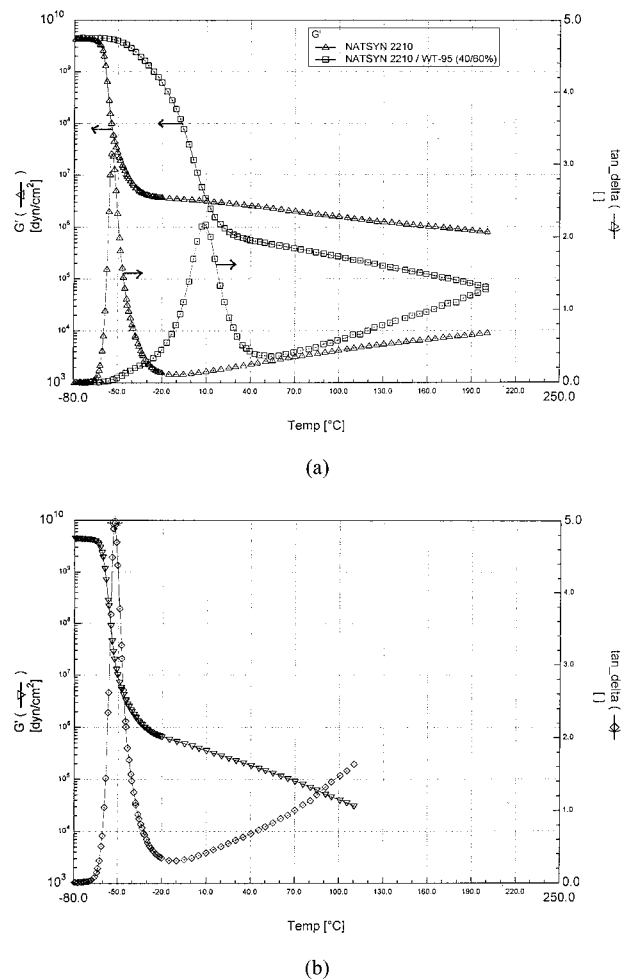
Figure 1   (a) DMA of *cis*-1,4 polyisoprene (NATSYN) and the WT-95® blend at 40/60 wt ratio. WT-95 is aliphatic tackifying resin (C5); (b) DMA of *cis*-1,4 polyisoprene (NATSYN) and napthanic oil blend at 40/60 ratio.

to yield high viscoelastic energy dissipation. The lack of cohesive strength could be inferred from the G' vs T curves at elevated temperatures which dropped off rapidly. Under small deformation, i.e., the start of the peeling process, the rubber/oil blend also did not give high viscoelastic energy dissipation. Chang[2] estimated that the DMA frequency ≈ 100 rad/s corresponded to 12 in./min peeling rate. According to the WLF principle, this peeling rate would correspond to looking at G'' at 5°C lower than room temperature (i.e., 20°C) since the DMA test was done at 10 rad/s. Lower G'' at peeling condition for the rubber/oil blend caused low viscoelastic energy dissipation which lowered peel energy. Note: $G'' = (G')(\tan δ)$.

Table I Viscoelastic Properties of Rubber/Tackifier and Rubber/Oil Blends

	Rubber[a]	Rubber/Tackifier[b]	Rubber/Oil[c]
T_g (°C)	−54	9	−52
Calculated T_g	—	7.58	−54
G_n^o (dyne/cm^2)	3.45×10^6	4.64×10^5	5.33×10^5
Calculated G_n^o (dyne/cm^2)[d]	—	4.2×10^5	4.2×10^5
T onset for rubbery region (°C)	−10	54	−10
M_e (g/mol)[e]	5685	52,708	36,903
G', 25°C (dyne/cm^2)	2.8×10^6	7.9×10^5	2.6×10^5
tan δ, 25°C	0.2	0.89	0.55
G', 25°C	3.0×10^6	1×10^6	3×10^5
G'', 20°C	6×10^5	1.3×10^6	1.74×10^5
90° peel (lbs./in.)	—	2	0.25

[a] Synthetic *cis*-1,4 polyisoprene (NATSYN 2210).
[b] 40/60 NATSYN 2210/WINGTAC 95 Blend.
[c] 40/60 NATSYN 2210/SHELLFLEX 371 Blend.
[d] Calculated using plasticizer model.
[e] Calculated using eq. (6).

