

# A Hot-Melt Pressure-Sensitive Adhesive Based on Styrene–Butadiene–Styrene Rubber. The Effect of Adhesive Composition on the Properties

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## SYNOPSIS

Hot-melt pressure-sensitive adhesives based on styrene–butadiene block copolymers with aliphatic and aromatic tackifying resins and plastifying oils have been analyzed. The importance of the resin structure in the compatibility with the block copolymer and the influence of the different paraffinic-naphthenic character of the oil in PSA performance have been shown. Ternary systems with a fixed polymer content (30%) and with variable resin and oil contents show a good miscibility over the whole range of compositions, and only one glass transition temperature was found in each composition. The relationship between chemical composition and bulk performance are expressed in terms of the viscoelastic behavior of the adhesives, measured by DMTA. It has been shown that at a given resin content there is a minimum on  $\tan \delta$  peak vs. temperature, the melt viscosities present a plateau region and the tack strength shows a maximum. An important conclusion is that phase separation is not a requirement for maximum tack; some restricted miscibility is enough, present in a few microdomains of the blend. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Hot-Melt pressure-sensitive adhesives are generally blends of block copolymers with modifying resins and other additives in order to improve the characteristics and performance.

The viscoelastic properties of the bulk adhesive depend on the chemical composition of its components and are related to the final properties of these materials.<sup>1–11</sup> In a general sense, the bonding and debonding processes that take place, corresponding to the adhesion to a surface and to the resistance to separation, respectively, are viscoelastic processes. Bonding takes place at low rates and at low deformation. On the contrary, debonding is a high rate and high deformation process. Because of these general rheological characteristics, the properties of the adhesive are strongly dependent on their composition, qualitative and quantitatively considered and, therefore, on the compati-

bility of the components in a system that it is multiphase.

As a consequence of the varied composition in the blends of the main component, elastomer, with tackifying resins and oils, the thermal transitions and the dynamic-mechanical relaxations may be very variable, conditioning the performance and final properties such as tack, peel strength, and shear strength. Thus, thermal transition measurements have been carried out by Differential Scanning Calorimetry (DSC) and the viscoelastic relaxations have been determined by Dynamic Mechanical Thermal Analysis (DMTA), by observing the differences in mechanical properties as a function of temperature.<sup>12–14</sup> Changes in the storage ( $E'$ ) and loss ( $E''$ ) moduli or in the  $\tan \delta = E''/E'$  have been used to characterize the behavior of both the pure components and the blends.

Earlier studies on natural rubber-based adhesives and the influence of low molecular weight resins have been carried out by using DMTA techniques, and have demonstrated the importance of these studies.<sup>1–3</sup> Similar studies of resins blended with

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**Table I** Description of the Elastomer

Parameter	Value
$M_n$	122000
$M_w$	149000
$M_w/M_n$	1.22
$T_{g\text{BUTADIENE}}$ , °C (DSC)	-85
$T_{g\text{STYRENE}}$ , °C (DSC)	+95
Bound styrene, %	30
Polymer type	Radial

styrene-isoprene-styrene block copolymers were reported by Krauss and co-workers.<sup>4,5</sup>

A more systematic analysis of rubber-resin blends, based on natural rubber and styrene-butadiene rubber was reported by Class and Chu.<sup>6-8</sup> They studied the relationship between the structure, concentration, and molecular weight of the resin and their effect on the viscoelastic properties of the rubber-resin composition. These authors also attempted to correlate the viscoelastic properties of the adhesive and its PSA performance.<sup>9</sup>

The main objective of this work is the analysis of hot-melt pressure-sensitive adhesives based on styrene-butadiene block copolymers with aliphatic and aromatic tackifying resins using an oil as a plasticizing component. This analysis includes the study of the correlation between adhesive properties and structural parameters. These correlations are fundamental in order to maximize the optimal performance or to predict the properties of commercial formulations.

## EXPERIMENTAL

### Materials

A commercial block copolymer SBS (Calprene, Repsol Química) was used in this study. Polymer

characterization data are given in Table I. Molecular weights were determined by gel permeation chromatography using universal calibration.

Commercial polymeric resins of low molecular weight, from Hercules Co., commonly used in the formulation of pressure-sensitive adhesives, were used. Their names and composition are: Piccotac 95: Aliphatic resin derived from petroleum monomers; Hercotac 205: Modified aliphatic resin; and Foralyn 110: Pentaerythritol ester of hydrogenated rosin.

Resins properties are shown in Table II. The infrared spectra of the three resins are given in Figure 1. The previously unreported aromatic character of Hercotac-205 is clearly shown.

Three oils, with paraffinic or paraffinic-naphthenic structure, were used as diluents. They have different content in paraffinic carbon. The most interesting properties are described in Table III.

Hot-melt adhesives were prepared by mixing the components in a 1 liter glass Büchi reactor at a temperature of 180°C. The order of adding the components to the reactor was the following: first the oil, resins, and antioxidant were poured into the reactor, and after 5 min the corresponding milled rubber was added. The blends were stirred during 30 min and minimizing contact with air by purging with nitrogen gas. A phenolic antioxidant, Irganox 1010, was used as a thermal stabilizer. The hot-melt adhesives were discharged from the mixer to a holding tank and were cooled to room temperature.

