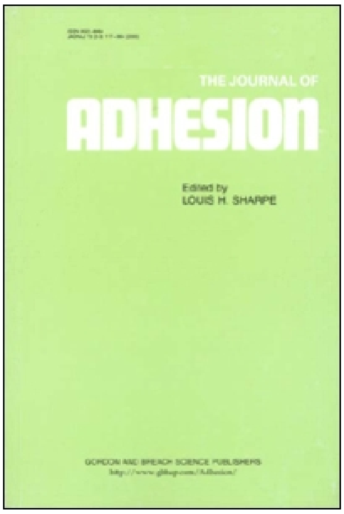

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Dynamic Mechanical and Thermal Analysis for the Determination of RFL Morphology

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From dynamic mechanical and DSC studies, we have concluded that resorcinol-formaldehyde-latex (RFL) adhesive systems are two-phase materials. This is consistent with the limited electron microscopy work published on these polymers. However, while finer details of RFL morphology have never been resolved by electron microscopy, a comparison of the dynamic mechanical results with theoretical models provides evidence that the RFL has an interpenetrating network (IPN) morphology. The resorcinol-formaldehyde thermoset provides a continuous glassy network, while the butadiene-styrene-vinyl pyridine terpolymer latex forms a continuous rubbery phase at ordinary use temperatures. The mechanical properties of the IPN are dominated by the volume fraction, chemistry, and thermal history of the RF thermoset. The dynamic mechanical properties of films made from ammonia-containing RFL adhesives are particularly sensitive to thermal history. This is consistent with the long-accepted belief that ammonia forms thermally unstable benzylamine linkages in the RF network.

INTRODUCTION

Resorcinol-formaldehyde-latex (RFL) adhesives have been used by the rubber industry for over 40 years. Yet they remain the single most important class of adhesive for bonding rubber to reinforcing cord. Despite the commercial importance of cord-rubber composites and the

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significant role of RFL adhesives in these composites, the understanding of RFL remains quite empirical. The absence of fundamental information results from the complexity of the rubber-to-cord adhesion problem. This problem brings together many poorly understood areas of science. Among them are the subjects like network formation in thermosetting polymers, multi-phase polymer morphology, polymer surface analysis, adhesion science, adhesion testing, the diffusion of vulcanizing agents, and vulcanization chemistry. While additional research and new techniques have greatly improved our understanding of many, if not all, of these subjects in the last several years, little effort has been made to bring this knowledge to bear on the problem of rubber-cord adhesion with RFL adhesives. Studies of a fundamental nature on this subject have been almost nonexistent in the open literature since the mid-1960's. Thus the time is right to examine this old problem in the light of new knowledge and techniques.

A fundamental study, however, must begin at the point where the existing, basic, experimentally-sound information ends and speculative, empirically-drawn conclusions start. For the RFL rubber-to-cord adhesion problem, this point occurs in our understanding of RFL as a material. Several aspects of the chemistry, morphology, and mechanical properties of RFL are subjects of either speculation or controversy. The present study seeks to clarify the morphology-property relationship in RFL.

The RFL morphology has received only brief attention in the literature. Chappius *et al.*[1], Fomchenkova *et al.*[2], and Dlugosz[3] have all examined RFL systems *via* transmission electron microscopy. There were many differences in the formulations and sample preparation techniques used by these workers in their respective studies. However, they all saw evidence that RFL is a two-phase material. The RF resin acts as a glassy network while the latex serves as a rubbery phase at normal use temperatures. But while the two-phase nature of these systems has been revealed, finer details of the morphology have yet to be investigated. It has not been previously established, for example, whether the two phase morphology is that of a continuous glassy phase, continuous rubbery phase or interpenetrating network. The answer to this question may be beyond the resolving power of electron microscopy. Furthermore, no serious effort has been made to study changes in morphology which accompany changes in RFL formulation. It should also be pointed out that at least one worker[4] has concluded that RFL is a single-phase material. Thus the question of RFL morphology is one which must be addressed if we are to understand these materials.

While the mechanical properties of RFL have been investigated as a function of such formulation variables as resin/latex ratio, formaldehyde/resorcinol ratio, and latex type, little fundamental knowledge has emerged. The overall picture is confusing, and many apparent contradictions arise when data obtained by independent researchers are compared. This situation results from two factors. One is the fact that the preparation techniques for making RFL films suitable for mechanical testing vary greatly. And in most cases, vulcanization agents are included in the RFL recipes. As a result, the effects of both the film preparation technique and the vulcanizing agents are superimposed on the effects of the RFL formulation variables. The second factor is that a typical RFL recipe consists of many variables. Since these variables are seldom adequately controlled between studies, comparing the results of independent researchers becomes much like comparing apples with oranges. The situation calls for a careful, well-controlled study of the mechanical properties of RFL films. The films must be prepared in a uniform way without vulcanizing agents. Only through experiments of this type can we hope to understand and explain these complex materials.

One experimental technique which can be used to investigate the effect of formulation changes on both the morphology and the mechanical properties of viscoelastic materials is the study of their dynamic mechanical behavior.[5] While dynamic mechanical studies have been conducted extensively on single phase and multiphase polymers, only one report has been published on the application of this technique to RFL. That work was done by Raumann[4], who contends that the dynamic mechanical results are consistent with a one-phase RFL. There are serious problems with Raumann's interpretation of the dynamic mechanical data. And it contradicts the overwhelming flow of evidence regarding RFL morphology. The need to understand the interrelationships among chemistry, morphology, and mechanical properties in RFL, and the apparent controversy regarding Raumann's dynamic mechanical results are compelling reasons why the current study on the effect of formulation changes on RFL dynamic mechanical properties was launched.

EXPERIMENTAL

Materials

All of the RFL aqueous dispersions used in this study were based on the following recipe:

5.0 gm Penacolite R2170 Resin (Koppers)
5.0 ml of 1.5% NaOH
5.0 ml of 28% NH_4OH
62.5 ml of 2508 × 25 latex (BFGoodrich)
2.5 ml of 37% formaldehyde solution
53 ml of distilled water

These ingredients were appropriately mixed. Then the resulting solution was allowed to mature 16–48 hours in a sealed glass container prior to use.

The formulation changes made in this recipe for the current study were variations in the latex/resin ratio and either including or excluding NH_4OH in the recipe. To study the effect of the latex/resin ratio on RFL film properties, the volumes of 2508 × 25 used were varied from 25 ml up to 250 ml as the latex/resin ratio by weight in the RFL was varied from 2/1 up to 20/1. To examine the role of NH_4OH, this ingredient was either included at the level specified in the above recipe or it was excluded altogether. We did not investigate the effect of intermediate amounts of NH_4OH in the RFL recipes.

Film preparation

The RFL films used in this study were prepared by casting the aqueous RFL dispersions prepared as described above onto a mercury surface. A 190 × 100 round Pyrex crystallization dish was filled with enough mercury to cover the bottom of the dish completely. It was then placed into a constant temperature water bath maintained at 65°C. Exactly 70 ml of the RFL solution was then poured onto the mercury surface. Bubbles which resulted from the pouring process were either broken or pulled to the edge of the dish so that uniform films could develop. To reduce the rate of water loss, a large funnel was inverted over the Pyrex dish. Reducing the rate of water loss provides more uniform films. The Pyrex dish was maintained at 65°C in the constant temperature bath until the films appeared dry (roughly 4 hours). The RFL films were then removed from the mercury surface and allowed to dry in the air overnight. Any mercury clinging to the resulting films was then vacuumed off. These films constitute the "as cast" series of RFL films.

Some of the "as cast" films were subsequently subjected to one of two possible thermal treatments. The first treatment was a compression molding process. Under this treatment the "as cast" RFL film was placed between two sheets of Mylar and the Mylar-RFL-Mylar sandwich was placed between two polished, preheated steel plates. This assembly was transferred to a press equilibrated at 175°C. The RFL was pressed at 20,000 lbs of force for 7 minutes. The resulting RFL films were very uniform with a glossy surface.

The second thermal treatment was much simpler. In this treatment the "as cast" RFL film was simply placed into a forced air oven at 220°C for 1.5 minutes. Films subjected to this treatment were not as aesthetically pleasing as the compression molded films. There is clearly some effect of either the higher temperature or the absence of pressure on the resulting properties of films cured by this thermal treatment.

Measurements

Dynamic mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-IIC (Toyo Measuring Instruments Co.). The temperature range was −100 to 200°C. The frequency used was 11 Hz. Samples were heated at a rate of 1–2°C/min under nitrogen.

DSC measurements were carried out on a Perkin–Elmer Model DSC II. Scanning speed used was 20°C/min. Rubbery phase glass transition studies were conducted by scanning a temperature range of −150 to 50°C. Cyclohexane, water, and benzoic acid were used as calibration standards in this work. RF resin cure studies were conducted by scanning a temperature range of 0 to 300°C. Benzoic acid, iridium, and tin were used as the calibration standards for this part of the study.

RESULTS

In order to study the effects of latex/resin ratio, thermal history, and ammonia on the material properties of RFL, we have examined five different sets of RFL films. These sets are: 1) *Series AA*, as cast RFL films prepared with ammonia, 2) *Series AP*, ammonia-containing RFL films pressed at 175°C, 3) *Series AO*, ammonia-containing RFL films cured in a forced air oven at 220°C, 4) *Series NA*, as cast RFL films prepared without ammonia, and 5) *Series NO*, RFL films prepared without ammonia and cured in a forced air oven at 220°C. The latex/resin ratio of the RFL samples was varied from 2/1 to 20/1 by weight within each series. To identify samples, the following shorthand notation will be used throughout this report. Each sample will be designated by the letter combination for its series (AA, AP, AO, NA, or NO) and a number from 2 to 20 to denote the parts of latex to one part of resin by weight. So AA5 is an as cast RFL prepared with ammonia and having a 5/1 latex/resin ratio.

