

The Viscoelastic Properties of Natural Rubber Pressure-Sensitive Adhesive Using Acrylic Resin as a Tackifier

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Received 19 March 2002; accepted 18 June 2002

ABSTRACT: Acrylic tackifier resins were prepared by free radical polymerization. A natural rubber base was prepared from Standard Malaysian Rubber through mechanical milling. The acrylic tackifier was blended with the rubber base in various ratios. The blends were coated onto strips of paper and tested for shear and peel strengths. Circular samples of the blends were cast onto release paper and their viscoelastic properties studied using DMTA. On plotting storage modulus G' against frequency, differences between the low fre-

quencies and high frequencies explain the change in pressure-sensitive adhesive (psa) properties as the percentage of tackifier resin was varied. Blends with good psa have higher loss tangent at higher frequencies. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2118–2123, 2003

Key words: viscoelastic properties; natural rubber; pressure sensitive adhesives; acrylic resin; tackifier

INTRODUCTION

Pressure sensitive adhesive (psa) is defined as a viscoelastic material, which in a solvent free state, remains permanently tacky at room temperature.¹ Such material will adhere instantaneously to most solid surfaces with the application of very slight manual pressure. It is well known that the properties of psa are strongly dependent on their viscoelastic properties. During bonding, the adhesive must be brought into intimate contact with the substrate on a molecular scale.² For this to happen, the adhesive should have proper flow and wetting characteristics. For good tack, the adhesive has to be viscous during the bonding stage. It is essential to relax the stress created in the adhesive when it is made to conform to the topographic irregularities of the adherend. If the bond deformations were only elastic and recoverable, the stored stress would assist external stress in the rupture of the bond.³ Thus, bonding is a low rate process at low deformation while debonding is a high rate process at high deformation. The shear strength test is essentially a creep test carried to high deformation.

The rate of separation of the adhesive from the substrate is important for all psa properties including tack. If the rate of deformation is too high, no flow or yield can occur. The system then behaves elastically

and the film ruptures. At lower rates the adhesive can flow and yield forming strings of adhesive.

Generally psa can be made by blending a low molecular weight resin and an elastomer such as natural rubber. The resin is described as a tackifier if by adding it to rubber; the resulting composition has the properties of a psa. Most common tackifiers used in natural rubber formulations are amorphous material at room temperature and have a softening point ranging from room temperature to 150°C. They usually have molecular weights in the range of 200 to 5000 and a structure that is large and rigid. The increase of tack with the addition of such hard polymers is coincident with the formation of a second phase.⁴ This two-phase theory was first proposed by Wetzel, who investigated psa of natural and synthetic rubber with rosin ester tackifiers. He explained the characteristic variation of tack with different proportions of tackifier by the formation of a two-phase system. At low resin concentration (<40%), tack is only slightly raised over that of natural rubber. This is due to the resin being completely soluble in rubber. The rapid rise of tack above 40% tackifier is, according to Wetzel, due to rubber being saturated with resin and the development of a second phase consisting of resin and low molecular weight rubber. This disperse phase is assumed to have a much lower viscosity than the rubber phase and thus have better wetting properties. The second phase continues to develop until the maximum amount of low molecular weight material has dissolved in the disperse phase resin. This is the point of maximum tack. Further increase of resin content causes increasing brittleness in the resin phase until a phase inversion

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occurs. The continuous phase becomes nontacky and is unable to wet the adherend. Electron microscopy has shown the existence of the two phases.

Viscoelastic properties of the rubber-resin systems have been studied by various researchers.⁵⁻¹¹ However, these publications were mostly related to the effects of viscoelasticity on peel strength using conventional tackifiers. This report describes the change of shear and peel strength due to changes of viscoelastic properties using a tackifier which by itself has good psa properties.

EXPERIMENTAL

Materials

The natural rubber used was Standard Malaysian Rubber (SMR5). The monomers used were commercial grades supplied by Elf Altochem. The other chemicals used were standard laboratory reagents.

