

Studies on Oil Distribution in Polymer Blends

KAZUO NAITO,^{1,*} NORIO WADA,² SAKAE INOUE,³ and TOSHO NISHI⁴

¹R&D Division, Bridgestone Corporation, 3-1-1, Ogawahigashi Kodaira, Tokyo 187, Japan, ²Bridgestone/Firestone Inc., 50 Century Blvd., Nashville, Tennessee 37214, ³3-30-6, Tsudachou, Kodaira, Tokyo 187, Japan, and ⁴Department of Applied Physics, Faculty of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

SYNOPSIS

Oils and resins are widely used in rubber industries to improve or control the mechanical properties, viscoelastic behavior, processability, and tackiness of a rubber compound. Very few fundamental studies have been reported on the function and the mechanism of oils and resins in a rubber mixture. In this article oil or resin distribution to each phase in an immiscible binary elastomer blend was studied by measuring the change of thermodynamical parameters, such as glass transition temperature, melting point of crystallines, and heat at melt of each polymer component. Several independent approaches give consistent results. It was found that aromatic oil was favorably distributed to the polystyrene-butadiene (SBR) phase of an SBR/natural rubber (NR) blend. Similarly, unequal distribution of resin in a blend was observed for a natural resin (rosin) and a petroleum resin. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Oils and resins are widely used in rubber industries to improve or control the mechanical properties, viscoelastic behavior, processability, and tackiness of rubber compounds.^{1,2} A high loading of filler becomes possible with oil. Normally, the oils and resins employed in rubber compounds are complex mixtures of various materials,³ making it difficult to characterize them. Very few fundamental studies have been reported on the function and mechanism of oils and resins in rubber mixtures. The first systematic research was carried out by one of the authors¹ on the role of oils and resin in rubber compounds. However, to our knowledge, the distribution of oils or resins to each phase of an immiscible binary rubber blend has not been studied. In this article the change of thermodynamic properties of the polymer component was measured when oils or resins were added to an immiscible elastomer blend.

EXPERIMENTAL

Materials

The elastomers used were natural rubber (NR, RSS no. 1), *cis*-1,4-polybutadiene (Japan Synthetic Rubber Co., BR01), and polystyrene-butadiene rubber (Japan Synthetic Rubber Co., SBR 1500). Naphthenic oil (Japan Petroleum Co., spindle no. 2), aromatic oil (Japan Synthetic Rubber Co., JSR AROMA), rosin (Taisha Pine Spirit Oil Co.), and petroleum resin (Esso, Piccodiene) were mixed with elastomers, as shown in Table I.

The oils and rubbers were mixed by a Plastograph (Brabender Corporation) at a rotor speed of 70 rpm for 10 min. Resins (up to 10 phr) were also compounded by using the Plastograph. A 3-inch-diameter roll mill was employed for mixing 30 and 50 phr resins. The amount of oil or resin added to rubber was measured using the weight gain after compounding. This was also checked by measuring the density of the compound precisely. As indicated in Table II, these values agree with each other.

* To whom correspondence should be addressed.

Table I Compounding Recipe of Samples

	1	2	3	4	5	6	7	8	9	10	11	12
NR	100	100	100							50	50	
BR				100	100	100				50		50
SBR							100	100	100		50	50
Oil or resin	10	30	50	10	30	50	10	30	50	50	50	50

Parts per hundred rubber (phr) by weight.

High-Resolution Nuclear Magnetic Resonance and Infrared Spectroscopy Analysis

To characterize the structure of oils and resins used, high-resolution nuclear magnetic resonance (NMR) and infrared (IR) spectrographic studies were carried out. Carbon tetrachloride was used as the solvent in NMR analysis at a resonance frequency of 60 MHz (JEOL minimer 60MC). In the IR measurement, a Hitachi EP-2 spectrometer was used. Naphthenic and aromatic oil were supported by a sodium chloride disc, and a KBr disc method was used for rosin and Piccodiene in the analysis.

