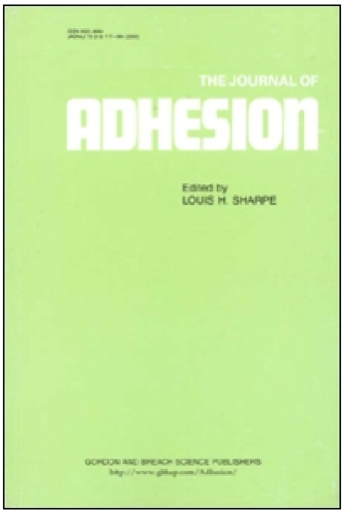

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Pressure Sensitive Adhesive Properties and Miscibility in Blends of Poly(vinyl ethylene-co-1,4-butadiene) with Hydrogenated Terpene Resin

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The pressure sensitive adhesive (PSA) properties of two samples of poly(vinyl ethylene-co-1,4-butadiene) (V-BR) (vinyl content: 47.4 and 60 wt%) blended with hydrogenated terpene resin (CLEARON P125) were measured on blend compositions having CLEARON P125 contents (by weight) of 10%, 30% and 50%. The maximum values of 180° peel adhesion, rolling ball tack and probe tack were observed with a V-BR/CLEARON P125 70/30 blend, whereas the maximum values of holding power were obtained with a 50/50 V-BR/CLEARON P125 blend. In these blends, the miscibility between V-BR and CLEARON P125 was confirmed by means of SEM, DSC and light scattering. The influences of surface tension and dynamic mechanical properties on PSA properties were investigated. The surface tension values were essentially the same in all the V-BR/CLEARON P125 blends. Minimum values of storage modulus G' and loss modulus G'' at room temperature in V-BR/CLEARON P125 blends were obtained with a 70/30 blend. Thus, it is believed that in V-BR/CLEARON P125 blends, 180° peel adhesion and tack are related to the dynamic mechanical properties.

KEY WORDS poly(vinyl ethylene-co-1,4-butadiene), hydrogenated terpene resin, miscibility, surface tension, dynamic mechanical properties, blend, pressure sensitive adhesive properties.

INTRODUCTION

Pressure sensitive adhesives (PSAs) are utilized in the packaging, printing, medical, electrical and automobile industries.[1-4] It is well known that they are composed of blends of elastomers, such as natural rubber and synthetic rubber, with tackifying resins. There are three main types of tackifying resins: (a) rosin and rosin derivatives, (b) terpene resins, and (c) hydrocarbon resins.

The PSA properties of the rubber/resin blends depend on the viscoelastic properties,[5,6] surface tension[7] and the miscibility between rubber and resin.[8] Especially, Akiyama[8] explained the tackiness mechanism using the phase diagrams in blends of styrene-isoprene-styrene block copolymer (SIS) with two tackifying resins, such as a terpene and a styrenic resin. Then, he found that the SIS/terpene resin blends

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and SIS/styrenic resin blends displayed lower critical solution temperature (LCST) phase behavior and upper critical solution temperature (UCST) phase behavior, respectively. Finally, he concluded that good tackiness at room temperature was obtained with a blend near the critical composition on the phase diagram. He also found that large concentration fluctuations based on the micro dispersed morphology provided maximum tackiness.

It was also reported that poly(vinyl ethylene-co-1,4-butadiene) (V-BR) possessed an excellent balance of rebound resilience and wet skid resistance as tire tread material.[9] We took note of V-BR having wet skid resistance which gave interesting possibilities for a new adhesive made from blends of this rubber with tackifying resins. The PSA properties of blends of V-BR with various tackifier resins were studied in relationship to their miscibility, dynamic mechanical properties and surface tensions.[10-15] The V-BR (70.4 wt% vinyl content)/resin blends exhibited an LCST phase diagram with critical temperature ($T_c = 80°C$) and excellent peel adhesion at room temperature was obtained near the critical composition.[10,11] The V-BR/terpene resin blends were judged to be miscible because of the single glass transition temperature T_g on DSC thermograms.[12] The (50/50) blend of V-BR (47.4 wt% vinyl content) with terpene resin revealed excellent PSA properties and we obtained values of the storage modulus $G' = 10^6$ (dyn/cm^2), and $T_g = -20°C$. The surface tension of V-BR/terpene resin blends did not change with vinyl content and blend ratio.[13] Therefore, it is probable that the PSA properties of the V-BR/terpene resin blends were influenced by the dynamic mechanical properties. In the previous study,[14,15] blends of the V-BR with 54.3 wt% vinyl content with hydrogenated terpene resin (CLEARON P125) were investigated and PSA properties and miscibility were determined. The PSA properties of V-BR/hydrogenated terpene resin blends were lower than those of V-BR/terpene resin blends.[14] It was presumed that the difference between surface tension and T_g of the resins influenced the PSA properties. The V-BR/hydrogenated terpene resin blends exhibited UCST phase behavior as determined by means of DSC and light scattering measurements.[15] Then, it was confirmed that the V-BR/hydrogenated terpene resin blend displayed a "Miscibility Valley"[16] when the vinyl content of V-BR was varied.

