

Miscibility and pressure-sensitive adhesive properties of poly(vinylethylene-co-1,4-butadiene)/terpene resin blends

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The pressure-sensitive adhesive properties of miscible blends of poly(vinylethylene-co-1,4-butadiene) (V-BR) with terpene resins were investigated on varying both the random copolymer composition (vinyl content) and the blend composition. The V-BR with 47.4 wt% vinyl content was found to be a remarkable rubber for use as a base polymer for a blend adhesive. In V-BR(47.4)/terpene resin blends, excellent pressure-sensitive adhesive properties were revealed for 50/50 blends. The good results for the adhesive properties were interpreted in terms of the dynamic mechanical behaviour of the blends.

(Keywords: miscibility; blends; dynamic mechanical properties; adhesives)

INTRODUCTION

Pressure-sensitive adhesive properties of blends of elastomers with low-molecular-weight, amorphous tackifiers have been investigated in relation to miscibility in multicomponent polymer mixtures. It is well known that some very effective tackifiers for blend adhesives revealed only a homogeneous morphology by some well known methods^{1,2}. For example, in blends of natural rubber (NR) with tackifiers, two grades of poly(β -pinene) and one hydrocarbon resin based on poly(dicyclopentadiene) showed only a homogeneous phase by electron microscopy, and also dilatometry revealed only a single T_g over the whole composition ranges. On the other hand, Wetzel and coworker³⁻⁵ reported heterogeneous phases, where the disperse phase consisted of resin with some low-molecular-weight rubber and the continuous phase consisted of rubber saturated with resin. It was suggested by Wetzel that maximum tack could be observed when the maximum amount of low-molecular-weight rubber had dissolved in the dispersed resinous phase. In our previous study, the miscibility of blends of rubber with tackifiers was also reported on the basis of phase equilibria, in which the blends exhibited phase-separation behaviour⁶⁻⁸ with rising temperature. This led to the conclusion that the adhesive property at room temperature was better in the close vicinity of the critical composition in the phase diagram owing to large concentration fluctuations. Thus the effective factors for adhesion may be classified as follows. (1) In immiscible blends, morphological and concentration fluctuation contributions to the adhesive properties may play an

important role. (2) In miscible blends, the effect of tackifier can influence the adhesive properties either via its effect on surface energetics or via an effect on bulk viscoelastic properties (elastic modulus and loss factor) of the adhesive⁹⁻¹².

In achieving favourable adhesive properties of bulk adhesives, viscoelastic properties in general range from $G' = 10^5$ to 10^7 dyn cm⁻² at room temperature and T_g from -30 to -20°C . Bonding in the adhesives is a low-rate process at low deformation, which occurs when the pressure-sensitive adhesive is brought into contact with a surface: while debonding is a high-rate process in a tack or peel test, considering the thickness of the adhesive. The shear strength test is a creep test carried out at high deformation. Thus, the viscoelastic behaviour of an adhesive controls its response in adhesive testing and is an important factor in determining practical performance. The viscoelastic properties of rubber-resin pressure-sensitive adhesive systems have been reported and reviewed elsewhere^{11,12}.

We direct our attention to the excellent viscoelastic properties of poly(vinylethylene-co-1,4-butadiene) (V-BR)¹³⁻¹⁵ as a new base polymer^{7,8} for pressure-sensitive adhesives. V-BR with high vinyl content has been reported to exhibit an excellent balance between rebound resilience and wet skid resistance for tyre tread¹⁶. In addition, the adhesive properties can be controlled via the viscoelastic properties of the base polymer on changing the vinyl content in V-BR.

In this study, the performance of new pressure-sensitive adhesives was examined with V-BR/terpene resin (Nirez series) blends, both by ball tack measurements (J. Dow method) and by peel strength at 180° . The 50/50 blend

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of V-BR containing 47.4 wt% vinyl groups (V-BR(47.4)) with terpene resin was found to have the best adhesive properties of all V-BR/terpene resin blends studied. The adhesive properties were interpreted in terms of the bulk viscoelastic properties.

EXPERIMENTAL

The polymer samples used in this study were V-BR(10), V-BR(47.4) and V-BR(70.4) supplied by Nippon Zeon Co. Ltd. The figures in parentheses represent the vinyl contents (in wt%) of V-BR. The V-BR(10) ($M_w=285\,000$, $M_w/M_n=1.09$), V-BR(47.4) ($M_w=214\,000$, $M_w/M_n=1.03$) and V-BR(70.4) ($M_w=232\,000$, $M_w/M_n=1.05$) were prepared by polymerizing 1,3-butadiene in hexane or benzene with an n-butyllithium catalyst in combination with diglyme (diethylene glycol dimethyl ether) at 40°C. The tackifiers used were various Nirez resins supplied by Dainippon Ink and Chemicals Inc. Their molecular characteristics are shown in Table 1.