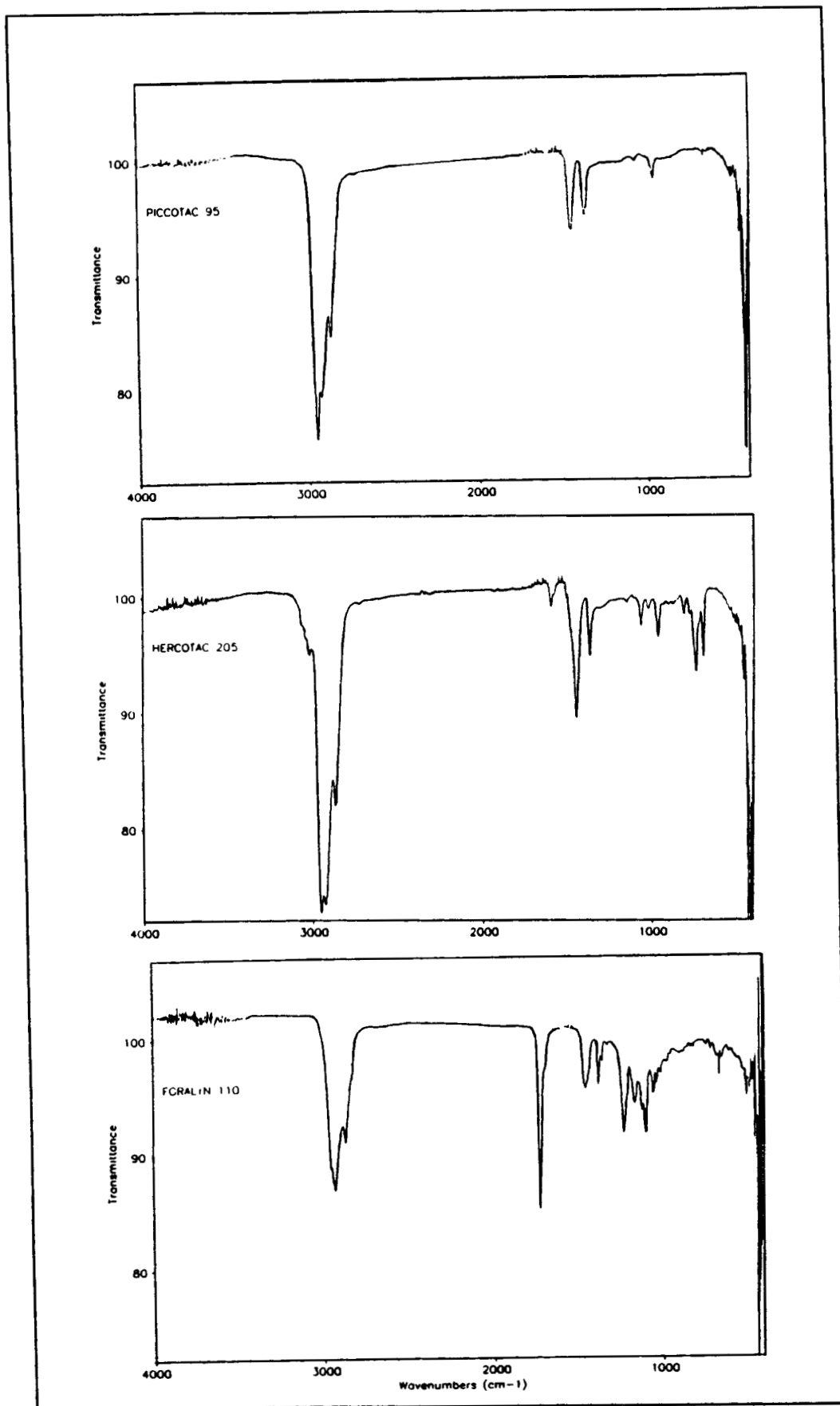
## Methods

### Apparent Viscosity (Brookfield Viscosity)

Apparent viscosity was measured in a Brookfield Synchro-Lectric Viscometer Model DV-II with a Brookfield Thermosel System to accurately measure the viscosity at elevated temperatures, 160 and

**Table II** Description of Resins

	Piccotac 95	Hercotac 205	Foralyn 110
$M_w$	1500	1400	885
$M_n$	870	815	740
$M_w/M_n$	1.72	1.72	1.20
$T_g$ , °C (DSC)	47.0	44.0	59.6
MMAp, °C	95	35	5
DACP, °C	47	-10	-40
Drop softening point, °C	96	107	106
Softening point ring & ball, °C	95	95	103



**Figure 1** FT-IR spectra of Foralyn-110, Hercotac-205, and Piccotac-95 resins recorded at room temperature.

**Table III** Description of Oils

	Oil-1	Oil-2	Oil-3
Paraffinic carbons, %	73	69	62
Naphthenic carbons, %	24	25	32
Aromatic carbons, %	3	6	6
Viscosity at 100°C, ctsk	4.5	11	11
Viscosity at 40°C, ctsk	24	100	135
DSC: $T_g$ , °C	-85	-70	-61

180°C. A SC4-31 spindle was used to measure a viscosity range of 300 to 100,000 cps.

### Thermal Properties

The glass transition temperatures were measured using a Mettler TA4000 Differential Scanning Calorimeter with a DSC 30 furnace at a heating rate of 10°C/min. The transition temperatures were recorded as the midpoint of the endothermic shift in the DSC curve corresponding to the increase in specific heat, on the second heating run.

Drop softening points were measured in a FP-83 Mettler furnace. A 6.35 mm sample cup was over-filled on a brass plate with 0.5 g of the adhesive pitch. The temperature of the cup was then increased by approximately 45°C above the expected softening point for a few minutes in order to fit the adhesive into the appropriate geometry. The sample cup was then cooled down to room temperature. The drop softening point determination was made by elevating the temperature from 40°C to the softening point at a rate of 5°C/min.

### Dynamic Mechanical Properties

*Sweep Temperature.* The dynamic shear storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of the adhesives were measured at a frequency of 1 Hz and from -100 to 30°C at a ramp rate of 2°C/min. These measurements were carried out using a tension-compression mode at constant dynamic force on a Perkin-Elmer DMA 7. Except for a few experiments, the measurements were recorded for a range of frequencies from 0.2 to 10 Hz.

### Adhesives Performance

*Peel Test (180°).* Films, approximately 0.025 mm thick, were compression molded at 160°C between 0.1 mm thick aluminum film. Strips with dimensions 25 × 30.5 mm (22.9 mm of bonded length) were cut from the compression molded sheets. The measurements were carried out in an Instron Tensometer

model 4301. The grip separation rate was 254 mm/min for all of the specimens. Peel or stripping values were taken after 127 mm from the initial peak (close to half of the bonded area).

*Polyken Probe Tack Test.* Films, approximately 0.06 mm thick, were compression molded at 160°C between silicone release paper and 0.76 mm thick polyester film. The equipment used for the measurements was a Polyken Probe Tack Tester. In this type of test a probe of precisely defined surface composition and dimension was brought into contact with the adhesive film for 5 s (dwell time) under fixed-load conditions, during which the tacky film deforms and "wets" the surface of the probe with which it is in contact. The probe was then pulled off the film at a rate of 2.5 cm per second and the force, in grams, was recorded. As with other tack tests, the film thickness and room temperature parameters must be accurately controlled.

## RESULTS AND DISCUSSION

### General Characteristics of Hot-Melt Pressure-Sensitive Adhesives Based on SBS Rubbers

This study has been carried out on hot-melt pressure-sensitive adhesives, HMPSA. These are ternary systems, including in their compositions the block copolymer, resins, and plasticizers, instead of the most general analogs, solution pressure-sensitive adhesives based on binary systems, including only polymers and resins.

The SBS block copolymer is the principal component in this type of adhesive. Because of the two phase morphology,<sup>15</sup> the polystyrene end-blocks and the elastomeric midblocks, at room temperature the polystyrene blocks act as physical crosslinks tying the elastomer into a three-dimensional network, thereby providing high cohesive strength and elasticity.

Resins are a critical component in HMPSA based on SBS block copolymers because they can dramatically influence the adhesion characteristics and mechanical properties of the adhesives.<sup>6-8</sup> Due to the two-phase nature of the SBS block copolymer, the choice of the resin type is very important because the main properties depend on the compatibility of the resin with either the elastomeric or styrenic phase of the copolymer. Considering the various groups of resins used today in the adhesive industry there are several possibilities for the formulation of the final products and, consequently, it is possible

to modify the viscoelastic behavior of these materials.