In this study, the PSA properties of blends of two V-BRs with 47.4 and 60.0 wt% vinyl content with hydrogenated terpene resin (CLEARON P125) were measured. Next, the miscibility between V-BR and hydrogenated terpene resin and the UCST phase behavior was investigated. The effects of surface tension and dynamic mechanical properties on PSA properties were also examined.

EXPERIMENTAL

The poly(vinyl ethylene-co-1,4-butadiene) (V-BR) samples with 47.4 and 60 wt% vinyl content were supplied by Nippon Zeon Co. Ltd. Their molecular weights were $M_w = 214000$ ($M_w/M_n = 1.03$) and $M_w = 224000$ ($M_w/M_n = 1.04$), respectively. The V-BR was prepared by polymerizing 1,3-butadiene in hexane or benzene with n-butyl lithium catalyst in combination with diethylene glycol dimethyl ether at 40°C.

The hydrogenated terpene resin was CLEARON P125 $M_w=1200$ ($M_w/M_n=1.32$) made by Yasuhara Chemical Co. Ltd. The V-BR/CLEARON P125 blend films were prepared by knife coating 10 or 20 wt% toluene solution onto poly(ethylene terephthalate) (PET) film of 50 μm thickness. After the blend films were dried at 70°C for 120 sec, they were seasoned at 23±3°C and 65±5% RH for more than 7 days. Films were 20 μm thick after drying.

The measurements of PSA properties, such as 180° peel adhesion, rolling ball tack, probe tack and holding power were carried out according to JISZ0237. The 180° peel adhesion to stainless steel of samples was performed by use of Toyo Baldwin Co. Ltd. Tensiron/UTM-4-100. Both ball and probe were made of stainless steel. Measurements of 180° peel adhesion, rolling ball tack and probe tack were carried out at 23°C. The holding power was evaluated against stainless steel using a Nitto Rika Co. Ltd. NDS-100S creep tester at 40°C.

The miscibility between V-BR and CLEARON P125 was judged by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and a light scattering technique. The glass transition temperature T_g was obtained using a Du Pont 910-DSC with a heating rate of 10°C/min. The T_g's of the blends were determined as the intermediate temperature between the bottom and top points of intersection between the base line and tangential line at the inflection of the DSC thermograms. The surface morphology of the V-BR/CLEARON P125 blends was observed by use of a Hitachi, Ltd. S-430 type SEM. The cloud point was obtained at various cooling rates with a starting temperature of 170°C using an OPTEC GP-5 light scattering photometer. A He-Ne gas laser beam of 632.8 nm wavelength was applied vertically to the film specimen.

The critical surface tension γ_C of the V-BR/CLEARON P125 blends was evaluated by contact angle method using organic liquids as represented in Table I. The contact angle measurements were carried out using a Kyowa Kaimen Kagaku Co. Ltd. type CA-D apparatus.

The dynamic mechanical properties of the V-BR/CLEARON P125 blends were performed by a shearing method using a Rheometrics Co. Ltd. RDS-II instrument. The section areas and thickness of samples were 8 mm diameter and 6 mm, respectively. The frequency was 1 Hz. Several dynamic mechanical properties, such as the storage modulus, G', loss modulus, G'', and dynamic loss tangent, tan δ, were measured.

TABLE I
Surface tensions γ_L (dyn/cm) and polarity[a] $X_L{}^p$ of liquids

Liquid	γ_L	$X_L{}^p$
2-Methyl,2,4-pentanediol	27.0	0.540
2,3-Butanediol	30.7	0.657
1,2-Propanediol	36.5	0.695
1,3-Butanediol	37.8	0.646
1,5-Pentanediol	43.2	0.593
1,4-Butanediol	45.3	0.634
1,2-Ethanediol	46.5	0.737

a) Ref. 21

RESULTS AND DISCUSSION

The summarized properties of V-BR/CLEARON P125 blends are shown in Table II. Using both types of V-BR (47.4 and 60 wt% vinyl content) blends, maximum values of 180° peel adhesion, rolling back tack and probe tack were observed at a 70/30 ratio of rubber to resin, while the maximum of holding power was found at a 50/50 ratio. It is expected that the changes in PSA properties of the blends of V-BR with CLEARON P125 can be interpreted in terms of miscibility, surface tension and viscoelastic properties.

