The Viscoelastic Properties of Rubber–Resin Blends. I. The Effect of Resin Structure

J. B. CLASS and S. G. CHU, *Hercules Incorporated, Hercules Research Center, Wilmington, Delaware 19894*

Synopsis

Blends of elastomers with the proper concentration of appropriate low molecular weight resins exhibit performance as pressure sensitive adhesives. Viscoelastic properties, which may be related to adhesive performance, were measured on 1:1 blends of rubber and resin using a mechanical spectrometer. Significant differences in viscoelastic properties were observed depending upon the resin structure. On plots of G' and tan δ vs. temperature, the addition of a compatible resin produces a pronounced shift of the tan δ peak to a higher temperature and reduces the modulus in the rubbery plateau. An incompatible resin results in a minor shift in the tan δ peak of the elastomer along with the appearance of a second peak at higher temperature, attributed to a second phase which is predominantly resin. Also, the modulus is increased in the rubbery plateau. A polystyrene resin, M_w about 900, is shown to be incompatible with natural rubber but compatible with styrene–butadiene rubber. A cycloaliphatic poly(vinyl cyclohexane) resin, M_w about 650, prepared by hydrogenating the polystyrene resin, is compatible with natural rubber, but incompatible with styrene–butadiene rubber. An alkyl-aromatic poly(*tert*-butylstyrene) resin, M_w about 850, which is intermediate in aromaticity between the aromatic polystyrene resin and the cycloaliphatic poly(vinyl cyclohexane) resin, is compatible with both natural rubber and styrene-butadiene rubber. Therefore, the structure of the resin is very important in adjusting the viscoelastic properties of a rubber–resin blend to achieve pressure sensitive adhesive performance.

INTRODUCTION

Testing the performance of a pressure sensitive adhesive involves both the formation and destruction of a bond. For the typical tack, peel strength, and shear strength tests, the bonding conditions, such as the applied stress and dwell time, are specified, as are the debonding conditions of strain rate for tack and peel, and stress for time to failure in the shear test. To perform satisfactorily as a pressure sensitive adhesive, the material must respond to a deforming force in a prescribed manner during both bonding and debonding. It must adhere to the substrate during bonding and exhibit a measurable resistance to separation at debonding conditions. In each of these steps, both the rate and extent of deformation are important. Bonding is a low rate process at low deformation, when the adhesive is brought into contact with a surface, while debonding in the tack or peel tests is a high rate process at high deformation relative to the thickness of the adhesive. The shear strength test is essentially a creep test carried to high deformation. Thus, the viscoelastic behavior of the adhesive controls its response in adhesive testing and is a major factor in its performance.

Satisfactory pressure sensitive adhesive performance can be observed in a simple blend of a low molecular weight resin and an elastomer, such as natural rubber or styrene–butadiene rubber. A resin is described as a tackifier if by adding it to a rubber, the resulting composition has the properties

Journal of Applied Polymer Science, Vol. 30, 805–814 (1985)
CCC 0021-8995/85/020805-10$04.00

of a pressure sensitive adhesive. An effective resin will have a weight average molecular weight in the range of 300–2000. It will often be a brittle glass at room temperature, although softer resins may be useful. Glass transition temperatures (T_g's) range from about 0°C to about 70°C. The resin may be an oligomer of a cyclic monomer, such as styrene or a terpene, or of monomers which are believed to form cyclic structures during polymerization. These are the C_5 and C_6 mono- and diolefins which are present in certain petroleum streams. The resin may also be an ester of a cyclic organic acid such as rosin.

There have been a few earlier studies of the viscoelastic properties of rubber–resin pressure sensitive adhesive systems.[1-7] Sherriff and co-workers demonstrated the effect of adding low molecular weight resins to natural rubber.[1,2] Compositions were selected for study which exhibited pressure sensitive adhesive performance at an appropriate concentration of resin. Sherriff et al. found that addition of the resin to the rubber shifted the entry to the transition zone to a lower frequency, and also reduced the modulus in the rubbery plateau. Later, Aubrey and Sherriff examined the relationship between viscoelasticity and peel adhesion of rubber–resin blends.[3]

Kraus and co-workers reported on studies of resins blended with styrene–isoprene–styrene block copolymers.[4-7] These blends also exhibit pressure sensitive performance at the appropriate concentration. Kraus et al. showed that addition of a compatible resin increased the T_g of the rubbery midblock and decreased the plateau modulus.