Another utility of DMA data is to determine entanglement mol wt (M_e). M_e can be estimated from rubbery plateau modulus (G_n^o) as follows[14]:

$$M_e = \frac{\rho R T}{G_n^o} \qquad (6)$$

where ρ is density of the polymer or blend, R is 8.31×10^7 dyne-cm/mol °K, T is absolute temperature where G_n^o is located, and G_n^o is determined from G' at the onset of rubbery region (usually where tan δ reaches minimum following the prominent maximum). For crosslinked PSA, it is determined as a point of inflection in tan δ curve following the prominent maximum.

G_n^o can also be calculated by using the plasticizer model for compatible rubber/tackifier or rubber/oil blends as follows[15]:

$$G_n^o = [G_{n,\text{polymer}}^o]\phi^{2.3} \qquad (7)$$
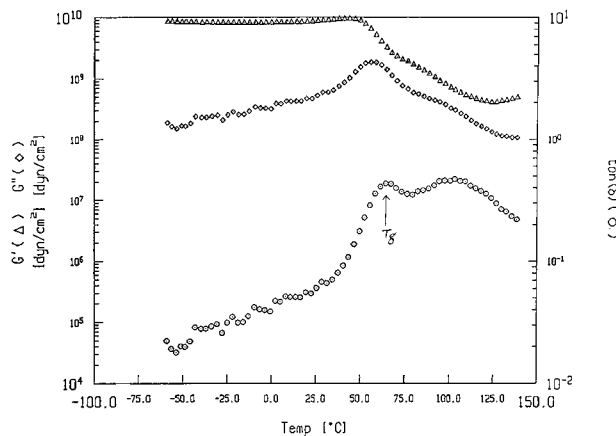
where ϕ is the polymer volume fraction.

As shown in Table I, M_e increased from 5685 to 52,708 for the rubber/tackifier blend and to 36,903 for the rubber/oil blend. The reported value of M_e for polyisoprene (untackified) was 3500.[16] The discrepancy (5685 vs 3500) came from the fact that drying the solvent cast film at 171°C for 15 min gave rise to discoloration, indicating some thermal degradation. The low molecular weight components could act as plasticizer to increase M_e. The reported values for inherently tacky poly(*n*-butyl acrylate) and poly(2-ethyl hexyl acrylate) PSAs were 26,000 and 130,000, respectively.[3,17] These seem to be in the same order of magnitude with the rubber/tackifier blend. High M_e value (10^4–10^5) is needed for PSA film to undergo fibrillation during the peeling process which significantly increases peel energy.[17]

Effect of Drying Condition on Morphology, Viscoelastic Properties, and Adhesion

In tackified acrylic emulsion PSA, one question needs to be answered is how the tackifier could achieve the state of mixing with the polymer given the fact that the tackifier has a high T_g (64°C) and there is no solvent or high shear device to aid in this process. Furthermore, commercial drying processes have very short residence times and limited temperature range (normally ≤121°C for 1/2 min). The DMA of tackifier impregnated in glass fiber cloths is shown in Figure 2. From the tan δ peak, the T_g was estimated to be 64°C.

After the particle contact film formation stage, the tackifier molecules could either diffuse from one tackifier particle to the other (assuming that $T_{\text{drying}} >> T_g$), or, as a competitive process, they could diffuse into the polymer. The relative rates of these two processes could be estimated by their diffusion coefficients. Tackifier self-diffusion coefficient above the T_g was reported to be 10^{-8} cm^2/s using spin echo NMR.[18] There was no experimental data available for the diffusion coefficient of the tackifier into the polymer so it had to be estimated. The translatory solvent friction coefficient (ξ_1) of ethyl alcohol into poly(methyl acry-

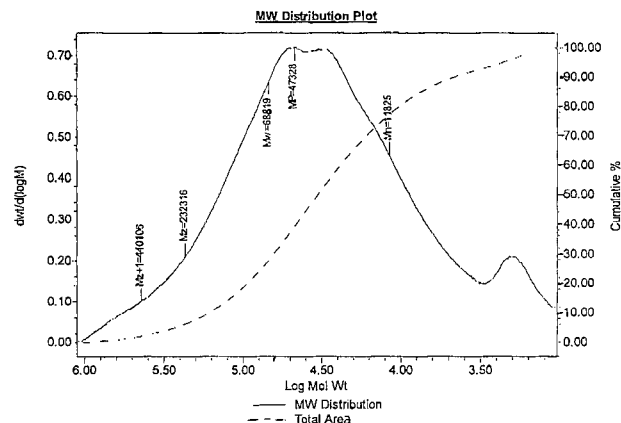**Figure 2** DMA of glycerol ester abietic acid impregnated in glass cloth.