Preparation of acrylic resin

The monomers 2-ethylhexyl acrylate and methyl methacrylate were washed in 2% sodium hydroxide solution twice to remove the inhibitors and then rinsed thrice with deionized water. A stock solution of chain transfer agent CBr_4 was prepared by dissolving 0.5 g of CBr_4 in 99.5 g of 2-ethylhexylacrylate. The monomers mixture consisting of 42.0 g of 2-ethylhexylacrylate, 6.0 g methyl methacrylate, and 6.0 g acrylic acid was placed in a 250-mL conical flask and mixed with 108.0 g ethyl acetate as solvent; 0.18 g of azobisisobutyronitrile initiator was then added, followed by 6.0 g of the stock solution of CBr_4 . The flask was purged with nitrogen and capped, and placed in a water bath set at 55°C. The temperature was held constant throughout the experiment. The content was stirred using a magnetic stirrer. The reaction was set to run for 24 h. At the end of the experiment, 1 mL of 10% solution of hydroquinone was added to stop further reaction.

Number-average molecular weight

Vapor pressure osmometry was used to determine the number average molecular weight of the resin. The resin was dried in vacuum and redissolved in toluene. An Osmomat model 070-B osmometer was used with concentration of the resin in toluene varying from 90 to 150 g/kg.

Preparation of rubber base

Standard Malaysian Rubber (SMR 5) was chosen as the rubber base for the pressure-sensitive adhesive (psa). It was milled using a laboratory two roll mill

with the roller gap set at 0.2–0.4 mm. The milled sheet was folded four times and then sent through the mill again. This was repeated 45 times. The rubber was dissolved in toluene to a concentration of 10%.

The viscosity of the milled rubber was determined using the Ubbelohde viscometer in a water bath adjusted to $30 \pm 0.01^\circ\text{C}$. The samples were dissolved in analar grade toluene at about 0.3% solids content. The solution was filtered through a 25-micron sintered glass filter. The weight of polymer retained by the filter was recorded as the gel content. 10.0 ml of the filtrate was measured into the viscometer and the solution flow times were determined. The viscosity average molecular weight (M_v) was determined using the Mark Houwink-Sakurada equation. For natural rubber in toluene at 30°C the values of the constants a and K were taken to be 0.67 and 5.02×10^{-4} respectively¹² for the calculation of M_v .

Preparation of the psa

Blends of the acrylic tackifier in the milled natural rubber were prepared in ratios of 10, 20, 30, 50, 70, 90, and 100%. Each of the blends was prepared as a toluene solution and coated onto paper strips for testing.

The flexible backing used was 100 μm (4 mil) paper laminated with a thin polyethylene layer. The polymer solution (10% solids) was spread onto the backing strips using a laboratory adhesive coating machine manufactured by Chemitest. This machine consists of an adhesive reservoir that feeds two accurately grounded stainless steel doctor rollers. These doctor rollers can be adjusted accurately and their gap monitored by a micrometer. The coating gap was set to give a wet film thickness of 2 mil (50 μm). After coating, the samples were allowed to dry in air for 1 week before carrying out further tests.

Testing of the adhesive strips

The adhesive strips were tested for shear strength in accordance to ASTM D3654-78 and the peel strength according to ASTM D3330. The load used for the shear test was 1 kg. The peel and shear strength were carried out immediately upon preparation of the tapes on the panels. The stainless steel panel used measured 5 in by 2 in wide with a bright-annealed finish. A steel roller 3.25 inches in diameter and 1.75 in wide covered with rubber 0.25 in thick and weighing 4.5 lbs was used to apply the tapes onto the panel. The tests were carried out at 25°C. The shear tests were carried out using a test stand that held the panel with the tape applied at an angle of 2° to the vertical. A universal testing machine with a 100 lbf load cell was used for measuring the peel strength. The pulling rate used was 12 inches per min. After each test, the plate was cleaned

