Dielectric Behavior of a Rubber-Toughened Epoxy Resin

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Synopsis

The dielectric behavior of amine-terminated butadiene acrylonitrile rubber/DGEBA epoxy resin blends of different formulations has been studied in the temperature range −120–160°C at 10 kHz. As indicated by the constancy of the glass transition temperatures of the two components, the degree of segmental mixing was very low or nil, irrespective of cure schedules. The intensity of the α-relaxation of the rubber was much less than that predicted by the simple series model (lower bound). This has been attributed to incomplete phase separation at gelation. Measurements carried out with a nonreactive rubber support this conclusion. Part of the rubber remains molecularly dispersed within the glassy matrix, thus contributing to the modification of the mechanical properties of epoxy resins brought about by reactive rubbers.

INTRODUCTION

Many experimental studies have been devoted to investigating mechanical properties, morphology, and toughening mechanisms of rubber-modified epoxy resins. Dielectric measurements have also been carried out in order to obtain additional data on the relaxational properties of these materials.

Hussain and McGarry[1] reported dielectric data on anhydride-cured epoxy/CTBN blends which, however, were of little help for clarifying the properties of the systems. Daly and Pethrich[2] used both dielectric and ultrasonic techniques to study relaxation phenomena in CTBN/epoxy blends over a wide temperature range. The same authors have also investigated the effects of adding various fillers to CTBN-based blends.[3] More recently, Khabibullin et al.[4] have utilized dielectric loss data to study the cure of carboxy-terminated nitrile rubber/epoxy blends filled with quartz sand.

Besides being useful for gaining better insight into the physical properties of multiphase epoxies, such data are also of practical importance, for instance in the field of shock-resistant insulation materials.

Rubbers with different terminal functionalities have also been studied and recent papers deal with fracture and other physical properties of amine-terminated rubber/epoxy blends that differ in composition and cure conditions.[5-7] The toughness of these materials is strongly influenced by the quantity and dimensions of the separated soft particles. Moreover, the reactions between resin and rubber can modify the mechanical behavior of the matrix, thus further influencing the properties of the blends.

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This paper reports the results of a study aimed at revealing possible interactions between the reactive amine rubber and the epoxy matrix.

EXPERIMENTAL

The epoxy prepolymer was a low molecular weight liquid diglycidyl ether of bisphenol-A (trade name Epon 828 by Shell Co.) with an equivalent weight of ~ 195. The amine-terminated rubber (ATBN) was a random acrylonitrile butadiene copolymer (trade name Hycar 1300X21 by B.F. Goodrich) with an acrylonitrile content of ~ 10% and an equivalent weight of ~ 1100. The nonreactive rubber was the type Hycar 1312 (B.F. Goodrich) with an acrylonitrile content of ~ 33%. The curing agent was reagent-grade piperidine.

Resin and rubber were first mixed and heated at 60°C for a short time, subsequently the hardener (5%) was added and the mixture thoroughly stirred. The resulting milky blend was then poured into a PTFE-coated tray and cured at constant temperature for 15 h. The mixtures clarified long before gelation. All formulations were postcured at 120°C for 15 h. It was impossible to prepare blends with more than 20% by wt of the nonreactive rubber since formulations of high rubber content separated before gelation and two-layer casts resulted.

Samples for dielectric measurements were machined to a thickness of 0.3/0.5 mm and were aluminium coated in vacuum. Measurements were
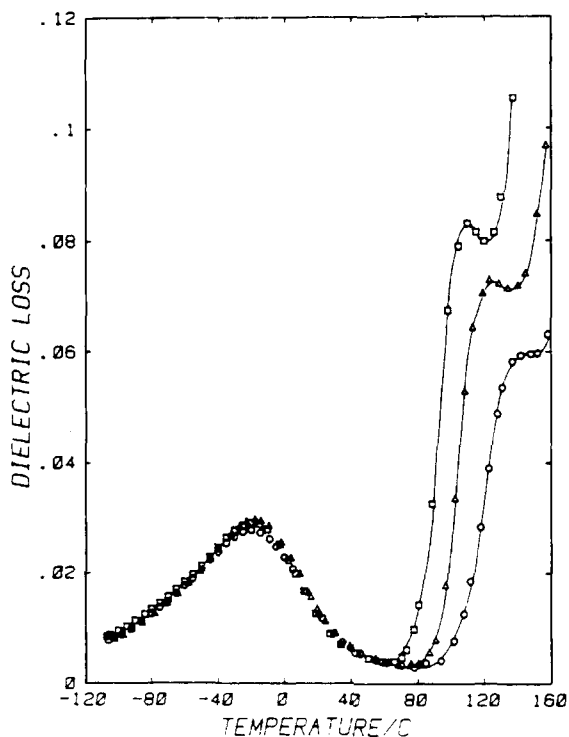