Firstly, the miscibility between V-BR and CLEARON P125 was investigated by DSC, SEM and light scattering. We point out[17] that miscibility or immiscibility of rubber/resin blends can be used to relate the PSA properties to the viscoelastic properties and surface tension as follows:

1) In miscible blends, when the value of surface tension of the rubber is equal to that of the resin, the PSA properties are evaluated by the viscoelastic properties.
2) In immiscible blends, it is necessary for the phase morphology, viscoelastic properties and averaged surface tension to be investigated.
3) When the phase transition temperature from miscible to immiscible is about room temperature, the influence of concentration fluctuation on PSA properties may be important.

Therefore, the miscibility of V-BR/CLEARON P125 blends is significantly related to their adhesive and viscoelastic properties.

The SEM photograph of 50/50 V-BR (47.4 and 60 wt% vinyl content)/CLEARON P125 blends are shown in Figure 1. The V-BR/CLEARON P125 blends exhibit a homogeneous surface morphology. In the range of 10 to 50 wt% CLEARON P125 content, the V-BR/CLEARON P125 blends are miscible as shown by the single peak on the DSC thermogram (see Table III). Temperature dependence of light scattering intensity at $2\theta = 21.4°$ for a 30/70 V-BR (47.4)/CLEARON P125 blend is shown in Figure 2. The light scattering intensity increases

TABLE II
Pressure sensitive adhesive properties in blends of V-BR with CLEARON P125

	V-BR (47.4)/CLEARON P125			V-BR (60)/CLEARON P125		
	90/10	70/30	50/50	90/10	70/30	50/50
180° peel adhesion (g/25 mm)[a]	30	1400	CF/1350	130	1200	750
Rolling ball tack (g)	<2	9	<2	2	7	<2
Probe tack (g/5 mm diameter)	104	397	75	84	323	23
Holding power (s)	CF[b] 20420	CF 13540	CF 52970	CF 25780	CF 58640	NC[c] 70000

[a] Dwell time, 24 h; mm, diameter
[b] CF: Cohesive failure of the adhesive layer
[c] NC: No creep

