

On the Internal Structure of Pressure-Sensitive Adhesives

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Synopsis

The internal structure of pressure-sensitive adhesives was studied using electron microscopy and measurements of mechanical loss, tensile modulus, viscosity, stress relaxation, and critical surface tension. The adhesives were blends of natural rubber and the pentaerythritol ester of hydrogenated rosin. Compositions containing up to 40 wt-% resin are homogeneous mixtures. The temperature dispersion of mechanical loss shows a single peak, and the peak value remains almost constant. When the resin concentration exceeds 40 wt-%, phase separation occurs. The disperse phase is resin containing a small amount of rubber. Two peaks, or a peak and a shoulder, appear in the temperature-loss peak curves. It is postulated that one of the peaks corresponds to the phase in which resin is uniformly dispersed in the rubber and the other peak corresponds to the resin phase which contains a small amount of rubber. Evidence for homogeneity in compositions containing 40 wt-% or less resin and of heterogeneity at higher concentrations of resin was also obtained from the electron microscope observations. The relationships between the internal structure of pressure-sensitive adhesives and viscosity, Young's modulus, the relaxation spectrum, tack, and critical surface tension are discussed.

INTRODUCTION

The internal structure of pressure-sensitive adhesives has been investigated by Hock¹ and Fukuzawa and co-workers.^{2,3}

Hock, on the basis of electron microscopy, reports that the tack of films of blends of natural rubber and the pentaerythritol ester of hydrogenated rosin is dependent more upon the development of a second phase, which probably consists of low molecular weight rubber dissolved in the resin, than upon the continuous phase consisting of rubber saturated with resin. Increasing the resin concentration evidently increases the amount of the second phase and, at the same time, the film's tack.

At maximum tack, presumably, the maximum amount of low molecular weight ends of the rubber has dissolved in the disperse resin phase. Further increases in resin concentration then result in phase inversion and a drop in tack.

Fukuzawa and co-workers, from observations with an electron microscope and from results of measurement of mechanical loss with a torsional pendu-

lum apparatus (TPA), reported that blends of natural rubber and polyterpene resins are perfectly mixed. Moreover, they reported that the T_g of the blends observed by TPA satisfies the Gordon-Taylor equation. They claimed that tackiness reaches a maximum value at 60 wt-% resin, because the samples wet the adherend more readily as the viscosity of the mixture decreases with increasing resin concentration.

The viscoelastic properties of pressure-sensitive adhesives have been studied by Fukuzawa and co-workers,³ Kaelble,⁴ and Dahlquist.⁵ However, these workers give no details as to the internal structure of their adhesive.

We studied the internal structure of pressure-sensitive adhesives by electron microscopy and by measurement of mechanical loss, tensile modulus, viscosity, stress relaxation modulus, and tackiness. The adhesive systems were blends of natural rubber and the pentaerythritol ester of hydrogenated rosin.

The observation with an electron microscope made heretofore on pressure-sensitive adhesives involved replication of the surface of pressure-sensitive adhesives, but the replica method observes only the surface and is not suitable for observing the internal structure of adhesive films. We fixed the adhesive film on a mesh and took photographs of the adhesive film on the mesh, thereby viewing the interior of the film and obtaining positive identification of internal structure.

EXPERIMENTAL

Materials

Masticated natural rubber was used as the elastomeric base of the pressure-sensitive adhesives. The viscosity-average molecular weight, determined in accordance with the intrinsic viscosity-molecular weight relationship for natural rubber in toluene found by Carter and co-workers⁶ was 5.72×10^6 ($[\eta]$ measured at 25°C). The pentaerythritol ester of hydrogenated rosin (Hercules Inc., U.S.A.) was used as the tackifier. Its molecular weight, determined by a cryoscopic method, was 900. Its softening temperature, determined by the Ring and Ball method,⁷ was 90°C.

Apparatus and Procedure

The electron microscope was a JME 6A (made by Japan Electron Optics Lab. Co. Ltd., Tokyo, Japan). A thin sample of required thickness for the experiments was prepared. Rubber and resin were dissolved in *n*-hexane at a fixed low concentration, 2-3 wt-%, stirred until homogeneous, then taken up on the mesh and dried to remove the solvent. Photographs of light field, dark field, and diffraction images were taken.

The temperature dispersion of mechanical loss was measured by Kaneko's method.⁸ Supported film specimens were made by permeating solutions in

n-hexane of 2-3 wt-% rubber and resin into filter paper and drying to remove the solvent. The measurement is based on the principle that the number of oscillations in the interval during which the maximum amplitude damps from its initial value to a given smaller value is inversely proportional to the logarithmic decrement of the oscillating systems (conjugated torsion pendulum).

A Koka-type flow tester (made by Shimazu Seisakusho Ltd., Kyoto, Japan) was used to measure the viscosity of the blends. The length-to-diameter ratio (L/D) of the nozzle used was 2, and the stress was 3.7×10^6 dynes/cm².

The stress relaxation modulus of the blends was measured by a strain gauge attached in a constant-temperature bath variable from -20° to 60°C . The thickness of the sample was 0.08 cm. By sliding the relaxation curves of modulus versus time obtained at various temperatures along the time axis to superpose with the relaxation curves obtained at 20°C , a master curve covering a much wider range of time could be constructed for each blend. The apparent activation energies of the relaxation processes were obtained from the shift factors.

The tensile strength was measured with a TOM 30-type tensile tester (made by Shinkoh Tsushin Kogyo Co. Ltd., Tokyo, Japan) using the same type of sample used in stress relaxation measurements.