There has been no prior study specifically of the relationship between the structure of the resin and its effect on the viscoelastic properties of the rubber-resin composition. Sherriff et al. reported that blends of natural rubber with the pentaerythritol ester of stabilized rosin exhibited two T_g's, determined by dilatometry, indicating two phases, at greater than 60% resin concentration.[1] The hydrocarbon resins examined showed only a single T_g in blends with natural rubber over the entire concentration range studied. However, Sherriff et al. reported viscoelastic studies only up to the 50% resin concentration.

EXPERIMENTAL

Aromatic resins were prepared from styrene and *tert*-butylstyrene by cationic polymerization. The cycloaliphatic poly(vinyl cyclohexane) resin was obtained by complete hydrogenation of the polystyrene resin. The resins are described in Table I.

The natural rubber and styrene–butadiene rubber used in this work are described in Table II. The natural rubber was shear degraded on a two-roll mill to reduce the Mooney viscosity to 53, a level appropriate for use in pressure sensitive adhesives. The styrene–butadiene rubber was Ameripol 1011 (BF Goodrich Rubber Co.). The styrene content was determined by infrared spectroscopy.

Molecular weight data were obtained by size exclusion chromatography using a Styragel column set, calibrated with polystyrene standards. Resins were run at room temperature in tetrahydrofuran. Natural rubber was run

TABLE I
Description of Resins

	PS[a]	PVCH[b]	PTBS[c]
$\overline{M}_n$	574	471	654
$\overline{M}_w$	917	644	835
$\overline{M}_w/\overline{M}_n$	1.60	1.37	1.28
T_g (DSC) (°C)	32	38	59

[a] PS is polystyrene resin.
[b] PVCH is poly(vinyl cyclohexane) resin.
[c] PTBS is poly(*tert*-butylstyrene) resin.

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.

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.

Rubber and resins were combined in toluene solution at a 1:1 solids ratio. This concentration was selected because pressure sensitive performance is observed at this ratio with an appropriate resin. The solutions were cast onto a release surface and allowed to evaporate at room temperature. The last trace of solvent was removed by drying for three days in a vacuum oven at 40°C. 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 μm thick, were obtained by microtoming at about 20°C below T_g.

The rubber–resin blends were examined on a dynamic spectrometer (Rheometrics, Inc.) in the parallel plate mode. Small diameter (8 mm) plates were used with a 2 mm gap. Storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) were plotted from 120°C down to the glassy region at 10 rad/s. Use of the small diameter plates allowed accurate data to be obtained from the glassy region to the rubbery plateau. The standard 25 mm diameter plates gave erroneous low modulus values for the glass because of instrument compliance, even though a compliance correction calculation was programmed for the instrument.[8] Data were obtained using the 8 mm diameter plates at 0.2% strain in the glassy region and at 2% in the rubbery plateau, both well within the linear viscoelastic range for

TABLE II
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

rubber–resin blends. This was confirmed by an examination of G', G'', and tan δ vs. strain for typical glass and rubbery samples. Although the data obtained on the glass is of the appropriate order of magnitude, the values may not be highly accurate. Difficulties with maintaining a bond between the glass and the plate over the complete surface may result in a lower G' than the true value. Also, during a temperature scan, the dimensions of the sample change as it is cooled, which prevents accurate calculation of the modulus. These relatively minor errors for the glasses, if present, would not affect the conclusions based on this study.

RESULTS AND DISCUSSION

Natural rubber and styrene–butadiene rubber were each combined with low molecular weight polystyrene resin, poly(vinyl cyclohexane) resin, and poly(*tert*-butylstyrene) resin. These resins, representing an aromatic, cycloaliphatic, and alkylaromatic structure, were selected to cover a range of aromaticity for hydrocarbon resins.