Glass Transition Temperature Measurement

A Perkin-Elmer model DSC-1B was employed to measure the glass transition temperature (T_g) of the oils, resins, NR, SBR, and their mixtures at a scanning speed of 8°C/min. The measurement was made twice for each sample to confirm the transition temperature. Figure 1 shows the measurement method to determine the typical T_g . For BR and its mixtures, a DTA (Rigaku Electric) modified for low-temperature measurement was used. As the coolant, a mixture of isopentene and liquid nitrogen was employed. The measurement was carried out at a scanning

speed of 4°C/min using quartz powder as a reference. In the measurement of T_g for BR/NR, BR/SBR, and their mixtures with oils or resins, the T_g of BR and an exotherm caused by the crystallization of BR (−80°C ~ −50°C) were observed during the first run (Fig. 2). Then the sample was rapidly cooled to −150°C and a second run was made to obtain the T_g values of NR and SBR, since these T_g values were masked by the exotherm of the BR at the first run.

Melting Point Measurement of Polybutadiene Crystals

Samples were cooled to −150°C and then heated at a scanning rate of 8°C/min in a differential scanning calorimeter (DSC) (Perkin-Elmer Model DSC-1B). The polybutadiene crystallized rapidly in the temperature region of −75°C to −45°C and it started to melt at around −20°C. The melting was complete below +5°C. The temperature at the peak of melting was defined as the melting temperature (T_m).

Crystallinity of Polybutadiene (BR)

As illustrated in Figure 3, an endotherm in the thermogram of BR at melting was observed, and the

Table II Density Measurement

		Calculated Density Based on	Observed Value by Density
		the Difference in Weight before and after Mixing	Gradient Column Measurement
NR plus naphthenic oil	10PHR	0.914	0.914
	30PHR	0.909	0.909
	50PHR	0.907	0.906
BR plus naphthenic oil	10PHR	0.902	0.902
	30PHR	0.900	0.900
	50PHR	0.897	0.898

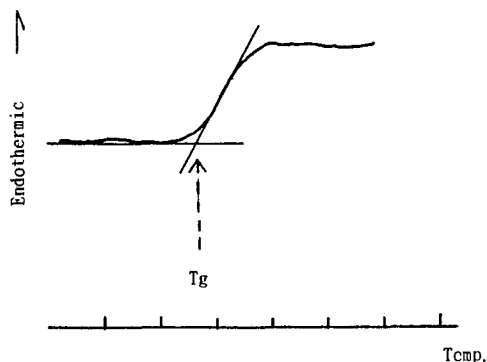


Figure 1 Experimental definition of the glass transition temperature (T_g).

area enclosed by the endotherm and the base line was defined as the crystallinity of the BR compound. About 15 mg of each sample was precisely weighed, and the crystallinity of the sample was corrected based on the weight.

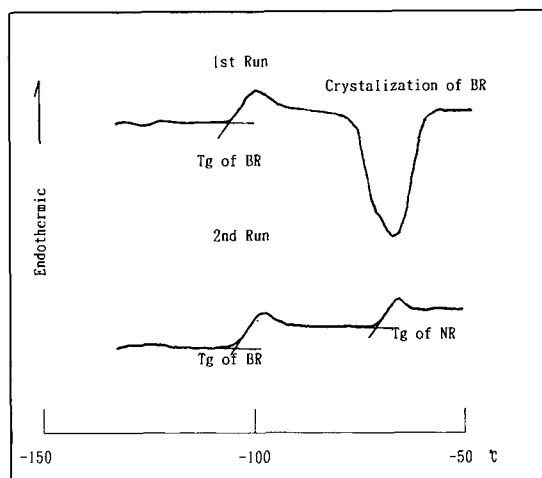
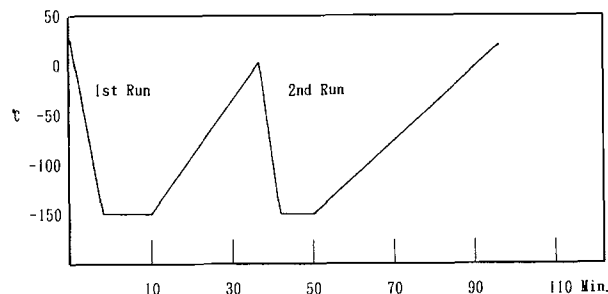


Figure 2 Experimental method of determining g of NR in BR/NR blend.

