

The Viscoelastic Properties of Rubber-Resin Blends. III. The Effect of Resin Concentration

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Synopsis

The viscoelastic properties of a rubber-resin blend, which influences performance of the blend as a pressure-sensitive adhesive, depend upon the structure of the resin as well as its molecular weight. The effect of the concentration of a compatible resin in the blend was examined using a mechanical spectrometer. Four types of resins were used. These are the rosin esters, polyterpenes, pure monomer resins such as polystyrene and poly(vinyl cyclohexane), and petroleum stream resins. Each was examined in blends with both natural rubber and styrene-butadiene rubber over a range of concentrations. It is shown that the temperature of the $\tan \delta$ peak for compatible systems can be predicted by the Fox equation, $T_g^{-1} = W_1 T_{g1}^{-1} + W_2 T_{g2}^{-1}$, where W_1 and W_2 are the weight fractions of the resin and rubber, respectively, and the T_g 's are the $\tan \delta$ peak temperatures in K. The plateau modulus G_N^0 for a blend can be identified as the G' value in the rubbery plateau at the point where $\tan \delta$ is at a minimum. The relationship between G_N^0 and G_N^0 , the plateau modulus for the undiluted elastomer, is shown to be proportional to the volume fraction of the elastomer raised to the 2.3-2.4 power for natural rubber with six different compatible resins. The exponent for styrene-butadiene rubber is 2.5-2.6 with four different resins. Using these relationships, both the $\tan \delta$ peak temperature and plateau modulus can be predicted for a rubber-resin system from data on the unmodified elastomer and on one typical rubber-resin blend.

INTRODUCTION

It is generally accepted that the viscoelastic properties of a composition reflects the bulk response which controls pressure sensitive adhesive performance. A representative pressure sensitive adhesive system may be a simple blend of an elastomer with a low molecular weight resin. Typical resins are described in Paper I of this study.¹ At specific ratios, these rubber-resin blends are pressure-sensitive adhesives, while at other concentrations they are not. Therefore, an examination of rubber-resin systems covering a range of concentrations allows properties to be determined on blends which exhibit pressure sensitive adhesive properties at appropriate concentrations, but not at others.

Paper I of this study was an examination of the effects of resin structure on the viscoelastic properties of blends of low molecular weight resins with natural rubber or styrene-butadiene rubber.¹ Aliphatic resins were shown to be compatible with natural rubber but incompatible with styrene-butadiene rubber, while aromatic resins were compatible with styrene-butadiene rubber but incompatible with natural rubber. Thus, the components must be similar in polarizability to form compatible systems. Paper II demonstrated the significance of the weight average molecular weight of the resin on viscoelastic properties.² For the systems studied, incompatibility appeared when the weight average molecular weight of the resin was in-

creased to greater than 1000. The work reported here is a study of the effect of the concentration of the resin diluent on the viscoelastic properties of the rubber-resin blends.

The temperature of the peak in $\tan \delta$ and the modulus in the rubbery plateau are two of the more recognizable features of dynamic property plots versus temperature. Earlier workers had shown that the addition of specific resins to elastomers shifted the $\tan \delta$ peak to higher temperatures, or equivalently shifted the transition zone to lower frequencies, and depressed the modulus in the rubbery plateau.³⁻⁷ The objective of this work was to determine the relationship between the concentration of a compatible resin in a rubber-resin blend and the shift of the $\tan \delta$ peak temperature and depression of the plateau modulus compared to the unblended rubber.

EXPERIMENTAL

Four types of resins were used in this work. The rosin-based resins are the glyceryl or pentaerythritol esters of hydrogenated rosin. The terpene resins are cationically polymerized terpenes such as α - or β -pinene. The C_5 resin is a cationically polymerized petroleum stream consisting primarily of C_5 and C_6 mono- and diolefins, branched and straight chain. The pure monomer resins are polymerized monomers such as styrene, α -methylstyrene, or vinyltoluene prepared as the homo- or copolymers. The poly(vinyl cyclohexane) resin was prepared by complete hydrogenation of a polystyrene resin. The specific resins used are described in Table I.

The natural rubber and styrene-butadiene rubber are described in Table II. The natural rubber was milled to a Mooney viscosity of 53, a level appropriate for use in pressure sensitive adhesives. The styrene-butadiene rubber was Ameripol 1011 (BFGoodrich Rubber Co.). The styrene content was determined by infrared spectroscopy.

TABLE I
Identification of Resins

	Symbol ^a	\bar{M}_w^b	\bar{M}_w/\bar{M}_n^b	T_g (°C) ^c
Rosin-based				
Glycerol ester of highly stabilized rosin	R-GLY	550	1.2	32
Pentaerythritol ester of highly stabilized rosin	R-PE-1	650	1.3	48
Pentaerythritol ester of stabilized rosin	R-PE-2	650	1.3	48
Terpene				
Poly (α -pinene)	α -PIN	650	1.4	68
Poly (β -pinene)		1600	2.6	62
Pure monomer				
Polystyrene		900	1.6	32
Poly (vinyl cyclohexane)	PVCH	650	1.4	38
Poly (<i>tert</i> -butylstyrene)	TBS	850	1.3	59
C_5 Stream				
Polymerized petroleum stream, low MW	C_5 LMW	1350	1.8	45
Polymerized petroleum stream, high MW	C_5 HMW	2850	2.8	41

^a Symbols for resins used for Figures 12, 13, 16, and 17.

^b Apparent molecular weight data based on polystyrene standards.

^c DSC data; first break on second heat.

TABLE II
 Description of Elastomers

<i>Natural rubber (milled smoke sheet)</i>	
Mooney viscosity (100°C)	53
\overline{M}_n	105,000
\overline{M}_w	266,000
$\overline{M}_w/\overline{M}_n$	2.53
T_g (DSC) (°C)	-66
<i>Styrene-butadiene rubber</i>	
Mooney viscosity (100°C)	53
Bound styrene (%)	25
T_g (DSC) (°C)	-57

Molecular weight and molecular weight distribution data for both the resins and the polymers were determined by size exclusion chromatography (SEC) using a Styragel column set, calibrated with polystyrene standards. Glass transition temperatures were determined by differential scanning calorimetry as the temperature of the first break on the second heat. Heating rate was 20°C/min.

The rubber-resin compositions were prepared in the required concentrations in toluene solution. These were cast onto a release surface and the solvent was allowed to evaporate at room temperature. Final drying was carried out at 40°C in a vacuum oven for 3 days. Complete absence of solvent was confirmed by thermogravimetric analysis. Photomicrographs of the blends were taken using phase contrast on a Zeiss WL light microscope at 490 \times . The samples, which were about 5 μ m thick, were obtained by microtoming at about 20°C below T_g .