The blend of low molecular weight polystyrene resin with natural rubber

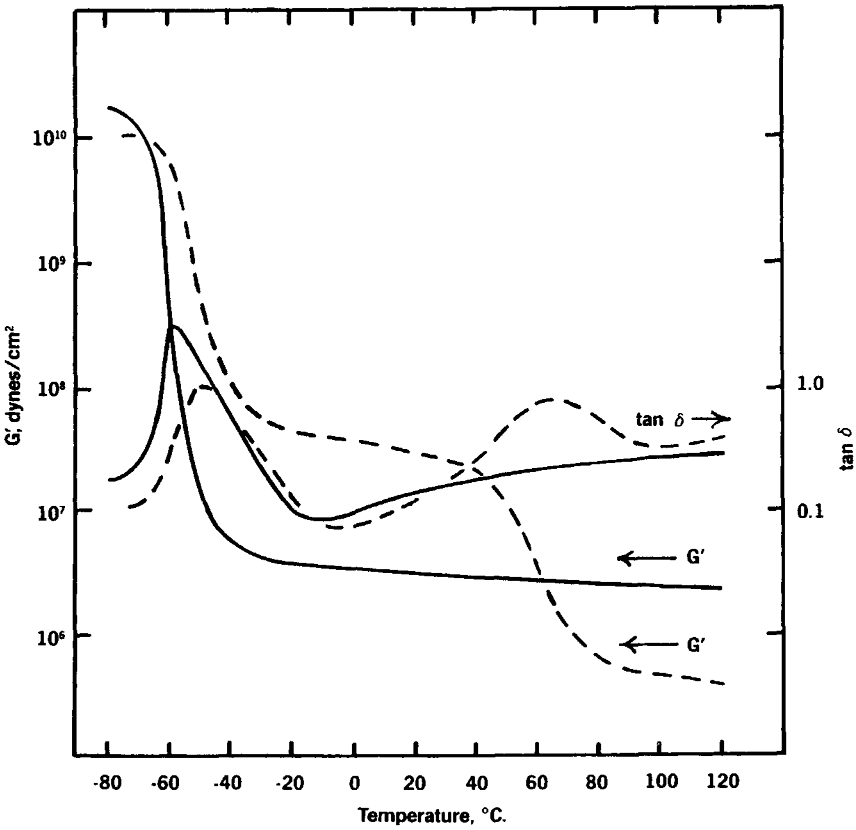

Fig. 1. G' and tan δ vs. temperature for a 1:1 blend of natural rubber with polystyrene resin: (—) NR; (- - -) NR:PS; PS $\overline{M}_w = 900$; PS $\overline{M}_w/\overline{M}_n = 1.6$.

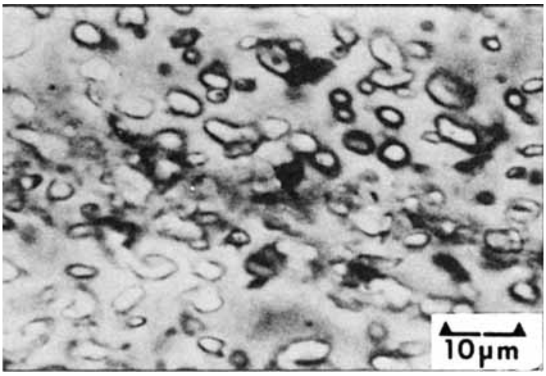

Fig. 2. Transmission photomicrograph of a 3:1 blend of natural rubber with polystyrene resin.

does not perform as predicted from earlier studies of pressure sensitive adhesive compositions. The plot of G' and tan δ vs. temperature, presented as Figure 1, does not show the expected shift of the temperature at which tan δ reaches a peak, nor does it show the depression of the storage modulus