Plasticizers are essential in compounding of the HMPSAs in order to achieve desirably low viscosities. Some liquid resins, such as polyisobutenes and particularly oils are used as plasticizers.<sup>16</sup> The main effect of oil addition is a significant decrease in the melt viscosity and the formation of softer compounds with improved tack. However, it also reduces adhesion and resistance to heat and deformation. Naphthenic-paraffinic oils with a low aromatic content are preferred in HMPSA formulations,<sup>17</sup> while aromatic oils are not used because their interaction with the polystyrene domains cause a drastic reduction in strength.

The polymer as an unsaturated block copolymer can be oxidized further. Any unsaturated resin or oil added to the formulation can create stability problems, particularly at the high temperature of processing and application. Therefore, the blends must be stabilized to avoid changes in viscosity and 5 phr of antioxidant (Irganox 1010) has been used.

In this analysis, the main component, the polymer, was kept in a constant proportion with respect to the resins or to the oils. In the first case, the resins and oils are analyzed depending on their chemical structure; and in the second case, the influence of the resin and oil content has been considered.

The two main methods used for the characterization of adhesive blends have been the analysis of the thermal transitions, the glass transition temperatures of the components and of the mixtures, by Differential Scanning Calorimetry (DSC), and the relaxations and differences in mechanical properties as a function of temperature using Dynamic Mechanical Thermal Analysis (DMTA).

The two techniques show different results as a consequence of differences in the frequency of measurements. Special emphasis will be placed on using the two techniques for determining the transition temperatures and the identification of the type of chain motions that are related with the structure of the adhesive components.

If the glass transitions of the components are considered by calorimetry,  $T_g$  is found to be lower than the values obtained by DMTA, as it is the general finding in polymers.<sup>18</sup> The relaxations found by DSC and DMTA can be compared, provided that the frequency difference among the two experiments is taken into account. In the general discussion it will be shown that these two techniques are in some way complementary.

The glass transition temperatures of the individual components has been measured by DSC and DMTA. However, due to the experimental conditions of the techniques used for DMTA measurements it has not been possible to determine the  $T_g$  of the resins, due to its rigidity at  $T < T_g$  or high fluidity at  $T > T_g$ . The same difficulties appear with the oils. Binary blends containing polymer-resin and polymer-oil were prepared in order to obtain the pure  $T_g$  for resins and oils. Assuming complete miscibility (only one  $T_g$  was measured for each blend), an additive rule was used to calculate the pure  $T_g$  values for Hercotac-205 and oil-3.

The requirements for good pressure-sensitive adhesive performance may be considered from the value of  $E'$  at room temperature,<sup>9</sup> the temperature at which the bond is formed during testing the PSA performance. In other words, the values of the glass transition temperature and of the moduli at the application temperature are essential requirements. These parameters are related to the rheological flow properties of the adhesive onto substrates within a short period of time, as such are related to the time-dependent wetting properties.

### Effect of the Resin Type

Three Hercules resins were selected due to the different compatibility with the block copolymer, in order to analyse the effect of the resin type on the properties of the adhesives.

Foralyn-110 (pentaerythritol ester of hydrogenated rosin) is compatible with the elastomeric block. The addition of resins of this type softens the polymer with the consequent reduction of the modulus at room temperature and increase in the tack of the mixture.

Hercotac-205 is a modified aliphatic resin that is compatible with the two blocks in the polymer, that is to say, with the styrenic end-block and the elastomeric midblock. As a consequence of the compatibility of this resin with the midblock, the addition of this resin increases the tack of the final adhesive, but the decrease of the modulus at room temperature is not apparent due to the end-block reinforcing character of the resin.

The third resin, Piccotac-95, is an aliphatic resin derived from petroleum monomers. It does not present compatibility with the SBS block copolymers. Therefore, this resin is used to increase the softening temperature. It has been included in the study in order to demonstrate not only that it is incompatible with the polymer but also to investigate the effect on the final adhesive properties.

**Table IV** Composition, Physical, and Adhesive Properties of the Blends with Three Different Resin Types

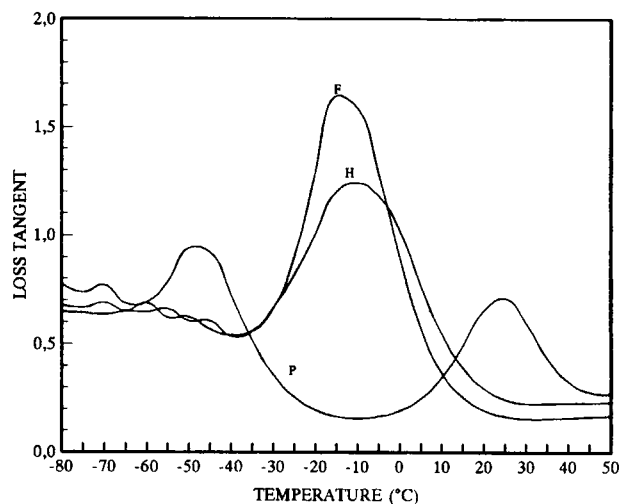
	F	H	P
<b>Formulations (%)</b>			
SBS	30	30	30
Foralyn-110	45	—	—
Hercotac-205	—	45	—
Piccotac-95	—	—	45
Oil-3	25	25	25
<b>Physical Properties</b>			
Glass transition temp (°C, DSC)	-49	-48	-70, -10
Glass transition temp (°C, DMA)	-12	-10	-47, 24
E' at 25°C (Pa <sup>a</sup> 10 <sup>-6</sup> , DMA)	1.9	2.3	4.5
Softening point (°C)	105	102	142
Melt viscosity (cps):			
-160°C	22338	26010	34400
-180°C	10950	13870	11250
<b>Performance</b>			
Polyken probe tack (g)	1295	1280	160
180° Peel (g/cm)	620	1030	510

<sup>a</sup> Antioxidant: IRGANOX 1010 (5 phr).

In order to analyze the effect of the resin type on the transitions, we have prepared three different blends with the three main components, maintaining the same proportion but changing the resin type in the blend (see Table IV). As it is known,<sup>19,20</sup> the compatibility between amorphous components is characterized by only one glass transition temperature; meanwhile, the incompatibility results in multiple glass transition temperatures. By using DSC and DMTA, the compatibility can be considered under these criteria.

In Figure 2, the changes in loss tangent with temperature is plotted for the three adhesives. Only one glass transition temperature, with one  $\tan \delta$  peak maximum temperature, appears for the blends with Foralyn-110 and Hercotac-205, indicating the existence of a compatible system. However, in the blend containing Piccotac-95, two different  $\tan \delta$  peaks are shown at  $-47$  and  $24^\circ\text{C}$ , respectively. This is strong evidence for incompatibility. In general, the intensities and the width of the peaks are related with the level of compatibility of the mixtures and, therefore, the most intense peaks correspond to higher levels of compatibility.