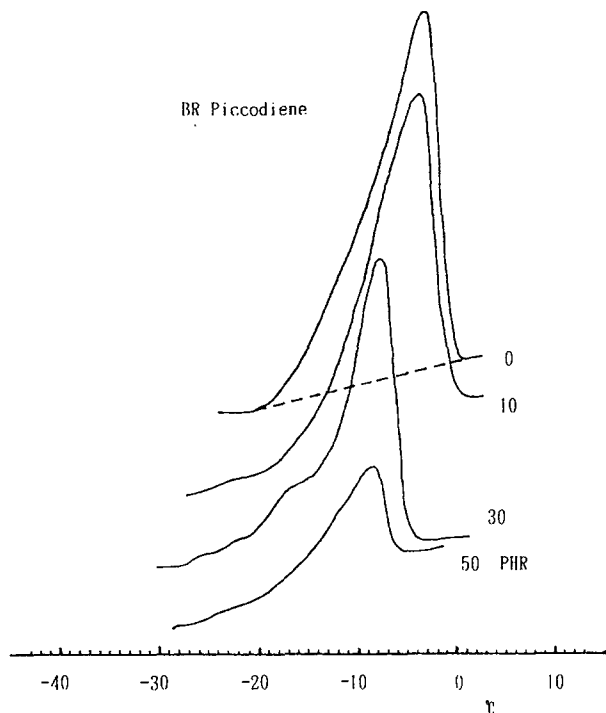


Figure 3 Endothermic thermogram of BR and BR/Piccodiene mixture. The dashed line defines the base for crystallinity measurement.

RESULTS AND DISCUSSION

Glass Transition Temperature Shift

The glass transition temperature (T_g) of a miscible polymer-plasticizer mixture is known to shift when the T_g values of components are different. This phenomenon has been explained by assuming that the free volume of a mixture is the sum of the free volume of the polymer and the plasticizer.⁴ Therefore, the T_g of a mixture is a function of oil. It is expected that the T_g shift of a polymer A may be smaller than expected while that of polymer B is larger than anticipated when an oil C preferentially mixes with polymer B (assuming the polymers are immiscible).

The thermograms for raw polymers, oils, and their mixtures are shown in Figures 4 to 6. The relationship between the T_g values of NR and SBR mixtures and the volume fraction of oil added are shown in Figures 7 and 8. From Figure 6, for example, for an NR : SBR, 50 : 50 and naphthenic oil 50 PHR mixture, the T_g of the SBR phase was -64°C , corresponding to the T_g when the oil was added to SBR alone at a volume fraction of 0.21 (Fig. 8, black dot). On the other hand, the T_g of the NR phase was

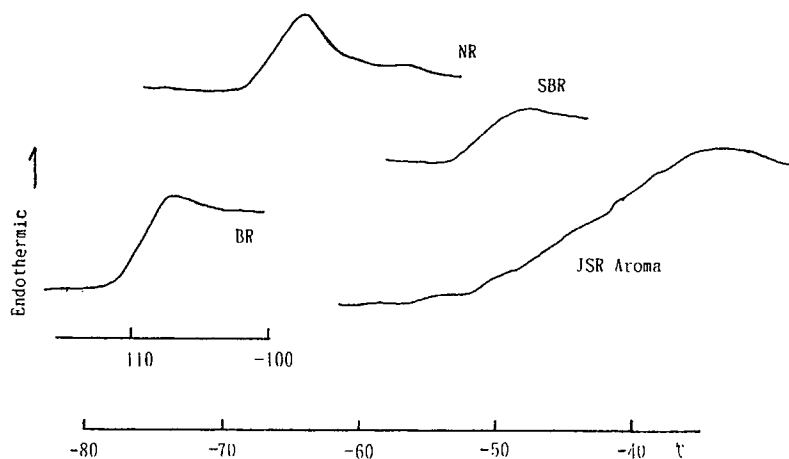


Figure 4 Thermogram of unblended polymers and aromatic oil.

-75°C (Fig. 6), corresponding to a volume fraction of 0.36 (Fig. 7, black dot). When a uniform distribution of oil is assumed, the volume fraction of oil in both phases should be approximately 0.29. This suggests that the oil was preferentially distributed to the NR phase of the immiscible NR/SBR blend. Similar results are observed for NR/SBR/rosin, NR/SBR/aromatic oil, and other systems. These results are summarized in Table III. For example, rosin was preferentially distributed in the BR phase of NR/BR, shown as BR in the bottom row of Table III. In this study all oils and resins employed, except the naphthenic oil, showed higher T_g than those of elastomers. The relationship between T_g and the

volume fraction of oil (up to 0.29) was found to be linear (Figs. 7 and 8).