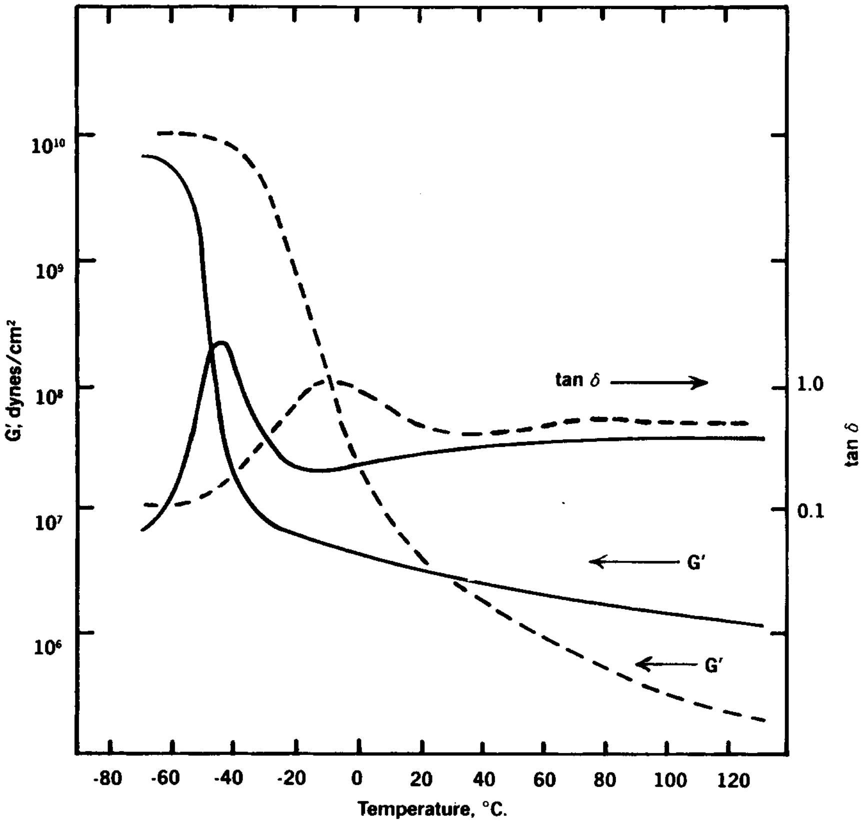

Fig. 3. G' and tan δ vs. temperature for a 1:1 blend of styrene–butadiene rubber with polystyrene resin: (—) SBR; (- - -) SBR:PS; PS $\overline{M}_w = 900$; PS $\overline{M}_w/\overline{M}_n = 1.6$.

in the plateau. However, it was known that this blend is not a satisfactory pressure sensitive adhesive. In Figure 1, the initial peak in tan δ shifts only about 10–15°C from the peak temperature shown for natural rubber, and G' in the plateau is elevated instead of reduced. Also, a higher temperature tan δ peak is apparent at approximately 60°C, suggesting the presence of a second phase. Microscopic examination of a 25% resin blend, presented in Figure 2, confirms the presence of two phases. Dispersed particles can be seen which range in size from about 2 to 5 μm. The assumption is that the resin is dispersed in a continuous rubber matrix. The higher temperature peak is produced by a phase which is predominantly resin but which contains a small amount of rubber, while the continuous phase which is represented by the lower temperature peak, is natural rubber perhaps with some low molecular weight resin dissolved in it. This incompatible behavior was unexpected for a resin having a weight average molecular weight of less than 1000.