The elastic moduli values ( $E'$ ) at various temperatures are shown in Figure 3. Once again, changes in the moduli are related with the compatibility of the

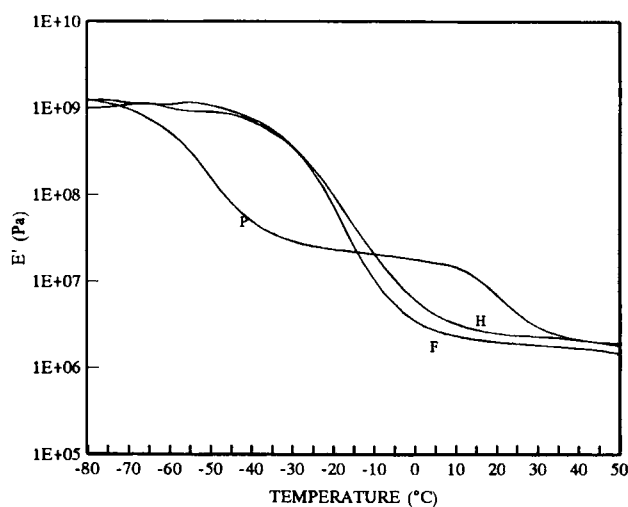


**Figure 2** Plot of loss tangent vs. temperature for three blends with three different resin types, containing: (F) Foralyn-110, (H) Hercotac-205, and (P) Piccotac-95.

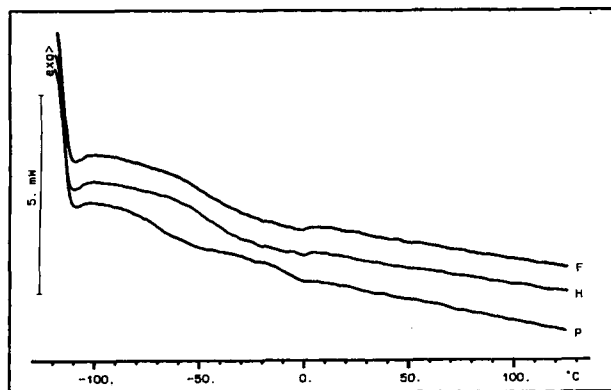
blends. Blends with Foralyn 110 and Hercotac-205 gave a change in moduli at  $10^\circ\text{C}$  and two changes with Piccotac-95 at temperatures  $-50$  and  $20^\circ\text{C}$ .

Similar results on the compatibility of the blends are obtained by DSC measurements as shown Figure 4.

The differences in compatibility behavior has a distinct effect on performance properties. The mid-block resin, Foralyn-110, is the most compatible resin with the butadiene phase, and consequently, the blend F has better tack value than the others. A similar value, for the tack measurement, is obtained for the blend H, with the modified aliphatic



**Figure 3** Plot of elastic moduli vs. temperature for three blends containing three resin types: (F) Foralyn-110, Hercotac-205, and (P) Piccotac-95.



**Figure 4** DSC thermograms of the three blends with different resin types.

resin; also, the peel strength for this blend is the best because of its compatibility with the styrenic end-block. The blend that includes the incompatible aliphatic resin shows the worst performance with low tack and peel values, but it has a high softening point. Therefore, this type of resin is used for increasing the upper service temperature limit of the adhesives.

### The Effect of Oil Structure

Three oils with different paraffinic or naphthenic-paraffinic character have been used in this study. As we mentioned before, some properties such as shear adhesion and 180° peel adhesion are reduced by increasing oil content but these properties could be improved by addition of an adequate resin. In this respect, we consider that not exceeding a 30% oil content in the blends provides a ratio that is high enough to examine clearly how it affects the different paraffinic or paraffinic-naphthenic character in the adhesives through their different behavior in dynamic mechanical measurements and in PSA performance. For this purpose, we have prepared three different adhesives with the three main components, maintaining the same proportion but changing the oil type in the blend (see Table V).

The glass transition temperatures of the adhesives have been determined by DSC and DMTA. In both types of determinations,  $T_g$  values increase in the order  $T_{gA1} < T_{gA2} < T_{gA3}$ , that is to say, in the same order as the values of the glass transitions of the pure oils used in the mixtures. Differences in  $T_g$  in the adhesives correspond with the differences related with both experimental methods, DSC and DMTA, as it was previously commented.

In Figure 5, the  $\tan \delta$  peaks at several temperatures are shown for the three blends. The maximum

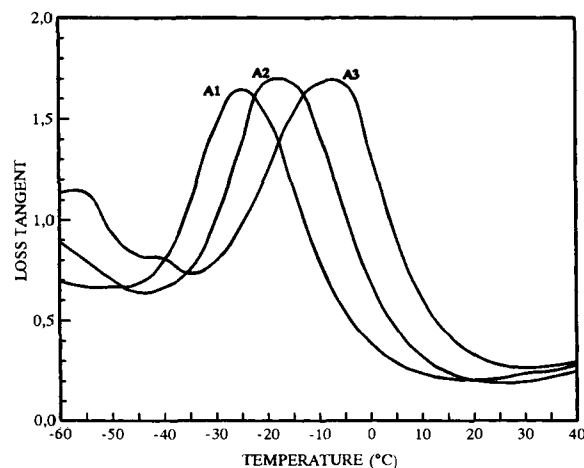
**Table V** Composition, Physical, and Adhesive Properties of the Blends with Three Different Oil Structure

	A1	A2	A3
Formulations (%)			
SBS	25	25	25
Hercotac-205	45	45	45
Oil-1	30	—	—
Oil-2	—	30	—
Oil-3	—	—	30
Physical properties			
Glass transition temp (°C, DSC)	-63	-55	-45
Glass transition temp (°C, DMA)	-24	-17	-7
$E'$ at 25°C (Pa <sup>a</sup> 10 <sup>-6</sup> , DMA)	1.3	1.5	1.6
Softening point (°C)	82	90	90
Melt viscosity (cps):			
-160°C	5350	7380	8700
-180°C	3100	4125	4550
Performance			
Polyken Probe tack (g)	615	1065	1445
180° Peel (g/cm)	430	525	525

<sup>a</sup> Antioxidant: IRGANOX 1010 (5 phr).

increases when the paraffinic character of the oil decreases. The height and width of the peaks do not show any significant difference with the type of oil.

Figure 6 shows the changes in elastic moduli,  $E'$ , with temperature. The values of the transition are lower as the paraffinic character of the oil increases, although the values of  $E'$  at above 20°C are similar.



**Figure 5** Plot of loss tangent vs. temperature for three blends with different oil structures, containing: (A1) oil-1, (A2) oil-2, and (A3) oil-3.