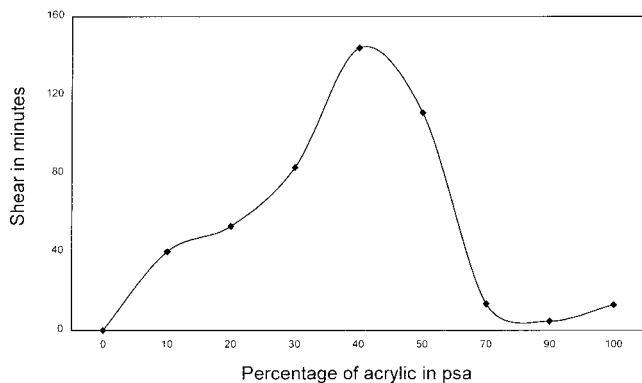


Figure 1 Shear strength vs. percentage of acrylic resin in the psa.

with acetone three times before the next sample was tested.

Fourier transform infrared spectroscopy

The FTIR spectra were recorded on a Perkin-Elmer FTIR 1600 instrument at 16 scans from 4000 to 400 cm^{-1} . The cast film method was employed, where films of the polymers were cast from their solution directly on sodium chloride cell by evaporating off the solvent using a hot air blower.

Temperature gradient phase diagram

The various blends of rubber and tackifiers at different proportions were dissolved in toluene. The solutions were visually inspected. Film samples were made by spreading the polymer solution onto glass slides and the solvent allowed to evaporate off. The films were checked for clarity or opacity. The samples were then placed in an oven and the temperature raised in a stepwise manner by 10°C every 24 h up to 150°C. The films were checked visually at each interval, sometimes with the help of a magnifying glass, to determine if any phase separation had occurred at the specified temperature.

DMTA determination of viscoelastic properties

Circular samples of the various blends were cast onto release paper in layers of approximately 0.1 mm. Each layer was allowed to dry for 2 days before casting the next layer. The thickness of each of the samples was built up to 1 mm. The storage modulus G' and $\tan \delta$ of the complex shear modulus were determined for each of the sample using a Perkin-Elmer dynamic mechanical thermal analyzer model DMTA 7. A parallel plate configuration consisting of two round metal plates of diameter 10.0 mm was used. The sample disc was loaded in between the plates. An environmental chamber surrounded the test fixture and maintained

the sample at $29 \pm 0.2^\circ\text{C}$. During the test, the top plate moved in an oscillatory manner with frequencies from 0.2 to 50 Hz in the compression mode. The bottom plate was fixed and transducers attached to it recorded the stress transferred through the sample. The viscoelastic properties were processed and calculated with the help of computer software.

RESULTS AND DISCUSSION

The acrylic resin used as tackifier had psa properties. The peel strength measured was 3.0 lbf/in and the shear strength was 13.3 min. The number average molecular weight M_n , as determined using vapor pressure osmometry, was 12,400.

The milled Standard Malaysian Rubber after passing through the mill 45 times had a gel content of 7.5% and a viscosity average molecular weight M_v of 269,000. It had no psa properties.

The results of the shear and peel strengths measurements of the psa comprising of mixtures of acrylic resin with the milled SMR were as shown in Figures 1 and 2.

Shear strengths (Fig. 1) start at 0 for a pure rubber, which has been milled 45 times. The shear strength increased steadily as the percentage of acrylic tackifier increased up to a maximum at 40%, above which the shear strength decreased fairly rapidly till a minimum at 90% acrylic tackifier. The shear strength of the acrylic resin alone was 13.3 min. The peel strength (Fig. 2) also increased from zero to a maximum at 40% tackifier and then decreased to a minimum at 90%. The peel strength of 100% acrylic resin was 3.0 lbf/in.

To obtain more information on the behavior of the adhesives, the shear storage modulus G' for various proportions of acrylic tackifier was studied. The storage modulus G' is defined as the stress in phase with the strain in a sinusoidal shear deformation divided by the strain; it is a measure of energy stored and recovered per cycle.¹³ G' at low frequency is related to the wetting and creep behavior of the adhesive. Thus, its value at low frequencies should preferably be low

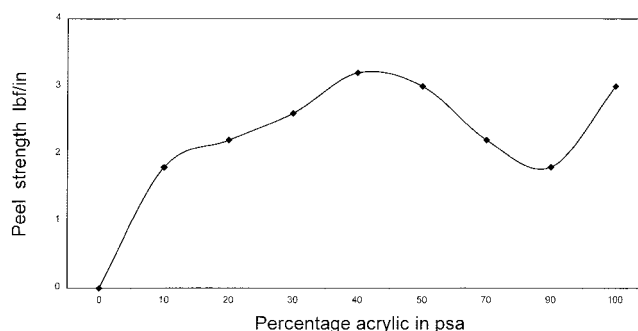


Figure 2 Peel strength vs. percentage of acrylic resin in the psa.