Dynamic measurements were made on a dynamic spectrometer (Rheometrics, Inc.) in the parallel plate mode using small diameter (8 mm) plates. G' , G'' , and $\tan \delta$ were plotted from the glassy region to 120°C at 10 rad/s. Frequency scans were run from 0.1 to 100 rad/s. The data for some of the samples were extrapolated in the glassy region to -80°C to simplify comparisons. This does not affect the conclusions since only data at the transition and in the rubbery plateau were involved. Further details of the dynamic measurements are in Paper I of this study.¹

DISCUSSION OF RESULTS

In considering the effects of resin concentration on the viscoelastic properties of rubber-resin blends, two questions are of interest. First, are the rubber-resin blends compatible over the entire concentration range and second, within the compatible range what is the effect of a resin diluent on the viscoelastic properties of the system.

Sherriff et al. reported that blends of natural rubber with the pentaerythritol ester of stabilized rosin exhibited two T_g 's, indicating two phases, at greater than 60% resin concentration.³ The hydrocarbon resins examined showed only a single T_g over the entire concentration range studied. However, Sherriff et al. reported viscoelastic studies only up to the 50% resin concentration.

Examination of natural rubber-poly(vinyl cyclohexane) resin blends and

styrene-butadiene rubber-polystyrene resin blends suggests that these systems consist of two phases at high concentrations of resin. Plots of $\tan \delta$ vs. temperature for the natural rubber-poly(vinyl cyclohexane) resin blends covering a range of concentrations are presented in Figure 1. The x -axis is scaled to the concentration of natural rubber. As the concentration of resin is increased, the temperature of the $\tan \delta$ peak increases from -58°C for undiluted natural rubber to 49°C for the composition containing 25% natural rubber. At this concentration, a lower temperature peak at -40°C becomes prominent and the irregular $\tan \delta$ plot between the two peaks (-40 – 49°C) indicates a complex multiphase system. The G' plots shown in Figure 2 also suggest that two phases are present in the blend containing 75% of resin. The extended drop of G' from the glassy region to the rubbery plateau over a wide temperature range supports the observation that more than a single $\tan \delta$ peak is present. Similar plots for styrene-butadiene rubber-polystyrene resin blends, presented as Figures 3 and 4, show behavior which is similar to the natural rubber-poly(vinyl cyclohexane) resin blends. Two phases appear to be present at high resin concentration, based upon two $\tan \delta$ peaks and the extended drop in G' over a wide temperature range.

The presence of two phases in the natural rubber-poly(vinyl cyclohexane) resin blend is supported by the photomicrographs presented as Figures 5–7. Figure 5, which is of the 25% resin blend, shows a single phase within the limits of detection of the microscopic system (about $0.5 \mu\text{m}$). The two circular structures in the center of the photo are artifacts of the sample preparation. Figure 6, the 50% resin blend, shows a small concentration

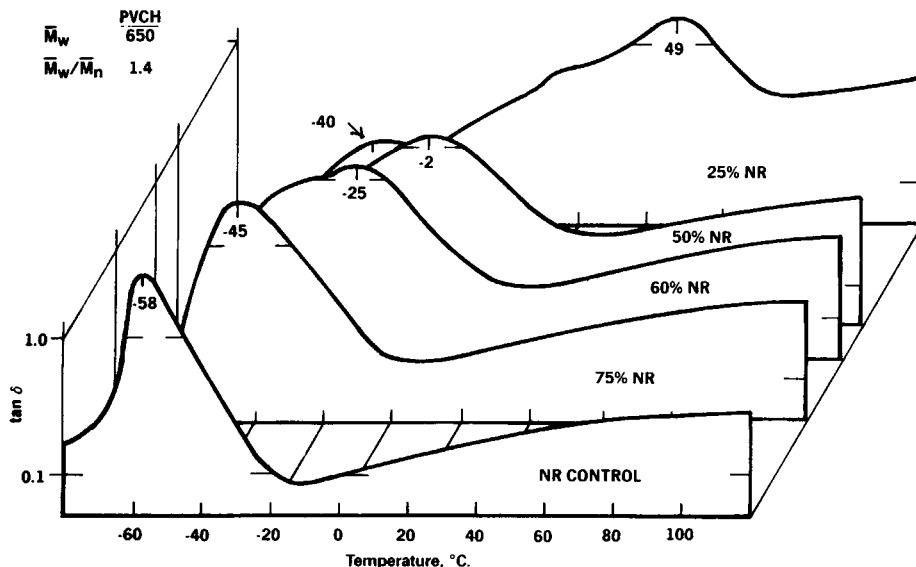


Fig. 1. Effect of concentration on $\tan \delta$ vs. temperature for blends of natural rubber with poly(vinyl cyclohexane) resin.

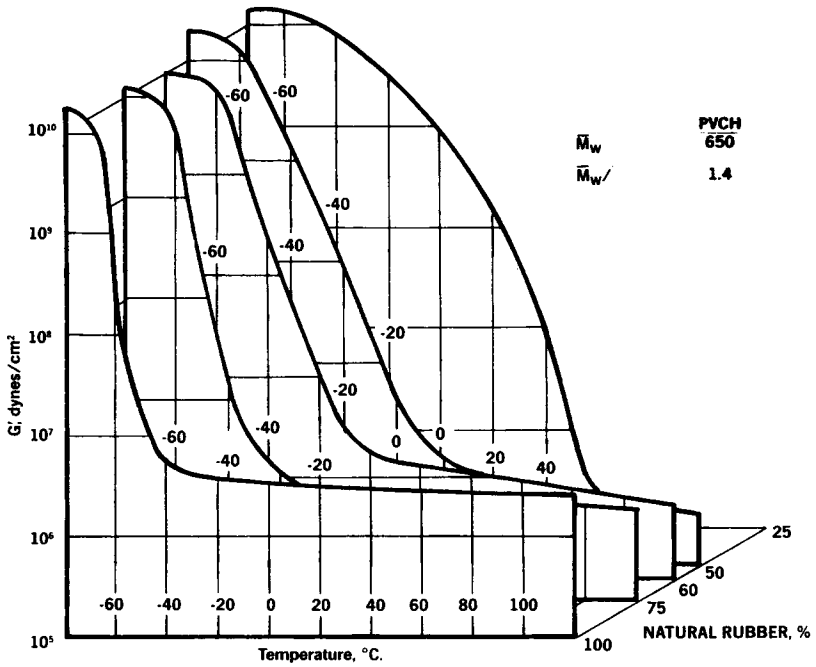


Fig. 2. Effect of concentration on G' vs. temperature for blends of natural rubber with poly(vinyl cyclohexane) resin.

