The Viscoelastic Properties of Rubber–Resin Blends. II. The Effect of Resin Molecular Weight

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Synopsis

In blends of rubber and low molecular weight resins, the compatibility of the system controls the viscoelastic properties and ultimately the performance of the composition as a pressure sensitive adhesive. The effect of the resin molecular weight on compatibility was examined by studying rubber–resin blends prepared from resins which represent a range of molecular weights. Viscoelastic properties were measured using a mechanical spectrometer on 1:1 blends of rubber and a series of polystyrene resins and poly(vinylcyclohexane) resins. Based on plots of G' and tan δ vs. temperature, blends of natural rubber and polystyrene resin show incompatibility at resin M_w of about 600 and above. Blends of natural rubber and poly(vinyl cyclohexane) are incompatible at resin M_w of about 1800, but are compatible at M_w of about 650. Blends of styrene–butadiene rubber and polystyrene resins are compatible at resin M_w of about 650 but appear to contain a low volume incompatible phase at M_w of about 900. Therefore, the compatibility of a rubber–resin blend depends upon the molecular weight of the resin. Even systems expected to be compatible will show evidence of incompatibility as the molecular weight of the resin is raised above some limiting value.

INTRODUCTION

It is generally accepted that the proper combination of viscoelastic parameters control the performance of a pressure sensitive adhesive. In earlier studies of the viscoelastic properties of rubber-resin pressure sensitive adhesive systems, it was shown that the addition of a low molecular weight resin to the elastomer shifted the entry to the glassy zone to a lower frequency in frequency scans, or equivalently to a higher temperature in temperature scans.[1-5] The resin also depressed the modulus in the rubbery plateau. It is believed that these changes in viscoelastic properties are related to pressure sensitive performance.

In Paper I of this series, it has been shown that the identity of the resin is important to its effect on viscoelastic properties.[6] Studies conducted with both natural rubber and styrene–butadiene rubber showed that a cycloaliphatic poly(vinyl cyclohexane) resin is compatible with natural rubber but not with styrene–butadiene rubber, while an aromatic polystyrene resin is compatible with styrene–butadiene rubber but not with natural rubber. An alkyl aromatic resin prepared from *tert*-butylstyrene is compatible with both natural rubber and styrene–butadiene rubber. Thus, the aromatic resin is compatible with the aromatic polymer, and the aliphatic resin is compatible with the aliphatic polymer.

Compatibility of the rubber–resin system is determined from temperature scans of the storage modulus (G') and the loss tangent (tan δ). For systems in which the glass transition temperature (T_g) of the rubber and resin are sufficiently different, compatibility is recognized by a pronounced shift of

a single peak in tan δ, compared to the peak observed for the unmodified elastomer. Also, G' in the rubbery plateau is depressed compared to the unmodified elastomer, regardless of the T_g of the resin diluent. For the natural rubber samples, this hypothesis was confirmed by a microscopic examination of a blend judged to be compatible and another judged to be incompatible.

All resins examined in Paper I had weight average molecular weights of less than 1000. Since natural rubber is soluble in aromatic hydrocarbon solvents yet incompatible with a low molecular weight aromatic oligomer such as a polystyrene resin, it is tempting to assume that the molecular weight of the resin is important to compatibility. Therefore, a study was undertaken to examine the effect of the molecular weight of the resin on compatibility.

EXPERIMENTAL

Higher and lower molecular weight analogs of the resins examined in Paper I of this study are examined in this work.[6] These were polystyrene resins and the poly(vinyl cyclohexane) resins prepared by complete hydrogenation of the polystyrene resins. Molecular weight data were obtained by size exclusion chromatography (SEC) using a Styragel column set, calibrated with polystyrene standards. The resins were run at room temperature in tetrahydrofuran. Glass transition temperatures were measured by differential scanning calorimetry. T_g was recorded as the first break on the second heat. Heating rate was 20°C/min. The SEC curves for the polystyrene resins along with the molecular weight, and T_g data are displayed in Figure 1. Figure 2 shows the poly(vinyl cyclohexane) resins which were prepared from the polystyrene resins.