Eutectic Melting Point Depression

It is well known that melting point depression occurs when a foreign material mixes with a crystalline one (assuming that the materials are miscible). The eutectic melting point depression is expressed as a function of volume fraction of polymer in the mixture and an interaction parameter (χ_1) between polymer and oil.⁵

The oil distribution in an immiscible polymer blend can be estimated when the relationship be-

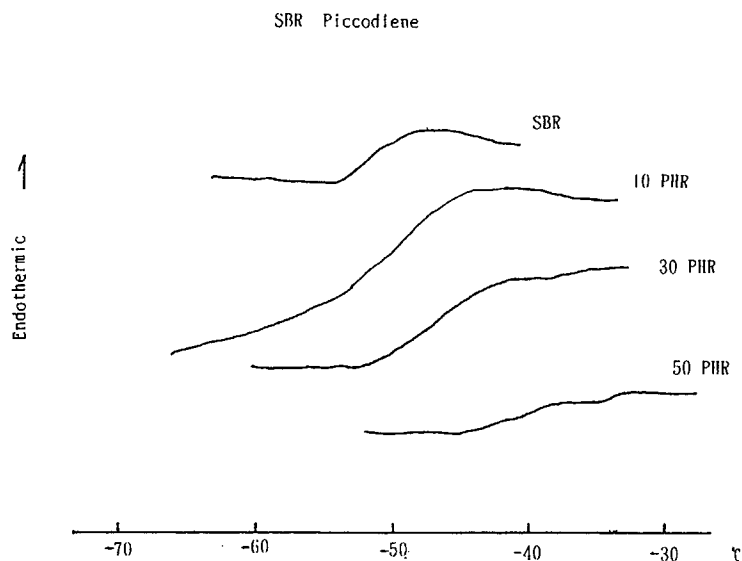


Figure 5 Thermograms showing the shift of T_g in SBR/Piccodiene blend.

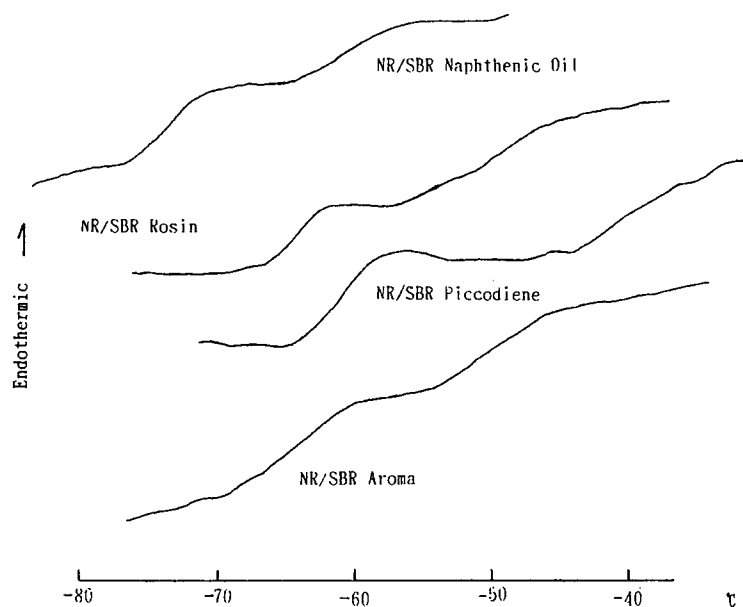


Figure 6 Thermogram of NR/SBR blends containing oil or resin. The NR/SBR naphthenic oil blend (top curve) shows the T_g of the SBR component to be -64°C and that of the BR to be -75°C .

tween the melting point depression and the volume of the oil or resin added is known. Cis-1,4-BR easily crystallizes in the temperature region between -70°C and -50°C and melts at -20°C to $+5^\circ\text{C}$. Assuming that an oil would preferentially mix with BR in an immiscible BR and other elastomer blend,

its melting point depression is expected to be larger than that of a uniform distribution. Figure 9 shows the thermogram of an aromatic oil and BR mixture. It can be seen clearly that the melting point of the mixture decreased as the volume fraction of the oil increased. The oil, rosin, and Piccodiene distribu-