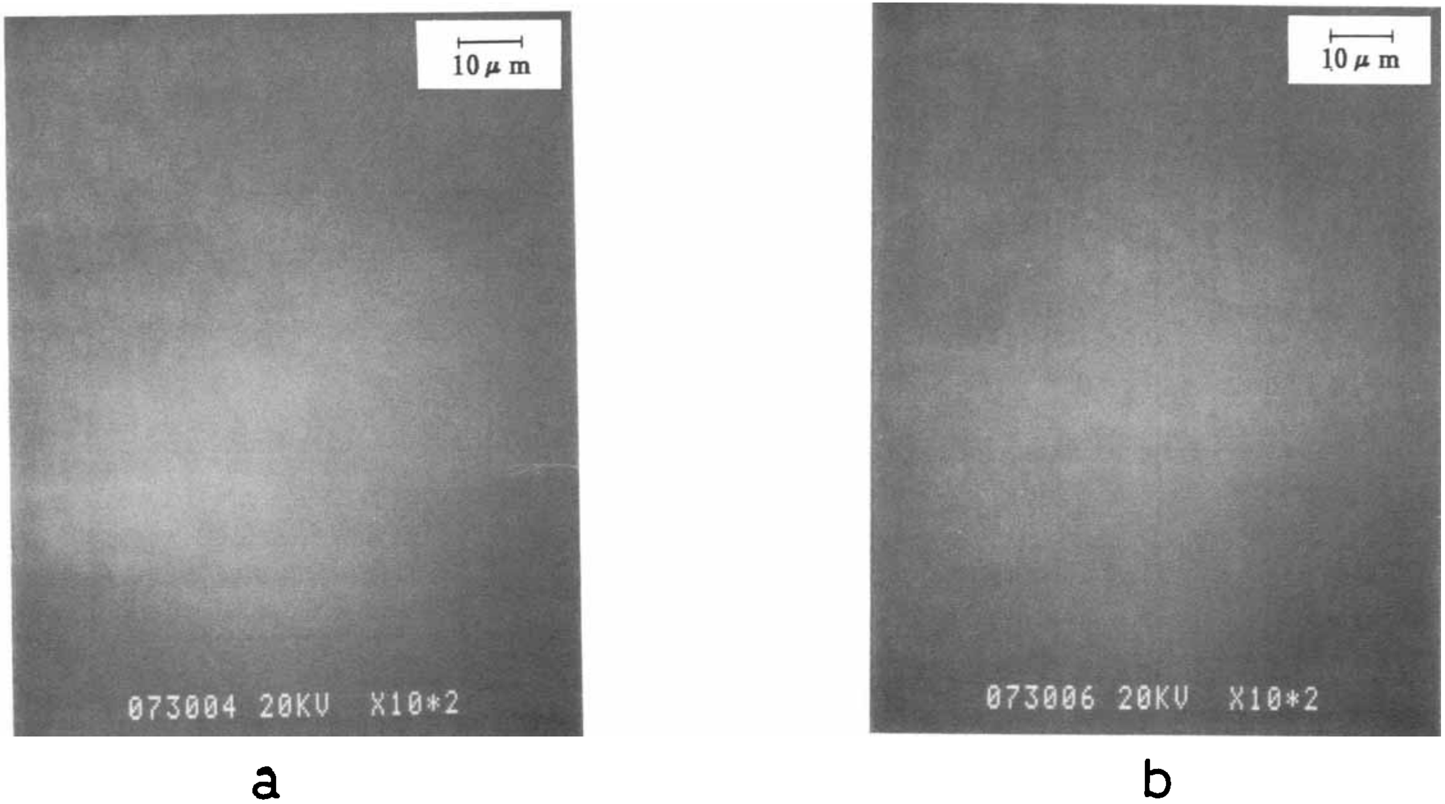

FIGURE 1 Scanning electron microscopy (SEM) photograph of 50/50 V-BR/CLEARON P125 blends. Vinyl contents (by weight): a) 47.4 wt%, b) 60 wt%.

TABLE III
Glass transition temperature, T_g, obtained by DSC

	V-BR (47.4)/CLEARON P125			V-BR (60)/CLEARON P125		
	90/10	70/30	50/50	90/10	70/30	50/50
T_g (°C)	−54	−45	−44.5	−41	−32	−23.5

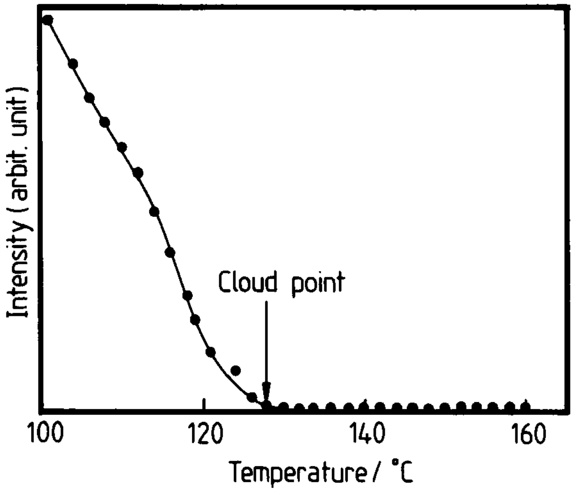

FIGURE 2 Temperature dependence of light scattering intensity for a 30/70 V-BR (47.4 wt% vinyl content)/CLEARON P125 blend.

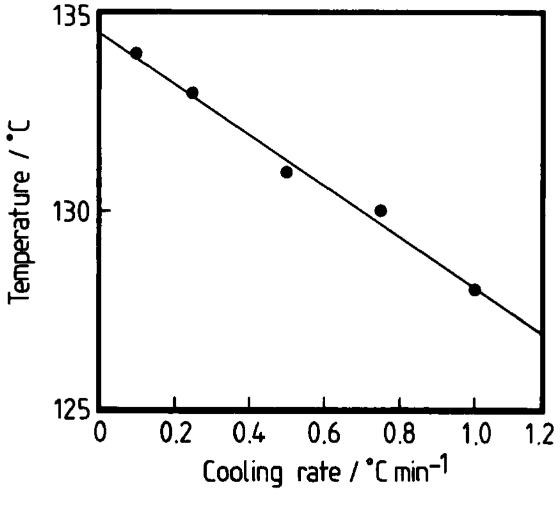

FIGURE 3 T_d vs. heating rate for a 30/70 V-BR (47.4 wt% vinyl content)/CLEARON P125 blend.