The natural rubber and styrene–butadiene rubber are described in Table I. The natural rubber was shear degraded to a Mooney viscosity of 53, which is an appropriate value for use as a pressure sensitive adhesive. The styrene–butadiene rubber was Ameripol 1011 (BFGoodrich Rubber Co.). The styrene content was determined by infrared spectroscopy. Glass transition temperatures were measured by differential scanning calorimetry. T_g was recorded
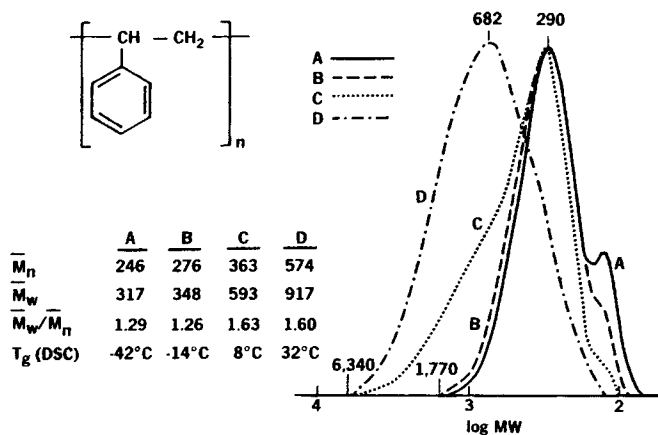

	A	B	C	D
$\overline{M}_n$	246	276	363	574
$\overline{M}_w$	317	348	593	917
$\overline{M}_w/\overline{M}_n$	1.29	1.26	1.63	1.60
T_g (DSC)	-42°C	-14°C	8°C	32°C

Fig. 1. Size exclusion chromatography data for polystyrene resins.
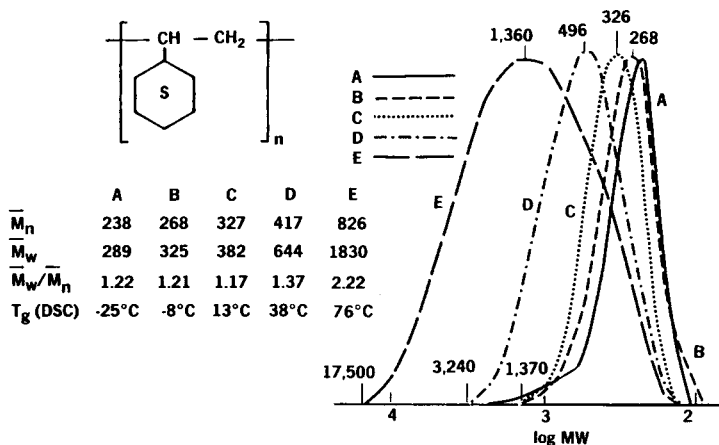
Fig. 2. Size exclusion chromatography data for poly(vinyl cyclohexane) resins.

	A	B	C	D	E
$\overline{M}_n$	238	268	327	417	826
$\overline{M}_w$	289	325	382	644	1830
$\overline{M}_w/\overline{M}_n$	1.22	1.21	1.17	1.37	2.22
T_g (DSC)	-25°C	-8°C	13°C	38°C	76°C

as the first break on the second heat. Heating rate was 20°C/min. As with the resins, molecular weight data were obtained by SEC using a Styragel column set, calibrated with polystyrene standards. Natural rubber was run at 140°C in 1,2,4-trichlorobenzene. Data could not be obtained on the styrene–butadiene rubber because of the gel content in the sample.

Each resin was combined individually with natural rubber and with styrene–butadiene rubber at 1:1 resin:rubber ratios. 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×. The samples, which were about 5 μ thick, were obtained by microtoming at about 20°C below T_g.

Dynamic measurements were made on a dynamic spectometer (Rheometrics, Inc.) in the parallel plate mode using small diameter (8 mm) plates. G', G'' and tan δ were plotted from the glassy region to 120°C at 10 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[6].