In Figure 1, the complex moduli (E*) spectra as a function of temperature are recorded for all of the series AO films studied. This figure is representative of the influence that latex/resin ratio has on the

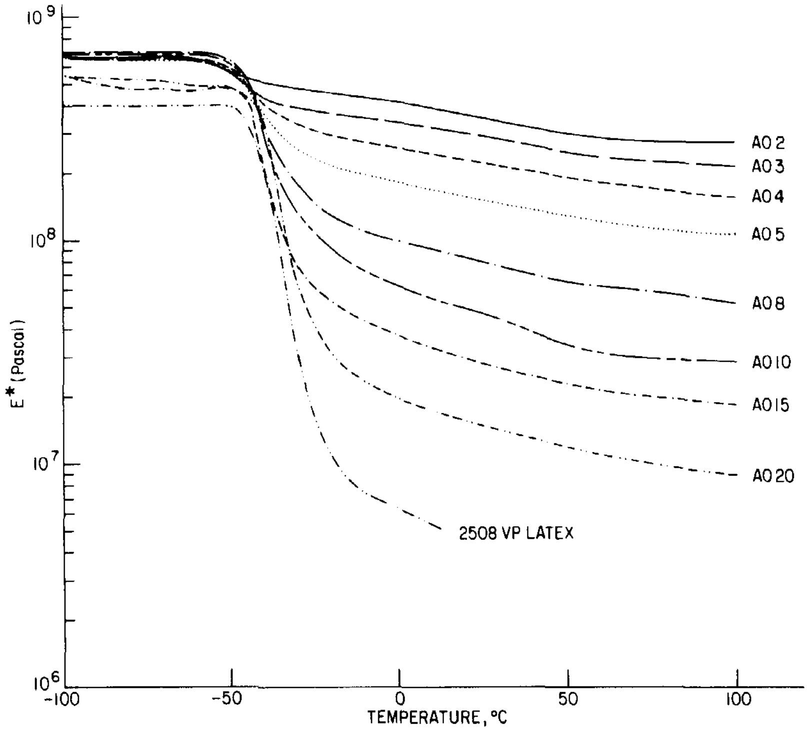

FIGURE 1 Complex modulus as a function of temperature for Series AO RFL films.

complex moduli of all the RFL series we examined. For the sake of comparison, the complex moduli as a function of temperature for the poly(butadiene-styrene-vinyl pyridine) terpolymer used as the latex component for each of the series is also included in Figure 1. For the starting latex, E^* undergoes a large decrease which begins when the test temperature is just above −50°C. This modulus drop corresponds to the glass-to-rubber relaxation in the latex terpolymer. In each of the five series of RFL films we examined, a similar drop in E^* occurs when the test temperature exceeds −50°C as shown in Figure 1 for the AO series. The extent of the E^* decrease within each series is very clearly dictated by the latex/resin ratio. As one would expect, the higher the ratio of latex to resin in a given series, the more closely the E^* behavior of that film approaches the E^* behavior of the terpolymer itself.

Figure 1 also shows a significant difference in the behavior of E^* as

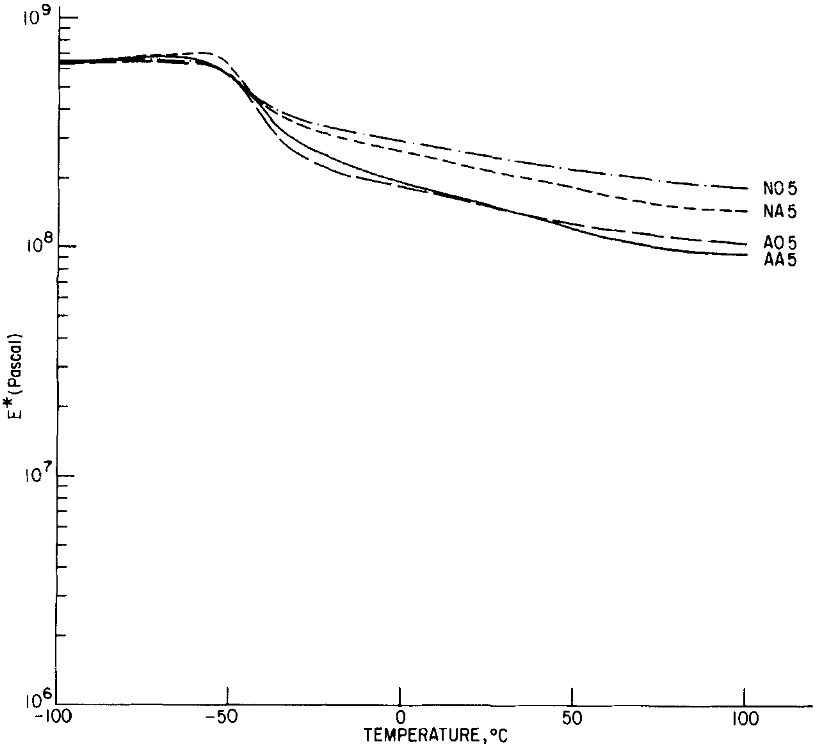

FIGURE 2 Comparison of E^* spectra for RFL films having a 5/1 latex/resin ratio.

a function of latex/resin ratio at temperatures below −50°C. By design, however, the Rheovibron is less operator sensitive and provides more reliable modulus data for leathery and rubbery materials than it does for glassy materials or materials below Tg. Therefore, due to the unclear trends in the *E** data in the sub-Tg region and the known instrumental limitations under these conditions, it would be unwise to infer much at all from the behavior of *E** below −50°C.

While Figure 1 does display, in a representative way, the influence of the latex/resin ratio on RFL moduli, it does not demonstrate the effects which thermal history and either the inclusion or exclusion of ammonia from the RFL can have on *E** results. These are displayed, however, in Figures 2 and 3. In Figure 2, *E**is plotted as a function of temperature for four series of RFL films, all having a 5/1 latex/resin ratio. The two conclusions that can be drawn from the comparison in

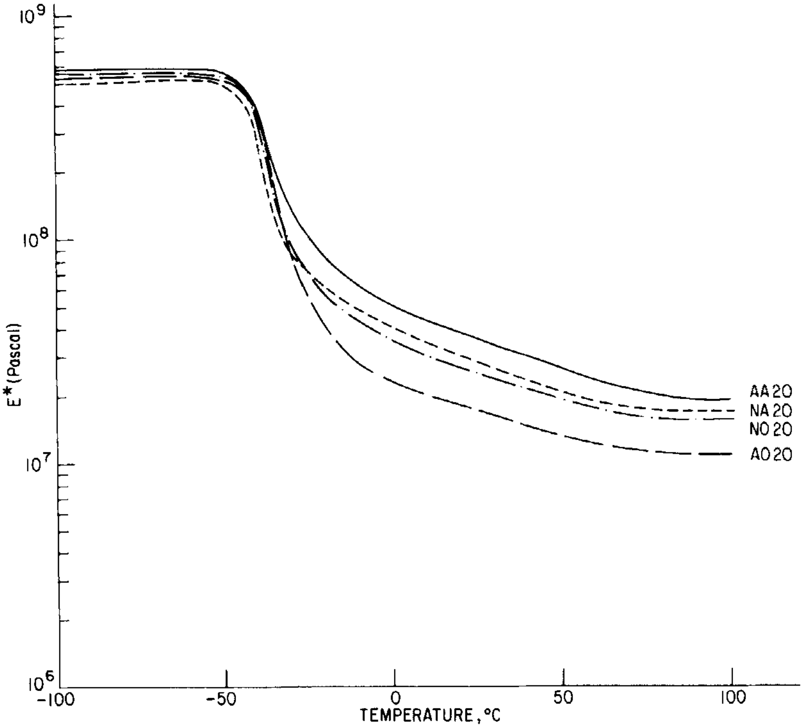

FIGURE 3 Comparison of *E** spectra for RFL films having a 20/1 latex/resin ratio.

this figure are 1) that ammonia-containing films have lower E^* values above the latex-phase Tg than do those prepared without ammonia, and 2) oven curing of the RF resin phase appears to increase the E^* values above $-50^\circ C$. When we examine the comparison of these same four series of samples but now at a 20/1 latex/resin ratio in Figure 3, the conclusions are different. In this case, the RFL films prepared without ammonia show virtually no effect from thermal treatment. But the RFL samples prepared with ammonia show a significant difference between the as cast and oven cured samples. A surprising *drop* in complex modulus accompanies oven curing of the ammonia-containing RFL. Perhaps even more surprising is the fact that at a 20/1 latex/resin ratio, the as cast film prepared with ammonia has a higher modulus than either of the two films prepared without ammonia. This is contrary to the behavior one would expect based on the conclusions drawn from the comparison of 5/1 latex/resin ratio RFL films in Figure 2. But these surprising results can be understood in light of the chemistry and theoretical models to be discussed shortly.

A typical plot of loss tangent (tan δ) as a function of temperature for these RFL films is displayed in Figure 4. Two relaxation regions are present. A low temperature relaxation is centered between -30

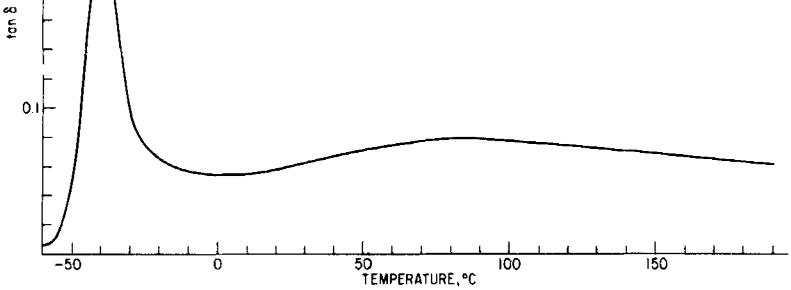

FIGURE 4 Tan δ as a function of temperature for sample AA5 displaying the α-relaxation at $-40^\circ C$ and the α′-relaxation centered about 85°C.

and −50°C which we have labelled the α-relaxation. A higher temperature relaxation is centered around 80 and 90°C, but is very broad and extends from 10 to 20°C to in excess of 150°C. We have labelled this the α′-relaxation. The α-relaxation peak decreases both in magnitude and in temperature as the latex/resin ratio is lowered. It obviously arises from molecular motion in the poly(butadiene-styrene-vinyl pyridine) terpolymer phase. In view of the fact that this terpolymer's glass transition occurs around −30°C, we have attributed the RFL α-relaxation to micro-Brownian segmental motion accompanying the glass transition of the terpolymer phase.