Blend samples of V-BR with tackifiers were stirred overnight in about 20 wt% toluene solution in the ratios shown. The solution was cast onto a coverglass to prepare as-cast films. The cast films were dried under vacuum at 40°C for a week.

For use in ball tack and peel strength measurements, the 20 wt% toluene solution was cast onto a poly(ethylene terephthalate) (PET) film and isotropically coated using a Lintec Corporation Universal Coating System. The films were dried at 90°C for 1 min according to the customary method. The sample thickness was about 30 μm. The measurements of tack and peel strength followed JIS-z0237. The ball tack measurements, based on the J. Dow method, were carried out at a fixed angle, $\theta=30^\circ$. The peel strength at 180° was measured using a Toyo Baldwin Co. Ltd Tensilon/UTM-4-100 with stainless-steel plate.

Molecular weights of the samples were determined by using a Toso Co. Ltd CP8000 system in 0.1 wt% tetrahydrofuran (THF) solution.

The T_g of the samples was measured using a Du Pont 990 system with 910 DSC at a heating rate of 10°C min⁻¹. Dynamic mechanical measurements of the samples were carried out using a Rheometrics RDS-II. The frequency was 1 Hz and the heating rate was 5°C min⁻¹.

Infra-red spectra were obtained on a JIR-100 FT-IR (JEOL). One-hundred scans at a resolution of 1 cm⁻¹ were signal-averaged and stored on a magnetic disc system.

RESULTS AND DISCUSSION

The infra-red spectra of six kinds of Nirez are shown in Figures 1 and 2. From results of peak attributions, the

Table 1 Molecular weights and T_g values of Nirez resins

	M_w	M_w/M_n	T_g (°C)
Nirez M85	1086	1.67	32
Nirez M105	1169	1.87	56.5
Nirez K105	1029	1.68	59
Nirez 1085	2447	2.53	53.5
Nirez 1100	1110	1.43	49
Nirez 1115	1210	1.54	65

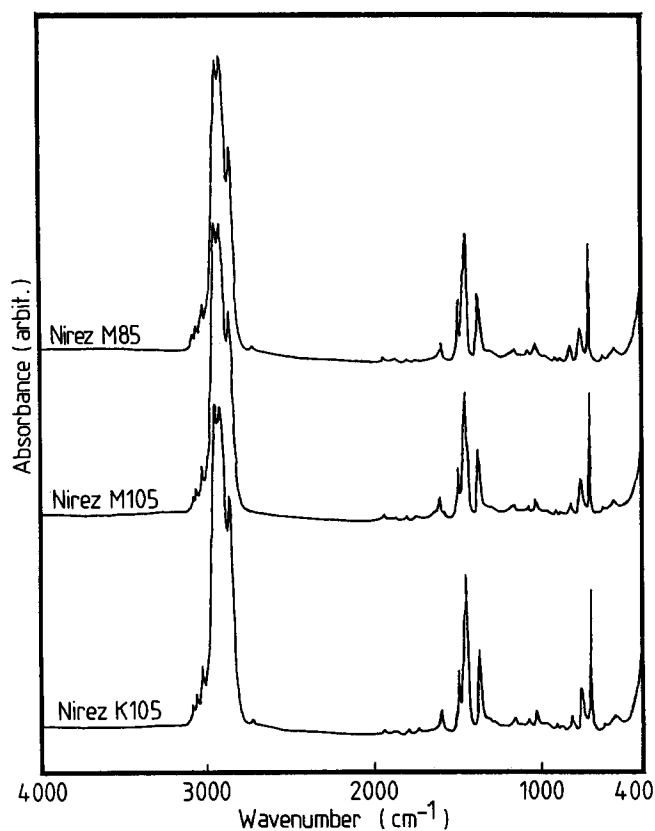


Figure 1 FT-i.r. spectra of Nirez M85, M105 and K105 recorded at room temperature