TABLE I
Description of Elastomers

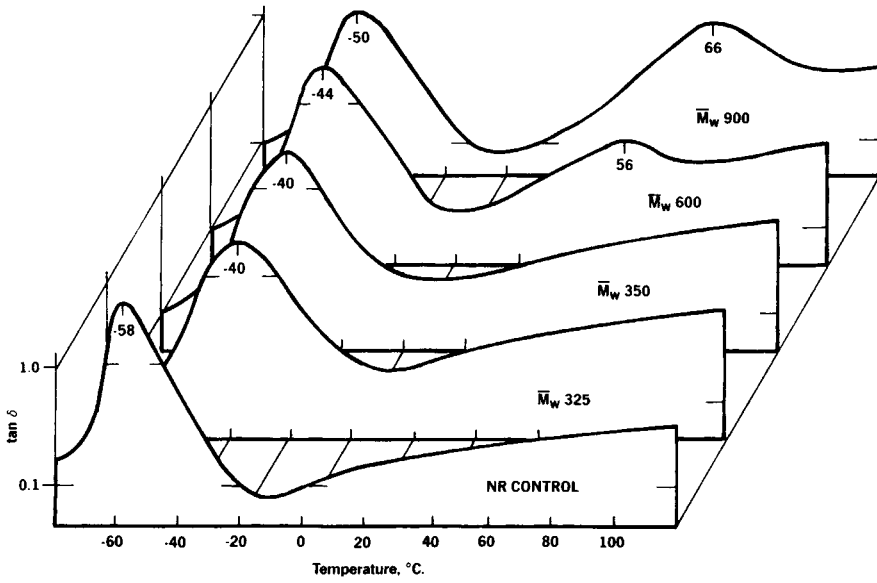| Natural rubber (milled smoke sheet)	
Mooney viscosity (100°C)	53
$\overline{M}_n$	105,000
$\overline{M}_w$	266,000
$\overline{M}_w/\overline{M}_n$	2.53
T_g (DSC) (°C)	−66
Styrene–butadiene rubber	
Mooney viscosity (100°C)	53
Bound styrene (%)	25
T_g (DSC) (°C)	−57

Fig. 3.   The effect of resin molecular weight on tan δ vs. temperature for 1:1 blends of natural rubber with polystyrene resins.
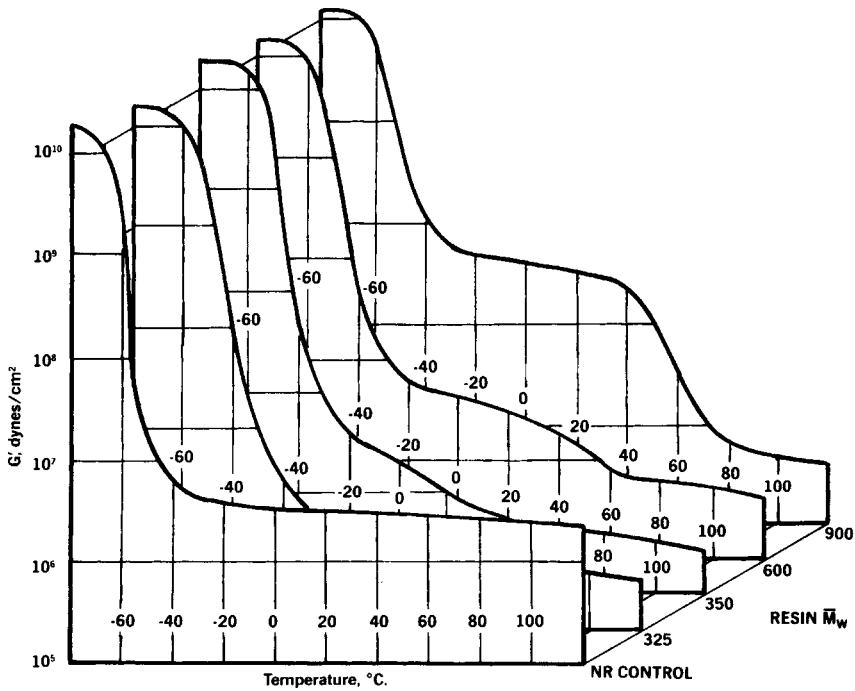
Fig. 4.   The effect of resin molecular weight on G' vs. temperature for 1:1 blends of natural rubber with polystyrene resins.
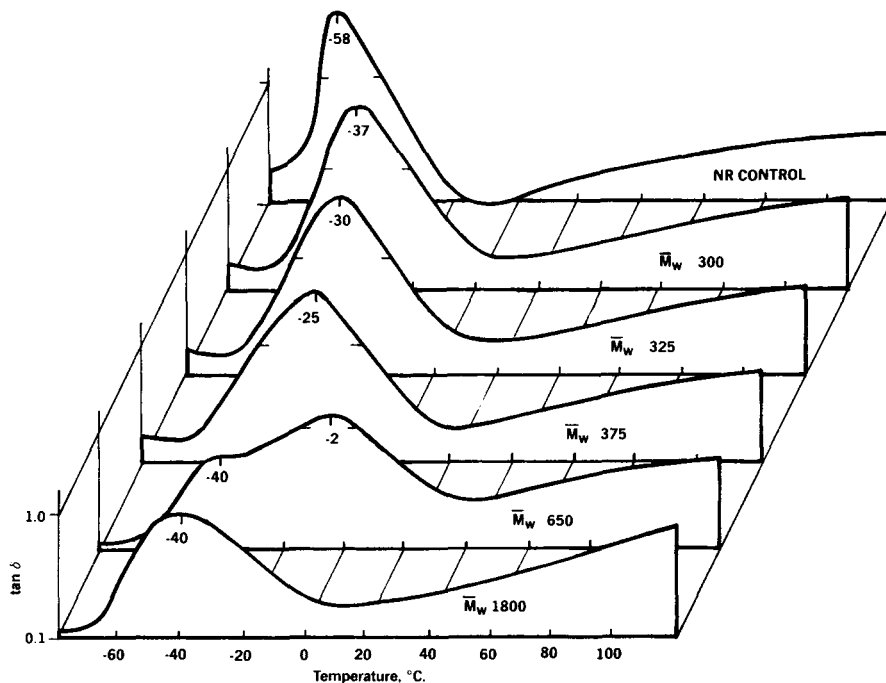
Fig. 5. The effect of resin molecular weight on tan δ vs. temperature for 1:1 blends of natural rubber with poly(vinyl cyclohexane) resins.