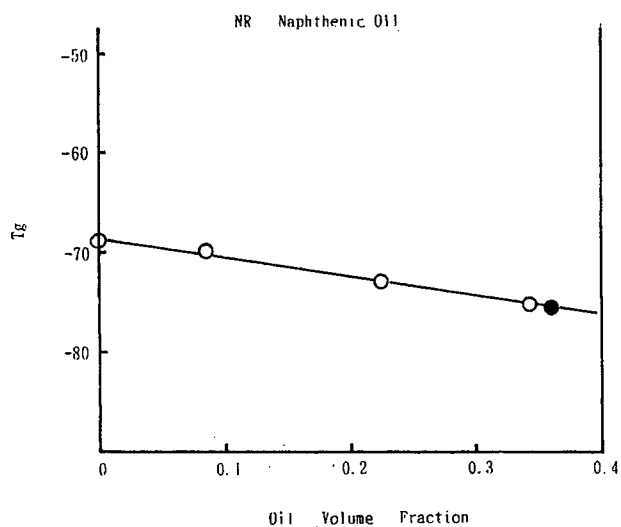


Figure 7 Relationship between T_g and volume fraction of oil in NR and naphthenic oil mixture. The solid dot is for the T_g of an NR/SBR mix with a 0.29 average volume fraction of naphthenic oil.

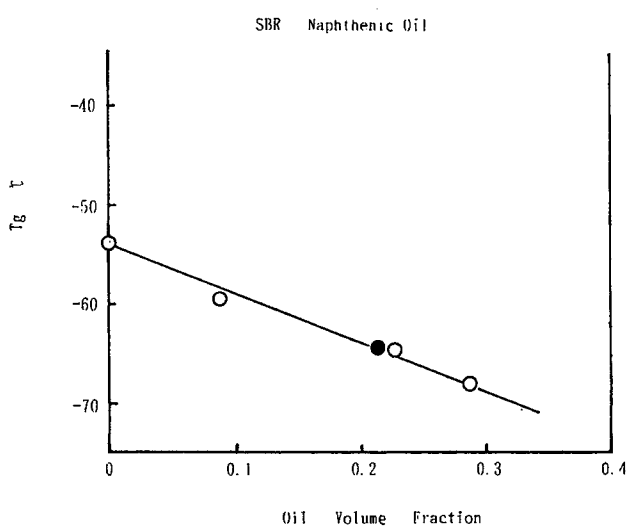


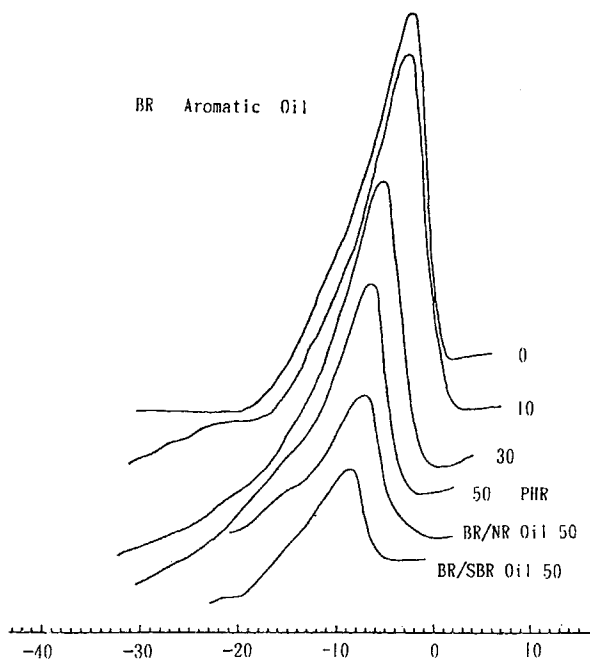
Figure 8 Relationship between T_g and volume fraction of oil in an SBR and naphthenic oil mixture. The solid dot is for the T_g of an NR/SBR mix with a 0.29 average volume fraction of naphthenic oil.

Table III Distribution of Oil or Resin Estimated by T_g Shift

Oil or Resin Added	Polymer Combination		
	NR/BR	NR/SBR	SBR/BR
Naphtenic oil	Vague	NR	Vague
Aromatic oil	Even	SBR	—
Piccodiene	—	SBR	—
Rosin	BR	SBR	BR

tions in BR/NR and BR/SBR measured using this method are summarized in Table IV.

It was found that the degree of melting point depression for BR-rosin was smaller than that of BR-Piccodiene. From the equation which expresses the relationship between the melting point depression and the volume fraction of oil (or resin), there are two possible causes for this difference in melting point depression. First, the volume per mole of rosin may be larger than that of Piccodiene. Second, the interaction parameter χ_1 in the equation may be larger for BR/rosin. Since the specific gravity and the average molecular weight per unit of the two materials are almost equal,³ the latter seems to be most probable. The existence of carboxyl polar groups in rosin causes a higher χ_1 value in a BR/rosin mixture.