The rate of jaw separation was 5 mm/min, and the temperature was 20°C .

The tackiness was measured with a previously described⁹ probe tack tester at 20°C . The sample was made as follows: Solutions in *n*-hexane of 10-15 wt-% of the rubber-resin blends were coated on a polyester film Lumirror (made by Toray Co. Ltd., Tokyo, Japan) and dried to remove the solvent. The thickness of the sample coatings was 0.049 ± 0.002 mm.

The critical surface tension was measured by Zisman's method.¹⁰ Solutions in *n*-hexane of 2 wt-% of the blends were coated on a glass microscope slide and dried to remove the solvent. Next, the drops of various liquids were placed on the coated slides and the contact angles were measured.

The liquids (and corresponding surface tensions) were water (73.8) glycerine (63.3), ethylene glycol (48.0), poly(ethylene glycol) 300 (45.5), and poly(ethylene glycol) 200 (42.0).

The surface tensions of the liquids were measured at 20°C with a Wilhelmy surface tensiometer, ST-1 type (made by Shimazu Seisakusho Co. Ltd., Kyoto, Japan).

RESULTS AND DISCUSSION

Temperature Dispersion of Mechanical Loss and Observations with Electron Microscope

Hock,¹ from electron microscope observations, found that in rubber-resins film having good tack, the tack is more dependent on the second phase that develops, which probably consists of low molecular weight rubber

molecules dissolved in resin, than on the continuous phase, which consists of rubber saturated with resin. Furthermore, he reported that the increase in tack is coincident with the formation of a second phase, this second phase becoming especially prominent at 60 wt-% resin concentration where the measured tack value of the film is high. However, observations were made only upon the replicated surfaces of the pressure-sensitive adhesives.

We have made observations of thin films with the electron microscope and have also measured the temperature dispersion of mechanical loss using compositions similar to Hock's.

Evidence from Mechanical Loss

The temperature dispersion of mechanical loss in blends of natural rubber and pentaerythritol ester of hydrogenated rosin is shown in Figure 1. The relation of the peak temperature to resin concentration is shown in Figure 2.

When two peaks, or a peak and a shoulder, appear in the temperature dispersion of mechanical loss, the peak or shoulder on the higher temperature side is associated with resin and that on the lower temperature side, with the rubber.

Natural rubber shows a primary dispersion at -65°C . This agrees well with Fukuzawa's results³ obtained by TPA. As the resin concentration increases to 10 wt-%, the loss peak temperature shifts from -65° to -54°C . The peak temperature remains almost unchanged though the resin concentration increases from 10 wt-% to 40 wt-%. At this resin concentration, the resin and the rubber are completely mixed and act as a single phase. When the resin concentration is increased to 60 wt-%, a shoulder (second peak) appears at -30°C .

It is believed that the main peak (first peak) at -42°C corresponds to the phase in which the resin is uniformly dispersed in the rubber, and the shoulder (second peak) at -30°C corresponds to a resin-rich phase which includes some rubber.

It is interesting to follow the behavior of these rubber-rich and resin-rich phases. As the resin concentration increases to 70 wt-%, the magnitude of the second peak becomes equal to that of the first peak. This means the phase containing mostly resin and the phase containing most of the rubber are clearly distinguishable. As the resin concentration becomes greater than 70 wt-%, the resin phase contains the major amount of resin, and its T_g rises. When the shoulder is at -10°C (90 wt-% resin concentration), it is estimated that the phase containing most of the rubber also contains an extensive amount of the resin.

We have no explanation for the peaks at -84°C (80 wt-% resin concentration) and -86°C (90 wt-% resin concentration). The relation of the loss peak temperature with resin concentration is summarized in Figure 2.

The torsion pendulum data allows us to postulate about the phases which exist in the mixture as a function of the resin concentration. For additions of resin to 40 wt-%, the mixture forms a homogeneous blend rich in rubber

with a single loss peak at about -53°C . When the mixture contains 60 wt-% resin, the peak of the rubber-rich phase has shifted to -42°C , and a shoulder appears at -30°C which is attributed to a newly formed separate phase rich in resin. As the resin concentration in the mixture increases to