RESULTS AND DISCUSSION

G' and tan δ plots vs. temperature for 1:1 blends of polystyrene resins with natural rubber suggest that incompatibility appears at resin molecular weights of about 600 and above. The tan δ curves for these blends are displayed in Figure 3. The z coordinate has no scalar significance. At the higher molecular weights of 600 and 900, the large second peak at about 60°C indicates the presence of a second phase. The major peak in tan δ has increased from about −58°C to only −44°C and −50°C, respectively. For the 325 and 350 molecular weight resins, the peak in tan δ for each blend has increased to −40°C. This suggests that there is at least partial compatibility of a low molecular weight component of the resin with natural rubber.

Figure 4 shows the G' curves vs. temperature for the same series of blends. A distinct elevation of the plateau modulus is observed for the blends containing the resins having the higher molecular weights of 600 and 900. There is a smaller rise in the modulus plot for the 350 molecular weight resin, but there are no signs of incompatibility for the 325 molecular weight resin.

The blends of natural rubber with the poly(vinyl cyclohexane) resins perform differently from blends containing the polystyrene resins. The tan δ plots vs. temperature for the poly(vinyl cyclohexane) resin blends are in Figure 5. As the molecular weight of the resins is increased, a distinct shift is observed in the major tan δ peak from −58°C to a maximum of −2°C for the molecular weight 650 resin. However, the blend prepared from the
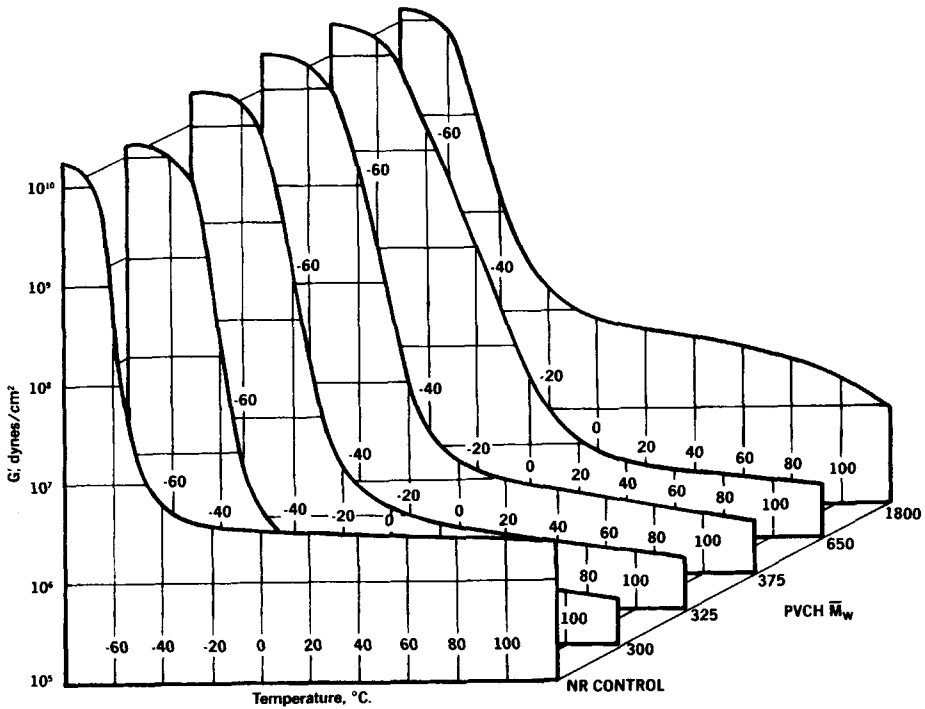
Fig. 6. The effect of resin molecular weight on G' vs. temperature for 1:1 blends of natural rubber with poly(vinyl cyclohexane) resins.