A blend of the same low molecular weight polystyrene resin with styrene–butadiene rubber gave the expected behavior of the tan δ peak and G', as shown in Figure 3. The tan δ peak temperature has shifted about 35°C and G' is depressed in the plateau compared to the unmodified rubber. A small second peak in the tan δ curve is evident at about 70°C, suggesting the

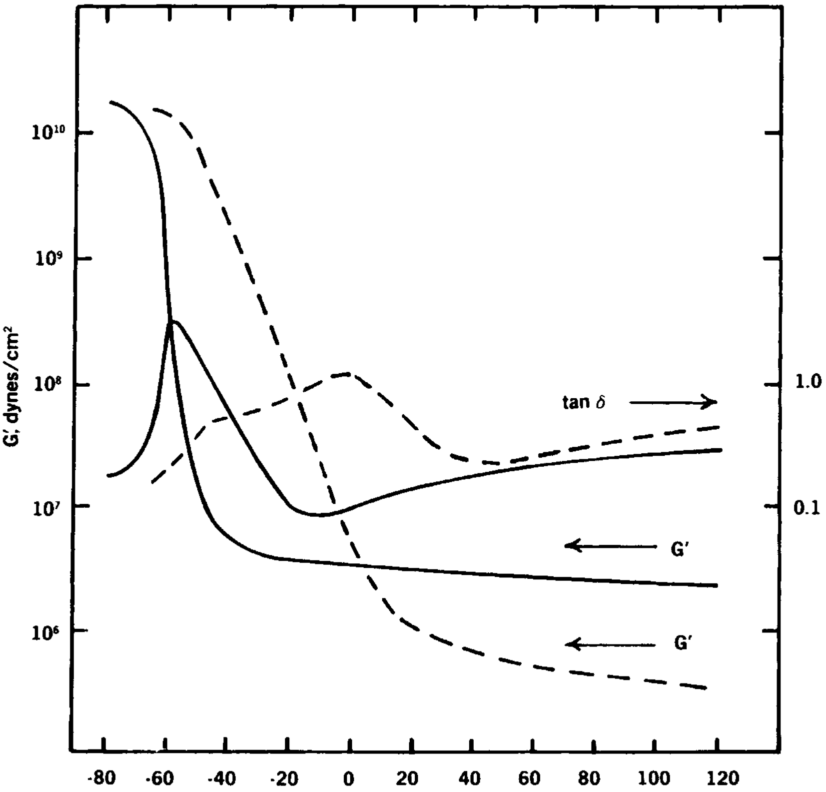

Fig. 4. G' and tan δ vs. temperature for a 1:1 blend of natural rubber with poly(vinyl cyclohexane) resin: (—) NR; (- - -) NR:PVCH; PVCH $\overline{M}_w = 650$; PVCH $\overline{M}_w/\overline{M}_n = 1.4$.

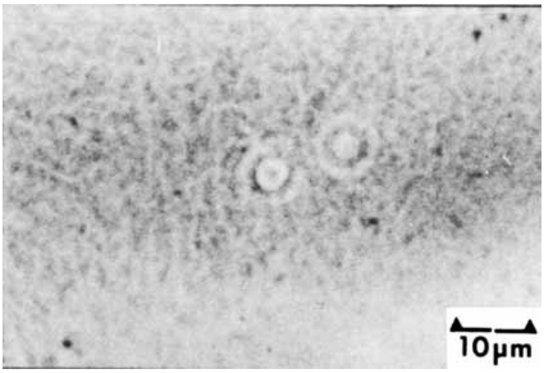

Fig. 5. Transmission photomicrograph of a 3:1 blend of natural rubber with poly(vinyl cyclohexane) resin.

presence of a small volume of a dispersed phase. The plot of tan δ and G' indicates that styrene–butadiene rubber and this sample of polystyrene resin are essentially compatible, as opposed to the incompatibility which is shown in the natural rubber–polystyrene resin blend.

The study was continued by examining the performance of a cycloaliphatic resin. This resin was obtained by complete hydrogenation of the