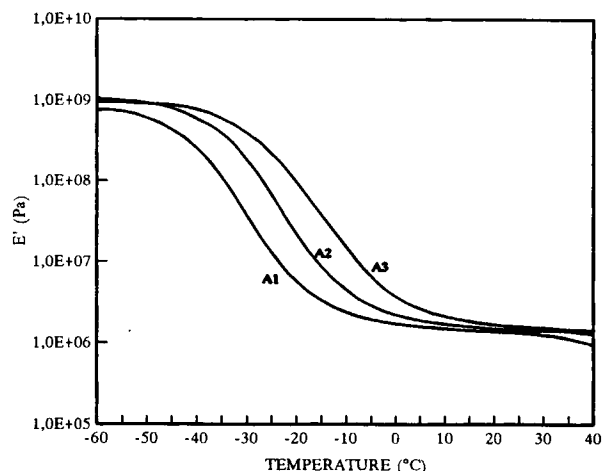
Other properties, such as the variation in melt viscosities at 160 and 180°C and the softening points, are related with the structure of the oil (see Table III). The melt viscosity of the oil-1 at 100°C is lower with respect to the other two oils. This causes the mixtures with oil-1 to present a lower viscosity than those of oil-2 and -3. In the same way, the softening temperature is lower for the blend containing paraffinic oil, due to the lower viscosity of oil-1. Moreover, in Figure 6 a decrease in  $E'$  is shown for the blend A1, at temperatures above 25–30°C. This fact is a clear indication of the lower value for the softening temperature.

The differences in paraffinic or paraffinic-naphthenic structure of the oils have a distinct effect on their PSA performances. The tack values increase from blend A1 to A3, in the same order as the  $T_g$  measured in the respective adhesives. The values obtained are in accord with the requirements of glass transition temperature for good PSA performance, found by Chu<sup>9</sup> for commercial PSA; the maximum tack appears to occur when the  $T_g$ , measured by DMTA, is within the range of -10 to 10°C with an appropriate value of  $E'$  at room temperature to "wet" the substrate. For the three adhesives tested, the values of  $E'$  at room temperature are similar and the best tack was obtained for the blend A3 with a  $T_g$  value of -7°C. On the other hand, in the peel test similar values are obtained for the three blends, being the lowest value for the one prepared with the oil-1. These facts should be related to the slight differences in moduli  $E'$  at room temperature and with the viscosity values at 40°C (see Table III) of the oil-1, lower than the other two, making softer the blend A1.

### The Effect of Resin and Oil Content

It is known<sup>3,4,8,9</sup> that at specific ratios the rubber-resin blends exhibit pressure-sensitive adhesive properties, while at other concentrations they do not. Considering the compatibility of rubber-resin blends, first, it is necessary to know if they are compatible over the entire concentration range and, second, within the compatible range what it is the effect of the resin content on the viscoelastic properties of the system and on the PSA performance.

Class and Chu<sup>8</sup> studied the effect of resin concentration in blends with natural rubber and styrene-butadiene rubber on the viscoelastic properties of the blends. Compatible rubber-resin systems may contain two phases at high resin concentration, and they showed that  $\tan \delta$  peak temperature and the plateau in the modulus of compatible rubber-resin



**Figure 6** Plot of elastic moduli vs. temperature for three blends with different oil structures: containing: (A1) oil-1, (A2) oil-2, and (A3) oil-3.

systems can be controlled by adjusting the amount of compatible low molecular weight resin blended with the elastomer. Other authors such as Krauss and co-workers<sup>4</sup> reported studies of resins blended with styrene-isoprene-styrene block copolymers; these blends also exhibit pressure-sensitive performance at the appropriate concentrations.

These previous studies examined the viscoelastic properties of solution prepared rubber-resin binary blends in PSA. In our case, as mentioned previously, for the hot-melt application low viscosities are necessary. Therefore, with rubber and resins, oil content must be considered. For this study, we have fixed the polymer content (30%) and the resin and oil content have been varied. Assuming that the structure of both components, resin and oil, influences the viscoelastic and adhesive properties of the system, as we observed in Effect of the Resin Type and The Effect of Oil Structure sections, it can be presumed that the final behavior of the adhesives depends on the resin content, which gives tack and/or cohesion according to the type of compatibility with the SBS copolymer, and on the oil content, whose main effect is to achieve desirably low viscosities.

In this part, only one resin and one oil have been used. The resin chosen was Hercotac 205 because of its best PSA performance in the proportion studied previously (45%) (in Effect of the Resin Type section) (see Table II). The same occurs with oil-3 (see Table III).

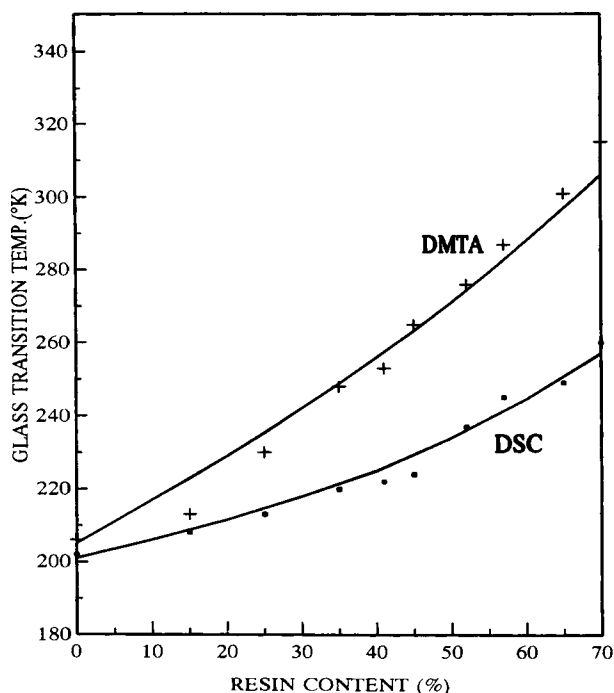
Six formulations were compared containing different resin and oil contents. Table VI summarizes the glass transitions, the physical properties, and



the performance results. It is worth pointing out the thermal behavior measured by DMA and DSC in these formulations. This behavior will be later related with their performance.

First, only one  $T_g$ , measured by DSC and DMA, has been obtained for each composition, and this provides good evidence for compatibility. In other words, the miscibility of these systems seems to be rather good. Figure 7 plots the  $T_g$  obtained by both techniques DSC and DMA, against the resin content. This figure also includes the glass transition temperatures obtained for four additional blends. Two of them contain the three main components with a 15 and 25% of resin content, and the other two correspond to the binary blends containing SBS-oil and SBS-resin, maintaining a 30% polymer content in each case.