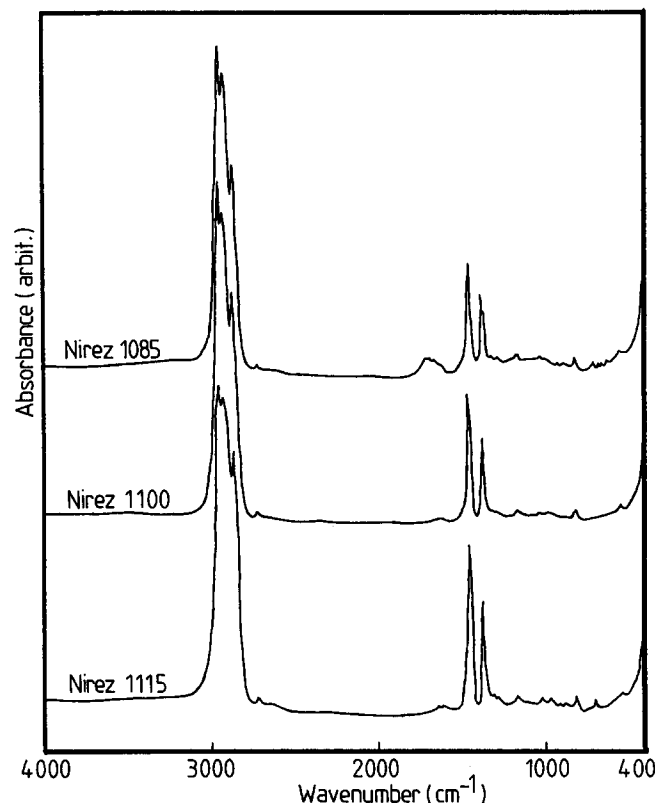


Figure 2 FT-i.r. spectra of Nirez 1085, 1100 and 1115 recorded at room temperature

Nirez resins obviously comprise carbon and hydrogen and were divided into two types: (1) Nirez M85, M105 and K105 have characteristic peaks at around 700–800 cm⁻¹ that are attributed to carbon-carbon double bonds or aromatic rings; while (2) Nirez 1085, 1100 and

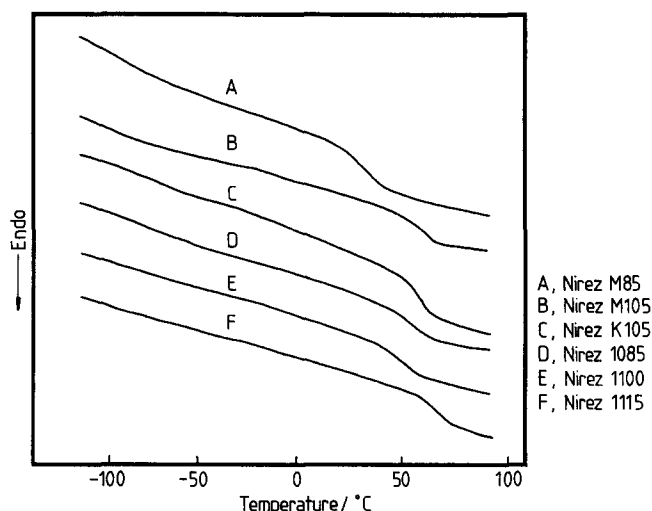


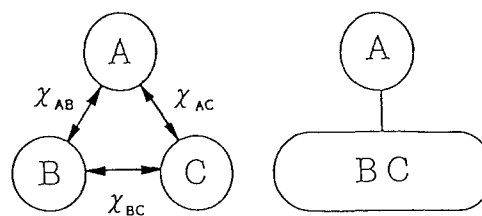
Figure 3 D.s.c. thermograms of each Nirez quenched by liquid N₂ after annealing at 100°C for 2 h

1115 show no evidence of a peak existing around 700–800 cm⁻¹. In Figure 3, the T_g values of various Nirez samples are found from d.s.c. thermograms. The T_g values were not clear in the first run because of the large endothermic melting peak of the crystalline part near T_g, except for Nirez M85. When the sample was quenched after annealing at 100°C for 2 h, at which the crystalline part of Nirez melted, the T_g appeared clearly. The T_g values of various Nirez resins are also shown in Table 1. Each Nirez has a different T_g, although their molecular weights are nearly equal to each other. Since the i.r. spectra of the samples were quite similar in Figures 1 and 2, respectively, the component units may be equivalent in the individual types. Thus, the thermal mobility of segments of the Nirez samples with the same component units can be restricted by certain structural modifications.

Since V-BR is a random copolymer composed of vinyl ethylene and 1,3-butadiene, three monomeric components should be considered in V-BR/Nirez blends, as shown in Figure 4. Here, we consider the effect of two composition parameters, i.e. random copolymer composition (vinyl content) and blend composition (Nirez content), on the phase diagram. In the present work, Nirez M85, M105 and K105 were excellent tackifiers for V-BR. Thus, the pressure-sensitive adhesive properties in blends of V-BR with the three Nirez resins that have peaks around 700–800 cm⁻¹ are investigated on changing both the vinyl content and the Nirez content as follows.

Nirez M85 is an amorphous tackifier at room temperature. Thus, there appears to be no influence on the bulk properties of the V-BR/Nirez M85 blends due to crystallinity. In Figure 5, the T_g values of the V-BR/Nirez 50/50 blends with various vinyl contents are found from the d.s.c. thermograms. It is clearly seen that miscibility of the blends is observed because of the single T_g. Since the T_g of random copolymers, i.e. V-BR, follows the Gordon–Taylor equation, the T_g of blends increases with increasing vinyl content.