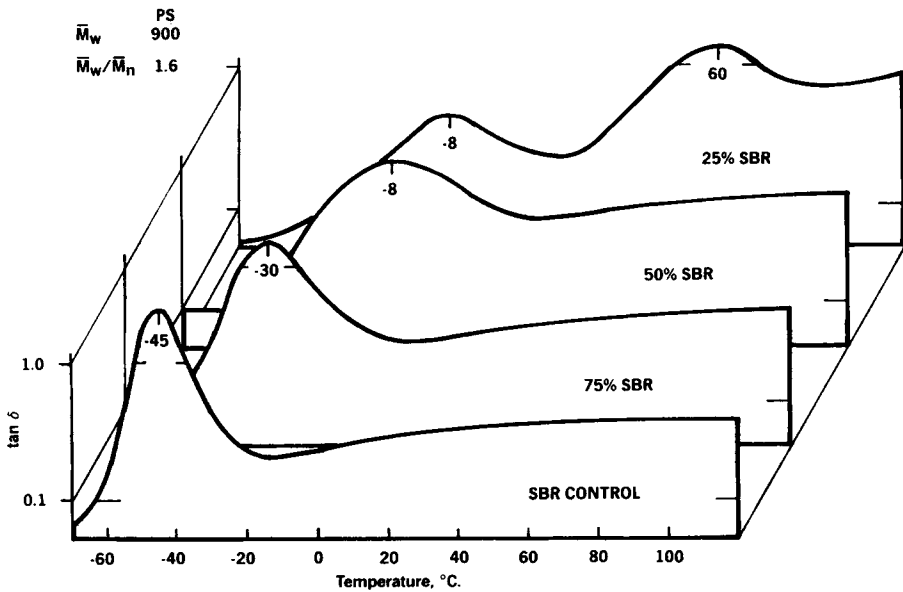


Fig. 3. Effect of concentration on $\tan \delta$ vs. temperature for blends of styrene-butadiene rubber with polystyrene resin.

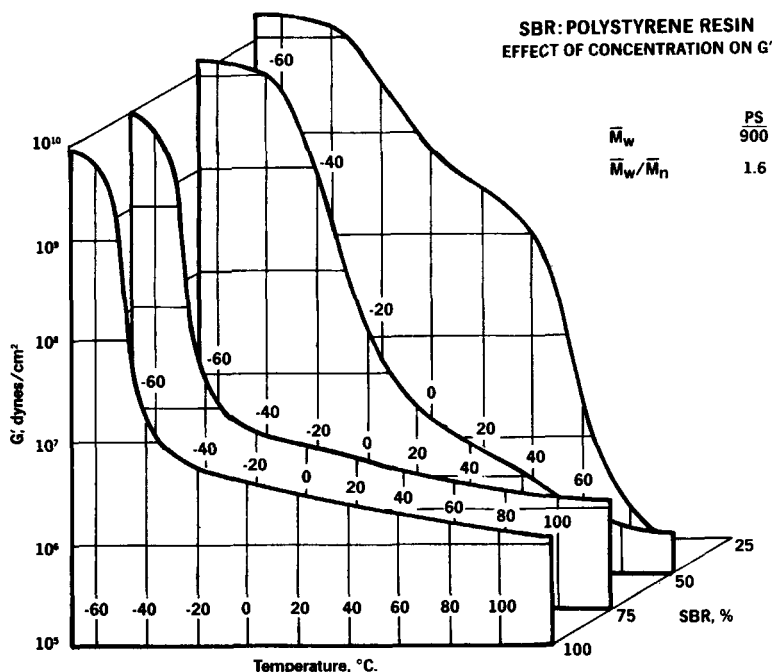


Fig. 4. Effect of concentration on G' vs. temperature for blends of styrene-butadiene rubber with polystyrene resin.

of light-colored specs about $1\ \mu\text{m}$ in size. Figure 7, the photomicrograph of the 75% resin blend, shows two phases where the light-colored phase may be present in higher concentration. We conclude that there is a limit to the amount of poly(vinyl cyclohexane) resin which can be dissolved in natural rubber and that a second, presumably resin-rich, phase is present above this concentration. We cannot assume, however, that incompatibility will be observed in all rubber-resin systems. Specific systems may be compatible at all concentrations depending upon the identity of the ingredients.

Withing the range of compatibility, temperature scans of rubber-resin systems show a progressive increase in the temperature at which $\tan \delta$

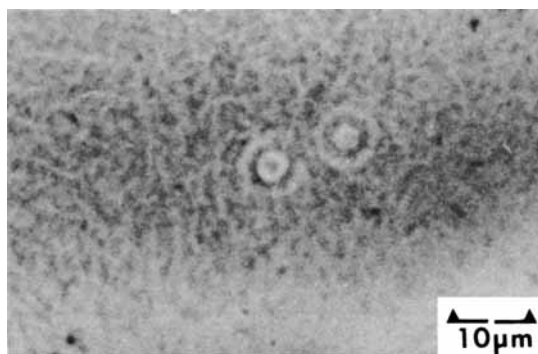


Fig. 5. Transmission photomicrograph of a 3:1 blend of natural rubber with poly(vinyl cyclohexane) resin.

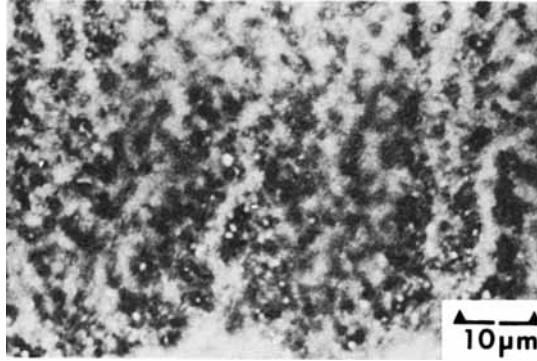


Fig. 6. Transmission photomicrograph of a 1:1 blend of natural rubber with poly(vinyl cyclohexane) resin.

reaches a peak and a progressive depression in the modulus of the rubbery plateau as the concentration of the resin is increased. A typical example of this behavior is shown in Figures 8 and 9 for natural rubber- C_5 stream resin blends. The $\tan \delta$ plots vs. temperature for the range of concentrations are shown in Figure 8. The z -axis is scaled to the concentration of natural rubber. The $\tan \delta$ curve for natural rubber is at the rear of this figure. The curves for compositions containing increasing amounts of resin are shown toward the front of the figure. The peak in $\tan \delta$ is shifted from -58°C to $+43^\circ\text{C}$ as the concentration of natural rubber decreases from 100% to 20%.

Figure 9 shows the G' plots for the same series of samples. On this figure the natural rubber is in front with the blends containing increasing concentrations of resin in the rear. Remembering that the base line of 10^4 dyn/cm² is ascending for the successive plots, it is easy to see that the plateau modulus is depressed by increasing concentrations of the resin.

Typical plots for blends of styrene-butadiene rubber with the glycerin ester of hydrogenated rosin are displayed in Figures 10 and 11. These figures show the same effects as seen for the natural rubber- C_5 stream resin system.

The systematic shift of the $\tan \delta$ peak temperature and depression of the plateau suggest a direct relationship of these properties to concentration.

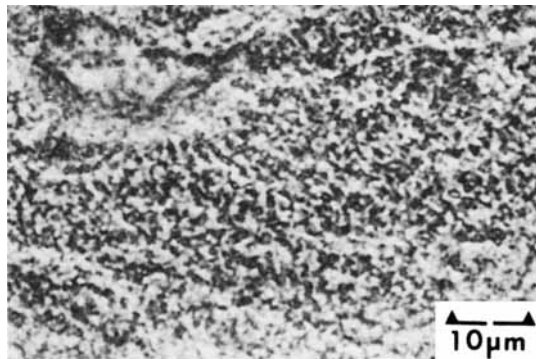


Fig. 7. Transmission photomicrograph of a 1:3 blend of natural rubber with poly(vinyl cyclohexane) resin.