resin having a molecular weight of 1800, has the major peak in tan δ at $-40°C$. Although a second peak in tan δ is not seen with this higher molecular weight resin, the tan δ value itself is elevated at about 120°C. This suggests that a second peak may be displayed if measurements had been made at temperatures above 120°C.

The G' curves for this series, presented as Figure 6, support this conjecture. The presence of two phases for the resin which has a molecular weight of 1800 is suggested by the marked elevation in the plateau. The lower
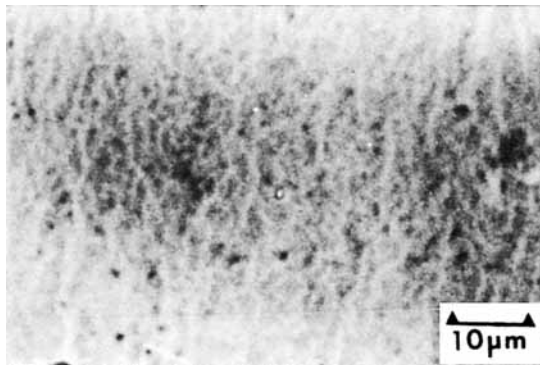

Fig. 7. Transmission photomicrograph of a 1:1 blend of natural rubber with a poly(vinyl cyclohexane) resin having an M_w of 300.
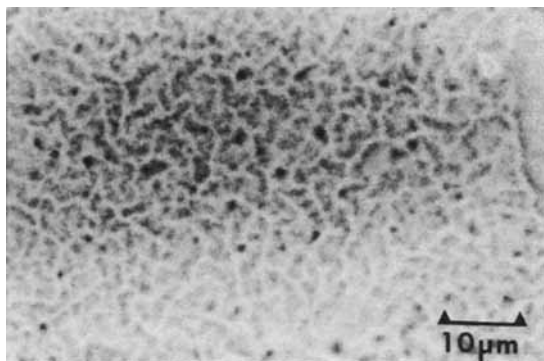
Fig. 8. Transmission photomicrograph of a 1:1 blend of natural rubber with a poly(vinyl cyclohexane) resin having an M_w of 325.

molecular weight resins show a depression of the plateau modulus consistant with compatible systems.

Photomicrographs confirm this interpretation of compatibility. Figures 7–10 show the photomicrographs for the 1:1 blends of natural rubber with the poly(vinyl cyclohexane) resins having weight average molecular weights of 300, 325, 650, and 1800. If there is incompatibility with the lower molecular weight resins (Figs. 7 and 8), the size of the dispersed phase is less than the resolution of the system (about 0.5 μm). The structure in Figures 7 and 8 is possibly due to shrinkage of the microtomed sections of the samples before microscopic examination. There may be an indication of incompatibility with the molecular weight 650 resin (Fig. 9), but this is not clear. Higher molecular weight components in this resin may have separated as a second phase in low concentration. A distinct two-phase system is seen in the blend containing the highest molecular weight resin (Fig. 10). Dispersed particles range in size from about 3 to 5 μm.