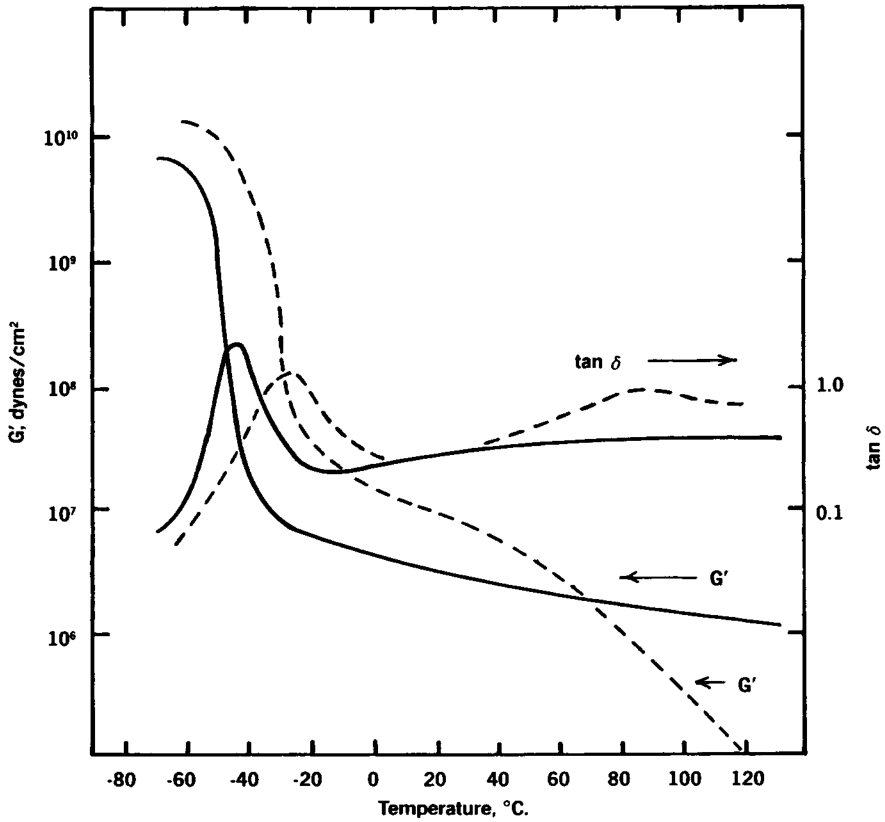

Fig. 6. G' and tan δ vs. temperature for a 1:1 blend of styrene–butadiene rubber with poly(vinyl cyclohexane) resin: (—) SBR; (- - -) SBR:PVCH; PVCH $\overline{M}_w = 650$; PVCH $\overline{M}_w/\overline{M}_n = 1.4$.

polystyrene resin to give a poly(vinyl cyclohexane) resin. When blended with natural rubber, the cycloaliphatic resin gave the predicted changes in viscoelastic properties. As shown in Figure 4, there is a shift of about 60°C in the tan δ peak temperature and a depression of the modulus in the plateau. A low temperature shoulder is seen at about −45°C on the tan δ plot. This probably results from a second phase which is present at low temperatures. The system may become a single phase as the temperature is raised or the second phase may remain as a low modulus, easily deformable dispersion. The photomicrograph of the 25% resin blend, shown as Figure 5, indicates that if a second phase is present, the particle size must be less than about 0.5 μm, the maximum resolution of the microscopic system. The two circles in the center of Figure 5 are artifacts produced during preparation of the sample for microscopy.

A blend of the poly(vinyl cyclohexane) resin with styrene–butadiene rubber is found to be incompatible as shown in Figure 6, similar to the blend of polystyrene resin with natural rubber.

After determining that the fully aromatic resin is compatible with styrene–butadiene rubber and incompatible with natural rubber, and the cycloaliphatic resin is compatible with natural rubber and incompatible with styrene–butadiene rubber, it is of interest to examine an alkylaromatic resin.