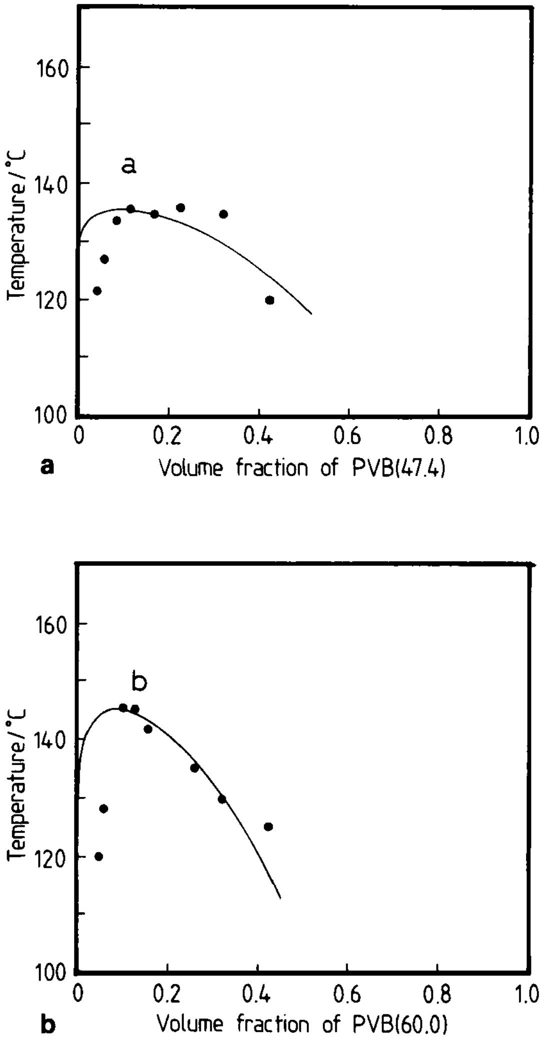

FIGURE 4 UCST phase diagram of V-BR/CLEARON P125 blends. The values of T_d (●) were obtained by cloud point measurement. The solid line represents a binodal curve calculated by using the Flory-Huggins expression. Vinyl content: a) 47.4 wt%, b) 60 wt%.

with decreasing temperature below 130°C. We defined the cloud point (T_d) as the temperature at which the scattering intensity begins to decrease. Since the T_d of the blend depended on the cooling rate, the cloud point was determined by straight line extrapolation to zero cooling rates shown in Figure 3. Figure 4a and Figure 4b show the cloud point *versus* blend composition plots. The relationship between cloud point and blend composition exhibits UCST phase behavior (convex curve) and the data were fitted to the binodal curve calculated according to Flory-Huggins free energy of mixing [χ_{12} parameter: V-BR(47.4) $\chi_{12} = -0.130 + 60.26/T$, V-BR(60) $\chi_{12} = -0.040 + 24.04/T$]. Because the V-BR/CLEARON P125 blends used in the measurements of pressure sensitive adhesive properties did not exhibit the peak in scattering intensity, it was judged that these blends were miscible. Therefore, from the results of SEM and light scattering measurements, we consider the effect of miscibility on PSA properties can be neglected for these V-BR/CLEARON P125 blends.

It is well known that the PSA properties, such as peel adhesion and tack, can be expressed as follows[18]

$$T = W_a \cdot B \cdot D \tag{1}$$

where T is the value of a PSA property, W_a the work of adhesion, B the bonding function and D the debonding function. Work of adhesion is influenced by the surface tension of pressure sensitive adhesives. The bonding function B increases as the storage modulus, G', and the loss modulus, G'', decrease, while the debonding function D increases with both increasing G'' and dynamic mechanical loss tangent, $\tan\delta$. Therefore, the evaluations of surface tension and dynamic mechanical properties are very important to evaluate the PSA properties.

The surface tension of solids can be estimated by a contact angle method using organic liquids. Zisman[19,20] found that the plot of $\cos\theta$ *versus* the surface tension of various liquids γ_L gives a good straight line. He determined the critical surface tension for wetting, γ_C (the γ_L value at $\cos\theta = 1$), by extrapolating the straight line. Since then, the γ_C values have been used as an indication of the surface properties such as the wettability, water repellency and tackiness. Recently, Saito[21] proposed a new equation between $\cos\theta$ and γ_L, which was expressed by interfacial interaction of solid-liquid as follows:

$$\log(1+\cos\theta) = -(0.5-a)\cdot\log(\gamma_L) + \log\{2\phi_X \cdot \gamma_S^{(0.5-a)}\} \tag{2}$$

where the $(0.5-a)$ is defined as the slope in the $\log(1+\cos\theta)$ *vs.* $\log(\gamma_L)$ plot, and the function ϕ_X corresponds to the bonding efficiency parameter of Kaelble and Uy.[22] The γ_C is estimated by the γ_L value at $\log(1+\cos\theta) = \log(2)$ by extrapolating the straight line. In poly(vinylidene fluoride-co-hexafluoro acetone) P(VDF-HFA),[23] poly(ethyl acrylate) PEA/P(VDF-HFA) blends,[24] and poly(vinyl ethylene-co-1,4-butadiene) (V-BR)/terpene resin blends,[13] we found that the plot of $\log(1+\cos\theta)$ and $\log(\gamma_L)$ exhibited the expected linear behavior and determined the reasonable critical surface tension for wetting, γ_C. The $\log(1+\cos\theta)$ *vs.* $\log(\gamma_L)$ plots of 70/30 V-BR(47.4)/CLEARON P125 (70/30) blend and 70/30 V-BR(60)/CLEARON P125 blend are shown in Figure 5a and Figure 5b. The relationships between $\log(1+\cos\theta)$ and $\log(\gamma_L)$ are shown in both figures. Reasonable values for γ_C can be estimated as the value of γ_L at $\log(1+\cos\theta) = \log(2)$ by extrapolation. The γ_C values in the V-BR/CLEARON P125 blends are given in Table IV. The γ_C values do not change in these blends. Therefore, we consider the influence of the work of adhesion W_a on the PSA properties can be neglected for the V-BR/CLEARON P125.