Figure 3 GPC of neat acrylic emulsion PSA (THF-soluble fraction) based on poly(2-ethylhexyl acrylate-*co*-vinyl acetate-*co*-dioctylmaleate-*co*-acrylic acid).

late) was reported as $10^{-3.69}$ dyne-s/cm.[19] Since the friction coefficient (ξ_1) is proportional to viscosity and viscosity of the tackifier at 121°C was three orders of magnitude higher than that of ethyl alcohol, hence ξ_1 for the tackifier in the polymer scales to $10^{-0.69}$. The diffusion coefficient (D_o) of the tackifier in the polymer could then be estimated[19] as:

$$D_o = \frac{RT}{6.023 \times 10^{23} \xi_1} \tag{8}$$

which gives D_o a value of 2.67×10^{-13}cm^2/s which is five orders of magnitude smaller than the tackifier self-diffusion coefficient. Based on this information, tackifier coalescence was more likely than mixing of tackifiers with polymer at 121°C.

It turns out, however, that this hypothesis is incorrect. The THF soluble fraction of the acrylic PSA contained a large fraction of low molecular weight, low T_g ($T_g = -10$°C) species. In fact, as shown in Figure 3, GPC analysis indicates greater than 70% of the sol fraction had molecular weights less than $2\times M_e$, where M_e is 30,000 g/mol; calculation and discussion is given in the next section. It is hypothesized that these oligomeric species were very mobile and they were diffusing into the tackifier molecules as soon as the particles were in contact with one another. This is particularly important in network polymers, because the gel fraction was left without the linear chains, and once these linear chains were tackified, they could no longer entangle with the gel fraction.

Tackified emulsion acrylic PSA containing 23 wt % tackifier was dried at well above and below

T_g of the tackifier, but well above the T_g of the polymer. The drying condition used was 121°C for 5 min, or 25°C for 1 day to ensure complete drying for the 25 μm thick films. DMA curves of the films dried at these two conditions are shown in Figure 4. Regardless of the drying conditions, DMA curves were remarkably similar with increased T_g for tackified PSA compared with the neat acrylic. Both conditions gave complete mixing indicated by a single T_g and no broadening of tan δ peaks compared with the neat sample. Contrary to this finding, an emulsion blend of polystyrene (PS) and polybutyl-acrylate (PBA) at 25 wt % PS, showed strong dependence on annealing temperatures.[20,21] Film dried at room temperature showed a single T_g (T_g of PBA) and lower rubbery G' indicating that PS particles were just acting as
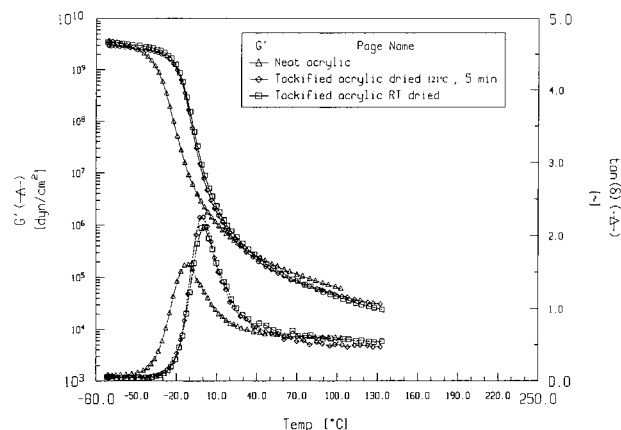
Figure 4 DMA of neat and tackified acrylic emulsion PSA.

**Table II   Effect of Drying Condition on PSA Properties[a]**

	Neat Acrylic (RT Dried, 1 day)	Neat Acrylic (121°C, 5 min)	Tackified Acrylic (RT Dried, 1 day)	Tackified Acrylic (121°C, 5 min)
Stainless steel				
Loop tack (lb./in.)	3.4	3.4	4.8	4.9 (stick-slip)
90° peel (lb./in.)	2.6	2.6	3.9	3.9 (stick-slip)
Shear holding power (h) (500 g × 1/2 × 1/2 in.)	3.0	3.0	0.7	0.7
HDPE				
Loop tack (lb./in.)	1.2	1.2	1.4	1.4 (stick-slip)

[a] 25 μm adhesive coated on 50 μm MYLAR.