The α′-relaxation is more complex. It decreases in magnitude as the latex/resin ratio decreases, which suggests that it, too, arises from

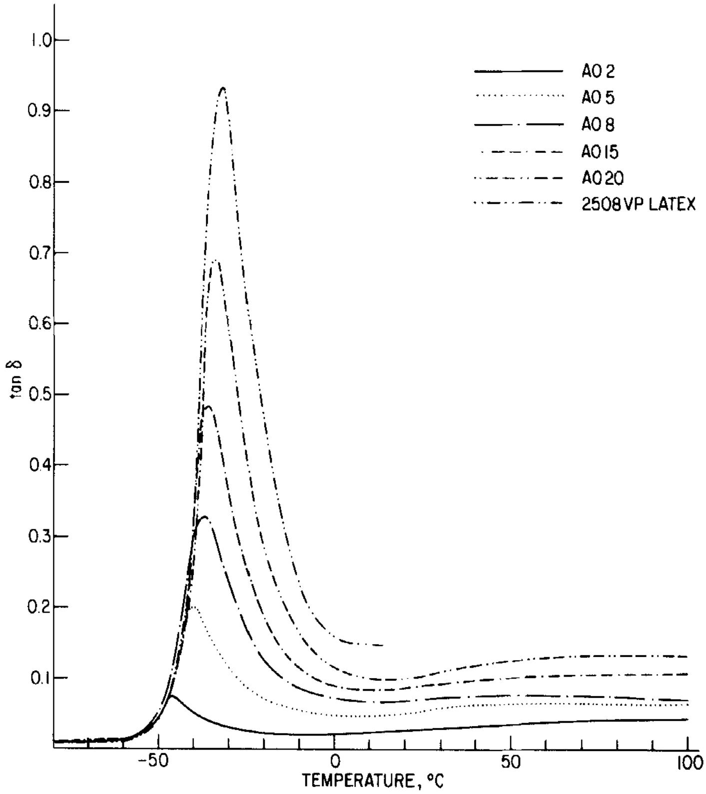

FIGURE 5 Tan δ as a function of temperature for Series AO RFL films.

molecular motions in the terpolymer phase. But this relaxation is very broad and occurs over the temperature range where one might expect to see molecular motions arising from the RF resin phase. This α'-relaxation is very likely composite in origin. Perhaps it involves cooperative motions of molecules above Tg in the rubbery terpolymer phase with motions of resin phase molecules below or near the resin phase Tg.

As mentioned above, the α-relaxation decreases both in magnitude and temperature with decreasing latex/resin ratio. This behavior is displayed in Figure 5 for the AO series films. For comparison the tan δ response of the poly(butadiene-styrene-vinyl pyridine) terpolymer is included in the figure. The decrease in α-relaxation magnitude with decreasing latex/resin ratio is easily understood. But not so easily understood is why T_α decreases as latex/resin ratio decreases. One might expect that if increasing RF thermoset would do anything, it would restrict the motion of terpolymer phase molecules and thus cause an increase in T_α as the resin phase increased in relative volume fraction. Dickie[5,6] has demonstrated, however, that when rubbery inclusions are

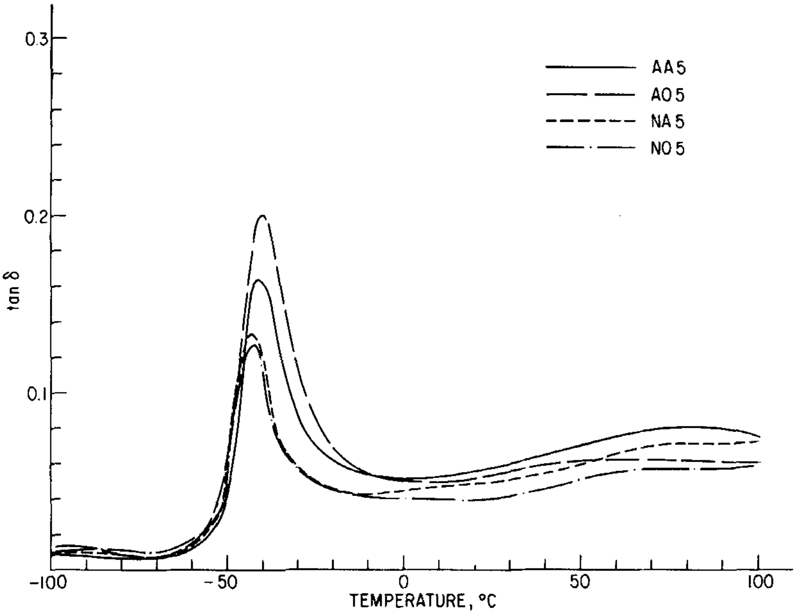

FIGURE 6 Comparison of tan δ spectra for RFL films having a 5/1 latex/resin ratio.

present in a continuous, glassy matrix, the rubbery phase Tg can behave exactly like the α-relaxation we've seen in the RFL films. This will be discussed further in the theory section of this report.

A comparison of tan δ results among the different RFL series we studied again highlights the impact which changes in thermal history and ammonia content can have on the properties of these materials. In Figure 6, tan δ results for four different series of RFL films, each having 5/1 latex/resin ratios, are compared. There is a significant difference in the magnitude of the α peak between those samples prepared with ammonia and those prepared without it. But for the RFL samples prepared without ammonia, thermal history has almost no effect on the α peak magnitude. The RFL films prepared with ammonia, though, show a significant impact of thermal treatment on the magnitude of the α-relaxation peak. For the α′-relaxation, thermal treatment reduces the size of the relaxation peak for both the ammonia-containing and the ammonia-free samples.

For RFL films having a 20/1 latex/resin ratio, the trend in tan δ behavior differs somewhat from the behavior displayed by the 5/1

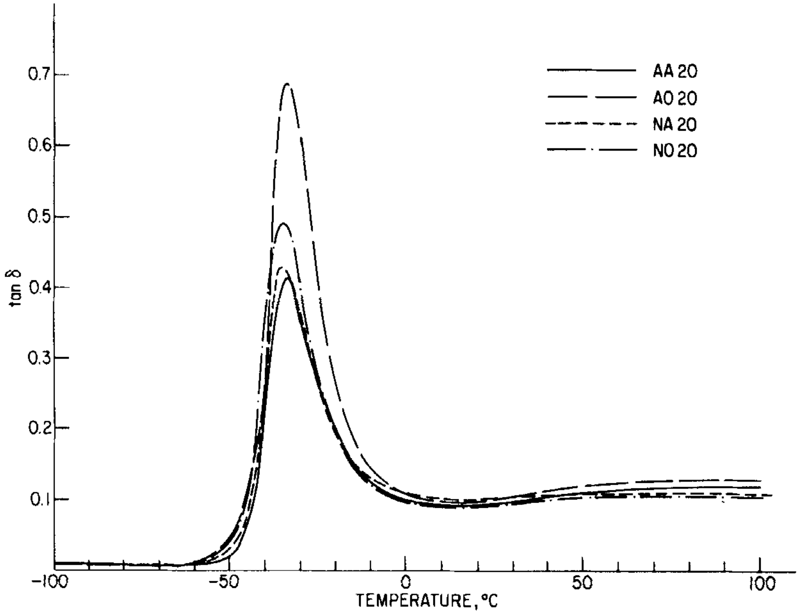

FIGURE 7 Comparison of tan δ spectra for RFL films having a 20/1 latex/resin ratio.

materials. This is illustrated in Figure 7. At this latex/resin ratio, thermal history has a noticeable impact on the α-relaxation peak magnitude of both types of samples. However, the difference in peak magnitude is much greater between as cast and oven-treated samples of the RFL prepared with ammonia than it is for the films prepared without ammonia. In the region of the α′-relaxation, the differences are so slight among the four samples that little can be discussed from the comparison.

DSC experiments have also been conducted with these RFL films. Figure 8a shows the initial DSC scan over the temperature range −120°C to 175°C for sample AA3. The glass transition of the latex terpolymer is readily detected at −51°C. Centered at 74°C, however, is an apparent broad endotherm. A second scan of this sample is shown in 8b. Here it is seen that on the second heat the endotherm is gone. Figure 8c shows the initital DSC scan for sample AO3. As with AA3, the glass transition of the latex terpolymer is readily seen at −51°C for this oven-cured counter-part. But for AO3, no endotherm exists at 74°C in the initial scan. The only difference in sample preparation between AA3 and AO3 is the fact that AO3 was oven cured at 220°C

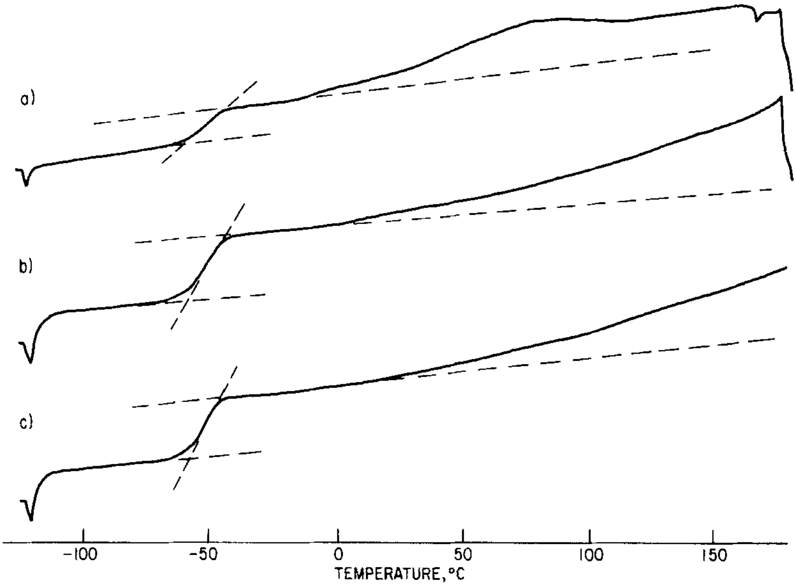

FIGURE 8 DSC scans of RFL samples run at 20°C/minute a) initial scan of sample AA3 b) second scan of sample AA3 c) initial scan of sample AO3.

for 1.5 minutes before it was examined in the DSC. The apparent endotherm at 74°C seen in the as cast sample is obviously related to thermally induced resin cure, but the relationship is not as simple as it might at first appear.