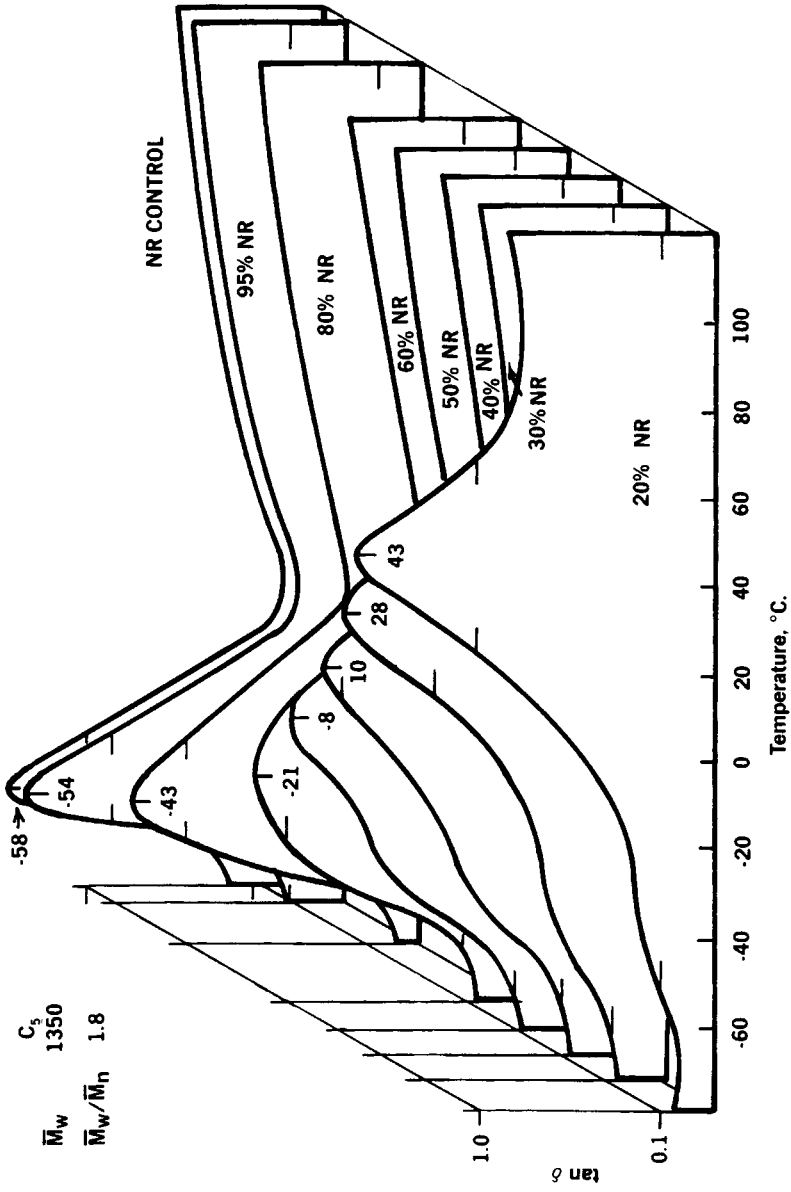


Fig. 8. Effect of concentration on $\tan \delta$ vs. temperature for blends of natural rubber with a C_s stream resin.

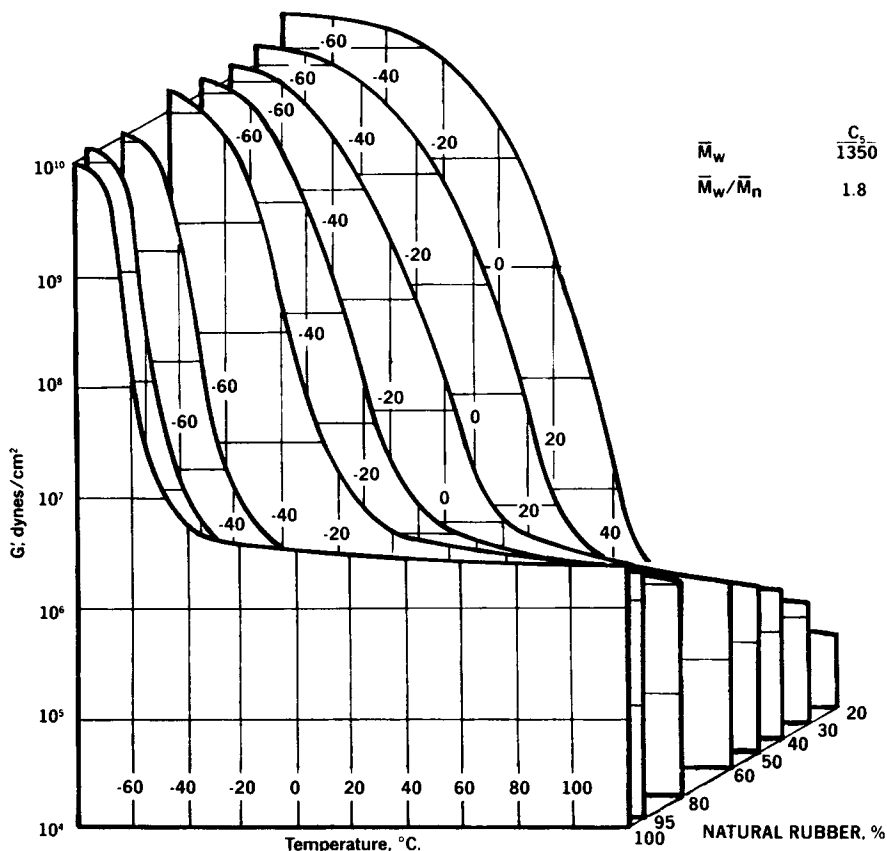


Fig. 9. Effect of concentration on G' vs. temperature for blends of natural rubber with a C_3 stream resin.

To examine this relationship, natural rubber was blended with six different resins covering a range of concentrations, and styrene-butadiene rubber was blended with four different resins. The temperature of the maximum in $\tan \delta$ and the modulus of the rubbery plateau were examined as a function of the concentration of the rubber and resin in the blends. As described earlier, all rubber-resin systems did not appear compatible at all blend ratios. Only data from compatible blends were included in this study.

Tan δ Peak Temperature

Tan δ peak temperatures were determined by reading directly from the temperature scans of the $\tan \delta$ curves. Data points were recorded at 4°C intervals, and so interpolation between points was carried out to estimate peak temperatures to approximately $\pm 1^\circ\text{C}$.