Blends of the polystyrene resins with styrene–butadiene rubber at 1:1 concentrations appear to be compatible. Figure 11 displays the tan δ values for this series of blends plotted vs. temperature. The tan δ peak temperature increased from $-45°C$ for the styrene–butadiene rubber control to $-10°C$ for the blend containing the resin which has a molecular weight of 600.
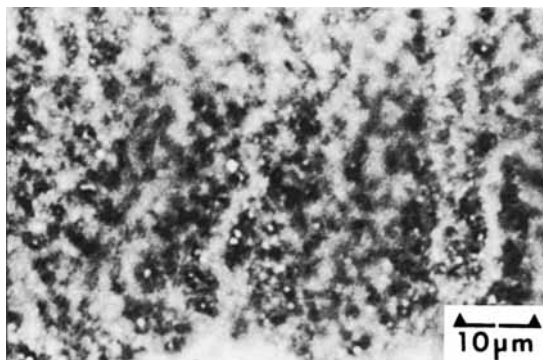

Fig. 9. Transmission photomicrograph of a 1:1 blend of natural rubber with a poly(vinyl cyclohexane) resin having an M_w of 650.
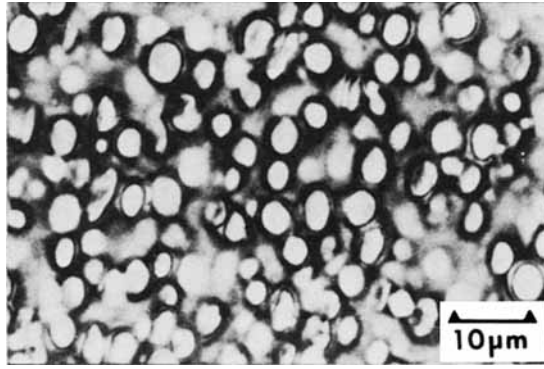
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Fig. 10. Transmission photomicrograph of a 1:1 blend of natural rubber with a poly(vinyl cyclohexane) resin having an M_w of 1800.

The tan δ peak temperature remained at −10°C for the blend containing the resin having a molecular weight of 900. This suggests that an incompatible phase appears at this molecular weight. The G' curves for the same series of blends are shown in Figure 12. A depression of the modulus is apparent for the blends containing the resins which have a molecular weight of 600 or less. The resin which has a molecular weight of 900 produces a slight elevation which again may indicate the presence of a small incompatible phase.

The series of poly(vinyl cyclohexane) resins was examined in blends at a 1:1 ratio with styrene–butadiene rubber. Although the styrene–butadiene rubber contains only 25% styrene, incompatibility with the poly(vinyl cyclohexane) resin is apparent especially at the higher molecular weights.
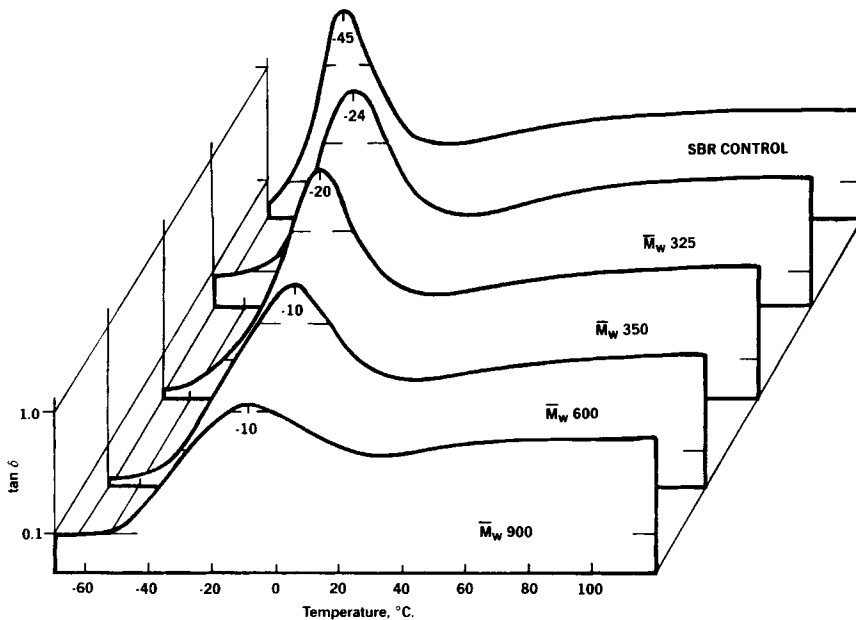