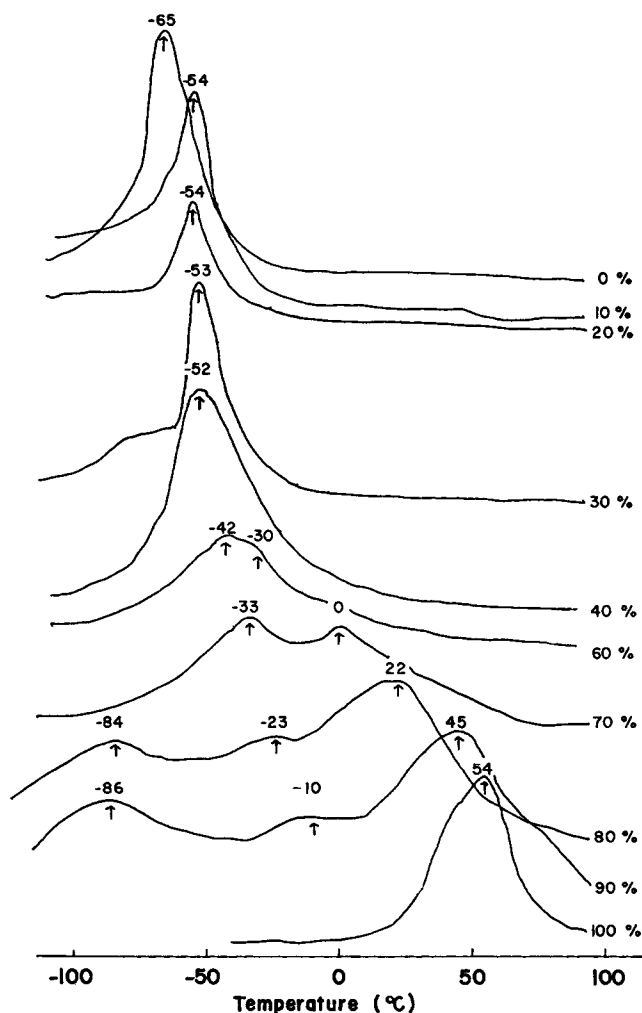


Fig. 1. Temperature dispersion of mechanical loss for blends of natural rubber and the pentaerythritol ester of hydrogenated rosin. Percentage figures refer to the concentration in wt-% of resin in each blend.

90 wt-%, most of the resin prefers to concentrate in the resin-rich phase. This is evidenced by the increasing intensity of the resin-rich peak and the decreasing intensity of the peak of the rubber-rich phase; also by the increasing spread in temperature between these peaks as resin concentration of the mixture increases. The increase in peak temperature of the phase

identified as rich in rubber indicates that a minor portion of the additional resin is still entering that phase.

A schematic representation of the phase relationships existing in the blends at various composition, as indicated by the temperature of the

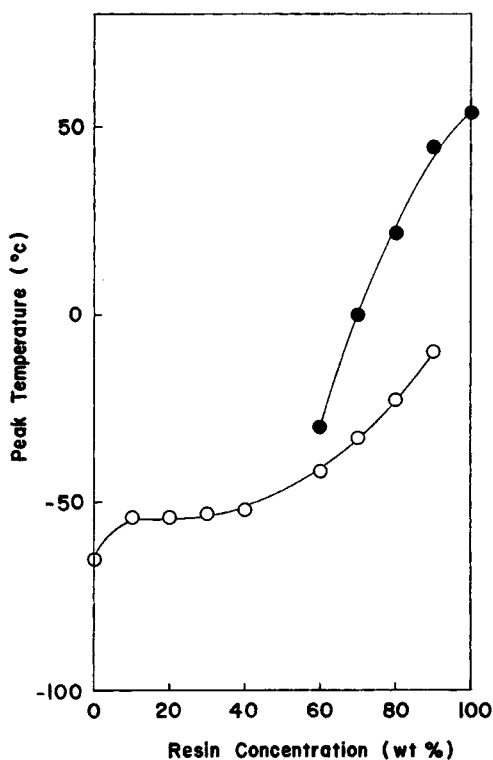


Fig. 2. Relationship between resin concentration and temperature of maximum mechanical loss: (O) rubber phase; (●) resin phase.

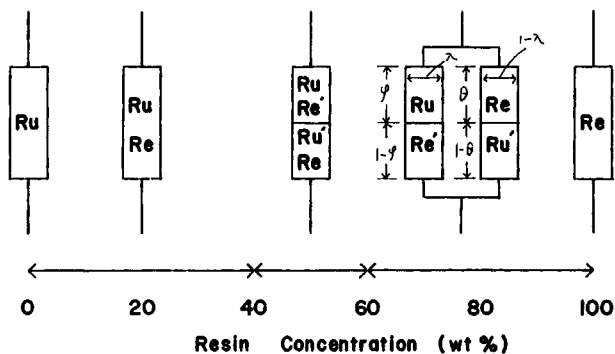


Fig. 3. Representation of adhesive structure in terms of blend composition and phase separation as interpreted from the dispersion of mechanical loss. Ru, Ru', Re, and Re' represent rubber, rubber-rich, resin, and resin-rich phases, respectively.

mechanical loss peaks, is shown in Figure 3. In this figure, the symbols Ru, Ru', Re', and Re refer to pure rubber, rubber-rich, resin-rich, and pure resin, respectively; ρ and θ show the ratios of Ru to Re' and to Re Ru', respectively; λ is the ratio of the rubber-like phase and resin-like phase.

Evidence from Electron Micrographs

The electron microscope photographs for the blends are shown in Figures 4 to 9. The photographs of Figures 4 and 5, 0% and 20% resin, respectively, show only variable degrees of shading indicating uniformity of com-

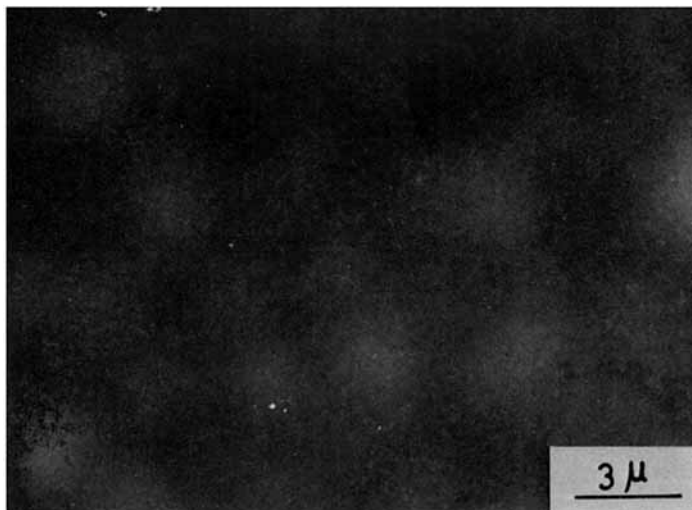


Fig. 4. Electron micrograph of 0 wt-% resin concentration.