The DMTA data show a linear region up to approximately 25% resin content, while the DSC data show a sharp increment in the range up to 40–45% resin content. With respect to these results, the linear increment of  $T_g$  with the resin content was predictable due to the highest glass transition value of the pure resin; also, the different slope for both curves is due to the different value of  $T_g$  for the pure resin obtained by DMTA and DSC measurements. The linearity of the experimental transition suggests, in principle, a good compatibility in the system and the relation between the glass transition and the resin content, can be predicted by any of the linear relationships established for the case of a multiple-component system. In this case, the system,



**Figure 7** Plot of glass transition temperatures measured by DSC and DMTA for blends with different resin contents. The resin content dependence of  $T_g$  follows the Utracki expression for  $K = 0.9$  (DMTA curve) and  $K = 0.5$  (DSC curve).

polymer-resin-oil, can be considered as a binary one, in which the first component corresponds to the polybutadiene phase and oil with a similar  $T_g$  and

**Table VI** Compositions, Physical and Adhesive Properties for Six Blends with Different Resin and Oil Contents

	A4	A5	A6	A7	A8	A9
Formulations (%)						
SBS	30	30	30	30	30	30
Hercotac-205	35	41	45	52	57	65
Oil-3	35	29	25	18	13	5
Physical properties						
Glass transition temp (°C, DSC)	-53	-51	-48	-36	-28	-24
Glass transition temp (°C, DMA)	-25	-20	-10	3	14	28
$E'$ at 25°C (Pa $\cdot 10^{-6}$ , DMA)	1.9	2.0	2.3	2.7	6.0	29
Softening point (°C)	95	99	102	108	110	123
Melt viscosity (cps):						
-160°C	12330	19020	26010	28500	31200	60100
-180°C	6510	10500	13870	14320	15600	28400
Performance						
Polyken probe tack (g)	770	915	1280	1090	940	90
180° Peel (g/cm)	540	870	1030	1390	1480	1975

\* Antioxidant: IRGANOX 1010 (5 phr).

the second component corresponds to the resin with a high  $T_g$  compared with the other two.

By using the expression derived by Utracki<sup>20</sup>

$$\ln T_g = (w_1 \ln T_{g1} + Kw_2 \ln T_{g2}) / (w_1 + Kw_2) \quad (1)$$

where  $w_1$  and  $w_2$  are the weight fraction of the elastomer-oil and the resin, respectively,  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the two components considered, and  $K$  is a ratio of the increment of the specific heat in the glass transition. The experimental curves are fitted with the value of  $K = 0.9$  and  $K = 0.5$  for the measurements obtained by the two methods, DMTA and DSC, respectively.

Also, by using the expression derived by Gordon-Taylor<sup>21</sup>

$$T_g = (w_1 T_{g1} + Kw_2 T_{g2}) / (w_1 + Kw_2) \quad (2)$$

where  $K$  corresponds to the ratio of the increment of the coefficient of volume expansion in the glass transition. The experimental data are fitted, in this case, with the value of  $K = 0.7$  and  $K = 0.4$  for the results obtained by DMTA and DSC, respectively.

In eqs. (1) and (2), complete miscibility of the ingredients is assumed over the whole range of resin content. However, the experimental and theoretical curves are slightly displaced for both methods, but a good agreement between experimental data and calculated values is found, being better for the DMTA than for the DSC data. This deviation from the calculated values could indicate that a certain loss of miscibility occurs in the system.

No phase separation was found in this system. This result agrees with those found by others,<sup>1,21</sup> in which only a single phase was detected. Moreover, blends of rubber with resins have shown the development of two phases at higher resin concentrations.<sup>1,22,23</sup> It has been pointed out<sup>23</sup> that phase separation occurs when the rubber phase is saturated with resin and that the tack strength depends upon the presence of this two-phase structure. However, this conclusion has been questioned<sup>24</sup> and an alternative approach has been attempted based on the use of the cohesive energy density or the solubility parameter for the qualitative prediction of miscibility between rubber and resins.

The analysis of the dynamic data allows one to consider other approaches. By increasing the resin content from 35 to 65% (corresponding to the decrease of the oil because the rubber content is maintained constant), the temperature at which  $\tan \delta$  presents a maximum is increased (Fig. 8). In general, there is also a broadening of the transition and a

clear decrease of the intensity of  $\tan \delta$  at compositions of around 45% of resin content. In principle, this result is not surprising because it appears in plasticized polymers; very early reports found the same phenomena in plasticized poly(vinylchloride).<sup>25,26</sup>

The transition temperature, related with the maximum in  $\tan \delta$  and with the half-widths of each curve, were associated with the solubility or compatibility of the plasticizer and the polymer. Although a simple relationship exists between the maximum in  $\tan \delta$  and the plasticizer content, there is not a simple relationship between the half-width and the volume fraction of the plasticizer. However, it has been pointed out that the broadening of the transition depends on the nature of the plasticizer and the interaction between the two components.<sup>20</sup> At a given concentration (about 40% in volume) there is a minimum in intensity correlated with the decreasing amount of plasticizer and the partial miscibility of the two components.

The same situation can be found in our data for a multicomponent system, although it must be pointed out that the butadiene phase and the oil have approximately the same  $T_g$  and only the resin has a high  $T_g$  compared with the other components. Therefore, the minimum at a composition around 45% in resin may represent the concentration at which the system presents restricted miscibility, with limited phase separation. In other words, when the oil content decreases this component cannot be considered as a solvent-type plasticizer.

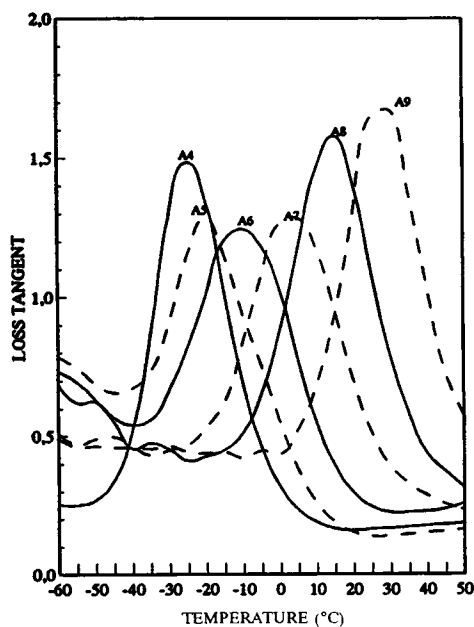


Figure 8 Plot of loss tangent vs. temperature for six blends with different resin and oil contents.

Moreover, the elastic modulus, another important viscoelastic parameter, was then plotted against the temperature (Fig. 9). The modulus at 25°C shows a clear increment with the resin content (Fig. 10). This fact can be attributed to the oil, which is the main softener component of the adhesive.

Finally, the properties of the adhesive must be discussed. As far as physical properties are concerned, the softening temperatures and the melt viscosities at 160 and 180°C will be commented.