The blend composition dependence of T_g in V-BR(47.4)/Nirez M85 blends is shown in Figure 6. The single T_g of the blends shifts smoothly depending on the Nirez M85 content. In Figure 7, the blend composition dependence of T_g for V-BR(47.4)/Nirez M85 is shown as a temperature–blend composition plot. When the blend



A; Nirez
 B; 1,3-butadiene CH2=CH-CH=CH2
 C; Vinyl ethylene CH=CH2

• Resin Nirez (terpene series)

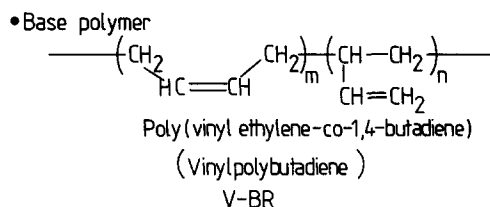


Figure 4 Schematic representation of segmental interaction for a V-BR/Nirez blend

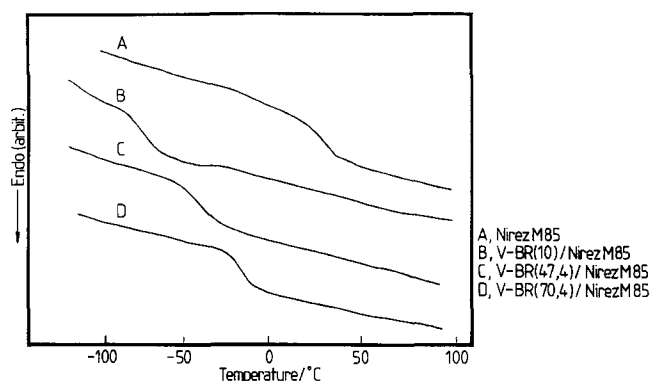


Figure 5 D.s.c. thermograms of blends of V-BR/Nirez M85 with various vinyl contents. T_g of the blends increases with increasing vinyl content

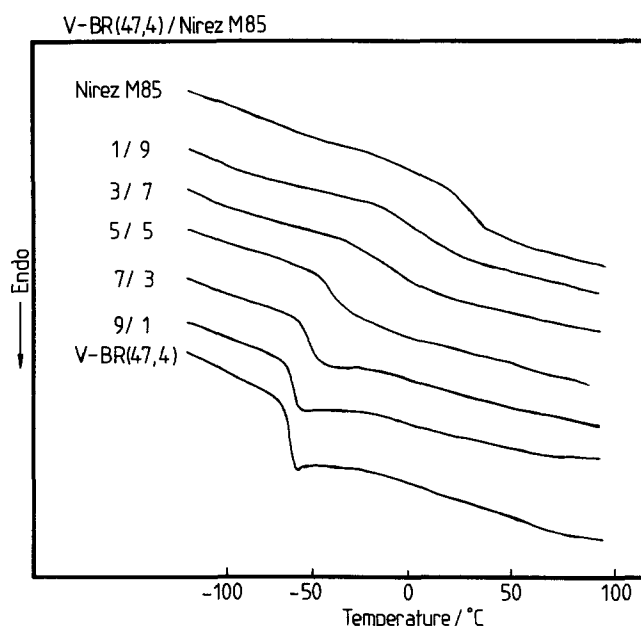


Figure 6 D.s.c. thermograms of V-BR(47.4)/Nirez M85 blends with various Nirez M85 contents. The single T_g of the blends shifts smoothly depending on the Nirez M85 content

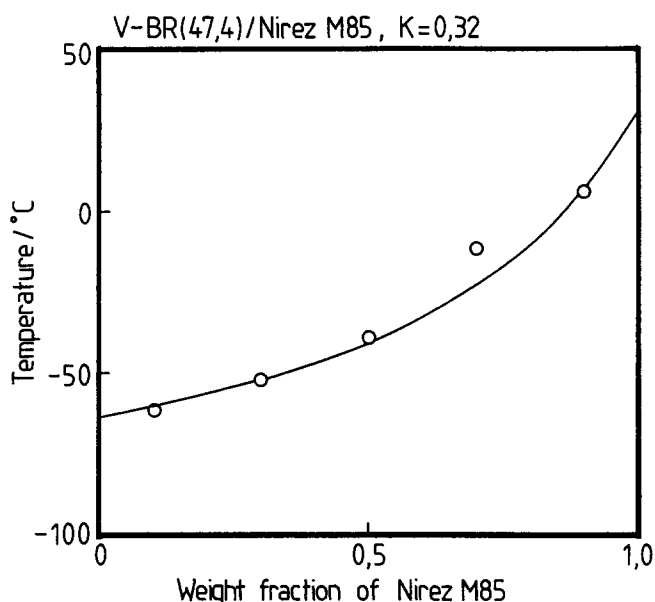


Figure 7 T_g of miscible V-BR(47.4)/Nirez M85 blends at room temperature. The composition dependence of T_g follows the Gordon-Taylor expression ($K=0.32$)