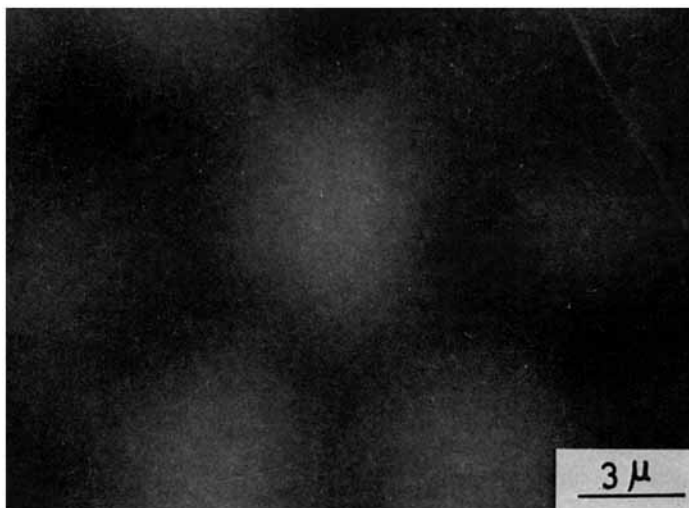


Fig. 5. Electron micrograph of 20 wt-% resin concentration.

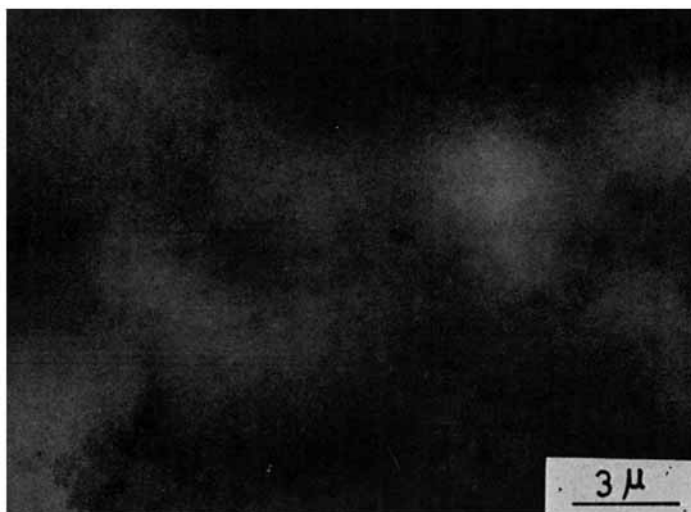


Fig. 6. Electron micrograph of 40 wt-% resin concentration.

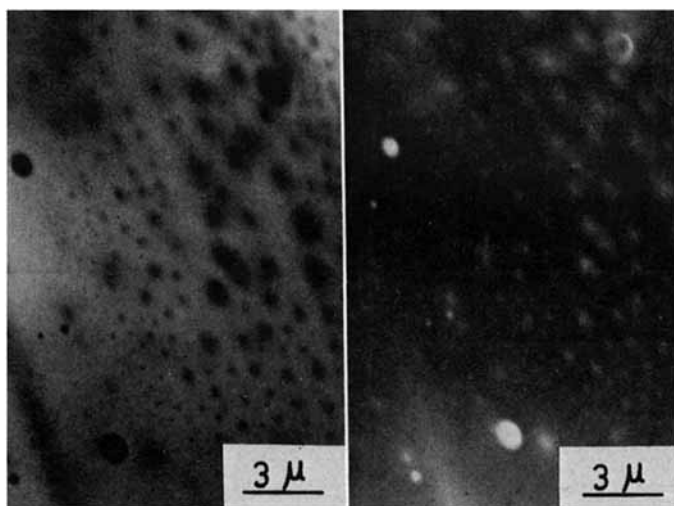


Fig. 7. Electron micrograph of 60 wt-% resin concentration. Left side, light field image; right side, dark field image.

position and a single phase. At a resin concentration of 40 wt-%, (Fig. 6) the resin-like phase is observed, but it is not distinct.

Figure 7 shows the 60 wt-% blend; the photograph on the left side is the light field image, that on the right side, the dark field image. The black spots, diameter 0.1-1.0 μ , shown in the light field image, appear in the dark field image as the white spots. Therefore, these spots are not impurities such as dust but show the existence of two phases.

A diffraction image of a spot taken at an oblique angle to the plane of the sample is shown in Figure 8. It shows a halo, indicating amorphous

structure. Its planar distances are 1.2 \AA and 2.1 \AA , values corresponding to the carbon-carbon bond distances and the diagonal distance of the benzene ring of abietic acid, the chief ingredient of the resin. This is evidence that resin particles also exist in the mixture.