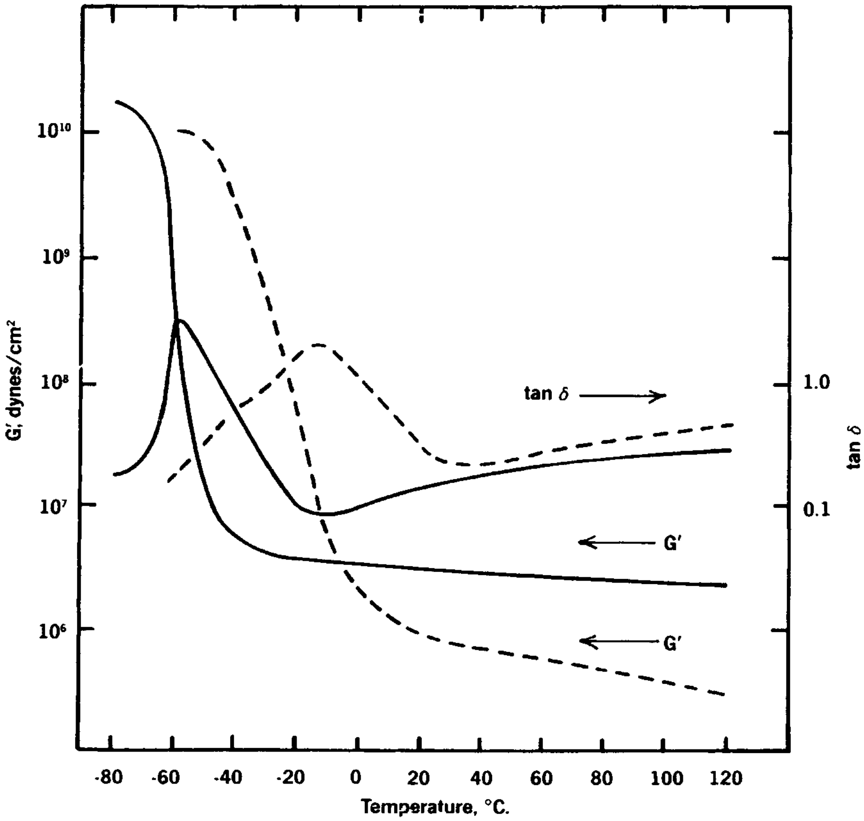

Fig. 7. G′ and tan δ vs. temperature for a 1:1 blend of natural rubber with poly(*tert*-butylstyrene) resin: (—) NR; (- - -) NR:TBS; TBS $\bar{M}_w$ = 850; TBS $\bar{M}_w/\bar{M}_n$ = 1.3.

A 1:1 blend of a poly(*tert*-butylstyrene) resin with natural rubber has viscoelastic properties, shown in Figure 7, which suggest compatibility. The tan δ peak temperature has shifted from about −60°C to about −10°C, and the modulus in the plateau has been depressed. This indicates that the *tert*-butyl group has reduced the aromaticity of the polystyrene resin sufficiently to produce the changes in the properties of natural rubber expected for a compatible system. The *tert*-butyl group, however, did not reduce the compatibility of the polystyrene resin with styrene–butadiene rubber. In the 1:1 blend, shown as Figure 8, the tan δ peak temperature has shifted approximately 50°C, and the modulus in the plateau is reduced because of the resin. The *tert*-butylstyrene resin is compatible with both natural rubber and styrene–butadiene rubber probably because its aromaticity is intermediate between the cycloaliphatic poly(vinyl cyclohexane) resin and the aromatic polystyrene resin.

CONCLUSIONS

The degree of compatibility of rubber–resin systems can be determined by measuring viscoelastic properties. Compatibility is identified by a pronounced shift of the tan δ peak temperature, associated with a depression in the storage modulus in the plateau. An incompatible system is confirmed by a minimal shift of the tan δ peak along with an increase in the storage