Various blending laws were evaluated in an attempt to develop an equation to predict $\tan \delta$ peak temperature. Of those examined, the reciprocal relationship proposed by Fox to explain the glass transition temperature of acrylic copolymers was found to be the most useful⁸:

$$T_g^{-1} = W_1 T_{g1}^{-1} + W_2 T_{g2}^{-1}$$

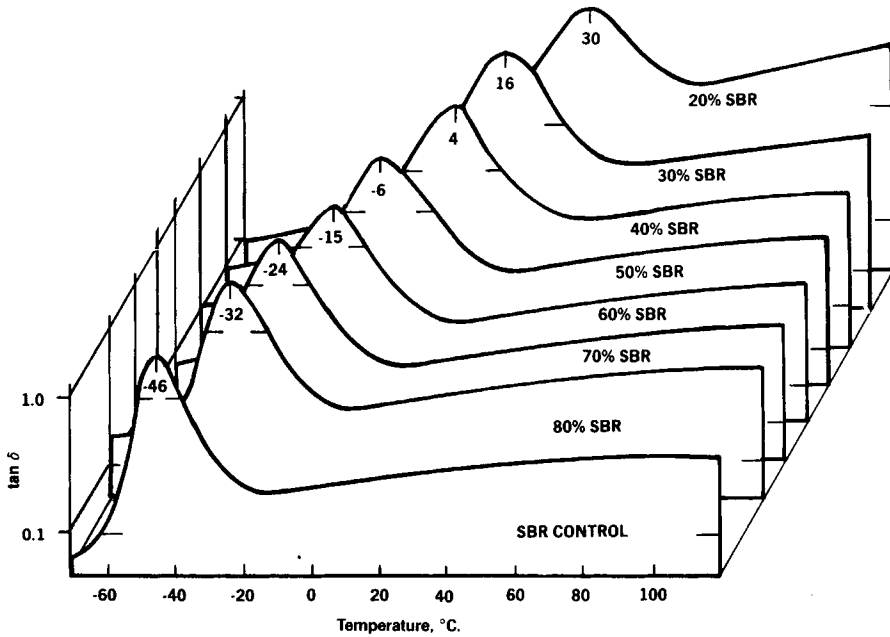


Fig. 10. Effect of concentration on $\tan \delta$ vs. temperature for blends of styrene-butadiene rubber with the glycerin ester of hydrogenated rosin.

W_1 and W_2 are the weight fractions of the the resin and rubber, respectively. T_g , T_{g1} , and T_{g2} are the glass transition temperatures of the blend and components, respectively, in K. In this work, T_g is replaced by the $\tan \delta$ peak temperature. To determine the applicability of the Fox equation, the appropriate plot is the reciprocal of the $\tan \delta$ peak temperature of the blend (K) vs. the weight fraction of the elastomer.

Fox plots for the natural rubber blends with the six different resins are shown as Figure 12, and the styrene-butadiene rubber with the four resins are in Figure 13. The resins are identified in Table I. The weight fraction coordinate for each resin has been displaced by 0.2 unit so that all of the blends can be displayed on a single figure. The predicted values for the $\tan \delta$ peak temperature, represented by the straight line plot, do not vary from the observed value by more than about 5°C. Because most of the discrepancies are observed at low resin concentration and are in the same direction, it is possible that further refinement of the equation could be made. However, this does not appear to be a fruitful exercise.

Thus, the Fox equation can be used to predict the temperature at which $\tan \delta$ reaches a peak for any concentration of a compatible rubber-resin system. All that is required is to determine the $\tan \delta$ peak temperature for two compositions. The undiluted elastomer and the 1:1 ratio blend are appropriate samples. Predictions of the $\tan \delta$ peak temperature can be made for all other concentrations from the straight line connecting these two points on a Fox plot.

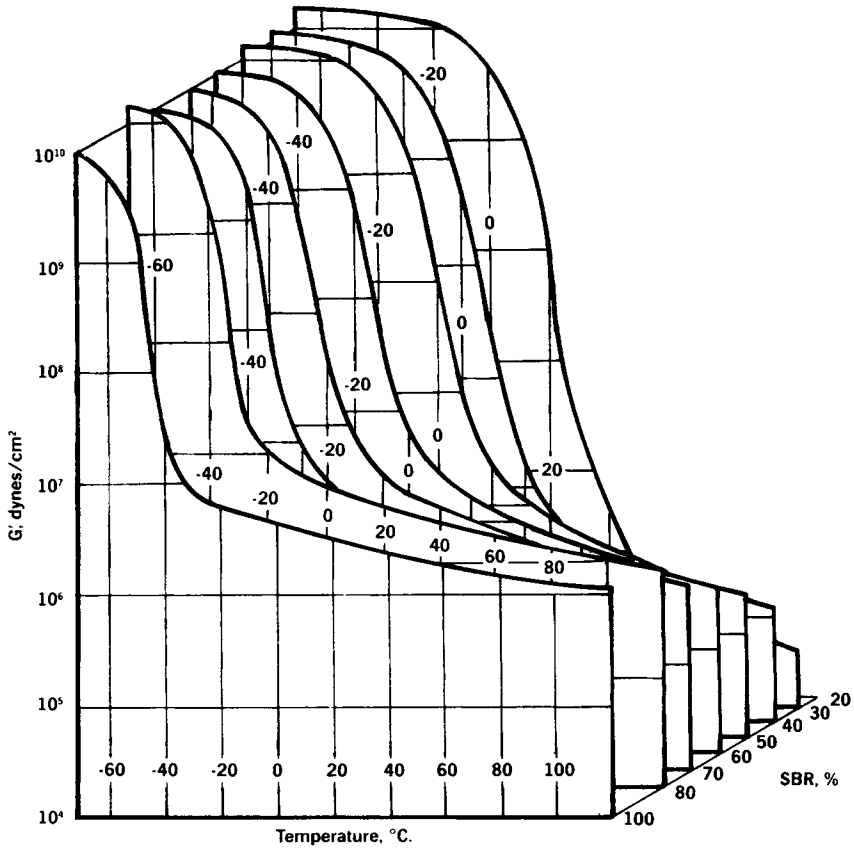


Fig. 11. Effect of concentration on G' vs. temperature for blends of styrene-butadiene rubber and the glycerin ester of hydrogenated rosin.

Plateau Modulus

The classical theory of rubber elasticity associates the plateau modulus G_N^0 with the concentration of network strands (ν_e) per unit volume⁹:

$$G_N^0 = g_n \nu_e RT$$

g_n is a numerical factor assumed to be 1. For an uncrosslinked elastomer, the strand concentration is equivalent to the density of the undiluted polymer divided by the molecular weight between entanglements:

$$G_N^0 = g_n (\rho / M_e^0) RT$$

In a diluted system, the strand concentration is represented by the polymer concentration divided by the molecular weight between entanglements:

$$G_N^0 = g_n (c / M_e) RT$$

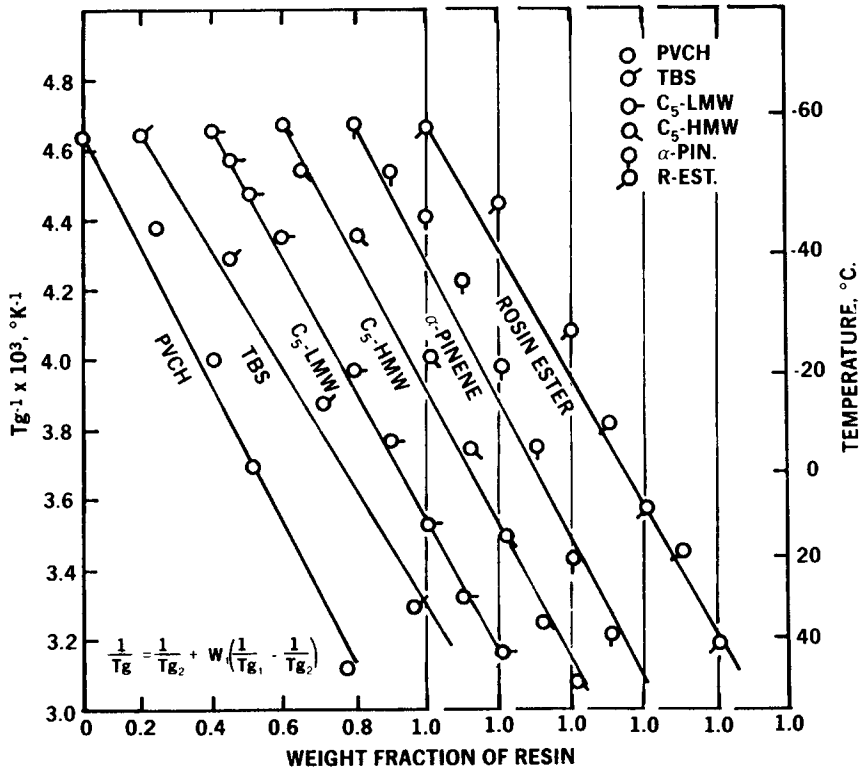


Fig. 12. $\tan \delta$ peak temperature vs. concentration for blends of natural rubber and low molecular weight resins.

Since the polymer concentration is its volume fraction (v_2) multiplied by its density ρ , and M_e in the diluted system is M_e^0 of the undiluted polymer divided by the volume fraction of the polymer (v_2), then the plateau modulus is proportional to the second power of the volume fraction of the polymer:

$$G_N^0 = (c/M_e)RT = v_2\rho(v_2/M_e^0)RT = v_2^2(\rho/M_e^0)RT$$

$$G_N^0 = v_2^2 G_N^{00}$$

A scaling law interpretation for dilute solutions by DeGennes suggests that the plateau modulus should be proportional to the 2.25 power of the concentration of the polymer.¹⁰ However, there is no reason to believe that rubber-resin systems should follow this behavior, especially at high rubber concentrations. Recent experimental data on polymer solutions have given values of about 2.2 and 2.^{11,12} Graessley and co-workers found 2.26 as the exponent for polybutadiene in different oils and 2.22 for hydrogenated polybutadiene in waxes.¹³

The only earlier study of rubber-resin systems was reported by Kraus, who examined SIS block copolymers.⁷ He obtained the value for G_N^0 from the storage modulus G' at the minimum slope of G' in the plateau. This was located at the minimum in $\tan \delta$ in the rubbery plateau on a temper-

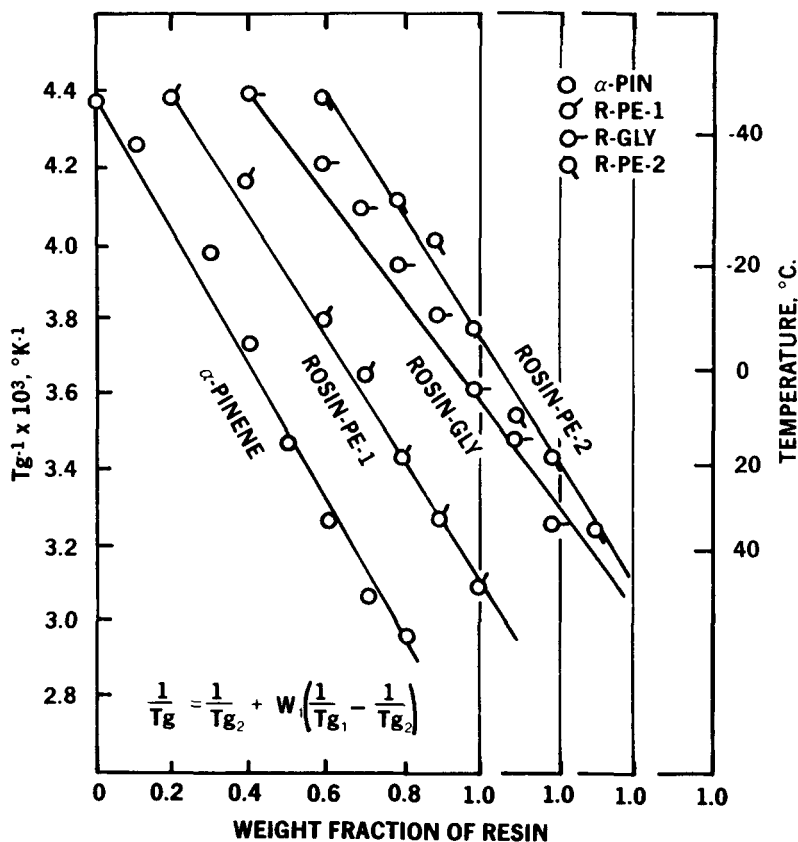


Fig. 13. $\tan \delta$ peak temperature vs. concentration for blends of styrene-butadiene rubber and low molecular weight resins.

ature scan of G' and $\tan \delta$. Kraus reported the exponent of the polymer volume fraction to be 2.3 and 2.6 for blends with the glycerin ester of hydrogenated rosin and a C_5 resin, respectively.

A similar procedure was used to identify the plateau modulus. The more traditional approach of determining G_N^0 by integrating the loss modulus G'' under the peak at the entry to the terminal zone could not be used with the highly entangled systems examined. The sample would begin to degrade before the terminal peak in G'' could be measured. The method used in this work is illustrated in Figure 14. First, the temperature at which $\tan \delta$ reaches a minimum in the rubbery plateau is located on a temperature scan of the sample. Then a frequency scan is run at this temperature to provide a more accurate determination of G' at the minimum in $\tan \delta$ as shown in the inset on Figure 14. This approach eliminates the dimensional changes which occur during temperature scans.