To examine the effects of thermal history on resin cure, DSC experiments were conducted on samples of the RF thermoset alone. The RF samples were prepared using the recipe described in the experimental section, but leaving out the 2508 x 25 latex. These samples were cast on a Teflon® surface at 50°C until solid, then dried overnight in a vacuum oven also at 50°C. The initial DSC scan of one such sample is shown in Figure 9a. The RF thermoset displays a glass transition at 88°C, followed by an endotherm with an onset temperature of 105°C (20°C/minute scanning rate). A study of the cure of phenol-formaldehyde resol systems by DSC, conducted by Chow and Steiner[7], concluded that the base-catalyzed phenol-formaldehyde network-forming reaction is endothermic. Thus the endotherm in 9a could be due either to further resorcinol-formaldehyde reaction or the the heat of vaporization of

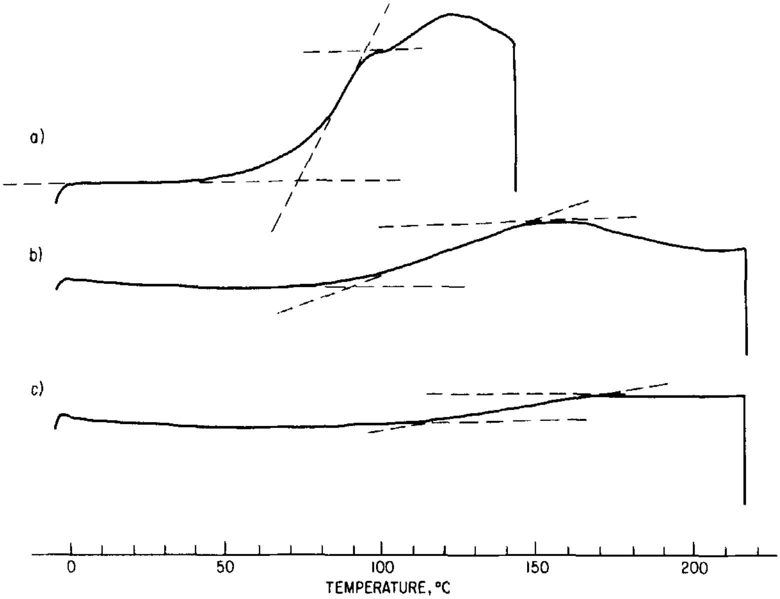

FIGURE 9 DSC scans of RF resin dried at 50°C. a) initial scan from 0° to 147°C. b) second scan of same sample taken up to 220°C. c) third scan of same sample again taken up to 220°C. Scans recorded at 20°C/minute.

residual water. Whatever its cause, the endotherm "peaks" at 125°C and the onset of an apparent exotherm occurs. The "exotherm" is just an artifact of the DSC experiment resulting from the loss of sample weight. The temperature range covered in this initial scan was 0 to 147°C. As soon at 147°C was reached, the sample was quenched immediately to 0° again. Once thermal equilibrium was restored, a second DSC scan was recorded. This scan is shown in 9b. In the second scan the temperature range studied was 0 to 220°C. In 9b it is seen that the Tg of the RF thermoset is shifted to 127°C and broadened significantly. The apparent exotherm beginning at 170°C is, like the "exotherm" observed in the first scan, caused by sample weight loss which takes place on heating. The weight loss is probably caused by the water given up as the resorcinol-formaldehyde condensation reaction is driven to completion.

A third DSC scan of the RF thermoset is shown in 9c. This scan displays the additional shift and broadening of the RF thermoset Tg caused by the thermal history. Such behavior is Ftypical for thermosets.

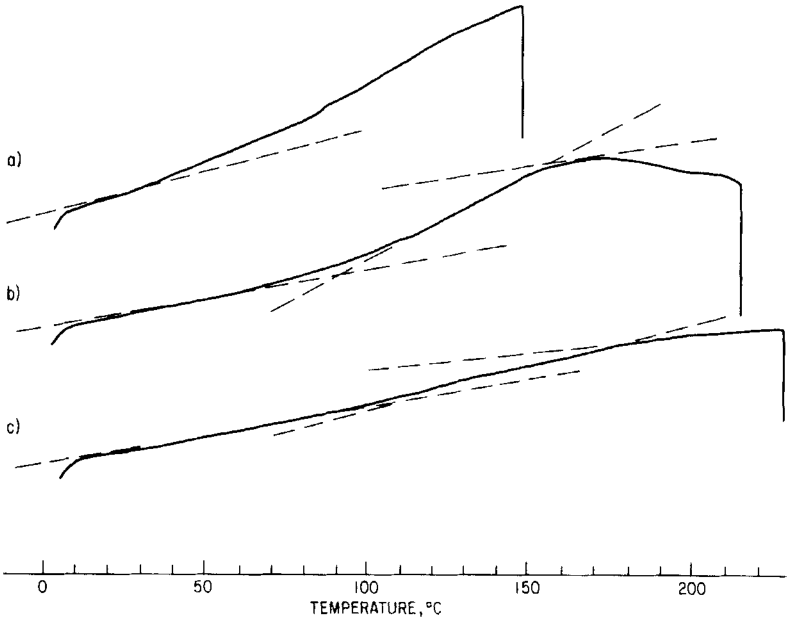

FIGURE 10 DSC scans of sample AA3 recorded at 20°C/ minute a) initial scan from 0° to 147°C. b) second scan from 0° to 220°C. c) third scan, again from 0° to 220°C.

Since the glass transition temperature of a polymer is influenced by molecular weight and crosslink density, the Tg of the thermoset increases and broadens as the extent of reaction increases. However, when the Tg of the thermoset begins to approach the temperature at which the cure reaction is occurring, the diffusion of reactants toward each other is restricted and the crosslinking reaction is slowed greatly. In such a case, the Tg of the resulting thermoset is dictated by the temperature at which the network-forming reaction occurs. However, when an incompletely cured thermoset is exposed to a higher temperature than it has ever previously experienced, additional reaction will occur until either the extent of network formation is complete or the Tg of the thermoset again approaches the temperature to which the sample is exposed. The shift of the RF thermoset Tg, demonstrated as a function of exposure temperature in Figure 9, emphasizes the importance which RFL cure temperature has in regard to ultimate RFL properties. The tremendous broadening which occurs in the Tg

TABLE I
Relaxation temperatures for RFL films determined by DSC[a] and Rheovibroa[b] experiments

Sample	Tg °C	T_α °C	Sample	Tg °C	T_α °C
2508 VP Latex	-50	-32			
AA2	-52	-43	AO2	-52	-47
AA3	-51	—	AO3	-50	-45
AA4	-51	-40	AO4	-51	-42
AA5	-50	-40	AO5	-50	-40
AA6	-51	—	AO6	-50	-39
AA8	-49	-40	AO8	-49	-37
AA10	-49	-38	AO10	-49	—
AA12	-49	-35	AO12	-48	—
AA15	-49	-33	AO15	-49	-36
AA20	-48	-33	AO20	-49	-34
NA2	—	-45	NO2	-54	—
NA3	-53	-45	NO3	-53	-45
NA4	-52	-44	NO4	-50	—
NA5	-52	-42	NO5	-51	-44
NA6	-51	-42	NO6	-51	-42
NA8	-50	-41	NO8	-52	-40
NA10	-48	-39	NO10	-50	-40
NA12	-50	-38	NO12	-49	—
NA15	-49	-36	NO15	-50	-36
NA20	-48	-35	NO20	-49	-35

[a] 20°C/min. scan rate
[b] 11 Hz. frequency

of the RF thermoset with increasing extent of reaction explains why a separate resin phase Tg is so difficult to observe in the RFL samples shown in 8b & c. The apparent endotherm observed in 8a, however, can now be understood to arise from a resin phase glass transition, accompanied by further RF condensation, water vaporization, and weight loss. This is further demonstrated in Figure 10 where a film of AA3 is subjected to the same series of DSC thermal treatments as experienced by the RF thermoset in Figure 9.

The poly(butadiene-styrene-vinyl pyridine) terpolymer phase glass transition temperatures determined by DSC for each of the RFL films studied are compiled in Table I. It is apparent that neither thermal history nor ammonia content have much impact on the DSC-evaluated, terpolymer phase glass transition temperatures. The latex/resin ratio, however, does appear to have a slight effect on the terpolymer phase Tg, causing a shift over a 4–5° range as the latex/resin ratio varies from 2/1 up to 20/1. For comparison the α-relaxation temperatures determined from the tan δ *vs.* temperature spectra of the RFL films are also included in the table. Here it is seen that while thermal history and ammonia content have a slight effect on T_α, the latex/resin ratio has a very significant effect. As latex/resin ratio is varied from 2/1 up to 20/1, T_α can vary as much as 13°C.

THEORY

The problem of predicting the elastic properties of multiphase polymers from the properties of the constituent phases has attracted the interest of theorists for many years. No theory now exists which can be universally applied to this problem. But a number of theories have been developed which work well in specific cases. In general, it is the morphology of a heterogeneous polymer-polymer composite that dictates which theory applies. One such theory, the Kerner theory[8], was developed for the case of a continuous matrix with spherical inclusions. Studies by Sperling and Friedman[9] and Davis *et al.*[10] have demonstrated that this equation works very well for sequential and latex interpenetrating networks (IPN) under the proper conditions. The Kerner equation for shear modulus is

$$G/G_m = [(1-v)G_m + (\alpha + v)G_i]/[(1-\alpha v)G_m + \alpha(1-v)G_i]$$

where G is the shear modulus of the composite, G_m is the shear modulus of the matrix phase, G_i is the shear modulus of the included phase, v is the volume fraction of inclusions and α is the function of the Poisson ratio (ν_m) of the matrix.

$$\alpha = 2(4 - 5\nu_m)/(7 - 5\nu_m)$$

For a latex IPN, the Kerner equation provides excellent agreement between theory and experiment at high volume fractions of rubbery lates spheres in a glassy matrix. But it fails for the inverted case of glassy spheres in a rubbery matrix.[10] The failure of the Kerner equation to predict composite properties adequately when glassy spheres comprise the discrete phase results from the fact that the Kerner theory neglects the problem of particle-particle interaction. For soft spheres in a hard matrix, the neglect of particle-particle interaction is not too serious an error. But for hard spheres in a soft matrix, it becomes a serious limitation.

In 1973, Dickie started with the Kerner equation for static shear modulus and made the appropriate substitutions to develop equations for the dynamic tensile quantities E^*, E', E'', and tan δ.[6] According to Dickie

$$E^*/E_m^* = \gamma[(1 - v)E_m^* + \beta(\alpha + v)E_i^*]/[(1 + \alpha v)E_m^* + \alpha\beta(1 - v)E_i^*] \qquad (1)$$

where

$$\beta = (1 + \nu_m)/(1 + \nu_i)$$

and

$$\gamma = (1 + \nu)/(1 + \nu_m)$$

The explicit expressions for E', E'', and tan δ are contained in Dickie's paper.