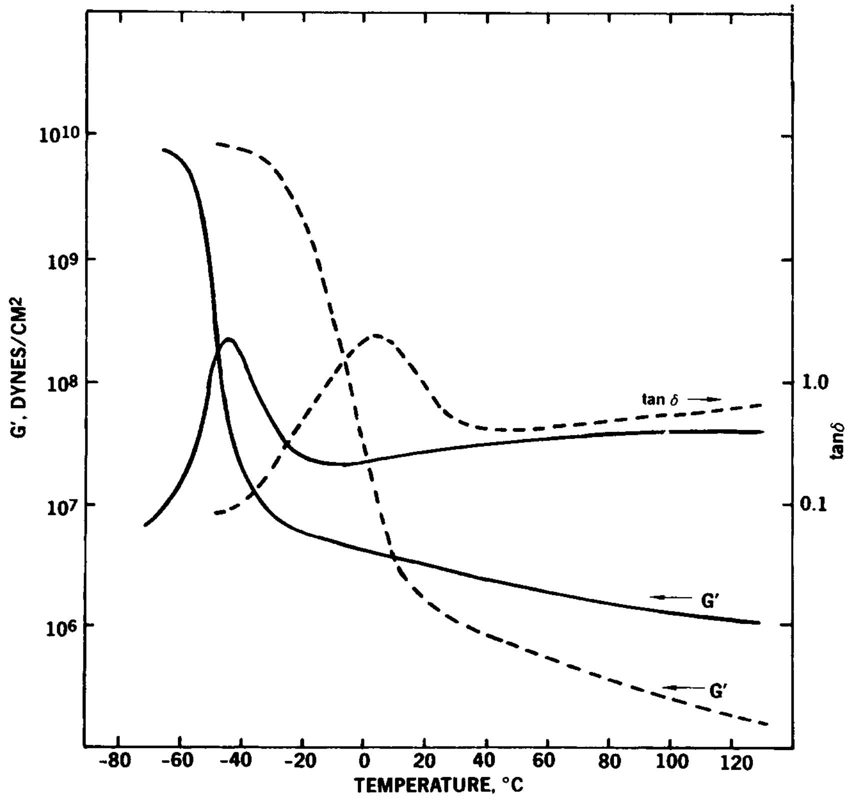

Fig. 8. G′ and tan δ vs. temperature for a 1:1 blend of styrene–butadiene rubber with poly(*tert*-butylstyrene) resin: (—) SBR; (- - -) SBR:TBS; TBS $\overline{M}_w = 850$; TBS $\overline{M}_w/\overline{M}_n = 1.3$.

modulus in the plateau. A second peak in tan δ may be apparent in the incompatible system.

Compatibility of rubber–resin systems requires that the rubber and resin are similar in polarizability. This is true even for resins which have weight average molecular weights of less than 1000. The aromatic polystyrene resin is incompatible with the aliphatic natural rubber, but compatible with the partially aromatic styrene–butadiene rubber. The cycloaliphatic poly(vinyl cyclohexane) resin is compatible with the aliphatic elastomer but incompatible with the aromatic elastomer. Poly(*tert*-butylstyrene) resin is compatible with both natural rubber and styrene-butadiene rubber.

From this work, we would expect that the compatible systems represent compositions which exhibit pressure sensitive adhesive performance at some ratio of rubber to resin. The incompatible systems, on the other hand, would not be pressure-sensitive. The addition of resin to the rubber is required to reduce the plateau modulus to a value low enough to form a bond under a light deforming stress, such as when a pressure sensitive substrate is pressed onto a surface. The addition of an incompatible resin, which elevates the modulus, obviously cannot supply the needed reduction to achieve pressure sensitive performance.

References

1. M. Sherriff, R. W. Knibbs, and P. G. Langley, *J. Appl. Polym. Sci.*, **17**, 3423 (1973).
2. D. W. Aubrey and M. Sherriff, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2631 (1978).
3. D. W. Aubrey and M. Sherriff, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2597 (1980).
4. G. Kraus, F. B. Jones, O. L. Marrs, and K. W. Rollmann, *J. Adhesion*, **8**, 235 (1977).
5. G. Kraus and K. W. Rollmann, *J. Appl. Polym. Sci.*, **21**, 3311 (1977).
6. G. Kraus, K. W. Rollmann, and R. A. Gray, *J. Adhesion*, **10**, 221 (1979).
7. G. Kraus and T. Hashimoto, *J. Appl. Polym. Sci.*, **27**, 1745 (1982).
8. M. Gottlieb and C. W. Macosko, *Rheol. Acta*, **21**, 90 (1982).

Received January 23, 1984
Accepted June 19, 1984