The softening temperature increases when the resin content increases (or the oil content decreases) (Fig. 11). This increment is due to the decrease of oil content, the component that softens the polymer. Regarding the melt viscosities of the blends, the additive mixing rule predicts that, in a homogeneous and miscible system, the viscosity increases with increasing the resin content or decreasing the oil content. In our data, this behavior is observed, although a plateau region appears, differing at the two temperatures that have been measured. The plateau is observed in the range of 45–55% resin content, and a resin/oil ratio of 45/25. This region is that in which the inflexion point of  $E'$  at room temperature appears and with the minimum of  $\tan \delta$  in the glass transition (see Fig. 10).

As it is known in polymer blend rheology,<sup>27–29</sup> mixing two polymers will result in an increase in viscosity above the mean value of the pure components. This behavior has been called a positive deviation from the mixing additive rule, and the opposite effect it is considered a negative deviation. Both types of deviations are simultaneously present in some systems, and for example, this is the case of polybutadiene–polyisoprene

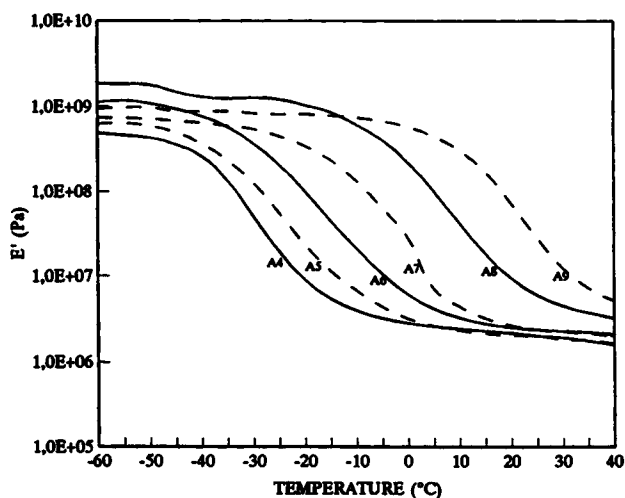


Figure 9 Plot of elastic modulus vs. temperature for six blends with different resin and oil content.

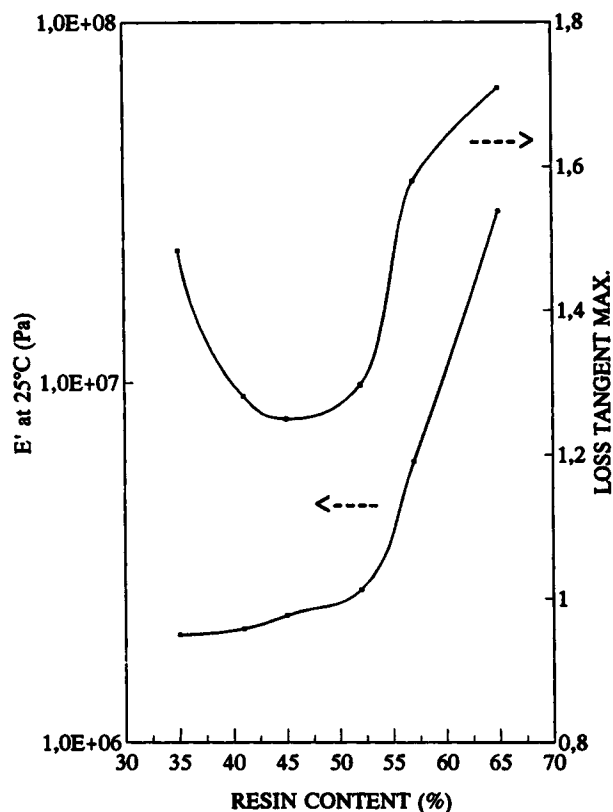
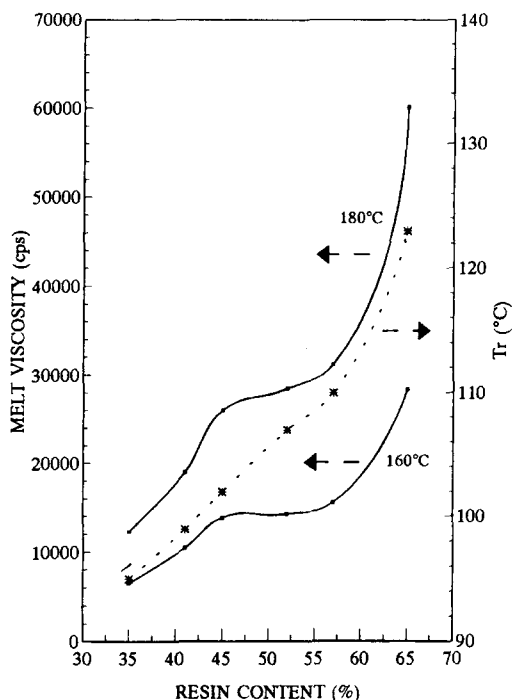


Figure 10 Plot of  $E'$  at 25°C and loss tangent maximum value for six blends with different resin content.

blends.<sup>30</sup> However, at present there is not a theoretical approach to explain the existence of maximum and/or minimum viscous behavior and, concomitantly, elastic properties. Further, it seems that there is no relationship between the miscibility and the deviations in the rheological functions.

The analysis of the performance properties (tack and peel strength) shows the behavior outline in Figure 12. The peel strength increases with the resin content, as expected, due to the increased cohesion of the adhesive. However, the dependence of the tack strength on the resin composition presents a maximum when the resin/oil ratio reaches a 45/25 value. The same general shape of this curve has been observed in many rubber–resin blends.<sup>5,21,31,32</sup>

Different explanations have been given for this behavior. Earlier results by Wetzel<sup>23</sup> were interpreted in terms of a two-phase model, and the maximum was considered to be due to a phase inversion. Other explanations have been related with the surface energies and the viscoelastic properties. Thus, as was discussed by Aubrey,<sup>24</sup> the bonding process in an adhesive depends on the surface energies and on the elastic moduli, and the debonding process depends again on the surface energies and on the energy dissipated within



**Figure 11** Plot of melt viscosities at 160 and 180°C and softening points vs. resin content.

the deformed adhesive ( $\tan \delta$ ). In the few studies that have been carried out, it seems that the change in the surface energy by adding a tackifier resin to a rubber is very small and it does not affect the tack value.

However, the analysis of the viscoelastic behavior leads to a more adequate explanation for the tack. The low modulus of the blend allows, in the bonding stage, intermolecular contacts, and the low value of  $\tan \delta$  corresponds to a high energy dissipation. In other words, the maximum in the tack appearing at a resin content of about 45–50%, corresponds to the same composition at the inflexion in  $E'$  at room temperature and a minimum in  $\tan \delta$  is found. This result seems to indicate that a gross phase separation is not a requirement for maximum tack. Some kind of restricted miscibility of the components is enough to form a few microdomains in the blend.