In subsequent work[11,12], Dickie attempted to apply these equations to heterogeneous polymer composites. He found that in order to get the optimum fit between experimental data and the calculated curves, it was necessary to account for particle-particle interaction. He did this by substituting the quantity ψv for v in equation (1) to get

$$E^*/E_m^* = \gamma[(1 - \psi v)E_m^* + \beta(\alpha + \psi v)E_i^*]/[(1 + \alpha\psi v)E_m^* + \alpha\beta(1 - \psi v)E_i^*] \quad (2)$$

where

$$\psi = 1 + v(1 - \phi_m)/\phi_m^2$$

and ϕ_m is the maximum packing factor. Dickie suggests that $0.8 \leqq \phi_m \leqq 0.83$ for rubbery inclusions in a glassy matrix. But it should be equal to about 0.6 for hard spheres in a rubbery matrix. In the limiting case of the Kerner equation, $\phi_m = 1$. Now this packing factor, or matrix-filler interaction parameter as Dickie calls it, plays the role of increasing the effective volume of the included material. The smaller ϕ_m is, the larger the effective volume of the filler material relative to its true volume.

The Dickie equations are of interest in the study of the dynamic mechanical properties of RFL films because they predict that for heterogeneous polymer composites having a continuous glassy phase and rubbery inclusions, the relaxation peak for the rubbery phase glass transition will shift to lower temperatures as the volume fraction of glassy matrix material increases. As shown in Figure 5 and by the data compiled in Table I, the temperature of the α-relaxation peak in the RFL films does decrease as the volume fraction of RF resin relative to rubbery terpolymer is increased. In view of Dickie's work, this suggests that RFL films have a continuous RF resin phase.

In order to apply Dickie's equations to RFL films, it would be necessary to know the values of E_i^*, E_m^*, v_m, and v_i. Generally ϕ_m would be determined by fitting the calculated curves to experimental data. Now E_i^* can be determined experimentally by running a Rheovibron experiment on a film of the poly(butadiene-styrene-vinyl pyridine) terpolymer. This, of course, was done and the results are included in Figure 1. And it is commonly assumed in calculations such as these that $v = 0.35$ for a polymer below its Tg and 0.5 for a polymer above its Tg. However, because the RF thermoset by itself is a very brittle material, we were not able to measure E_m^* experimentally. Therefore, we are forced to start with an RFL composite, make assumptions, and work in reverse to evaluate the properties of the resin phase before we can use Dickie's equations to predict the properties of other RFL compositions. To carry out this back-calculation of the resin properties, we first assume that Dickie's equations can describe the dynamic mechanical behavior of RFL films. Then we must 1) assume a value of ϕ_m and 2) choose either the resin phase or the latex phase to be continuous. If the latex phase is assumed continuous, the complex modulus of the resin would be calculated from the equation:

$$E_i^* = [(1 - \psi v)E_m^{*2} - (1 + \alpha\psi v)E_m^* E^*]/[\alpha\beta(1 - \psi v)E^* - \beta(\alpha + \psi v)E_m^*]$$

which is a simple algebraic rearrangement of equation 2 with $\gamma = 1$. However, the decrease in T_α as the resin volume fraction increases suggests that it is the RF thermoset phase which is continuous. Using this assumption, the exact expression for the complex modulus of the resin phase becomes

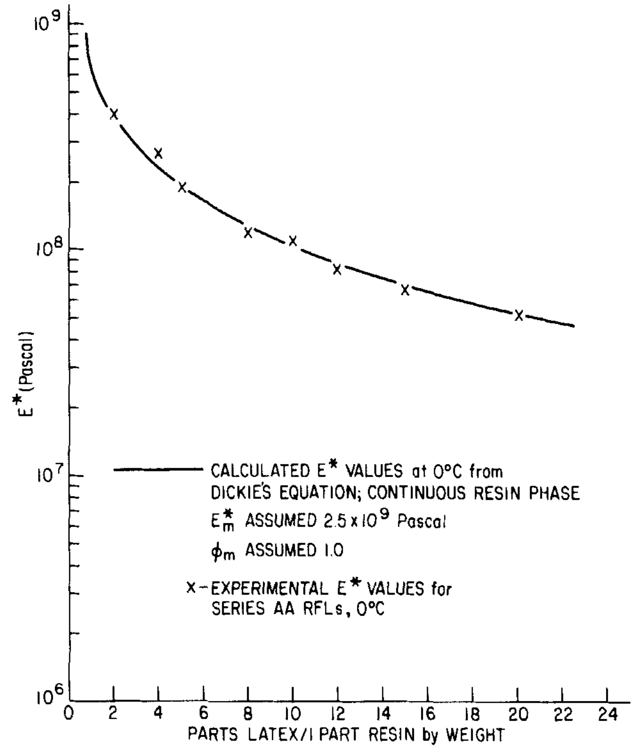

FIGURE 11 Comparison of calculated and experimental E^* data for Series AA RFL films with $\phi_m = 1$.

$$E_m^* = \{-[\beta(\alpha + \psi v)E_i^* - (1 + \alpha\psi v)E^*] \pm \{[\beta(\alpha + \psi v)E_i^* - (1 + \alpha\psi v)E^*]^2 + 4(1 - \psi v)^2\alpha\beta E_i^* E^*\}^{\frac{1}{2}}\}/2(1 - v)$$

which can be reduced to the much simpler expression

$$E_m^* = [(1 + \alpha\psi v)E^* - \beta(\alpha + \psi v)E_i^*]/(1 - \psi v) \tag{3}$$

with the assumption that E_i^*/E_m^* is negligibly small. For calculations above the glass transition temperature of the terpolymer phase, this assumption is reasonable.

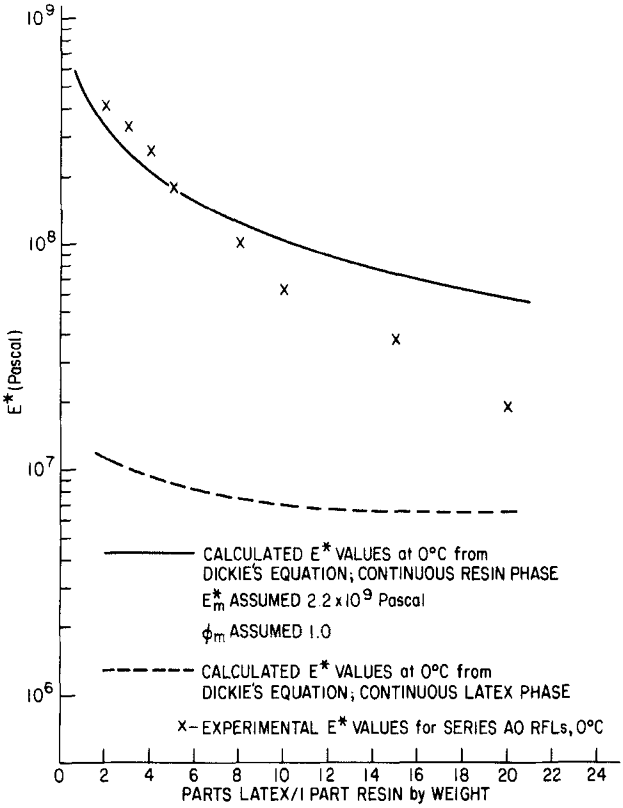

FIGURE 12 Comparison of calculated and experimental E^* data for Series AO RFL films with $\phi_m = 1$.

Since ϕ_m and E_m^* are both unknown, it is not possible to calculate a unique value of E_m^* from the experimentally determined complex modulus of a single RFL film. Instead, each assumed value of ϕ_m provides a different calculated value for E_m^*. As a first effort, then, it was decided to conduct the calculation of E_m^* using equation 3, the experimentally determined E^* for the 5/1 latex/resin ratio RFL of each series, and an assumed value for ϕ_m of 1.

Assuming $\phi_m = 1$ means there are no particle-particle interactions or packing problems between filler particles. In other words, the problem reduces to the complex tensile modulus expression of Kerner's equation. The comparison of calculated E^* curves with experimental data as a function of latex/resin ratio for the AA series and AO series RFL films are shown in Figures 11 and 12 respectively. For the ammonia-containing, as cast RFL films, the fit between experimental and cal-

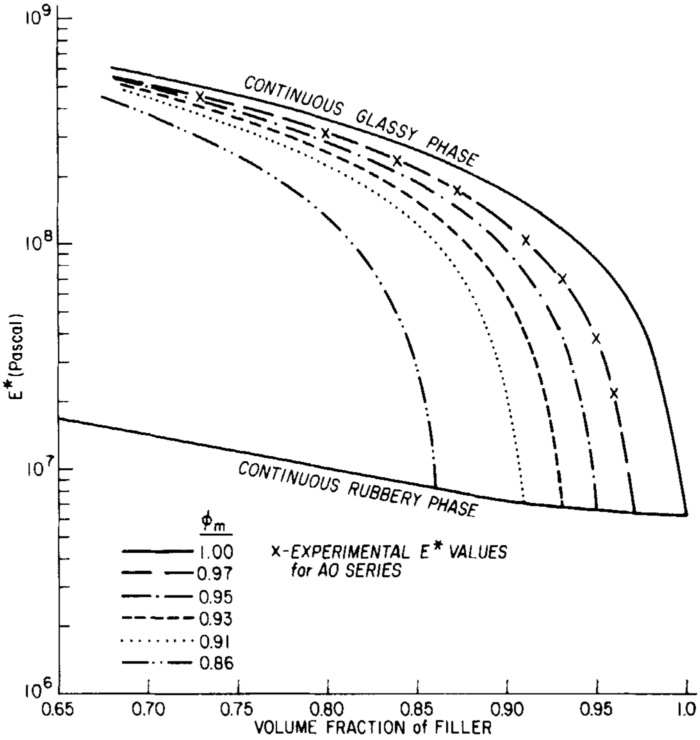

FIGURE 13 Effect of ϕ_m on complex modulus values calculated from Dickie's equation.

culated E^* values shown in Figure 11 is quite good. However, for the ammonia-containing, oven-cured RFL series, the correlation between calculated and experimental E^* values is only close at the low latex/resin ratios. There is no fit at all for higher latex/resin ratios as shown in Figure 12. And this behavior is representative of the trends seen in the AP, NA and NO series RFL films as well. For comparison, the E^* values calculated for the AO series films on the assumption of a continuous terpolymer phase and discontinuous RF resin phase morphology are also shown in Figure 12. Clearly the experimental E^* values at the higher latex/resin ratios fall between the two morphological extremes.