fillers. When annealing temperature was raised above the T_g of PS, the DMA curve showed 2 T_gs corresponding to those of PBA and PS. In addition, rubbery G' was significantly higher due to coalescence of PS particles forming interconnected morphology.
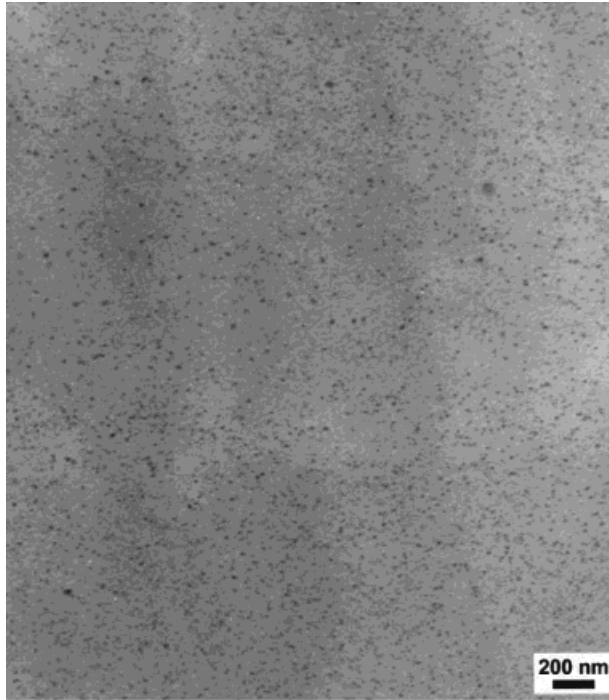
PSA properties as a function of drying condition of the films are shown in Table II. Tackified acrylic PSAs dried at room temperature and at 121°C for 5 min showed no difference in PSA properties. As expected, neat acrylic dried at two different conditions also showed no difference in PSA properties. Furthermore, the DMA data (Fig. 4) showed identical single T_g and no broadening in tan δ peak compared with that of the neat acrylic which indicates complete mixing was achieved probably due to fast diffusing species from soluble fraction of the polymer.

Morphological characterization was done on stained tackified acrylic PSA using TOM, backscattered SEM, and TEM. Os O_4 was used to react with the unsaturation of the tackifier (glycerol ester abietic acid) to give image contrast. Figure 5(a and b) show the presence of unmixed (still intact) large tackifier particles ($\approx$2–5 μm) in both RT and 121°C, 5 min dried film viewed by TOM. In both cases, they were present at much lower level than 23 wt % as shown later. Figure 6(a and b) shows TEM of microtomed RT and oven-dried samples. In both cases, the stained tackifiers are on the scale of a few nanometers which indicates molecular mixing. Figure 7(a and b) showed backscattered SEM of 25°C, 1 day and 121°C, 5 min dried samples. There are a few intact tackifier particles ($\approx$5 μm) on the surface of the oven-dried film while they are absent on the room temperature dried film. This may mean that drying above the T_g of the tackifier increases the tackifier's self diffusion coefficient to form coalesced particles
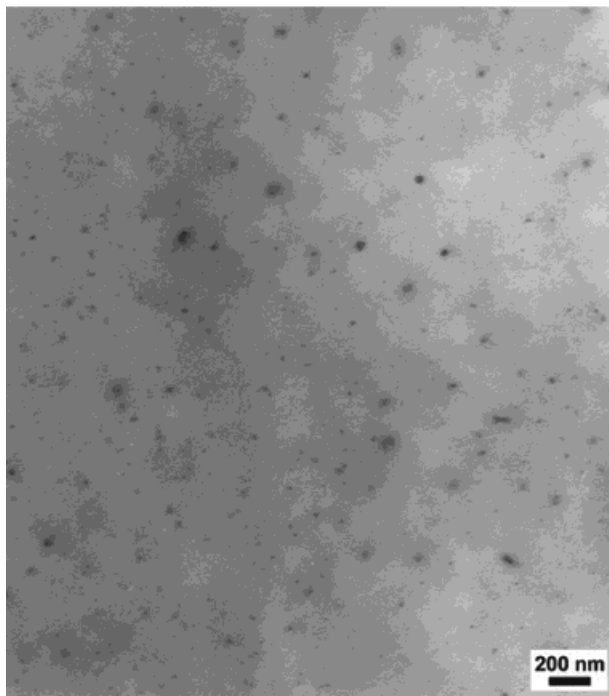

20 microns

(a)