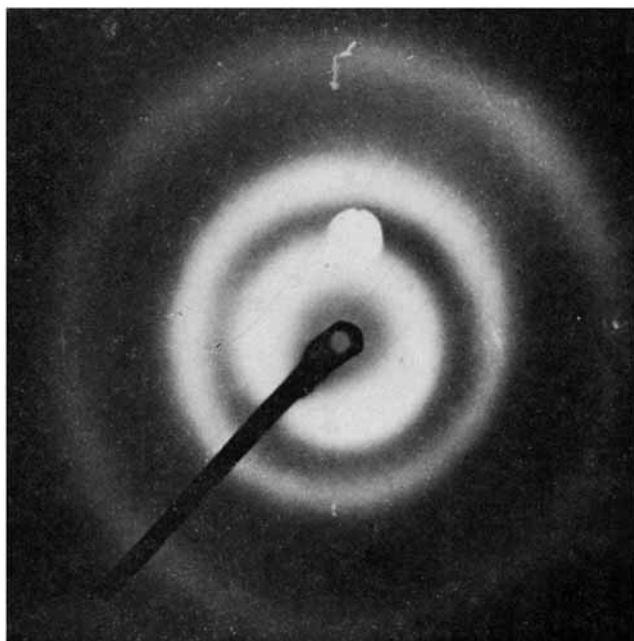


Fig. 8. Electron diffraction pattern of 60 wt-% resin concentration.

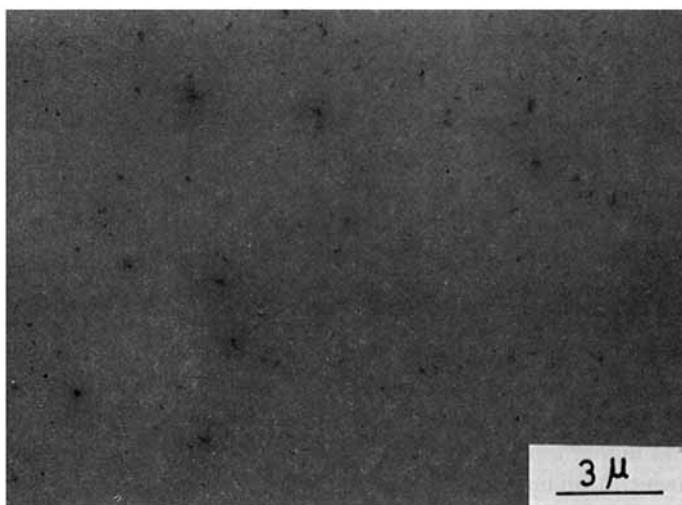


Fig. 9. Electron micrograph of 80 wt-% resin concentration.

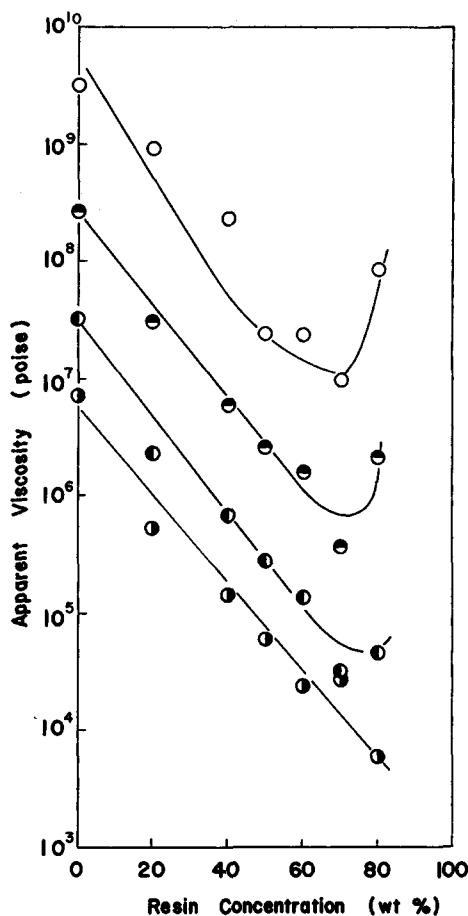


Fig. 10. Relationship between resin concentration and apparent viscosity at various temperatures: (○) 20°C; (●) 40°C; (●) 60°C; (●) 80°C.

The electron micrograph of the 80 wt-% resin blend is shown in Figure 9. Note that the diameter of the resin phase particles has decreased to 0.04–0.16 μ as total resin in the blend increases.

This electron micrograph evidence may be understood from the viewpoint of the phase relationships summarized in Figure 3.

Relationship Between Resin Concentration and Viscosity

Plots of the apparent viscosity obtained at various temperatures against the resin concentration are shown in Figure 10. In the lower temperature range, 20°–60°C, the viscosity has a minimum at a resin concentration of 70 wt-%. At higher temperature, 80°C, viscosity decreases continually as the resin concentration increases.

The viscosity behavior can be explained from the viewpoint of the phases which exist as a function of resin concentration. The viscosity of the

continuous phase decreases as the resin concentration increases because of the plasticizing effect of the resin.

This plasticizing effect of the resin appears to be independent of whether the rubber-rich or the resin-rich phase dominates or constitutes the continuous phase in the mixture.

In regard to the rubber-rich phase, one may refer again to Figure 2, to recall that the glass temperature of the continuous phase (rubber-rich phase) rises as the resin concentration increases; but the T_g at 90 wt-% of the resin is -10°C and is lower than room temperature, the initial temperature for our viscosity measurements.

In the resin concentration region where the resin-rich phase dominates, we may use the following argument. The softening temperature of the resin, T_s , obtained with the Ring and Ball method, is 96°C , and its glass transition temperature, T_g , obtained from the peak in the mechanical loss curve, is 54°C . The difference between T_s and T_g is 42°C .

If we assume that this 42°C difference between T_s and T_g holds for all resin-rich phases, we may calculate a T_s value for this phase as a function of concentration. These values are shown in Table I. Again, while the T_g of

TABLE I
Glass Transition Temperature and Softening Temperature of Resin-Rich Phase Obtained from Temperature Dispersion of Mechanical Loss

Resin concn., wt-%	Glass transition temp., (resin-rich phase) $^\circ\text{C}$	Softening temp., $^\circ\text{C}$
100	54	96*
90	45	87
80	22	64
70	0	42
60	-30	12

* Measured by Ring and Ball method.⁷

the resin-rich phase also rises as the resin concentration increases, it reaches only 22°C at 80 wt-% resin.