The importance of ϕ_m in the E^* calculations is demonstrated in Figure 13. It is seen that at the lower volume fractions of filler, ϕ_m has less influence on calculated E^* values than it has at higher volume fractions. This explains why the calculated and experimental E^* data in Figure 12 showed reasonable fit at the lower latex/resin ratios, but no fit at the higher volume fractions of terpolymer. Now in his work, Dickie assumed $0.80 \leqslant \phi_m \leqslant 0.83$ for a polymer composite having rubbery spheres in a glassy matrix. If we use ϕ_m values this small, however, we would predict that RFL films should follow the theoretical E^* curve for a continuous rubber phase morphology whenever the latex/resin ratio is above 4/1. It is clearly shown in Figure 12 that such is not the case. If we are to fit the experimental E^* values to curves predicted by Dickie's equations, the fit must occur using ϕ_m values that fall between 0.83 and 1.0. If such is accomplished then, considering the high volume fractions of latex in the RFL films studied, an argument can be made on the basis of packing geometry that the more closely ϕ_m approaches 1, the more likely the RFL morphology is that of an interpenetrating network of continuous RF resin and continuous terpolymer.

Since the E^* calculation is relatively insensitive to ϕ_m at low volume fractions of filler, and very sensitive to ϕ_m at high volume fractions (where ϕ_m approaches v), a procedure can be developed to determine a unique set of E_m^* and ϕ_m for each series of RFL films. This procedure is to assume $\phi_m = 1$ and calculate E_m^* for an RFL with a 5/1 latex/resin ratio as was done above to produce Figures 11 and 12. But instead of using this E_m^* value to generate E^* values for RFL films of other latex/resin ratios, this E_m^* value is used along with the experimental E^* value for the 20/1 latex/resin ratio film in the same series to calculate ϕ_m. A reiterative process is then used until a unique combination of

E_m^* and ϕ_m is found which fits the calculated E^* values to the experimental values at both latex/resin ratios. This E_m^*, ϕ_m combination is then used to calculate E^* for all the latex/resin ratios of interest. And a comparison of experimental and calculated values is made. The use of this procedure to compute E_m^* and ϕ_m means that our application of the Dickie equations to RFL films is reduced to nothing more than a two-parameter fit of the Dickie expression for E^* to the experimentally determined E^* values. However, while E_m^* would be expected to be temperature dependent, ϕ_m should be relatively independent of temperature. Therefore, once E_m^* and ϕ_m have been determined for one temperature, the procedure of relating calculated curves to experimental E^* values at other temperatures reduces to a single-parameter fitting

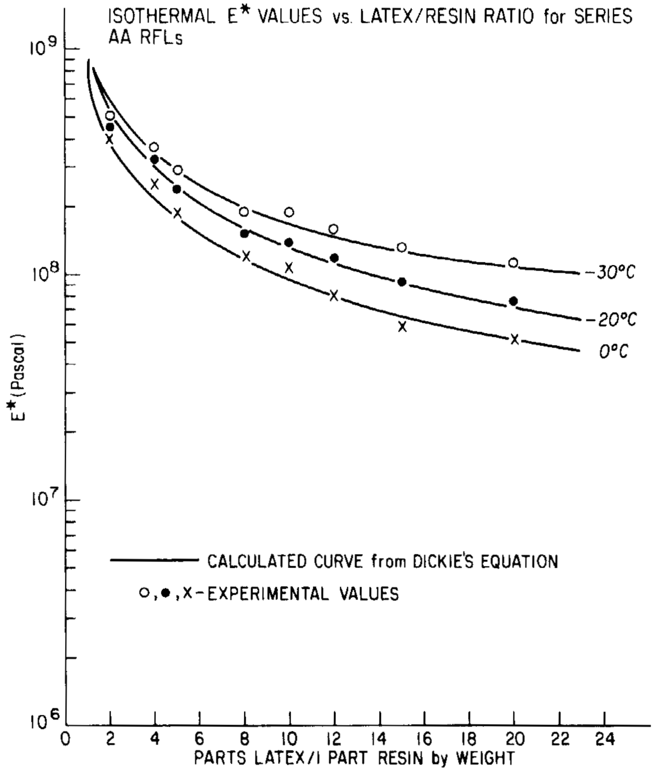

FIGURE 14 Isothermal E^* values as a function of latex/resin ratio for Series AA RFL films.

exercise. Figures 14 and 15 show that by using this procedure and allowing ϕ_m to approach 1, it is possible to fit experimental E^* values for RFL films to E^* curves predicted by Dickie's equation and assuming resin phase continuity. And the ϕ_m value determined at one test temperature (0°C) will allow a single parameter fit of the experimental and calculated data at other temperatures. This successful fit of experimental and calculated data with ϕ_m values approaching 1 very strongly suggests that the RFL samples are interpenetrating networks of continuous RF resin and continuous terpolymer with the glassy resin phase dictating the bulk properties. The E_m^* and ϕ_m values which provide the fit between experimental and calculated values for each series and each temperature are compiled in Table II.

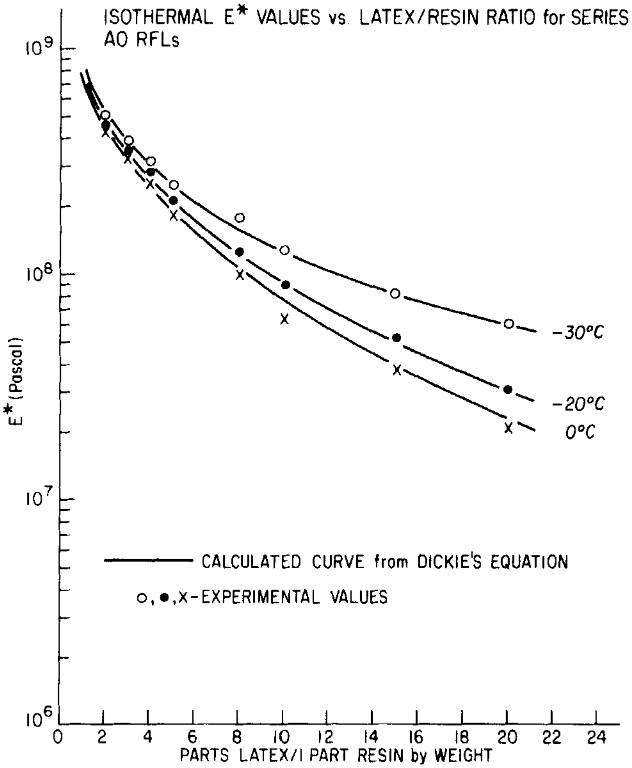

FIGURE 15 Isothermal E^* values as a function of latex/resin ratio for Series AO RFL films.

TABLE II

Effects of resin chemistry and thermal history on the E^*_m and ϕ_m values determined by curve fitting

Series	Ammonia In Recipe	Thermal History	ϕ_m	E^*_m at 0°C	E^*_m at −20°C	E^*_m at −30°C
AA	Yes	as cast @ 60°C	.995	2.4×10^9	3.2×10^9	3.4×10^9
AP	Yes	pressed 7 min. @ 175°C	.970	3.5×10^9	4.2×10^9	4.5×10^9
AO	Yes	cured 1.5 min. @ 220°C	.970	3.0×10^9	3.3×10^9	3.4×10^9
NA	No	as cast @ 60°C	.980	3.2×10^9	4.0×10^9	4.5×10^9
NO	No	cured 1.5 min. @ 220°C	.980	3.2×10^9	4.0×10^9	4.5×10^9

all E^* values in Pascal

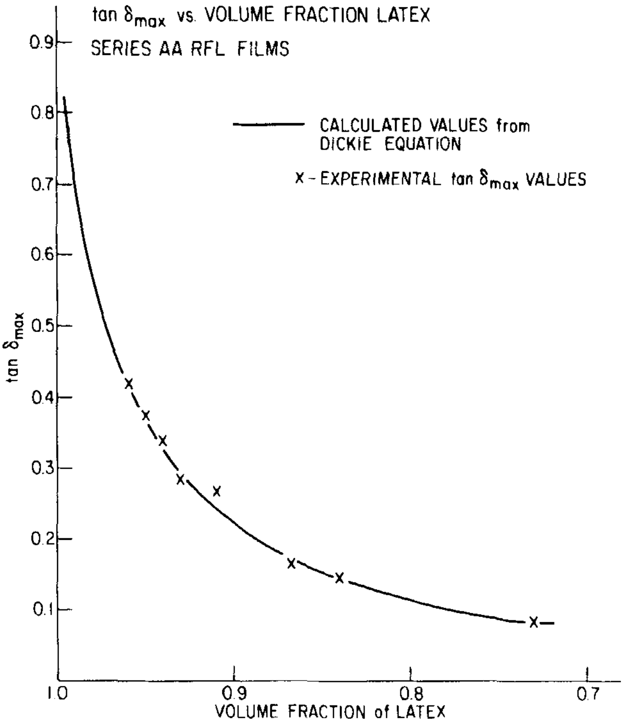

FIGURE 16 Tan δ_{max} as a function of latex volume fraction for Series AA RFL films.