Table 2 Glass transition temperatures and melting temperatures of samples

	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)
Nirez M85	22	32	
Nirez M105	47	56.5	68
Nirez K105	52.5	59	69
V-BR(10)	-100	-98	
V-BR(10)/Nirez M85	-81	-70	
V-BR(10)/Nirez M105	-80.5	-70	
V-BR(10)/Nirez K105	-79	-69	
V-BR(47.4)	-66	-63.5	
V-BR(47.4)/Nirez M85	-48.5	-39	
V-BR(47.4)/Nirez M105	-48.5	-37	
V-BR(47.4)/Nirez K105	-46	-36	
V-BR(70.4)	-39	-36.5	
V-BR(70.4)/Nirez M85	-22	-14.5	
V-BR(70.4)/Nirez M105	-21	-12	
V-BR(70.4)/Nirez K105	-22	-13	

composition is varied, the single T_g of the miscible blend systematically shifts between the T_g values for the pure V-BR(47.4) and Nirez M85. The open circles are T_g of the blends, and the full curve is the Gordon-Taylor expression^{17,18}:

$$T_g = \frac{T_{g1} + (T_{g2} - T_{g1})W_2}{1 + (K - 1)W_2} \quad (1)$$

where T_{g1} and T_{g2} are the T_g values of the pure V-BR(47.4) and Nirez M85, respectively, W_2 is the weight fraction of Nirez M85 and K is the ratio of the thermal expansion coefficients of the amorphous and glassy states. We chose K as a fitting parameter to achieve good agreement between experimental data and calculated values, i.e. $K=0.32$. Since the Gordon-Taylor expression assumes complete homogeneity, such agreement confirms that the V-BR(47.4)/Nirez M85 blend is miscible in the whole composition range. Results of d.s.c. measurements are tabulated in Table 2. Although three kinds of tackifier were used (Nirez M85, M105 and K105), the blends in which the vinyl contents are equal to each other have the same T_g value. With regard to the random copolymer composition, the T_g of the blends tends to increase on increasing vinyl content in V-BR.

For the miscible V-BR/Nirez blends mentioned above, the pressure-sensitive adhesive properties are also investigated in relation to the viscoelastic properties. The performance of pressure-sensitive adhesives is shown in Table 3. Although three types of Nirez were mixed with V-BR, the adhesive properties were identical to each other at the same vinyl content in V-BR. The peel strength, the ball tack and probe tack values, and the holding power for the V-BR/Nirez M85 50/50 blends with varying vinyl content are shown as a function of random copolymer composition. From the result of the 180° peel strength tests, cohesive failure of the adhesive layer appears to occur at lower vinyl content. On increasing the vinyl content, the peel strength increases and a debonding process in the adhesive starts to occur in an interface between the stainless steel and adhesive layer. On the other hand, the tack values decrease with increasing vinyl content. The holding power, furthermore, increases with increasing vinyl content in relation to cohesive strength in the adhesive layer, so that the

Table 3 Performance of pressure-sensitive adhesives in blends of V-BR with Nirez M85, M105 and K105

Sample	180° peel strength (g/25 mm) ^a	J. Dow ball tack	Probe tack (g/5 mm)	Holding power (s)
V-BR(10)/Nirez M85 50/50	CF/950 ^b	7	646	CF/9670
/Nirez M105 50/50	CF/700	8	898	CF/7890
/Nirez K105 50/50	CF/600	6	828	CF/7640
V-BR(47.4)/Nirez M85 50/50	2600	7	992	CF/17270
/Nirez M105 50/50	2400	6	730	CF/16940
/Nirez K105/50	2550	6	839	CF/13580
V-BR(70.4)/Nirez M85 50/50	2450	2>	185	NC shear 9.0 mm ^c
/Nirez M105 50/50	2250	2>	140	NC shear 9.0 mm
/Nirez K105/50	2500	2>	243	CF/54930
V-BR(47.4)/Nirez M85 70/30	1300	2>	159	CF/13770
/Nirez M85 30/70	CF/4700	6	385	CF/4260

^a Dwell time, 24 h

^b CF: cohesive failure of adhesive layer

^c NC: 70 000 s

V-BR(70.4)/Nirez blend shows the best holding power. In the V-BR(47.4)/Nirez M85 50/50 blend, the holding time is the longest of all the adhesives. Thus, in order to achieve the best balance between these properties, the V-BR(47.4)/Nirez M85 blend is found to be an excellent pressure-sensitive adhesive, compared with V-BR(10)/Nirez M85 and V-BR(70.4)/Nirez M85 blends.