Next, we examined the effect of the bonding function B and debonding function D on PSA properties for the V-BR/CLEARON P125 blends. Figure 6 shows the temperature dependence of storage modulus G' of three (90/10, 70/30 and 50/50) V-BR (47.4)/CLEARON P125 blends. G' for all blends decreases with rising temperature and the length of the plateau region decreases with increas-

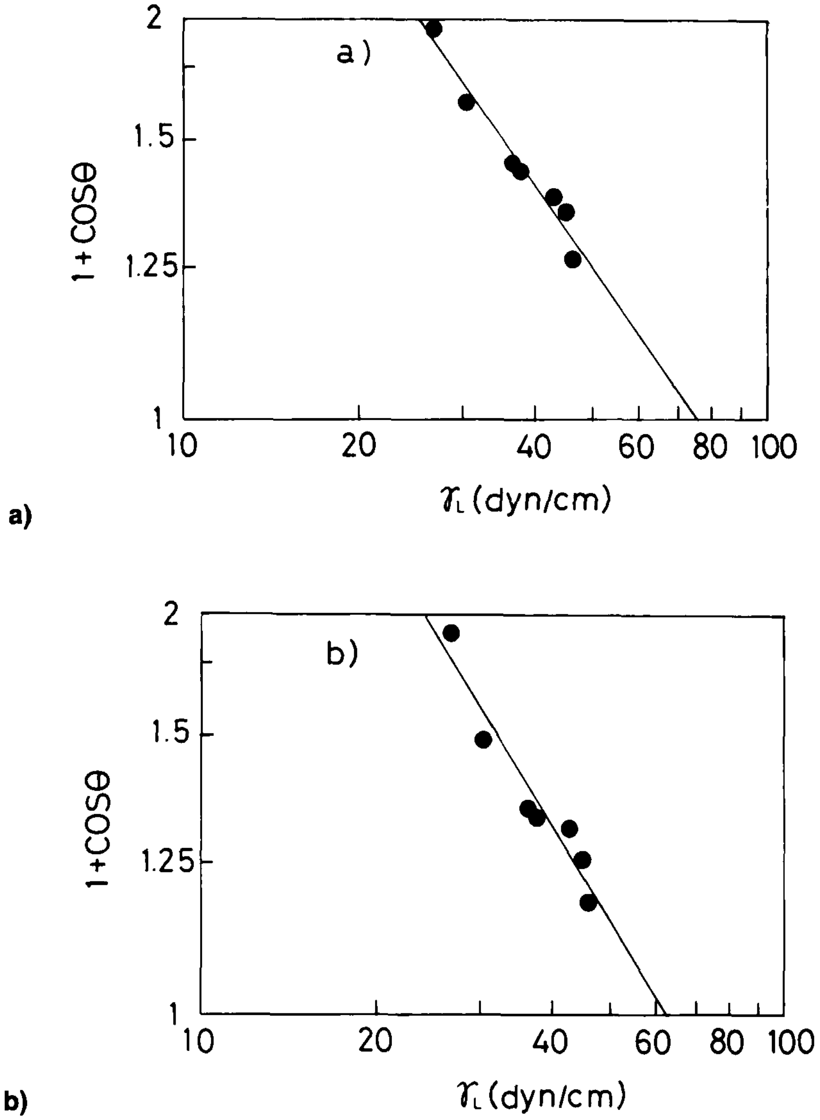

FIGURE 5 Log(1 + cos θ) *vs.* log(γ_L) plot of 70/30 V-BR/CLEARON P125 blends. Vinyl content: a) 47.4 wt%, b) 60 wt%.