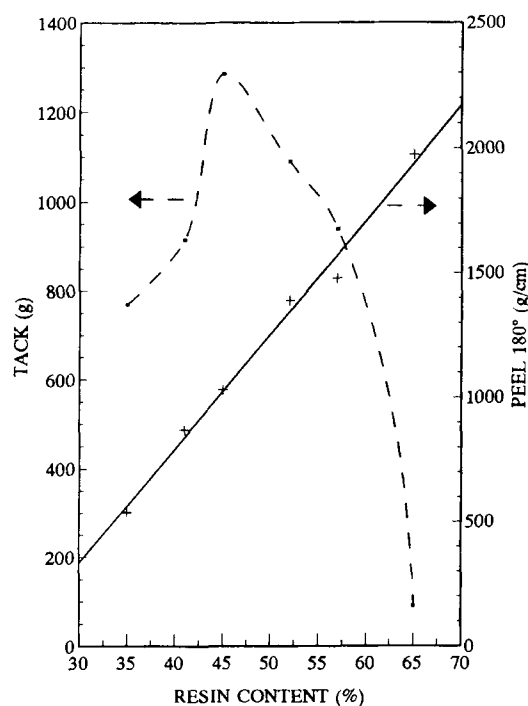
Other parameters such as the molecular weight of the elastomer and the relative content of the styrene or rigid blocks, together with the influence of the preparative methods used in the final mixing of the components should be studied in the future works.

## CONCLUSIONS

In this work, the effect of the adhesive composition on the properties of HMP SA based on styrene-butadiene-styrene rubbers has been analyzed.

The compatibility characteristics of the resin in the elastomer are directly related to the adhesive performance. To produce an adhesive with good tack, a resin must be found that has good compatibility with the midblock (the polybutadiene). Esters of rosin are particularly good as tackifiers for SBS. In case of aliphatic resin modified with aromatic groups, the compatibility is extended also to the endblocks (polystyrene) which confer good tack and better cohesive strength to the adhesive. An incompatible resin may also be added to an elastomer to impart other desirable properties, for example, higher softening point, but always to the detriment of the tack properties of the system.

The main effect of the oil addition is a significant decrease in melt viscosity and the formation of softer blends with improved tack. Naphthenic-paraffinic oils are preferred because of the enhanced compatibility. The values of the glass transitions of the oils are lower the higher the paraffinic character of the oil. Other properties such as the softening point and melt viscosity present lower values for the adhesives containing paraffinic oil. These facts are more important with a high oil content but they are also significant if the oil content is much lower than the concentration (30%) studied in this work. The oil structure and content depend on the desired adhe-



**Figure 12** PSA performance for blends with different resin and oil contents.

sive characteristics in order to achieve the best PSA performance.

The analysis of the properties in blends with a fixed polymer content (30%) and with different resin and oil contents, shows a rather good miscibility over the whole range of compositions. Only one  $T_g$  is found that can be fitted by several relationship, including Gordon-Taylor and Utracki ones.

However, around a given resin content (45–50%) there is a decrease of the intensity of the  $\tan \delta$ , correlated with restricted miscibility. Therefore, the melt viscosities increase with increasing the resin content but a plateau region appears in the range of 45–55% resin content. Also, a maximum at the same composition is found for the tack strength, which corresponds with variations in the viscoelastic parameters.

Differences in composition and miscibility between the rubber and the resins affect the adhesive behavior. DMTA is a powerful tool to establish correlations between structural parameters and adhesive properties.

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## REFERENCES.

1. M. Sherriff, R. W. Knibbs, and P. G. Langley, *J. Appl. Polym. Sci.*, **17**, 3423 (1973).
2. D. W. Aubrey and M. Sherriff, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2631 (1978).
3. D. W. Aubrey and M. Sherriff, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2597 (1980).
4. G. Krauss and K. W. Rollman, *J. Appl. Polym. Sci.*, **21**, 3311 (1977).
5. G. Krauss, K. W. Rollman, and R. A. Gray, *J. Adh.*, **10**, 221 (1979).
6. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 805 (1985).
7. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 815 (1985).
8. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 825 (1985).
9. S. G. Chu, in *Adhesive Bonding*, L. H. Lee, Ed., Plenum Press New York, 1991, p. 97.
10. C. L. Rohn, *Tappi J.*, **191**, March (1989).
11. G. Marin, Ph. Vandermaesen, and J. Komornicki, *J. Adhesion*, **35**, 23–27 (1991).
12. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Material*, Elsevier, New York, 1978.
13. C. Booth and C. Price, *Comprehensive Polymer Science, Vol. 1: Thermal Analysis*, M. J. Richardson, Ed. Pergamon Press, New York, 1989, p. 867.
14. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980.
15. W. B. Toig and P. A. Mancinelli, *Elastomerics*, Oct., 44–48 (1990).
16. S. Giordano, C. Padori, A. Riva, and L. Vitalini Sacconi, *Adhesive Age*, November, 32–38 (1994).
17. N. D. Keyzer, *Adesione*, **2**, 13–24 (1992).
18. D. J. Meier, Ed. *Molecular Basis of Transitions and Relaxations*, Gordon and Breach, New York, 1978.
19. D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, New York, 1976.
20. L. A. Utracki, *Polymer Alloys and Blends*, Houser Pub., Munich, 1989.
21. S. Kawahara, S. Akiyamada, and Y. Kamo, *Polymer*, **32**(9), (1991).
22. K. Kamagata, H. Kosaka, H. Hino, and M. Toyama, *J. Appl. Polym. Sci.*, **15**, 483 (1971).
23. F. H. Wetzel, *Rubber Age*, **82**(2), 291 (1957).
24. D. W. Aubrey, *Rubber Chem. Technol.*, **61**, 448–469 (1987).
25. K. Wolf, *Kunststoffe*, **41**, 89 (1951).
26. L. E. Nielsen, R. Buchdahl, and R. Levre, *J. Appl. Phys.*, **21**, 607 (1950).
27. C. D. Han, *Rheology in Polymer Processing*, Academic Press, New York, 1976.
28. L. A. Utracki and M. R. Kamal, *Polym. Eng. Sci.*, **22**, 96 (1982).
29. R. Sood, M. G. Kulkarni, A. Dutta, and R. A. Mash-elkal, *Polym. Eng. Sci.*, **28**, 20 (1988).
30. V. N. Kuleznev, O. L. Melnikova, V. D. Klykova, W. P. Skvortsov, and V. S. Flukkovskori, *Kolloid Zhuru*, **37**, 273 (1975).
31. M. Toyama, T. Ito, and H. Moriguchi, *J. Appl. Polym. Sci.*, **14**, 2039 (1970).
32. R. Bates, *J. Appl. Polym. Sci.*, **20**, 2941 (1976).

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