20 microns

(b)
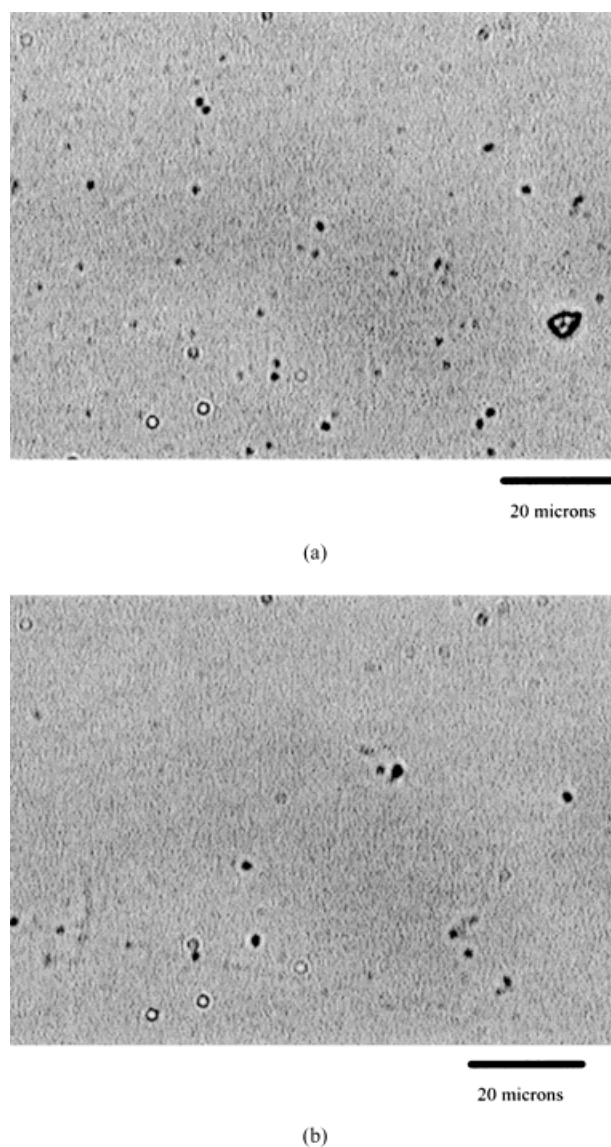
Figure 5   (a) Transmission optical micrograph of Os O_4 stained tackified acrylic dried at 25°C for 1 day; (b) transmission optical micrograph of Os O_4 stained tackified acrylic dried at 121°C for 5 min.

which are either squeezed to the surface by the film formation process, or smaller particles coalescing on the surface. This picture also assumes that solubility limit of the tackifier is reached at about 17% and the remaining 6% is in insoluble particles as shown below. As shown in Table II, film dried at 121°C for 5 min showed a stick-slip peel pattern which might be attributed by reduced contact area caused by the large tackifier particles occupying the surface.
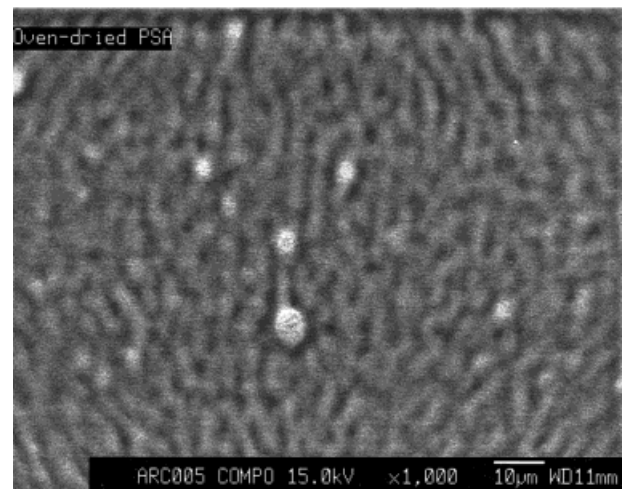

Figure 6   (a) Transmission electron micrograph of Os O$_4$ stained tackified acrylic dried at 25°C for 1 day; (b) transmission electron micrograph of Os O$_4$ stained tackified acrylic dried at 121°C for 5 min.

Figure 7   (a) Scanning electron micrograph (backscatter) of Os O$_4$ stained tackified acrylic dried at 25°C for 1 day; (b) scanning electron micrograph (backscatter) of Os O$_4$ stained tackified acrylic dried at 121°C for 5 min.
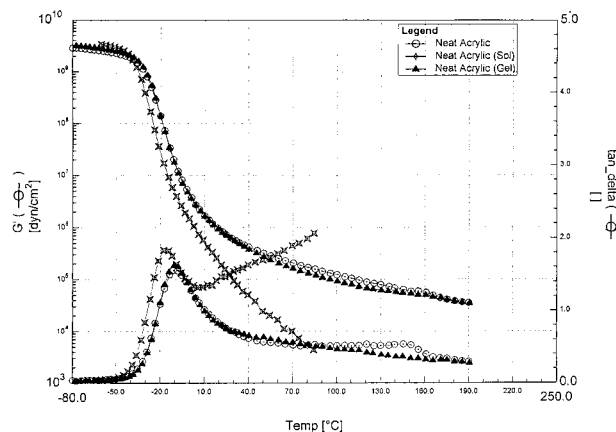
Figure 8 DMA of neat emulsion acrylic PSA, its THF-soluble (sol) and THF-insoluble (gel) fractions. Acrylic PSA is based on poly(2-ethylhexyl acrylate-*co*-vinyl acetate-*co*-dioctylmaleate-*co*-acrylic acid).