Blends of natural rubber with a paraffinic oil were examined to evaluate this method for determining G_N^0 . Examination of polymer-oil systems by other methods gave values of 2-2.3 for the exponent of the polymer volume

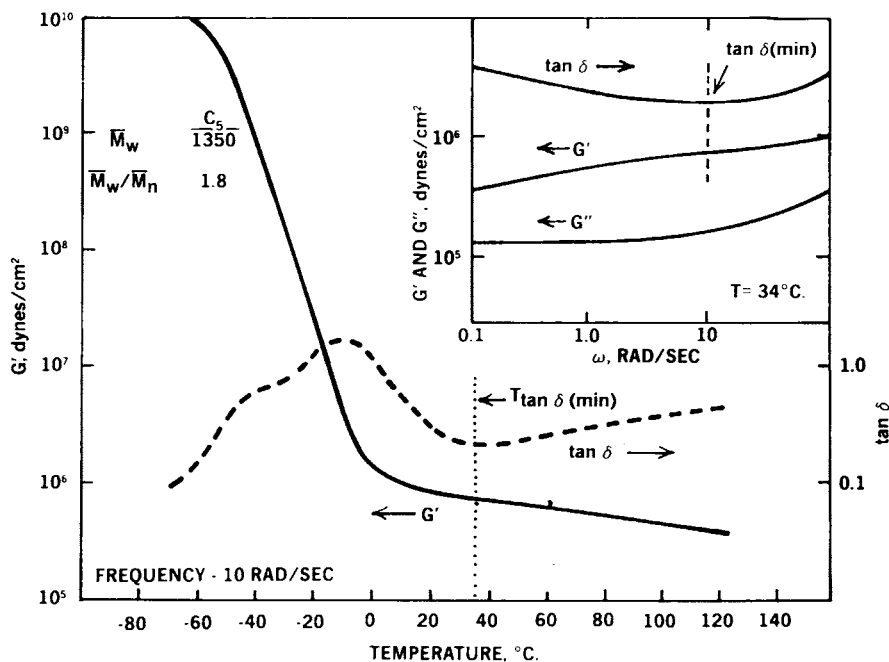


Fig. 14. G' (—) and $\tan \delta$ (---) vs. temperature for a 1:1 blend of natural rubber with a C_5 stream resin. This demonstrates the location of the plateau modulus at the temperature at which $\tan \delta$ is a minimum in the plateau.

fraction, as previously described. $\tan \delta$ and G' scans were run on compositions covering a range of concentrations. G_N^0 was located on individual plots as the value G' at the minimum in $\tan \delta$ in the plateau. The bilogarithmic plot of G_N^0 vs. v_2^2 , for natural rubber-paraffinic oil, as shown in Figure 15, has a slope of 1.19, which is equivalent to an exponent of 2.38. This agreement with prior work supports the validity of the method.

Bilogarithmic plots of G_N^0 vs. v_2 , the volume fraction of elastomer, are presented in Figure 16 for natural rubber-resin blends and in Figure 17 for styrene-butadiene rubber-resin blends. The resins are described in Table I. On these figures, the $\log v_2$ coordinate for each resin has been displaced by 0.2 unit to allow the data from all of the blends to be displayed on a single figure. The slope of the line drawn through the points on these $\log G_N^0$ vs. $\log v_2$ plots for each composition represents the exponent of the volume fraction of rubber.

As indicated in Figure 16, the exponents of the volume fraction of natural rubber, fall between about 2.25 and 2.45 for all compositions. This is in the range of values reported by other workers. In Figure 17, the exponents for the blends with styrene-butadiene rubber are seen to be slightly higher at about 2.45–2.65.

To demonstrate the sensitivity of determining the volume fraction exponent by the method used in this work, the line through the points for the blends of natural rubber with the lower molecular weight C_5 resin (Fig.

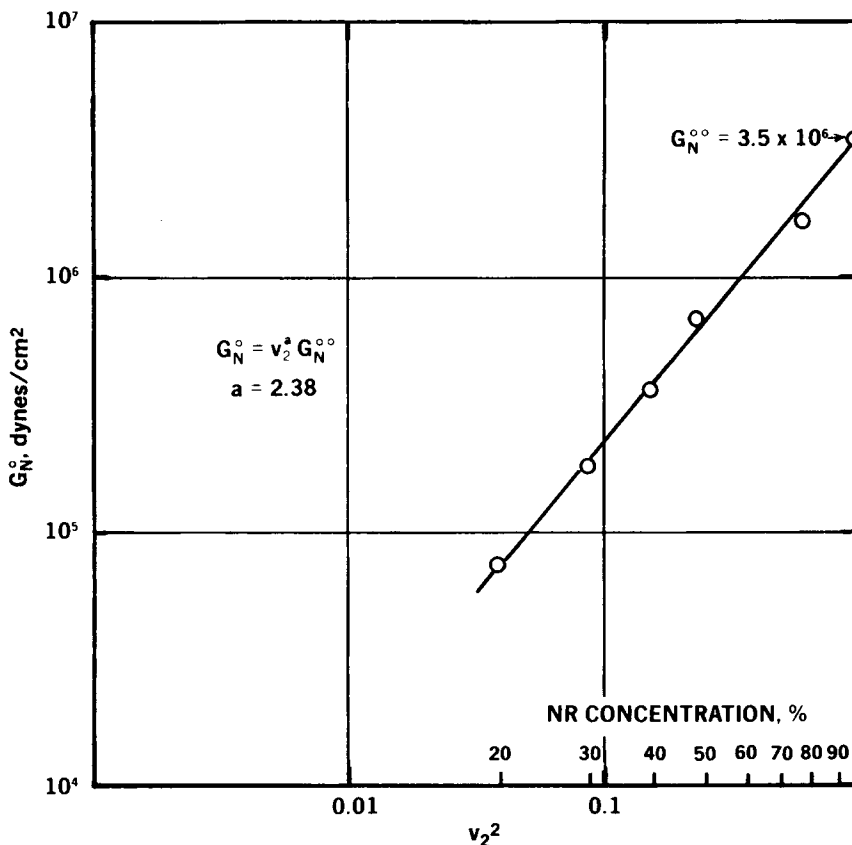


Fig. 15. Plateau modulus vs. polymer volume fraction squared for blends of natural rubber with an aliphatic oil.

16) has been drawn in two segments. The overall exponent for a single line drawn through all the points is 2.28. Extension of the initial slope at low resin concentrations would give an exponent of 2.18. The lower segment at higher resin concentrations gives an exponent of 2.42. This suggests that the second decimal place by this method may not be significant.

From the work reported here, low molecular weight resins affect the plateau modulus of natural rubber or styrene-butadiene rubber in the same manner as predicted from studies of concentrated polymer solutions. The high T_g of the rubber-resin blends affects the temperature range for the rubbery plateau, but does not affect the value of the plateau modulus.

The plateau modulus for compatible rubber-resin blends can be estimated from the exponent of the polymer volume fraction, which relates plateau modulus of a blend to that of the undiluted elastomer. This can be determined from measurements made on the elastomer and a single blend, for example, the 1:1 ratio. If the exponent is in the range of about 2-2.5, then the estimate can be made with confidence. A smaller exponent or a negative exponent, resulting from an increase in modulus on dilution, suggests that the system is incompatible so the estimate is not valid.