TABLE I
Shear Storage Modulus, G' , (MPa) for Various Proportions of Acrylic Resin in Natural Rubber Measured with at Specific Frequency Sweep

Percentage of acrylic in psa	Frequency					
	50 Hz	40 Hz	30 Hz	20 Hz	10 Hz	0.2 Hz
0%	0.83	0.95	1.04	1.09	1.10	0.80
10%	1.40	1.48	1.51	1.53	1.48	1.00
20%	1.58	1.65	1.65	1.65	1.55	1.03
30%	1.90	2.09	2.10	2.02	1.90	1.10
40%	2.35	2.40	2.40	2.30	2.10	1.10
50%	3.03	3.20	3.20	3.05	2.75	1.20
70%	4.15	4.10	4.00	3.90	3.55	1.50
80%	4.40	4.40	4.40	4.25	3.35	1.80
90%	7.50	6.70	6.20	5.80	5.10	1.90
100%	6.00	5.40	5.20	4.60	4.00	1.51

so that the adhesive will be soft enough to flow and wet the substrate during the bonding process. G' at high frequency (around 50 Hz) may be related to the peel or quick stick properties of the pressure-sensitive adhesives. The storage modulus at high frequencies should be high for good pressure-sensitive adhesives because it depicts the resistance to deformation at peeling.¹⁴ G' for pure milled natural rubber was at the lowest for each frequency. As the acrylic resin is increased, the G' had increased across the entire frequency range. This behavior is what would be expected from reinforcing filler. It indicates that the acrylic psa was incompatible with the natural rubber phase. Blends of natural rubber with a compatible tackifying resin are expected to behave in a different way. As the concentration of resin increase, the G' of the blend should decrease.¹⁴

The blends with increasing peel and shear strengths (10 to 40% acrylic resin in natural rubber) all have low G' from 1.0 to 1.1 MPa at 0.2 Hz. This showed that the psa samples have good wetting properties at bonding. On the other hand, G' of samples with 50–90% acrylic resin start to increase with higher acrylic content, in-

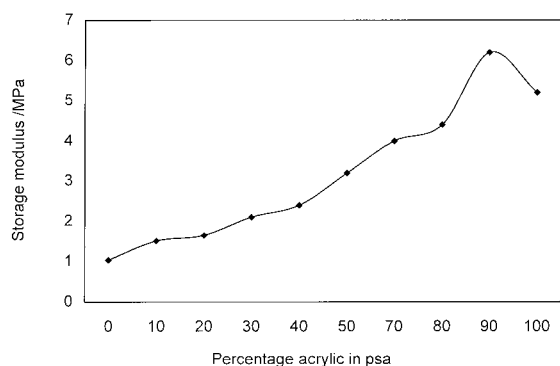


Figure 3 Storage modulus vs. % acrylic in adhesives measured at 30 Hz.

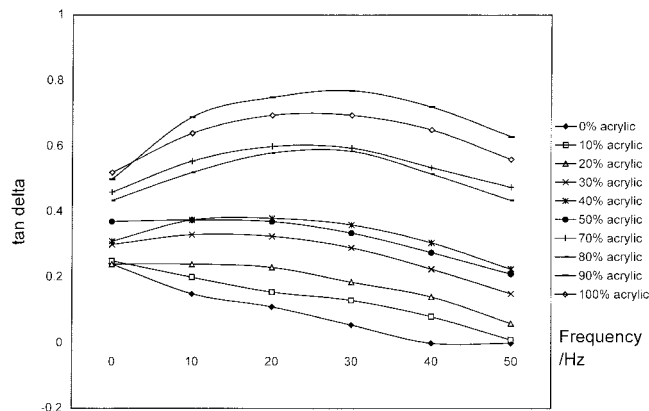


Figure 4 $\tan \delta$ vs. frequency for various blends of acrylic with natural rubber.

dicating that the wetting during bonding is decreasing, as shown in Table I.