We may also recall that in the region of 70 wt-% resin, where the electron micrograph detected the existence of resin particles, the viscosity of the blend increases, probably due to the filler effect of the resin particles.

Plots of the apparent viscosity against the reciprocal of the absolute temperature are shown in Figure 11. At 0-40 wt-% resin concentration, the plot for each composition exhibits two straight-line segments with different slopes.

Plots of the apparent activation energies calculated from slopes against concentration are shown in Figure 12. The activation energy of the rubber and the temperature of the inflection point are shown, with the results of other investigators,^{11,12} in Table II. According to the studies of Koide and

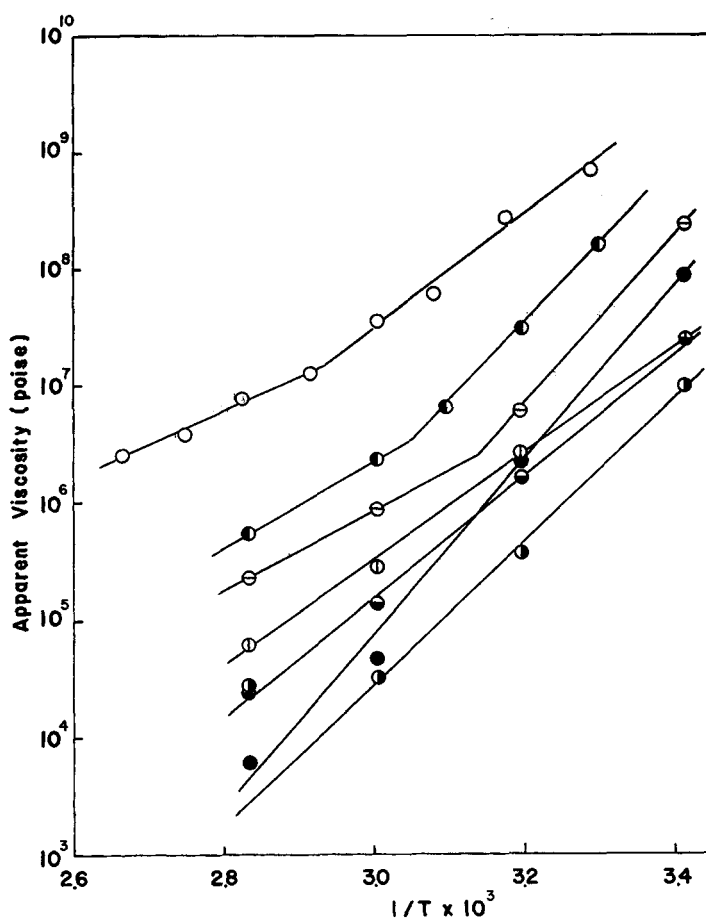


Fig. 11. Arrhenius plots of temperature dependence of apparent viscosity at various resin concentrations: (○) 0%; (●) 20%; (⊖) 40%; (⊕) 50%; (⊗) 60%; (⊙) 70%; (●) 80%.

co-workers,¹¹ the segmental flow unit increases in size as the temperature falls, the activation energies for flow slowly increase, and two straight lines with different slopes appear.

If this idea is applied to the blends of rubber and resin, the segmental unit for flow increases as the temperature falls, and the inflection point appears just as for rubber alone because only one phase exists until the resin concentration reaches 40 wt-%. But, with increasing resin concentration, the inflection point moves to the lower temperature side and the activation energies at the lower temperatures increase.

Above 40 wt-% resin, the flow resistance is lower at temperatures above room temperature, the segmental flow unit decreases in size, and the inflection point disappears. Because the activation energy for the flow of resin is larger than the activation energy for the flow of rubber, the activation en-

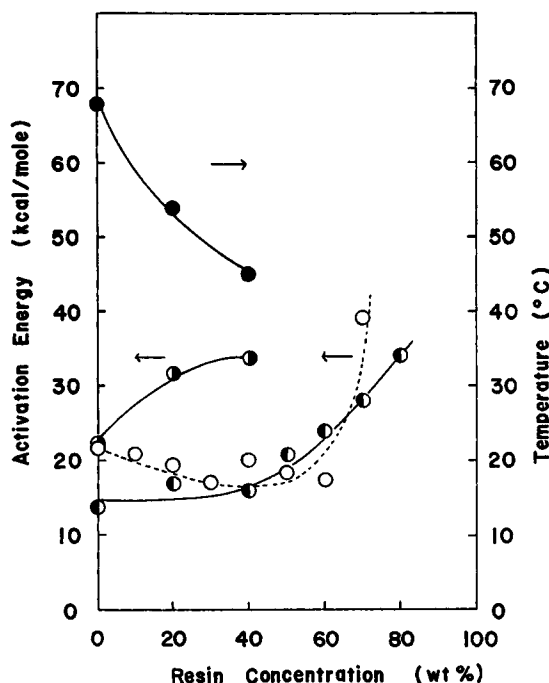


Fig. 12. Relationship between resin concentration and activation energy; also between resin concentration and temperature at inflection point: (●) activation energies obtained from viscosity vs. temperature in lower temperature range; (○) activation energies obtained from viscosity vs. temperature in higher temperature range; (○) activation energies obtained from shift factors of stress relaxation measurements; (●) inflection point of viscosity vs. temperature.

ergies for the blends abruptly increase when the resin concentration exceeds 40 wt-%.