In the V-BR(47.4)/Nirez M85 blends, the blend composition dependence of the adhesive properties was also examined. The peel strength and tack value for V-BR(47.4)/Nirez M85 on varying the Nirez M85 content are shown in Table 3. The peel strength increases with increasing Nirez M85 content, but cohesive failure of the adhesive layer takes place at higher Nirez M85 contents. With regard to the blends for which debonding occurs at the interface between the stainless steel and the adhesive layer, the V-BR(47.4)/Nirez M85 50/50 blend has better peel strength than the 70/30 blend. Considering the increase of peel strength with increasing Nirez M85 content and the cohesive failure of the adhesive layer at high Nirez M85 content, the maximum ball tack and probe tack values for the V-BR(47.4)/Nirez M85 blend are found as a function of blend composition. The maximum tack value occurs for the 50/50 composition. The holding power is good, corresponding to the results of peel strength and tack measurements. The longest holding time is also shown in the 50/50 composition. The 50/50 blend has the best adhesive properties of the various blend compositions. So, on changing both copolymer and blend compositions, the V-BR(47.4)/Nirez M85 50/50 blend is the most excellent adhesive of all.

In order to evaluate the relation between adhesive properties and viscoelastic properties, the dynamic mechanical behaviour of both V-BR/Nirez M85 blends and V-BR were examined by rheometry. Figure 8 shows the temperature dependence of $\tan \delta$ for various vinyl contents of the V-BR/Nirez M85 blends. The most striking change in mechanical behaviour with vinyl content is the location of the viscoelastic spectrum on the temperature scale. The maximum in $\tan \delta$ shifts to higher temperature with increasing vinyl content. The temperature at the maximum in $\tan \delta$, T_{Dmax} , is -38°C for V-BR(10)/Nirez M85, -14.6°C for V-BR(47.4)/Nirez M85 and 2.5°C for V-BR(70.4)/Nirez M85 blends,

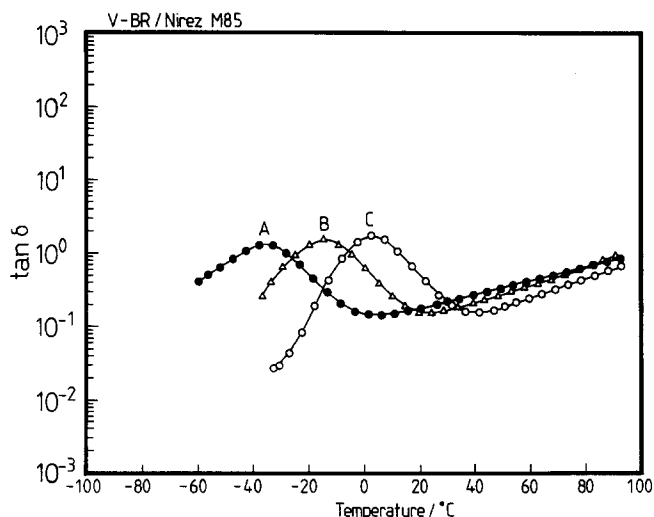


Figure 8 Plot of $\tan \delta$ versus temperature in V-BR/Nirez M85 50/50 blends containing (A) 10, (B) 47.4 and (C) 70.4 wt% vinyl units

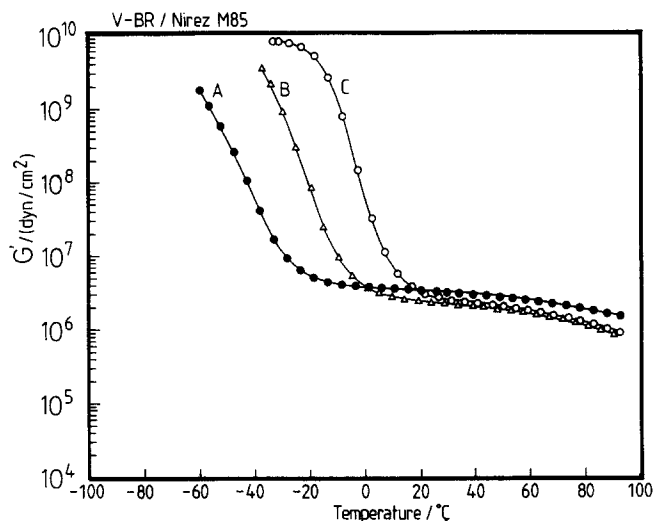


Figure 9 Plot of G' versus temperature in V-BR/Nirez M85 50/50 blends containing (A) 10, (B) 47.4 and (C) 70.4 wt% vinyl units