TABLE IV
Critical surface tension, γ_C, in blends of V-BR with CLEARON P125

	V-BR (47.4)/CLEARON P125			V-BR (60)/CLEARON P125		
	90/10	70/30	50/50	90/10	70/30	50/50
γ_C (dyn/cm)	24.0	25.3	24.9	23.8	24.0	24.4

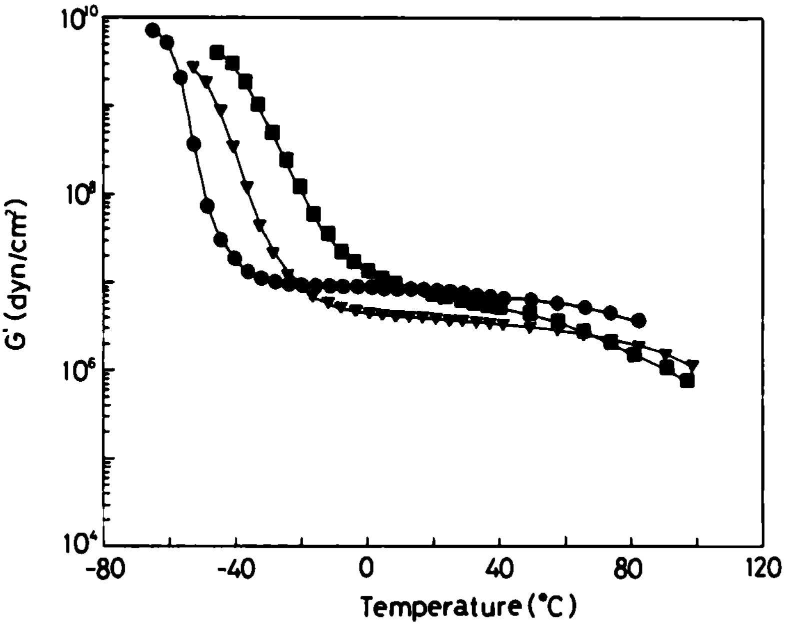

FIGURE 6 Temperature dependence of storage modulus, G', for V-BR (47.4 wt% vinyl content)/CLEARON P125 blends. CLEARON P125 content (by weight): (●) 10%, (▼) 30%, (■) 50%.

ing CLEARON P125 content. Also, the lowest value of the plateau modulus G_e is exhibited by the 70/30 V-BR (47.4)/CLEARON P125 blend. The loss modulus G'' *vs.* temperature plots for V-BR/CLEARON P125 blends (as shown in Figure 7) are similar to the G' *vs.* temperature plots in Figure 6. The curve of the dynamic loss tangent tan δ *vs.* temperature for the V-BR (47.4)/CLEARON P125 blends are represented in Figure 8. The maximum point of tan δ (T_{Dmax}) shifts towards higher temperatures with increasing CLEARON P125 content, which relates to the glass transition temperature, T_g. In general, the minimum value of tan δ at temperatures above T_{Dmax} is related to the molecular weight between entanglements, M_e, by the expression[25]

$$(\tan \delta)_{\min} = 1.04\,(2\cdot M_e/M_n)^{0.80} \tag{3}$$

where M_n is the number-average molecular weight. Since the value of $(\tan \delta)_{\min}$ increases with increasing CLEARON P125 content, the value of M_e derived from equation (3) also increases with increasing CLEARON P125 content. As suggested by Toyama,[3] it is thought that the entanglement between V-BR polymer chains is affected by the "rolling effect of resin" based on the reduced interchain friction in the mixtures.

The dynamic mechanical properties (G', G'') at 23°C and the maximum value of tan δ (T_{Dmax}) for the V-BR/CLEARON P125 blends are shown in Table V. From the results of PSA properties and dynamic mechanical properties as shown in Tables II and V, it is found that 70/30 V-BR/CLEARON P125 blends having minimum values of G' and G'' exhibit the best 180° peel adhesion and tack properties. When

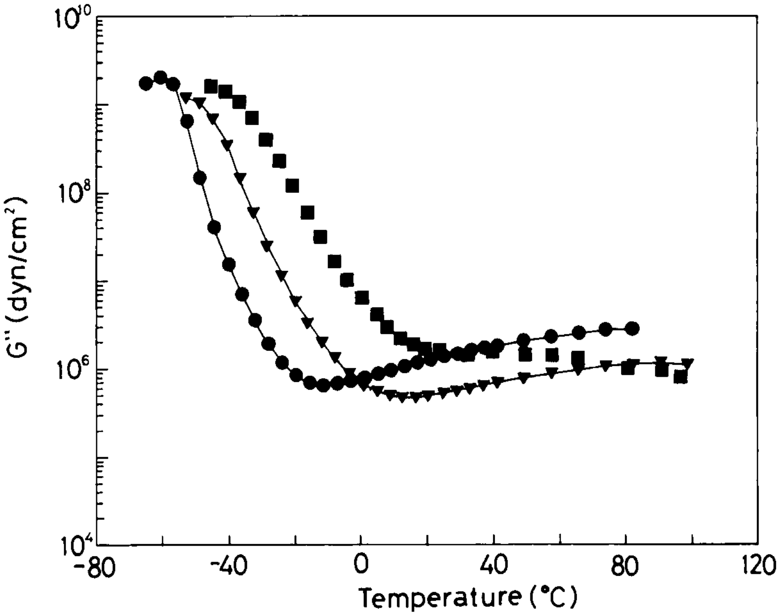

FIGURE 7 Temperature dependence of loss modulus G'' for V-BR (47.4 wt% vinyl content)/CLEARON P125 blends. CLEARON P125 content (by weight): (●) 10%, (▼) 30%, (■) 50%