**Figure 9** Thermogram of aromatic oil and BR.**Table IV** Distribution of Oil or Resin Estimated by Melting Point Depression

Oil or Resin Added	Polymer Combination	
	NR/BR	SBR/BR
Aromatic oil	BR	BR
Piccodiene	BR	—
Rosin	BR	even (BR?)

Crystallinity

As mentioned in the previous paragraph, BR easily crystallizes and the degree of crystallinity is influenced by adding oil or resin when this oil or resin is miscible with BR. Thus, the extent of preferential distribution of an oil in a BR and other elastomer blend can be estimated, when the relationship between the crystallinity of BR and the volume fraction of the oil is known.

The degree of crystallinity of raw BR was normalized by weight. A comparison of crystallinity was made between BR and BR with oil added. Calculation of the crystallinity was done based on the assumption that the change in crystallinity was caused by the volume of oil added. Thus,

$$C_m = C_b(1 - V_{oil}) \quad (2)$$

where C_m is the crystallinity of the BR and oil mixture, C_b is the crystallinity of BR, and V_{oil} is the volume fraction of oil. Table V shows the comparison between the two values, calculated and observed.

The observed crystallinity for a BR/NR and Piccodiene blend is much smaller than that of the calculated one. This result implies preferential distribution of Piccodiene to the BR phase. These conclusions are summarized in Table VI. The crystallinity observed sometimes exceeds the calculated one. Two possible causes for this are that (1) there was an experimental error in crystallinity measurement, or (2) the oil may have accelerated the crystallization of the BR.

Infrared Spectroscopy and High-Resolution NMR Analysis

Oils and resins for rubber formulation are normally composed of several complex components. For example, naphthenic oil is a mixture of normal paraffin, isoparaffin, alkyl cycloalkene, alkyl benzene, and

Table V Comparison of Apparent Crystallinity of BR between Calculated (Based on Volume Effect) and Observed

Oil or Resin Added	Polymer Combination			
	NR/BR		SBR/BR	
	Calculated	Observed	Calculated	Observed
Naphtenic oil	—	—	10.6	12.7
Aromatic oil	9.2	9.9	9.4	5.4
Piccodiene	10.5	1.7	—	—
Rosin	8.8	4.3	9.9	6.4

aromatic condensed hydrocarbons. Few studies have been made of their structures and properties. Figure 10 illustrates IR and NMR spectra of the oils and resins used in this study. Compared with naphthenic oil, aromatic oil contains more aromatic structures. This difference may explain the preferential distribution of the aromatic oil to the SBR phase in NR/SBR and BR/SBR blends.

Density of Mixtures

The density of a mixture can be expressed by the following equation¹:

$$\frac{1}{\rho} = \frac{1 - V_{oil}}{\rho_r} + \frac{V_{oil}}{\rho_{oil}} + \frac{L \times V_{oil}(1 - V_{oil})}{\rho_r \rho_{oil}} \quad (3)$$

where ρ is the density of the mixture, ρ_r is the density

of rubber, ρ_{oil} is the density of oil, and L is the interaction parameter.

In eq. (3), L is an empirical interaction parameter. A decrease in volume is observed when the rubber and oil molecules of some mixtures attract each other, resulting in a negative value of L . For NR-naphthenic oil and BR-naphthenic oil, as seen in Table I, the calculated density coincides with the observed value to three decimal places. This implies that the interaction between the oil and the polymer is small in these cases. Applying eq. (3), L was found to be nearly zero for SBR/naphthenic oil and NR/naphthenic oil mixtures.¹ On the other hand, for SBR/rosin and NR/rosin, L was -0.064 and -0.028 , respectively; and for aromatic oil, L was -0.007 with SBR and $+0.014$ with NR. This supports the conclusion that the distribution of oil or resin in immiscible elastomer blends is as tabulated in Table VII.