respectively. This is, of course, primarily a reflection of the T_g values of random copolymers obtained by d.s.c. as mentioned above. The shape of the $\tan \delta$ peak is unchanged in spite of increasing T_{Dmax} . The minimum value in $\tan \delta$ at temperatures above T_{Dmax} , in general, decreases with decreasing molecular weight¹⁹⁻²³. The minimum value is expressed²⁴ by:

$$(\tan \delta)_{\min} = 1.04(2M_e/\overline{M}_n)^{0.80} \quad (2)$$

where \overline{M}_n is the number-average molecular weight and M_e is the molecular weight between entanglements. Since the V-BR copolymers have almost identical \overline{M}_n , the blends of V-BR with Nirez are suggested to have the same M_e . The $\tan \delta$ minimum should appear around the mid-point of the rubber plateau regime, at which the G' curve shows a point of inflection. Then, the temperature is inversely proportional to the frequency. It is interesting that the minimum for V-BR(47.4)/Nirez M85 lies around 20°C . The temperature dependence of G' is demonstrated in Figure 9. Little difference in G' for the blends with various vinyl contents is found at 20°C , the performance of the adhesives being measured at that temperature. The values of G' at 20°C and T_{Dmax} are expressed as a function of the vinyl content in Figure 10. Owing to low T_{Dmax} , the V-BR(10)/Nirez M85 50/50 blend has a higher G' at 20°C in the rubbery state due to the 1,4-butadiene, whereas the V-BR(70.4)/Nirez M85 50/50 blend also has higher G' at 20°C due to high T_g . As the V-BR(47.4)/Nirez M85 has lower G' at 20°C , the dynamic mechanical behaviour of V-BR(47.4)/Nirez M85 50/50 blend is suitable for yielding a pressure-sensitive adhesive. In contrast with the blends, the V-BR copolymers have higher G' at 20°C in the rubber condition and have lower T_{Dmax} . As shown in Figure 11, V-BR(47.4) has the highest G' at 20°C . Thus, on account of loading Nirez M85 into V-BR(47.4), favourable dynamic mechanical behaviour in V-BR(47.4) can be achieved, so that the V-BR(47.4)/Nirez M85 blend exhibits the most excellent adhesive properties.

With regard to the V-BR(47.4)/Nirez M85 blends, the blend composition dependence of $\tan \delta$ is shown in Figure 12. As is clearly seen, T_{Dmax} and the molecular weight between entanglements increase with increasing Nirez M85 content. The increase of T_{Dmax} is interpreted by

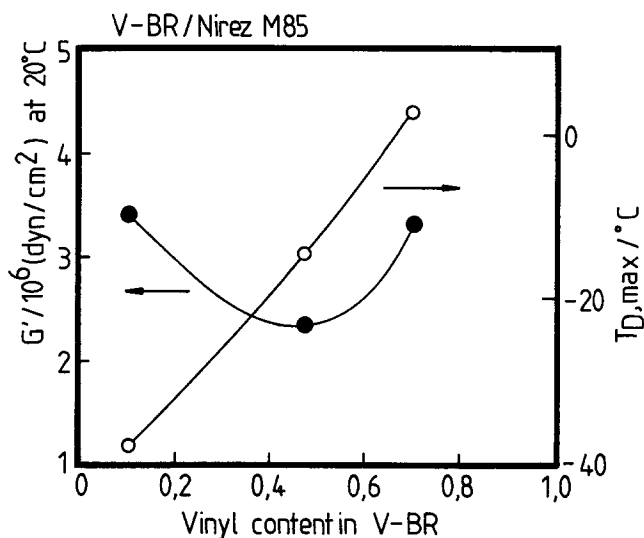


Figure 10 Effects of polymer mixing on both G' at 20°C and T_{Dmax} as a function of vinyl content

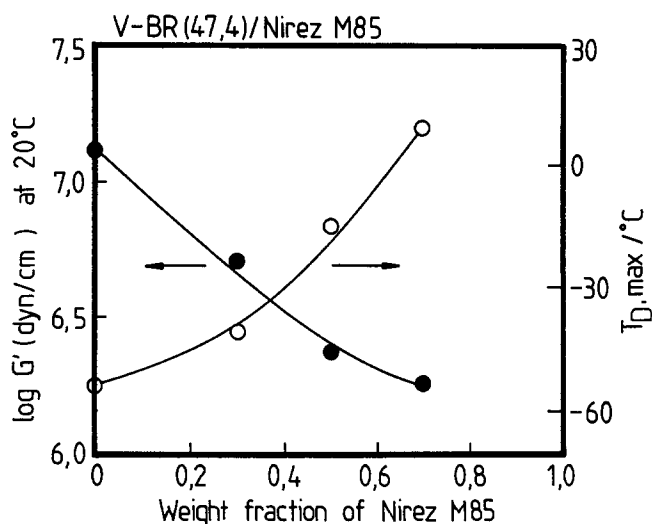


Figure 13 Effects of polymer mixing on both G' at 20°C and T_{Dmax} as a function of Nirez M85 content. The decrease of G' at 20°C and the increase of T_{Dmax} are confirmed with increasing Nirez M85 content