The storage modulus at 30 Hz (Fig. 3) showed a steady rise in synchrony with the rise of peel and shear strength for blends from 0 to 40% acrylic tackifiers. Above 40% of acrylic tackifier the shear and peel strength starts to fall even though the storage modulus continue to increase. This could be explained by the loss in wetting properties as indicated by the increase in storage modulus at 0.2 Hz for blends with more than 50% acrylic.

$\tan \delta$ is a measure of energy lost to energy stored in a cyclic deformation. It is the ratio of the loss modulus to the storage modulus.¹³ The $\tan \delta$ was plotted against frequency as shown in Figure 4. The curve for pure rubber has higher $\tan \delta$ at low frequencies than at high frequencies. The $\tan \delta$ for increasing percentages of acrylic tends to increase with increase from low to mid frequencies as opposed to the results for pure rubber. The values at mid frequencies increased faster than those at higher and lower frequencies.

Figure 5 shows that the FTIR spectrum of pure acrylic tackifier has a C=O peak at 1726 cm^{-1} , which was absent in the natural rubber. On the other hand,

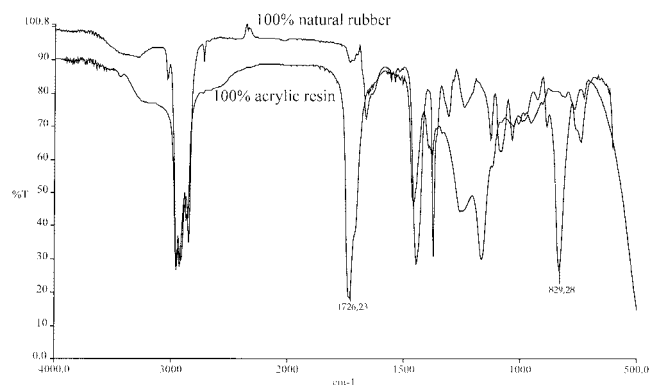


Figure 5 FTIR spectra of 100% acrylic resin and 100% natural rubber.

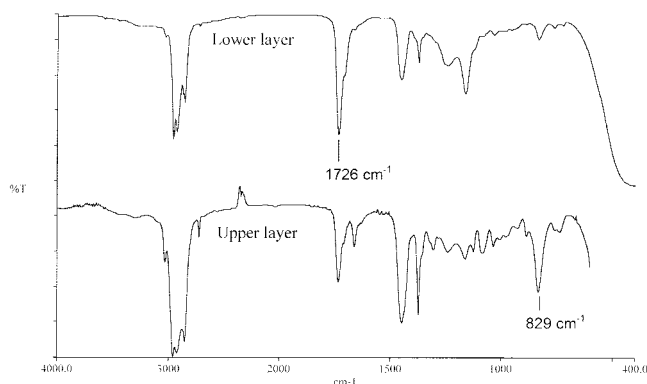


Figure 6 Blend of 50% acrylic resin and 50% natural rubber in toluene allowed to stand for 2 weeks until phase separation was observed. The upper layer consists of the rubber phase saturated with dissolved acrylic resin, while the lower layer consists mainly of the acrylic resin with very little natural rubber.

the spectra of pure rubber has a peak at 829 cm^{-1} due to $\text{C}=\text{C}$ double bond, which was absent in the acrylic resin. As such, these peaks could be an indication of the relative proportion of one component in the other.