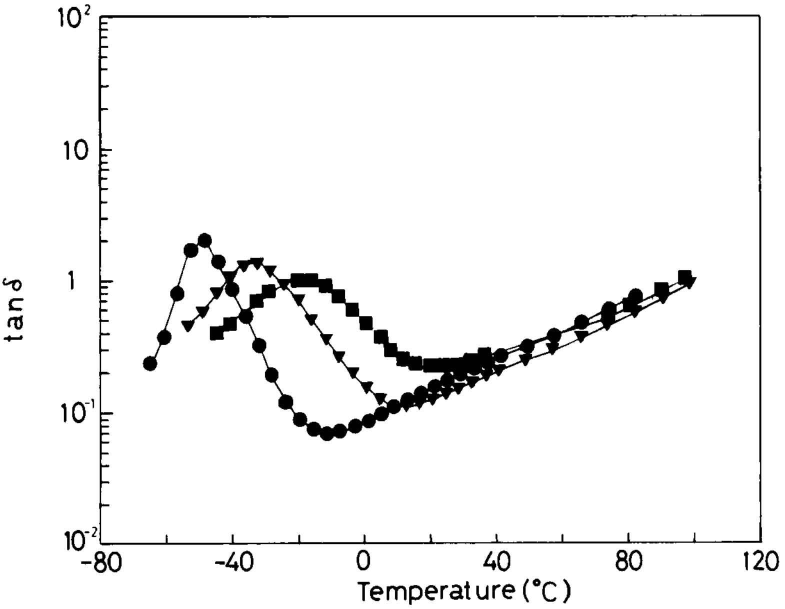

FIGURE 8 Temperature dependence of dynamic loss tangent, tan δ, for V-BR (47.4 wt% vinyl content)/CLEARON P125 blends. CLEARON P125 content (by weight): (●) 10%, (▼) 30%, (■) 50%

TABLE V
Dynamic mechanical properties at 23°C and glass transition temperature, T_{Dmax}, in blends of V-BR with CLEARON P125

	V-BR (47.4)/CLEARON P125			V-BR (60)/CLEARON P125		
	90/10	70/30	50/50	90/10	70/30	50/50
$G' \times 10^{-6}$ (dyn/cm^2)	7.93	3.81	6.85	7.89	3.70	9.09
$G'' \times 10^{-6}$ (dyn/cm^2)	1.26	0.49	1.52	9.60	0.42	3.63
T_{Dmax} (°C)[a]	−48.3	−32.2	−20.0	−34.0	−19.9	−0.8

[a]Temperature at which tan δ is maximum

the plateau modulus $G_e \leqq 3.3 \times 10^6$ (dyn/cm^2) (the Dahlquist criterion), the intimate contact area between the adhesive and substrate is established completely. In this case, the bonding function B is constant. Tse[18] found that blends of styrene-diene triblock copolymer with various 5-carbon aliphatic resins show constant values of the work of adhesion, W_a, and bonding function, B. The values of PSA properties are proportional to the debonding function, D. Then, he pointed out that the value of loop tack, quick stick, and peel adhesion correlate with loss modulus, G''. In this study, all V-BR/CLEARON P125 blends do not fulfill the Dahlquist criterion and the maximum values of 180° peel adhesion, rolling ball tack and probe tack are obtained in 70/30 V-BR/CLEARON P125 blends having the minimum G' and G''. We think that the values of 180° peel adhesion and tack in the V-BR/CLEARON P125 blends are influenced by the bonding function, B.

CONCLUSIONS

In blends of V-BR (vinyl content: 47.4 and 60 (wt%)) with hydrogenated terpene resin (CLEARON P125), pressure sensitive adhesive properties were investigated. The maximum values of 180° peel adhesion and tack were obtained with 70/30 V-BR/CLEARON P125 blends. The effects of miscibility, critical surface tension for wetting, γ_C, and dynamic mechanical properties were examined through the work of adhesion, W_a, bonding function, B, and debonding function, D. In the blends in which CLEARON P125 content was 10%, 30% and 50% (in wt), the miscibility between V-BR and CLEARON P125 at room temperature was confirmed and the γ_C values were constant. On the other hand, the 70/30 V-BR/CLEARON P125 blends exhibited minimums in G' and G''. Therefore, based on the dynamic mechanical properties, it was thought that the 180° peel adhesion and tack of the V-BR/CLEARON P125 blends were influenced by the bonding function, B.

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