Effect of Tackifier Addition on Viscoelastic Properties and Adhesion

In this section, PSA properties of neat and tacki-fied emulsion acrylic will be compared against SIS based hot melt PSAs. The results will be discussed in terms of the six most significant molecular parameters [T_g, M_e, M_c, mol wt of the THF-soluble fraction (uncrosslinked chains), % polymer network in the adhesive, and network morphology] that affect PSA properties.

DMA curves of the neat acrylic PSA film, its THF-extracted gel and sol fractions are shown in Figure 8. It is clear that the soluble fraction contained mostly low molecular weight species (oligomers) since tan δ values in the rubbery region were greater than 1. This was confirmed by the GPC data (Fig. 3) where M_w = 68,819, and M_n = 11,825. Entanglement mol wt (M_e) was then calculated using eq. (6) from G_n^o of the sol fraction and the value was 30,913 g/mol. Hence, as shown in Figure 3, greater than 70% of the sol fractions were species with mol wt less than $2 \times M_e$. To provide mechanical strength, mol wt of a polymer must be greater than $2 \times M_e$[14] and therefore most of the soluble fraction could be considered as plas-ticizer.

An examination of DMA curves for the adhe-sive (emulsion cast) vs the gel fraction revealed the presence of structured latex morphology in the adhesive (see Fig. 8). The rubbery G' (i.e., G' at $T \geq 30°C$) of the adhesive was higher than that of the gel fraction. Furthermore, there was a T_g peak at 150°C (small tan δ peak) corresponding to

that of polyacrylic acid. Reported value for T_g of polyacrylic acid determined by DSC at 20°C/min heating rate was 130°C.[22] The 20°C difference between DMA T_g (tan δ peak) and DSC T_g was consistent with the data measured earlier for tackifier. DSC T_g of the rosin ester tackifier done at 20°C/min heating rate was 44°C while DMA T_g was 64°C.

Mol wt between crosslink points (M_c) of the gel fraction was determined by swelling the gel in toluene. Using eq. (3), M_c was determined to be 52,000 g/mol (ϕ = .0656, χ = .347). Using a Soxhlet apparatus, THF extraction of the adhe-sive resulted in 50% insoluble (gel). If the mean particle diameter of the neat acrylic emulsion was 200 nm and half of the volume was occupied by the network, the mean end-to-end distance of each crosslink segment (mol wt 52,000) would be estimated as 10 nm and hence each network in-side a particle would have ≈16 segments. Thus, these micro-networks had molecular dimension equivalent to a polymer having ≈10^6g/mol mol wt. The chain ends from the micro-networks could entangle with the uncrosslinked chains which in turn could entangle with other chain ends from another particle after film formation because M_c > M_e.

DMA curves of the neat and tackified emulsion acrylic films are shown in Figure 4. Taking T_g of the neat acrylic as −10°C (263°K) and T_g of the tackifier as 64°C, the calculated T_g for the tacki-fied acrylic at 23 wt % tackifier was 4°C. The DMA T_g (tan δ peak) was 0°C and the difference could be attributed to ≈6 wt % undissolved tacki-fiers when calculated using eq. (5) (Fox equation). This finding is supported by the TOM data shown in Figure 5(a and b).

An important issue in tackification of emulsion acrylic PSA is whether or not the tackifiers could plasticize the network or they mainly stayed in the uncrosslinked chains. The rubbery plateau modulus (G_n^o) for the neat acrylic was 9×10^5 dynes/cm² and that for the tackified acrylic was 2.6×10^5 dynes/cm². Using eq. (7), the calculated G_n^o for the tackified acrylic (23 wt % tackifier) would be 4.93×10^5 dynes/cm². Therefore, over plasticization had occurred which means that most of the tackifiers were located outside the networks. An estimate of M_e for the tackified acrylic could be calculated using eq. (6) from the DMA data shown in Figure 4 and the value was approximately 93,000 g/mol. Note that both en-tanglement and crosslinking contribution were included in this approximation since the tackified