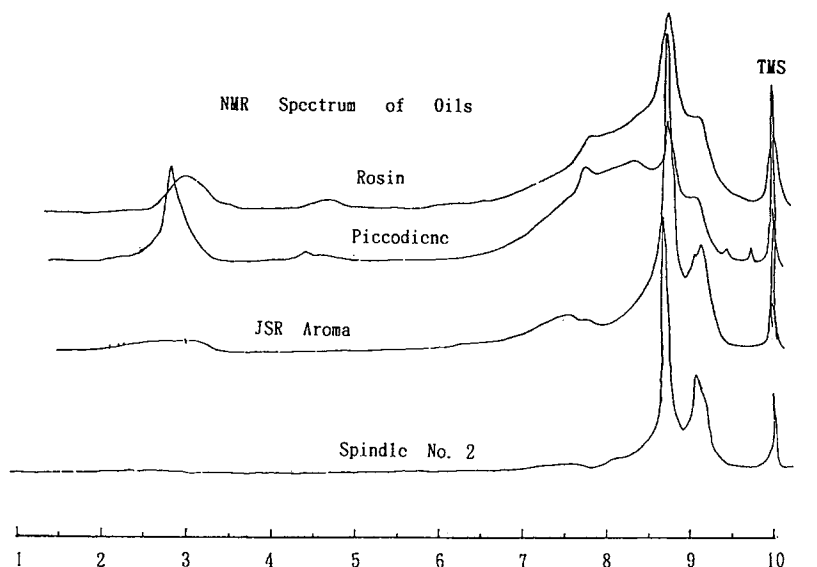


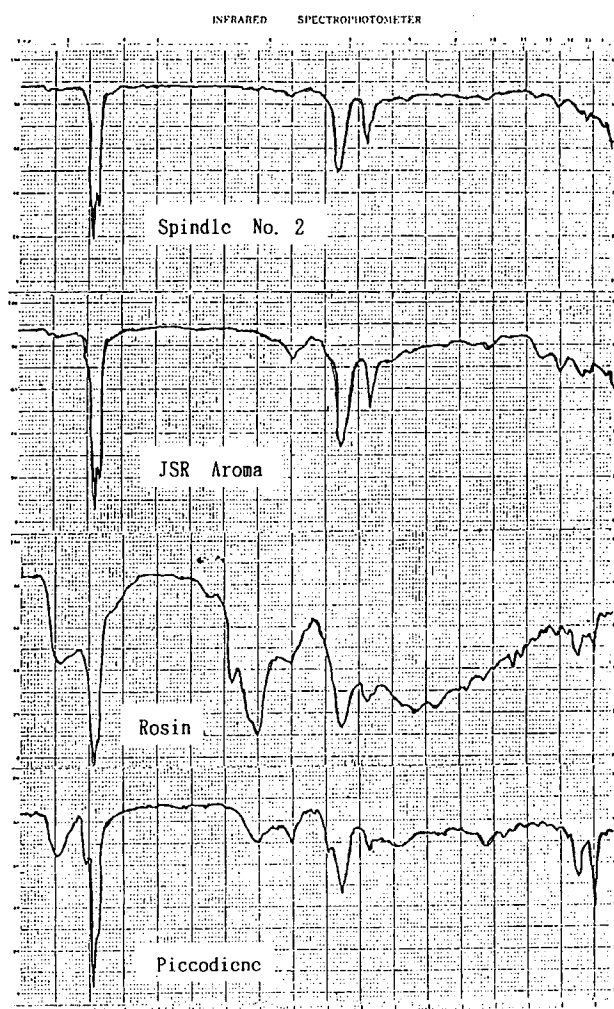
Figure 10 NMR spectra of oils and resin.

Table VI Oil or Resin Distribution Estimated by Crystallinity

Oil or Resin Added	Polymer Combination	
	NR/BR	SBR/BR
Naphthenic oil	—	Even
Aromatic oil	Even	BR
Piccodiene	BR	—
Rosin	BR	BR

Table VII Oil or Resin Distribution Collectively Estimated by Three Different Methods

Oil or Resin Added	Polymer Combination		
	NR/BR	NR/SBR	SBR/BR
Naphthenic oil	Slightly BR	NR	Slightly BR
Aromatic oil	Slightly BR	SBR	BR
Piccodiene	BR	SBR	—
Rosin	BR	SBR	BR

**Figure 11** IR spectra of oils.

CONCLUSIONS

The distribution of oils and resins in immiscible elastomer blends has been measured by the shift in glass transition temperature T_g (Table III), the melting point depression (Table IV), and the change in the crystallinity (Table V) of the components. The three independent approaches to determination of the oil/resin distribution in immiscible polymer blends are summarized in Table VII. All three methods give the same distribution. These present a consistent picture of the oils or resins being preferentially mixed by one of the components of the blends.

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