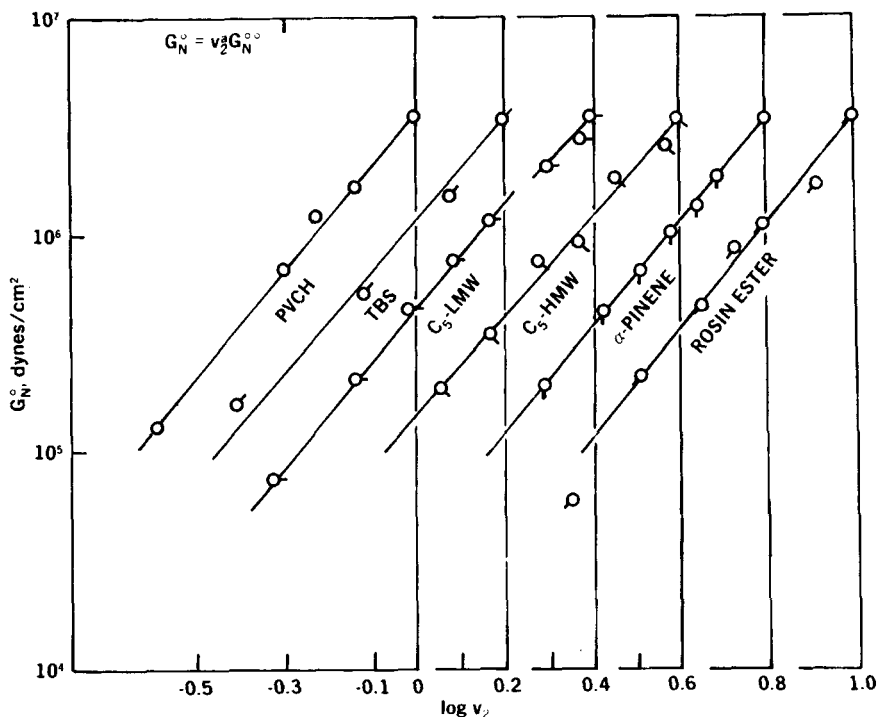


Fig. 16. Plateau modulus vs. log of the polymer volume fraction for blends of natural rubber with low molecular weight resins. (○) PVCH, $a = 2.38$; (○) TBS, $a = 2.30$; (○) C_5 -LMW, $a = 2.28$; (○) C_5 -HMW, $a = 2.24$; (○) α -PIN, (○) R-EST, $a = 2.42$. log V_2 shift is 0.2 unit:

V_2	log V_2
0.9	0.05
0.8	0.10
0.7	0.15
0.6	0.22
0.5	0.30
0.4	0.40
0.3	0.52
0.2	0.70

CONCLUSIONS

Plots of G' and $\tan \delta$ vs. temperature for nominally compatible rubber-resin systems indicate that compositions may contain two phases at high resin concentrations. Blends of both natural rubber-poly(vinyl cyclohexane) resin and styrene-butadiene rubber-polystyrene resin appear to contain two phases at 75–80% resin. This behavior may not be general but may occur only with specific rubber-resins systems.

The $\tan \delta$ peak temperature and the plateau modulus of compatible rubber-resin systems can be controlled by adjusting the amount of compatible

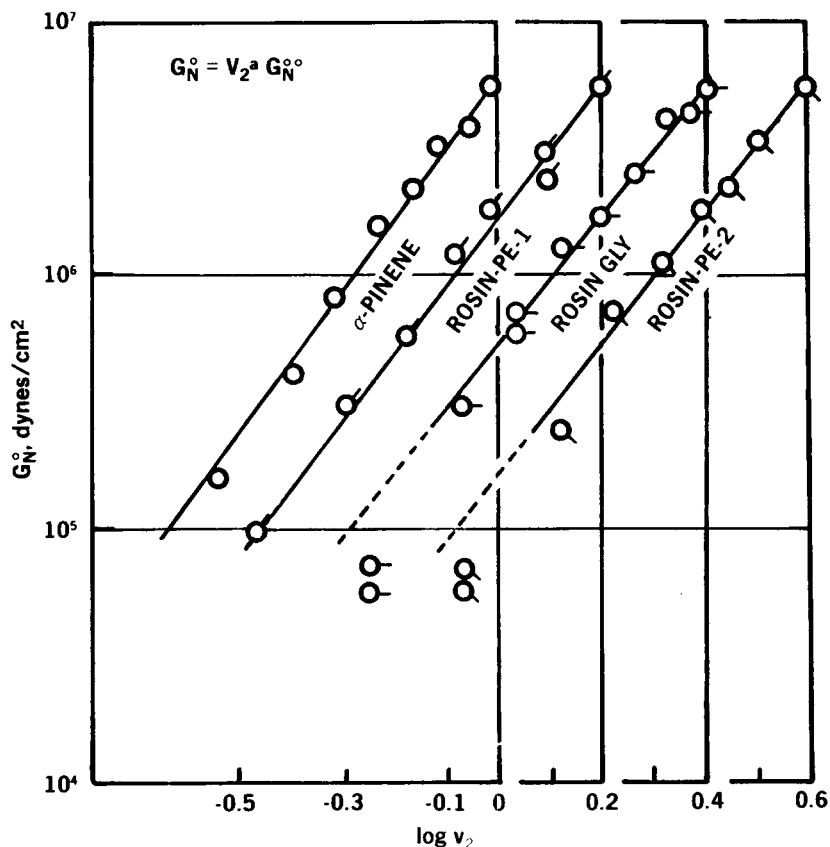


Fig. 17. Plateau modulus vs. log of the polymer volume fraction for blends of styrene-butadiene rubber with low molecular weight resins: (○) α -PIN, $a = 2.66$; (○) R-PE-1, $a = 2.60$; (○) R-GLY, $a = 2.46$; (○) R-PE-2, $a = 2.48$. $\log v_2$ shift is 0.2 unit:

V_2	$\log V_2$
0.9	0.05
0.8	0.10
0.7	0.15
0.6	0.22
0.5	0.30
0.4	0.40
0.3	0.52
0.2	0.70

low molecular weight resin blended with the elastomer. Both the identity and concentration of the resin affect the temperature at which $\tan \delta$ reaches a peak in the transition zone, while only the concentration of the resin and not its identity is important in determining the plateau modulus. However, the identity of the resin does affect the temperature at which the plateau modulus occurs on a plot of storage modulus vs temperature.

The $\tan \delta$ peak temperature can be estimated by the reciprocal blending law proposed by Fox. It can be determined from measurements made on the unblended rubber and on a single blend with resin, such as a 1:1 ratio. A line drawn between these two points on a Fox plot can be used to estimate the $\tan \delta$ peak temperature for all compositions.

The plateau modulus for a compatible system can be determined from the storage modulus at the temperature at which $\tan \delta$ is a minimum in the rubbery plateau. This temperature is first identified on a plot of storage modulus and $\tan \delta$ vs. temperature, and then a frequency scan is run isothermally to accurately determine G' at the minimum $\tan \delta$.

The exponent of the elastomer volume fraction, which relates the plateau modulus of the blend to that of the undiluted elastomer, is determined from a bilogarithmic plot of plateau modulus vs polymer volume fraction. The exponent is about 2.3–2.4 for the natural rubber blends examined and 2.5–2.6 for styrene–butadiene rubber blends. Plateau modulus can be predicted for all concentrations of a diluted compatible rubber system from values determined on two compositions. For example, plateau modulus of the undiluted elastomer and a 1:1 blend can be used to calculate the exponent of the elastomer volume fraction. If this value is in the range of 2–2.5, then the relationship $G_N^0 = v_2^{\alpha} G^0$ can be used to calculate plateau modulus for all other concentrations. If the exponent is lower than 2 or possibly negative, indicating incompatibility, then the plateau modulus cannot be calculated.

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