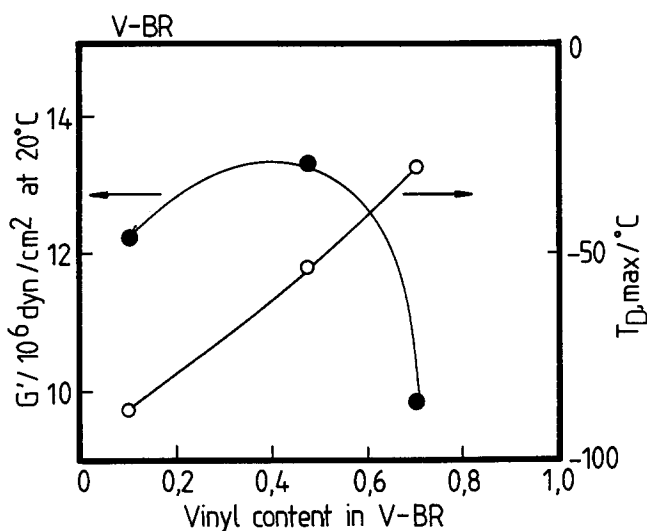


Figure 11 Plot of G' at 20°C and T_{Dmax} of V-BR with varying vinyl content

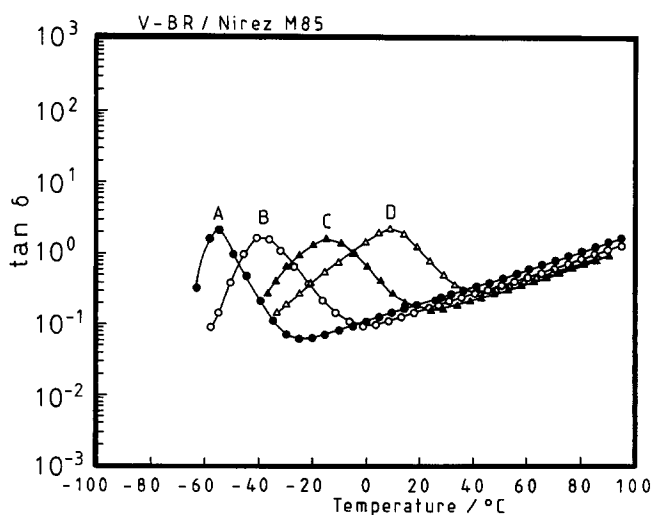


Figure 12 Plot of $\tan \delta$ versus temperature in V-BR(47.4)/Nirez M85 blends with various Nirez M85 contents

restricting segmental mobility: V-BR(47.4) is surrounded by Nirez M85. Since the molecular weight between entanglements increases with increasing Nirez M85 content, the wetness property of the blend should ensure good bonding with stainless steel. But, the higher molecular weight between entanglements may reduce cohesive association in the adhesive, so that cohesive failure of the adhesive layer occurs on increasing the Nirez M85 content. We note that the minimum in $\tan \delta$ for 50/50 blends lies around room temperature. The blend composition dependences of G' at 20°C and T_{Dmax} are shown in Figure 13. The decrease in G' at 20°C and the increase in T_{Dmax} are obviously observed with increasing Nirez M85 content.

Similar results of pressure-sensitive adhesive properties related with dynamic mechanical behaviour are also obtained in both V-BR/Nirez M105 and V-BR/Nirez K105, though given in abbreviated form here.

CONCLUSIONS

The miscibility of V-BR/Nirez blends was investigated by d.s.c. and dynamic mechanical behaviour. V-BR copolymers with all vinyl contents were miscible with Nirez M85, M105, K105, 1085, 1100 and 1115. Among them, Nirez M85, M105 and K105 were suitable resins for pressure-sensitive adhesives with V-BR. We found that V-BR(47.4) was a remarkable rubber as the base polymer for the adhesive. In V-BR(47.4)/Nirez M85 blends, excellent pressure-sensitive adhesive properties were yielded for 50/50 blends. Such results for the adhesive properties were interpreted in terms of the dynamic mechanical behaviour of the blends. Since the T_g or T_{Dmax} of the blend stood near -20°C , the point of inflection of the G' curve and the minimum in $\tan \delta$ appeared at around room temperature. Thus, the V-BR(47.4)/Nirez M85 50/50 blend was the most favourable for use as an adhesive.

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