While the E^* calculation is sensitive to the value of ϕ_m, especially at higher volume fractions of latex, the Dickie expression for tan δ is even more sensitive to the ϕ_m value. Therefore ϕ_m values obtained from the curve fitting of calculated and experimental E^* values have been used to calculate tan $\delta_{\max}$ as a function of latex/resin ratio for each series of RFL films studied. The comparisons of calculated and experimental results are shown in Figures 16 and 17 again for the series AA and series AO RFL samples. The excellent agreement between calculated and experimental tan $\delta_{\max}$ values using the same values for ϕ_m compiled in Table II suggests that ϕ_m must have true physical significance. The effect of ϕ_m on tan $\delta_{\max}$ suggests that the magnitude of the RFL α-relaxation peak is a sensitive measurement not of the true volume fraction of latex in the RFL, but of the effective volume fraction. This effective volume fraction of terpolymer includes free volume

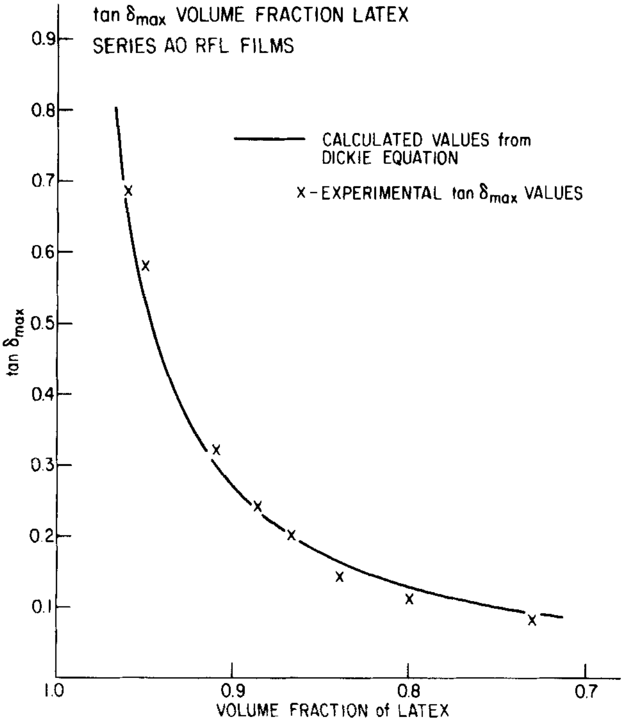

FIGURE 17 Tan $\delta_{\max}$ as a function of latex volume fraction for Series AO RFL films.

contributions from the resorcinol-formaldehyde thermoset phase. The extent of branching in the RF phase, the "tightness" of the RF network, the molecular mobility of the RF thermoset and interaction between RF and terpolymer all influence the magnitude of this free volume contribution.

DISCUSSION

Electron micrographs of various RFL systems agree that RFL adhesives are two-phase materials. However, finer points of RFL morphology have been beyond the resolving power of electron microscopy. The study reported here offers thermal and dynamic mechanical evidence for the two-phase morphology of RFL systems. But beyond that, the successful application of Dickie's equations to the RFL films studied provides the first evidence that RFL adhesives contain a continuous RF resin network and suggests that the morphology is that of an interpenetrating network of continuous RF thermoset/continuous terpolymer. The discussion to follow will highlight the DSC and dynamic mechanical evidence for two-phase morphology, critically examine the application of the Dickie equations to RFL, attempt to explain the chemical and physical significance of the E_m^* and ϕ_m values determined, and briefly explore the implications of this work to adhesion of rubber to cord.

Evidence for a two-phase morphology

DSC dynamic mechanical experiments are frequently used to differentiate between single-phase and multi-phase morphologies in systems such as block copolymers and polymer blends. For single-phase systems, these experiments reveal a single glass transition at a temperature intermediate between the glass transition temperatures of the corresponding homopolymers. For two-phase systems however, two distinct glass transitions are observed. These will either occur at the same temperatures as the Tg's of the corresponding homopolymers, or for partially compatible systems, at temperatures between the extremes of the two Tg's. An RFL is really a blend of an unsaturated latex with an *in situ* polymerized resorcinol-formaldehyde thermoset. From the DSC results displayed in Figure 8 it can be concluded that the RFL must be a two-phase system. For the as cast films, the glass transitions of both the latex phase and the resin phase are distinct in the initial DSC scan. However, as demonstrated in the DSC work with the RF thermostet alone (Figure 9), the Tg of the resin phase is almost masked by the endotherm which results from either heat of water vaporization or additional RF condensation. The additional RF condensation which takes place on thermal treatment causes resin phase molecular weight increase, additional crosslinking, and subsequently a rise in the resin phase Tg. Complete cure of the RF phase produces a resin phase Tg which is so broad that in an RFL, where the resin is "diluted" with latex, the resin phase Tg is difficult to resolve by DSC. This knowledge though, combined with the fact that a distinct latex phase Tg is present in every RFL studied and the fact that the latex phase Tg is essentially unaffected by latex/resin ratio, resin phase chemistry or RFL thermal history, all add up to support a two-phase morphology.

A simple analysis of the dynamic mechanical results provides further evidence of the two-phase morphology. The tan δ as a function of temperature for the starting terpolymer latex shows an α-relaxation at -32°C. This is identified as molecular motions accompanying the terpolymer glass transition. Every RFL studied shows an α-relaxation in approximately the same temperature range. The RFL α-relaxation can be assigned to relaxation processes occurring in the terpolymer phase because the magnitude of the α-relaxation peak within each RFL series is clearly proportional to the volume fraction of terpolymer in the RFL. Since RFL modulus drops in conjunction with this relaxation, the extent of modulus drop within each series increases as the volume fraction of terpolymer in the RFL increases, and DSC results clearly indicate a Tg in the region of the α-relaxation, it is obvious that the α-relaxation arises from molecular motions which accompany the glass-to-rubber transition in the terpolymer. In Table I though, it is clear that the temperature at which the α-relaxation occurs decreases as the volume fraction of resin in the RFL is increased. Since DSC work has shown that the resin phase Tg is much higher than that of the terpolymer, the α-relaxation would be expected to shift to higher temperatures with increasing volume fraction of resin if there were any tendency toward a single-phase morphology. The decrease in α-relaxation temperature with resin content can be explained by Dickie's analysis.[6] But even without Dickie's work there is sufficient evidence in the behavior of the α-relaxation to conclude that RFL adhesives are two-phase materials.

Of course, one normally expects to see two glass transitions in the tan δ spectra of two-phase materials. For RFL films, it is tempting to assign the α'-relaxation to the resin phase Tg. The α' peak is broad and occurs in the same temperature range as the broad resin phase Tg detected by DSC. However, the magnitude of the α' peak varies with latex/resin ratio and thermal history in a way which suggests that it arises from a composite mechanism. Part of the α'-relaxation probably does result from the resin phase Tg. Perhaps the latex contribution to the composite relaxation mechanism results from latex/resin interactions such as those proposed by Shmurak.[13] But whatever the source of α', there is sufficient evidence just in the behavior of the α-relaxation to conclude that RFL adhesives are two-phase materials. The absence of a distinct resin phase Tg in the dynamic mechanical spectra does not upset this conclusion.

The only previous report on the dynamic properties of RFL films is the work of Raumann.[4] On the basis of a single experiment, Raumann concluded that the dynamic mechanical response of an RFL film displayed no evidence to suggest a two phase morphology. However, Raumann's work did not look at the tan δ spectra at sufficiently low temperatures to detect the α-relaxation. Thus Raumann's conclusion that the RFL is a single phase material was based on incomplete dynamic mechanical data. The ability of our work to point out Raumann's mistake removes any remaining doubt about the two phase nature of RFL adhesives.

Detailed RFL morphology—critical assessment of the theoretical treatment

Because the dynamic mechanical properties of the isolated RF thermoset cannot be measured directly (it is too brittle to handle), we had to arrive at an E_m^* value for the resin phase by working backward. This procedure required two major assumptions. These are 1) that the complex modulus of an RFL film can be described by Dickie's equation and 2) that the resin phase is a continuous phase in an RFL. The first assumption was validated by the fact that we could fit the calculated curves to experimental E^* values over a broad range of latex/resin ratios. And even though this fit started as a two-parameter fit of the data, it became a single-parameter fit for all test temperatures other than that used for the reiterative calculation of ϕ_m. The ϕ_m value was shown to be a valid parameter by its ability to provide excellent fit between calculated and experimental tan $\delta_{\max}$ values. And the E_m^*

values arrived at through the curve-fitting exercise are realistic, believable values which increase with decreasing test temperature, as one would expect.

The other major assumption is the assumption that the resin phase is continuous. Of course, this choice was originally prompted by the decrease in T_α that accompanies increased volume fraction of resin in the RFL films studied. But efforts to fit experimental E^* data with curves calculated on the assumption of a continuous latex/discontinuous resin morphology were totally unsuccessful. No combination of E_m^* and ϕ_m could be found to give a fit over the whole range of latex/resin ratios. In fact, the experimental E^* values of the RFL films are so much higher than the complex modulus of the starting latex, that the only way positive E_{resin}^* values can be calculated when this morphology is assumed, is when ridiculously low values of ϕ_m are used in the calculation. Obviously the resin phase will not have a negative modulus, and it is hard to imagine a resin phase which manifests an effective volume 5–12 times its true volume. And even if we could accept such large effective volumes (low ϕ_m) it is still not possible to fit calculated curves to experimental data over the entire range of latex/resin ratios studied. Furthermore, successful application of Dickie's equations to RFL films with the assumption of a continuous latex/discontinuous resin phase morphology would require that T_α increase as the resin phase volume fraction is increased. This, of course, is opposite to the trend observed experimentally.

Before leaving this subject, it must also be recalled that Dickie's equations were derived from the original Kerner expressions. But Kerner's theory was developed for a heterogeneous composite of *spherical* inclusion in a continuous matrix. While it is easy to accept the fact that latex particles included in an RF resin matrix would be spherical, it is probably not valid to assume spherical RF resin inclusions in a continuous latex phase. Thus, even if the continuous latex/discontinuous resin morphology were correct, Dickie's equations would probably not hold up. If Dickie's equations are to be applied to RFL adhesives at all, it must be on the assumption of resin phase continuity.

Many of the assumptions made in the use of Dickie's equations center on the Poisson's ratio. It is assumed that the Poisson's ratio of the composite is equal to that of the matrix, that the elastic Poisson's ratio can be substituted for the complex Poisson's ratio (implicit in Dickie's derivation) and that for a glass $v = .35$ while for a rubber $v = .50$. The choice of $v = .50$ is a standard assumption for polymer above its Tg, as is the choice of $\upsilon = .35$ for a polymer below Tg. But Dickie has shown that values of E^* and tan δ predicted by his equations are relatively insensitive to the value of υ chosen for the matrix. Therefore these assumptions are really not very important to the application of Dickie's equations to the RFL materials.