Fig. 11. Effect of resin molecular weight on tan δ vs. temperature for 1:1 blends of styrene–butadiene rubber with polystyrene resins.

These results, which are not shown, are similar to those obtained for the blends of the polystyrene resins with natural rubber.

CONCLUSIONS

The compatibility of a low molecular weight resin with an elastomer depends upon the molecular weight of the resin. In the blends examined, incompatibility is evident from plots of tan δ and G' vs. temperature at weight average molecular weights greater than 1000. This is found even for resins which are expected to be compatible with the elastomer based on polarizability considerations. A higher molecular weight resin does not depress the plateau modulus compared to the elastomer with no resin added, nor does it shift the tan δ peak temperature. To the contrary, the plateau modulus is increased, the tan δ peak does not shift, and a second peak in tan δ is usually apparent. This behavior is consistent with the presence of a dispersed incompatible amorphous phase. However, even resins which are considered to be incompatible may have a significant compatible fraction at low molecular weights. For example, a blend of low molecular weight polystyrene resin with natural rubber shows a small but distinct shift in the tan δ peak temperature of the natural rubber. Therefore, there is a molecular weight at which compatibility of any resin can be observed and above which compatible behavior is not evident.
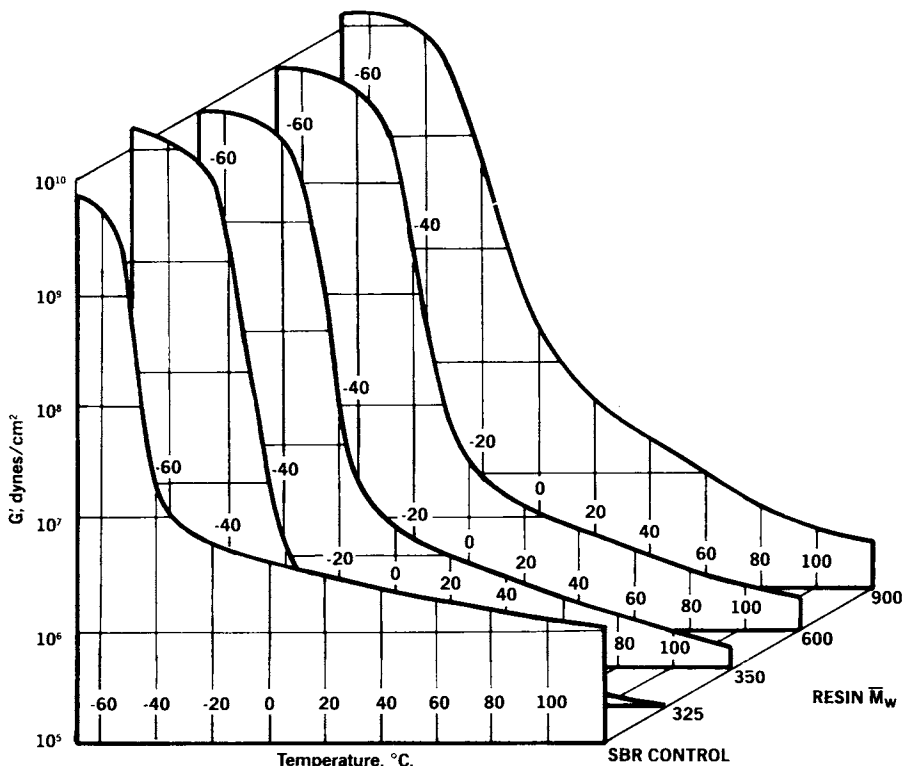

Fig. 12. Effect of resin molecular weight on G' vs. temperature for 1:1 blends of styrene–butadiene rubber with polystyrene resins.

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