Activation energies for the relaxation process obtained from the shift factor take a minimum value at 60 wt-% resin concentration and abruptly increase at 70 wt-% resin concentration. The viscosity of the resin-rich phase, which becomes the continuous phase at high resin concentrations,

TABLE II
Activation Energies and Inflection Point for Viscous Flow
of Natural Rubber at Elevated Temperatures

Activation energy, kcal/mole			Inflection point, °C	
In lower temp. range	In higher temp. range			
22.2	13.7	68	this work	
21.6	11.7	60	ref. 11	
10.0	2.0	50	ref. 12	
—	9.9	—	ref. 13	

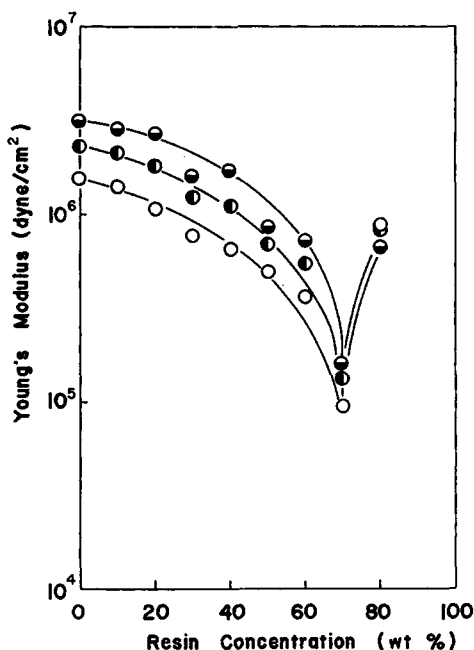


Fig. 13. Relationship between resin concentration and Young's modulus: (○) 50% elongation; (◐) 100% elongation; (●) 200% elongation.

decreases as the resin concentration increases, and the relaxation becomes fast. Above 70 wt-% resin, the activation energies for the relaxation process increase markedly owing to the strong interactions within the resin phase.

Relationship Between Resin Concentration and Tensile Modulus

The relationship between resin concentration and the tensile moduli at 50%, 100%, and 200% elongation is shown in Figure 13. The tensile modulus decreases as the resin concentration increases, taking a minimum value at 70 wt-% resin, then abruptly increasing at 80 wt-% resin. Moreover, the tensile modulus becomes almost independent of strain at 80 wt-% resin. When the resin concentration reaches 80 wt-%, the T_g of the resin-rich phase reaches 22°C and the blends become resin-like. The tensile modulus of the blends then abruptly increases. The strain independence of the tensile modulus at 80 wt-% resin can be explained by the fact that the T_g of the rubber phase, which is the continuous phase, is -23°C, and the T_g of the resin phase, which is the dispersion phase, is 22°C. The blends are completely mixed at the lower concentration of the resin, but the resin-rich phase is formed in the rubber-rich phase as the resin concentration increases. At resin concentrations below 80 wt-%, the tensile modulus decreases as the resin concentration increases, due to the plasticizing effect of the resin. When the resin concentration approaches 80 wt-%, the blends

become resin-like. If the sample is elongated at a low rate at room temperature, the rubber-rich phase, being the continuous phase, slips through the disperse phase, and the tensile modulus takes an almost constant value as the strain increases.

Relationship Between Resin Concentration and Relaxation Spectrum

The relaxation spectra of the various blends obtained from first approximation analysis of stress relaxation master curves are shown in Figure 14. The level of the rubbery plateau is lower the higher the resin concentration, and, above 40 wt-% resin, the width of the rubbery plateau, indicative of the degree of entanglement, becomes narrower. At the 70 wt-% resin concentration, the rubbery plateau almost disappears.

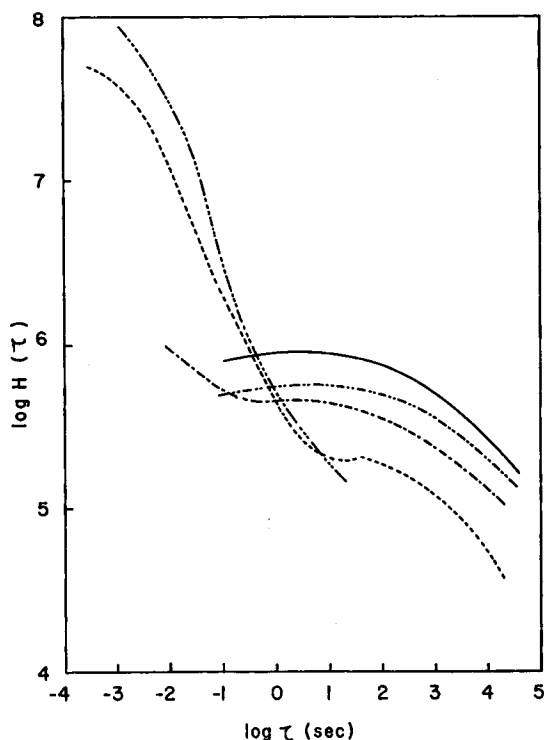


Fig. 14. Relaxation spectra of blends. Resin concentrations: (—) 0 wt-%, (-----) 20 wt-%; (-·-·-·) 40 wt-%; (—) 60 wt-%; (—) 70 wt-%.