There has been another assumption implicit in all the above work. That is the assumption that the resin phase properties should be the same regardless of latex/resin ratio, just as long as the chemistry and thermal history of the resin phase is not changed. Since the RF phase is polymerized *in situ*, this may or may not be a valid assumption. The successful fit of calculated curves to experimental data over a wide range of latex/resin ratios using a fixed value of E_m^* for each series and each temperature however, suggests that this assumption is not too bad.

In the derivation of equation 1, Dickie was forced to make some assumptions. Among these are: 1) there is perfect adhesion between matrix and inclusions, 2) the size and spatial distribution of the inclusions are random, and 3) the effective properties of the constituent phases of the composite may be replaced by their properties in bulk. Dickie addressed these assumptions in his work[6,11,12] so we will not elaborate further. But there is no reason to believe that any of these assumptions are violated in the RFL systems.

Effects of resin chemistry and thermal history of E_m^* and ϕ_m

As shown in Table II, the curve fitting procedure leads to E_m^* and ϕ_m values which vary with the chemistry of the RF thermoset and the thermal history experienced by the RFL. But are these values reasonable? And is there any significance to the way they change? We believe the answer to both questions is yes.

At the temperatures for which E_m^* has been determined, the RF thermoset is definitely below its Tg. The range of E_m^* values calculated for these resorcinol-formaldehyde thermosets is $2.4 - 4.5 \times 10^9$ Pascals. While we have no values available for the modulus of a resorcinol-formaldehyde thermoset with which to make comparisons, we do know that the tensile elastic modulus range of unfilled phenol-formaldehyde thermosets is commonly reported as $5 - 7 \times 10^9$ Pascal.[14,15] In view of the differing chemistry, the fact that the RF thermosets are polymerized *in situ* in the RFL systems, and the fact that modulus is affected by molecular weight and crosslink density, the E_m^* values determined

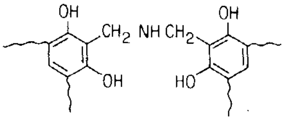

FIGURE 18 Benzyl amine linkage in RF thermoset.

through the curve-fitting procedure are certainly reasonable. Furthermore, the E_m^* values increase with decreasing temperature just as one would expect.

While the RFL films prepared with ammonia in the recipe show significant effects of thermal history on the E_m^* and ϕ_m values determined, the RFL systems prepared without ammonia show no such effect. This behavior is consistent with the long-held belief that ammonia can be incorporated into the resin network. According to the empirical observations of Wilson[16] and a reaction scheme proposed by Van Gils,[17] ammonia can react during the network-forming step to yield benzyl amine linkages such as those shown in Figure 18. But these linkages are thermally unstable and Wilson has proposed that at the elevated temperatures used for drying and heat setting RFL dipped cords, the benzyl amine linkages decompose to simple methylene bridges. This is probably not exactly correct. When phenol-formaldehyde novolacs are linked by benzyl amine groups, decomposition of the benzyl amine linkages begins around 140°C. But the exact decomposition reactions are not understood. And even at temperatures in excess of 200°C the resins still contain significant levels of nitrogen. For the purposes of this discussion, it is not necessary to know the exact chemistry. But it is important to know that benzyl amine links do form and are broken by heat. This explains why RFL films prepared with ammonia are very dependent on thermal history, while those prepared without ammonia are not.

Since the —CH_2NHCH_2— links are surely more flexible than methylene bridges, it is apparent why the as cast RFL films prepared with ammonia yield the lowest E_m^* values. When samples containing the benzyl amine groups are heated, though, the flexible —CH_2NHCH_2— links are removed and E_m^* values increase. When both heat and pressure are applied to the benzyl amine-containing RF resins, the resin phase becomes even stiffer than those RF thermosets prepared without ammonia. Perhaps pressure drives the RF condensation to an extent of reaction beyond that achieved by heat alone. Or possibly the application of pressure influences the chemistry of resin recombination following the thermal decomposition of benzyl amine links, by restricting the loss of decomposition products.

The influence of resin chemistry and thermal history on ϕ_m is very interesting. The original Kerner equation, which neglects particle-particle packing, has an assumed ϕ_m of 1. But Dickie proposed that when discrete, soft, spherical inclusion occurs in a hard matrix, ϕ_m should be between 0.80 and 0.83. To fit our calculated curves to the experimental results however, required ϕ_m values from 0.970 to 0.995. At the high volume fractions of latex rubber used in the RFL films studied, it would be impossible to have packing factors this large unless the latex particles are enjoying a considerable amount of contact with each other. What this really means is that not only is the resin phase continuous, but the latex phase is continuous as well. Thus the RFL is an interpenetrating network of RF thermoset with latex rubber. And the glassy resin phase dominates the mechanical properties. The continuity of the terpolymer latex phase allows the diffusion and subsequent reaction of vulcanizing agents in the adhesive.

The smaller ϕ_m is, the larger the effective volume of the latex phase. According to the Burakova model of RFL colloid chemical behavior[18,19] the RF resin intimately coats the surface of the latex particles in the aqueous dispersion. As water is removed, the RF condensation is driven toward network formation. This mechanism explains how so small a volume fraction of resin can provide a continuous phase in the final RFL. When flexible, benzyl amine linkages are included in the resin, the ability of the resin to conform to the surface of the latex particles is improved. As a result the final RFL probably contains less free volume. Since free volume acts to increase the effective volume of the latex phase, the less free volume present, the higher ϕ_m is. When an RFL containing benzyl amine linkages is heated, the loss of decomposition products and the breaking of network bonds causes the actual resin volume to shrink. The net effect is an increase, however, in the effective volume of the latex phase (ϕ_m decreases from .99 to .97). While this change seems minor, it has a large effect on the dynamic mechanical properties of RFL films, especially at higher latex/resin ratios. The ϕ_m of the series NA and NO RFL films prepared without ammonia, is intermediate between that of the as cast, ammonia-containing RFL and the thermally treated, ammonia-containing samples. And like the E_m^* values, ϕ_m does not change between the as cast and oven-cured samples when ammonia is removed from the RFL recipe. The intermediate ϕ_m value in these ammonia-free films probably occurs because RF thermosets prepared without ammonia are stiffer and thus less able to conform to the surfaces of latex particles. Therefore, the RFL free volume (and latex phase effective volume) is greater in as cast films prepared without ammonia. But since these resins contain no benzyl amine linkages, oven treatment does not affect their volume so ϕ_m does not change.

Implications for rubber to cord adhesion

The surface properties of multi-phase polymer systems have only recently come under study. ESCA analysis of multi-phase polymers has shown that the low surface energy component preferentially segregates to the surface.[20]. But while all systems studied to date display this qualitative behavior, the quantitative aspects can be influenced by many variables. To date, no ESCA studies on interpenetrating polymer networks have been published. But contact angle studies on polyurethane-epoxy IPN have been reported by Frisch *et al.*[21] These studies suggest that the IPN has very unusual surface properties. Thus, there is reason to believe that the IPN morphology of RFL adhesives will influence their surface properties. If such is the case, the chemical and thermal factors we have shown to influence morphology, will also impact the ability of RFL adhesives to bond rubber to cord.

In addition to surface effects however, the IPN morphology of RFL adhesives will affect the ability of vulcanizing agents to diffuse from coat rubber stocks into the RFL adhesive on a cord. Since it is generally accepted that the bonding between RFL adhesives and rubber results from the covulcanization of unsaturated carbon-carbon linkages in the latex with the $C = C$ bonds in the rubber, the ability of vulcanizing agents to diffuse into the RFL terpolymer phase is crucial. Furthermore, the extent of vulcanization which occurs in the continuous rubbery phase of the IPN morphology will certainly influence the ultimate RFL mechanical properties in service.

Knowledge of the RFL morphology is thus clearly important to understanding how these adhesives work. This background should serve as a useful starting point in learning more about the fundamental properties of these commercially important adhesives.

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APPENDIX

The central topic of this work is the two-phase, interpenetrating network morphology of RFL adhesives. Generally, evidence for morphology comes from electron microscopy work. Previous studies[1,2,3] have used transmission electron microscopy to examine RFL morphology. These studies have all found evidence that RFL adhesives are two-phase materials. Our own efforts at transmission electron microscopy on microtomed sections of RFL are represented in Figure A. The two phase morphology is evident from the contrast between dark and light areas in the sample. But phase continuity cannot be distinguished. By itself this micrograph adds nothing to our understanding of RFL morphology that was not already evident in the work of Chappuis *et al.*,[1] Fomchenkova *et al.*[2] and Dlugosz.[3] But taken together with the mechanical data presented in this paper, it highlights the additional morphological insight gained from the fitting of experimental mechanical data to theoretical expressions. For this reason it has been included here as suggested by one of the reviewers of this paper.

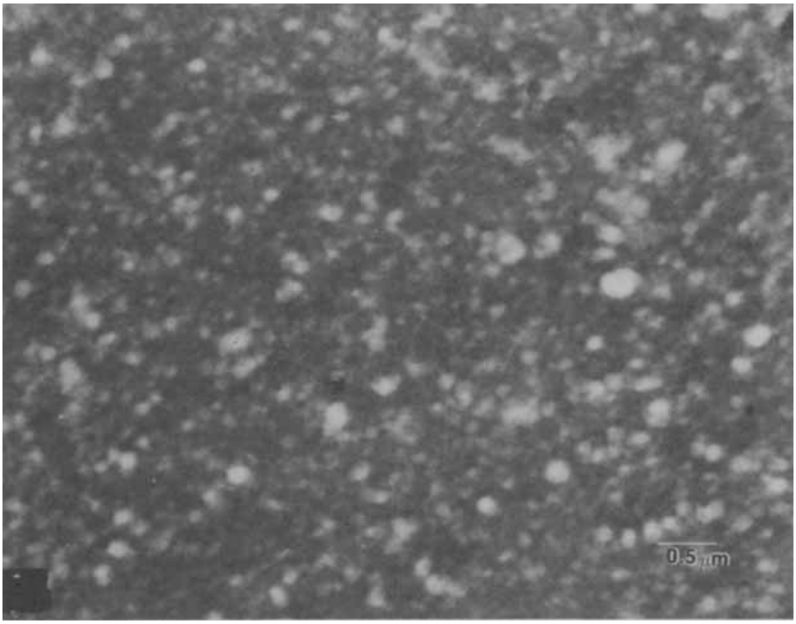

FIGURE A Transmission electron micrograph of an unstained, microtomed section of RFL film, sample AO5. Electron microscopy work was done by Ron Smith.