The miscibility of the components was checked by allowing phase separation of the mixture by standing undisturbed for 2 weeks. Two fractions of different compositions were observed. Examination of the top fraction of the phase separated 50% acrylic mixture (Fig. 6) showed that the ratio of peaks at 1726 cm^{-1} to the peak at 829 cm^{-1} to be 0.986. The spectrum of the blend with 10% acrylic tackifier had a A_{1726}/A_{829} peak ratio of 1.2. Thus, the top fraction of a 50% acrylic tackifier/rubber mixture upon standing for 2 weeks has about slightly less than 10% acrylic tackifier. The spectrum of the bottom fraction (Fig. 6) has a very small peak at 829 cm^{-1} compared to the peak at 1727

cm^{-1} . This showed that rubber was much less soluble in the acrylic tackifier. This observation differs from the original Wetzel theory, which states that the onset of pressure sensitive properties of the tackifier is brought about by low molecular fractions of the base material dissolving in the tackifier. The above findings can explain why the storage modulus of the 100% acrylic psa was actually lower than the modulus of the 90% acrylic tackifier blend despite the fact that rubber is a softer material. For the 90% acrylic tackifier blend, the continuous phase will be the acrylic. The addition of rubber to the acrylic polymer will cause some low molecular weight acrylic to dissolve in the rubber. This will make the continuous phase of acrylic harder, and is reflected in the increased storage modulus. The rubber in the dispersed phase does not affect the overall modulus sufficiently.

Phase diagrams could be used to investigate the degree of miscibility between components. Blends, depending on the miscibility, were classified into miscible type, lower critical solution temperature type, upper critical solution temperature type and immiscible type.¹⁵

Table II represents a phase diagram for blends of acrylic tackifier and natural rubber. The pure materials (0 and 100% acrylic) were clear at all temperatures. At room temperature it was shown that phase separation occurred at concentrations of more than 20% acrylic. As the temperature was increased the phase separation occurred at higher percentages until at 150°C when the blends were miscible at all ratios. As such this system exhibits an upper critical solution temperature, i.e., the components are miscible at elevated temperatures but phase separation occurs at lower temperatures. This is typically found in blends of polymer/oligomer systems.

TABLE II
Phase Diagram of Blends of Acrylic Resin with Natural Rubber

Temp $^\circ\text{C}$	Percentage of acrylic								
	0%	10%	20%	30%	40%	50%	70%	90%	100%
30	C	C	H	H	H	H	SH	SH	C
40	C	C	H	H	H	H	SH	SH	C
50	C	C	H	H	H	H	SH	SH	C
60	C	C	SH	H	H	H	SH	SH	C
70	C	C	SH	H	H	H	SH	SH	C
80	C	C	SH	H	H	H	SH	SH	C
90	C	C	SH	H	H	H	SH	C	C
100	C	C	SH	H	H	H	SH	C	C
110	C	C	SH	H	H	H	SH	C	C
120	C	C	SH	H	H	H	SH	C	C
130	C	C	C	SH	SH	SH	C	C	C
140	C	C	C	SH	SH	SH	C	C	C
150	C	C	C	C	C	C	C	C	C
160	C	C	C	C	C	C	C	C	C

C = clear; SH = slightly hazy; H = hazy.

CONCLUSION

Acrylic pressure sensitive adhesive can be used as a tackifier for natural rubber-based adhesives. They form two phases, but unlike traditional tackifiers, natural rubber do not dissolve to any considerable extent in the acrylic. The mixture can be described by a phase diagram of upper critical solution type.¹⁵ However, the original two-phase theory of Wetzel, which states that tack is developed by low molecular weights of the base dissolving in the tackifier, does not apply.⁴ The behavior of the adhesive can be adequately explained by its viscoelastic properties. For a good pressure-sensitive adhesive, the ratio of storage modulus at high frequencies to low frequencies should be high. They also have a higher loss tangent at high frequencies than at low frequencies. The pure acrylic pressure sensitive resin had a shear strength of 13 min and peel strength of 3.0 lbf/in. On the other hand, natural rubber-based PSA with acrylic resin as a tackifier exhibited better shear strength of up to 144 min and the peel strength of 3.2 lbf/in. In this system besides molecular weights, the existence and proportion of a second phase significantly influences the properties of the pressure-sensitive adhesive.

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