Relationship Between Resin Concentration and Tackiness

The relationship between resin concentration and tack as measured with the probe tack tester is shown in Figure 15. The tack value increases with the resin concentration up to 60 wt-% but is independent of the contact time. Above 60 wt-% resin, the tack value becomes dependent on the contact

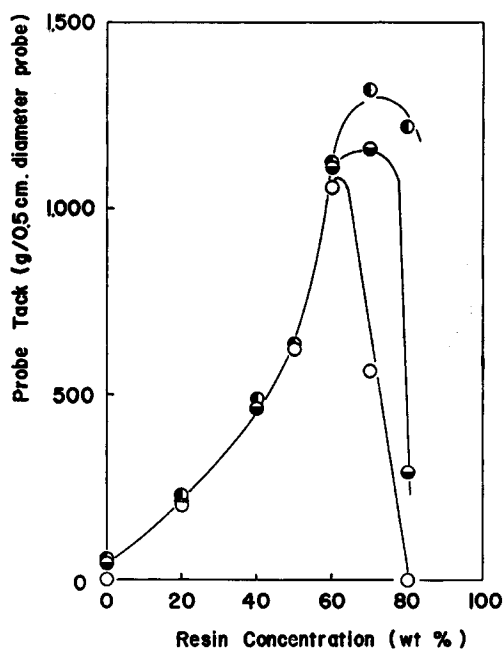


Fig. 15. Probe tack value as function of resin concentration. Contact time: (O) 0.2 sec; (◐) 2.0 sec; (●) 20 sec.

time. The viscosity, measured at 20°C, takes a minimum value at the 70 wt-% resin concentration. The adhesive's ability to wet the adherend therefore reaches a maximum at this concentration, hence the maximum in the tack value.

When the contact time is very short, the resin-rich phase (T_g is 42°C) does not make full contact with the probe, and the tack value is rather low.

It was previously reported⁹ that the Rolling Ball Tack (contact time about 10^{-2} – 10^{-3} sec) has a maximum value at 40 wt-% resin. Bull and co-workers¹⁴ also reported the tack maximum at 40 wt-% resin (natural rubber-poly(β -pinene) resin) using a rotating drum technique.

When the contact time is very short, the contact between adherend and adhesive is something less than perfect. The T_g of the resin-rich phase is higher than that of the rubber-rich phase, and though the viscosity of the system as a whole is down, the viscosity of the resin-rich phase is high and wetting is incomplete.

Hock¹ reported that the resin phase including low molecular weight rubber contributes to wetting. But if it is assumed that the rubber phase including the resin contributes to wettability, then the resin phase including low molecular rubber rather interferes with wetting at short times of contact.

At a longer contact time, the maximization of the tack at 70 wt-% of the resin concentration coincides with the formation of resin aggregates in

the sample, because a tacky thin layer of the sample is pulled away from the solid adhesive surface, and the sample shows a higher resistance to flow.¹⁵

Relationship Between Resin Concentration and Critical Surface Tension

The relation between resin concentration and the critical surface tensions of the blends is shown in Figure 16. The measurement of the critical surface tension (γ_c) of a tacky surface is very difficult, and the γ_c value does not necessarily reflect the internal structure. Figure 16 shows that γ_c is almost constant until 40 wt-% resin is reached, then slowly increases as the resin concentration exceeds 40 wt-%.

It may be concluded that when the resin concentration does not exceed 40 wt-%, the resin and the rubber mix completely and form a homogeneous phase, hence γ_c is almost constant. Above 40 wt-% resin, the resin and

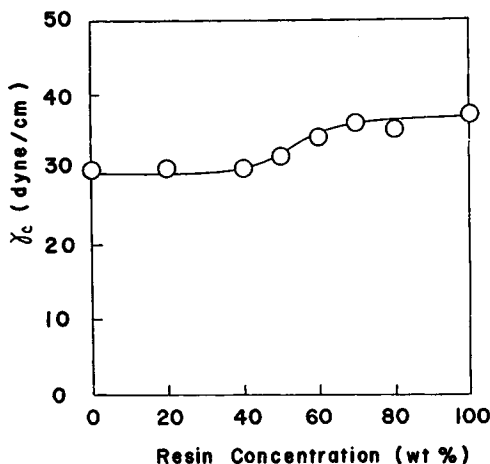


Fig. 16. Relationship between resin concentration and critical surface tension γ_c .

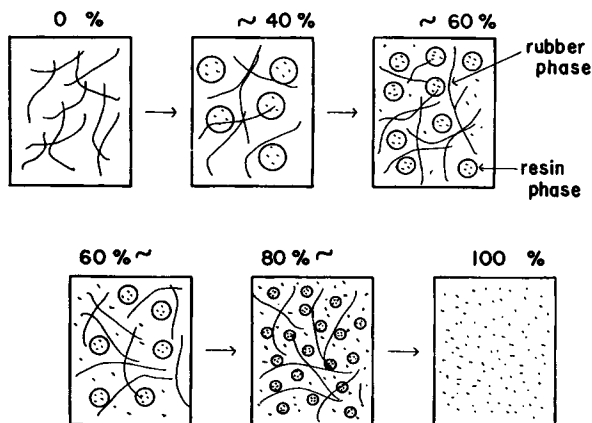


Fig. 17. Schematic representation of structures of blends of rubber and resin.

low molecular weight rubber form a separate phase in the rubber phase, and γ_c increases as the resin concentration increases.

The schematic representation of the structures of the blends of rubber and resin is shown in Figure 17.

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