Table III   PSA Properties[a] of Neat and Tackified Emulsion Acrylic PSAs Vs SIS-Based Hot Melt PSA and Their Molecular Parameters

	Neat Acrylic	Tackified Acrylic	SIS-Hot Melt[b]
T_g (°C)	−10	0	10
% polymer network	50	38.5	20
M_e (g/mol)	30,000	≈ 93,000	52,000
M_c (g/mol)	52,000	52,000	170,000[c]
M_w of the nonnetwork	68,819	68,819 + 940 (bimodal)	100,000 + 940 (bimodal)
Network architecture	Discrete, entangled	Discrete, separated	Continuous
Stainless Steel			
Loop tack (lb./in.)	3.4	4.9 (stick-slip)	6
90° peel (lb./in.)	2.6	3.9 (stick-slip)	5
Shear holding power (h)	3.0	0.7	20
LDPE			
90° Peel (lbf/in.)	0.42 (stick-slip)	0.50 (stick-slip)	1.65

[a] Twenty-five micron PSA coated on 50 μm MYLAR.
[b] Fifty percent diblock SIS. SIS/tackifier/oil 40/50/10. Styrene content 15%, $M_w = 200,000$.
[c] Estimated value for physical network due to PS association.

acrylic contained both the sol and gel fraction. Under this scenario, $M_e > M_c$, which means in tackified acrylic, the chain ends emanating from the micro-networks did not entangle with the chains from the soluble fraction. As a result, cohesive strength of the tackified acrylic is expected to be significantly lower than that of the neat acrylic.

PSA properties of the neat and tackified emulsion acrylic PSA are compared against SIS/SI based hot melt PSA in Table III. The hot melt PSA was made of (SIS/SI)/tackifier/oil at 40/50/10 blend composition. M_w of the triblock was 200,000 g/mol and the diblock was 100,000 g/mol and triblock to diblock ratio was 1 : 1. The styrene content was 15%. Based on this information, the % polymer network (physical) in the PSA formulation was estimated to be 20% and $M_c \approx 170,000$ g/mol. M_e could be estimated as 52,000 g/mol for the polyisoprene block (see Table I). Note that network formation was due to PS domain association in SIS.

As shown in Table III, both loop tack and 90° peel off stainless steel were increased by the addition of 23 wt % tackifier into the neat emulsion acrylic, but the shear holding power was decreased by 4×. This is consistent with the DMA finding where in tackified acrylic, the micro-networks were no longer entangled with the uncrosslinked chains since $M_e > M_c$. On the other hand, in SIS hot melt PSA, the shear holding power was much higher than the emulsion acrylic although the % polymer network in the adhesive

was lower. Network continuity was probably the reason for the enhanced cohesive strength.

The addition of 23 wt % tackifier did not bring any improvement in 90° peel off LDPE in emulsion acrylic PSA. The peel off LDPE was much inferior to that of SIS-based hot melt PSA. Since most of the tackifiers were located outside the micro-networks, therefore, the micro-networks remained unplasticized. Adhesion to low energy substrate requires significant viscous flow onto the crevices (hills and valleys) of a substrate to obtain excellent mechanical anchoring and unplasticized networks are too rigid to comply with this requirement.

CONCLUSIONS

Tackified emulsion acrylic PSA dried at 25°C for 1 day, or, at 121°C for 5 min (tackifier's T_g = 64°C) did not show any difference in their PSA and viscoelastic properties. Mixing of the tackifier and polymer took place during film formation via rapid diffusion of uncrosslinked (THF − soluble) − low T_g (T_g = −10°C) acrylic chains (M_w = 68,000; M_n = 11,825; M_e = 30,000) into the tackifiers. From experimental observation of the adhesive film morphology and DMAs, T_g estimation using the Fox equation, the solubility limit of the tackifier in the polymer was estimated to be ≈17 wt %.

The presence of micro-gels (50 wt %) inside the acrylic latex particles led to discrete networks in
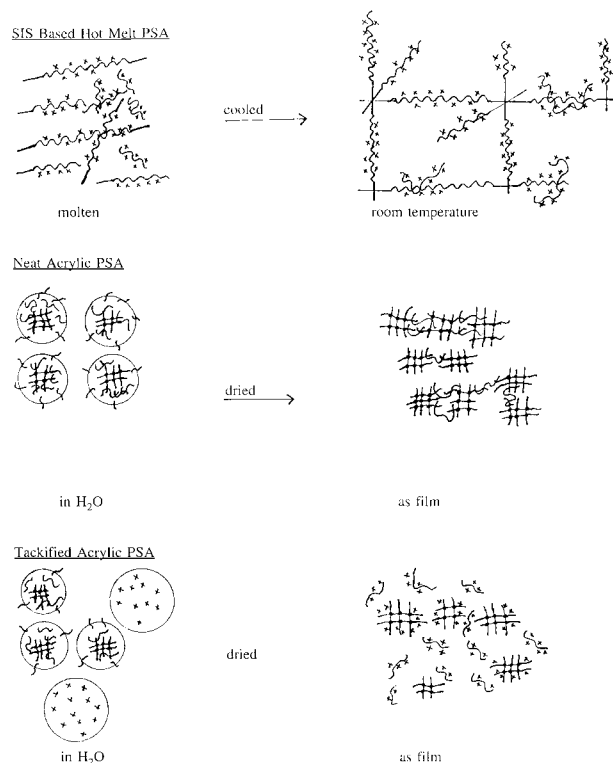
Figure 9   Schematic morphology of PSA films.

the PSA film. In the neat acrylic, these networks could entangle with the uncrosslinked chains since $M_c > M_e$, while in tackified acrylic, these networks could *not* entangle with the un-crosslinked chains since $M_c < M_e$. As a result, shear holding power of the tackified acrylic (23 wt % tackifier) was 4× lower than the neat acrylics. Another disadvantage of having micro-gels formed inside the latex particles prior to film formation was that the tackifiers would not be able to tackify the networks, which resulted in only weak improvement in adhesion on low energy substrates such as HDPE or LDPE. Contrary to this, SIS-based hot melt PSA, where the tackifiers were placed inside and outside the physical network, could give high shear holding power and excellent adhesion on low energy substrates. Schematic morphology of SIS-based hot melt PSA, neat and tackified emulsion acrylic PSA are shown in Figure 9.

REFERENCES

1. Dahlquist, C. A. In Adhesion: Fundamentals and Practice; Eley, D. D., Ed.; McLaren: London, 1966.
2. Chang, E. P. J Adhes 1991, 34, 189.
3. Zosel, A. Colloid Polym Sci 1985, 263, 541.
4. Satas, D. Handbook of Pressure Sensitive Adhesives; Van Nostrand Reinhold: New York, 1989.
5. Delgado, J.; Clemmens, L. M.; Sheridan, M. M. Proceeding of the International PSA Technoforum, Tokyo, Japan, 1997; p. 33.
6. Delgado, J.; Kinning, D. J.; Lu, Y. Y.; Tran, T. V. Proceedings of the 19th Adhesion Society Meeting, 1996; p. 342.
7. Charmeau, J. Y.; Berthet, R.; Grigreau, C.; Holl, Y.; Kleitz, E. J Adhes Adhes 1997, 17, 169.
8. Lovell, P. A.; Shah, T. H. Polym Commun 1991, 32, 98.
9. Anderson, C. U.S. Pat. 3, 769, 254, 1973. 10 Bernard, M. U.S. Pat. 5, 623, 011, 1997.
11. Lombardi, R. A. Paper, Film, Foil Converting 1988, 62, 74.
12. Sehgal K. C.; Sherwin, M. A. First World Congress Pressure Sensitive Tape Council Meeting, Chicago, IL 1992, 5, 85.
13. Sperling, L. H. Introduction to Physical Polymer Science; John Wiley & Sons: New York, 1985.
14. Coleman, M.; Graf, J.; Painter, P. Specific Interactions and the Miscibility of Polymer Blends; Technomic Publishing Co.: Lancaster, PA, 1991.
15. Wool, R. P. Polymer Interfaces Structure and Strength; Hanser/Gardner Publications, 1995.
16. Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. Macromolecules 1994, 27, 4639.
17. Zosel, A.; Ley, G. Macromolecules 1993, 26, 2222; Int J Adhes Adhes 1998, 18, 265.
18. Paiva, A.; Foster, M.; Von Meerwall, E. J Polym Sci Part B 1998, 36, 373.
19. Ferry, J. D. Viscoelastic Properties of Polymers; John Wiley & Sons: New York, 1961.
20. Cavaille, J. Y.; Vassoille, R.; Thollet, G.; Rios, L.; Pichot, C. Colloid Polym Sci 1991, 269, 248.
21. Hidalgo, M.; Cavaille, J. Y.; Guillot, J.; Guyot, A.; Pichot, C.; Rios, L.; Vassoille, R. Colloid Polym Sci 1992, 270, 1208.
22. Lovell, P. A.; El Aasser, M. S. Emulsion Polymerization and Emulsion Polymers; John Wiley & Sons: New York, 1997;Chapter 18.