Fig. 1.   Loss factor vs temperature for neat resin cured at: (○) 60°C; (△) 120°C; (□) 160°C.
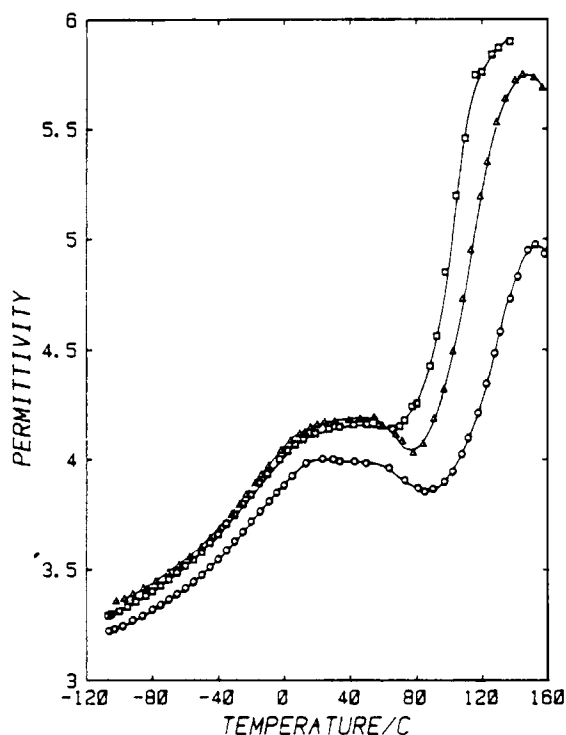
Fig. 2.   Dielectric permittivity vs temperature for neat resin cured at: (O) 60°C; (△) 120°C; (□) 160°C.

carried out with a G.R. Capacitance Assembly model 1620-A, in the temperature range −120–160°C. The heating rate was about 1°/min. Experimental results are presented at a frequency of 10 kHz.

Shear moduli were measured with a Clash-Berg torsiometer. SEM examination was made with an ISI-DS300 microscope on samples impacted at room temperature and gold coated.

RESULTS

Dielectric properties of fully cured neat resin are presented in Figures 1 and 2. In the explored temperature range, two relaxation phenomena were observed. That at high temperature (α), connected with the glass transition, appeared to be sensitive to cure conditions. The α peak progressively shifted to lower temperatures with increasing Tcure, indicating that the crosslink density was influenced by the cure temperature. Other properties, such as hardness and heat distortion temperature, were also modified.[6] The α peaks were not completely resolved due to the onset, on the high temperature side, of ionic conduction.

The low temperature peak (β) was centered at −18°C, and was not influenced by Tcure. The short-range motions that give rise to this process were therefore unaffected by the crosslink density. It has to be pointed out, however, that all formulations were given a final postcure that could have
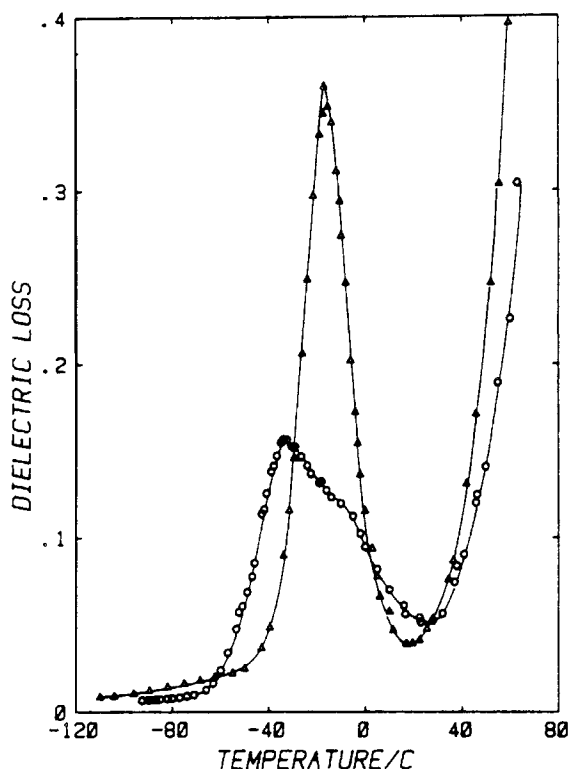
Fig. 3. Loss factor vs temperature for neat rubber. (O) amine-terminated (ATBN); (△) nonreactive.

eliminated any small difference brought about by the different cure temperatures. Also, the relaxation strength did not show any change, only the absolute values of ε' being slightly displaced.

The glass transition temperatures, as indicated by the maxima in Figure 3, were $-38°C$ and $-18°C$ for the ATBN and the nonreactive rubber, respectively. The difference reflects the diverse acrylonitrile content of the two rubbers which also influenced the height of the α peaks and the relaxation strength (Fig. 4). Slightly above room temperature, ionic conduction became predominant.

In the case of ATBN blends, the low temperature relaxation resulted from the superposition of the α peak of the rubber on the β peak of the resin (Fig. 5). Because the temperatures of the two processes were very close, the composite nature of the peak was barely noticeable. Its intensity increased on increasing the amount of rubber, although no simple additivity was found. The same trend was observed for the.dielectric permittivity (Fig. 6).

Similar results were obtained with the nonreactive Hycar (Figs. 7 and 8). The β process of the resin was completely hidden by the α process of the rubber, since both occurred at $-18°C$ and the latter was much stronger than the former.
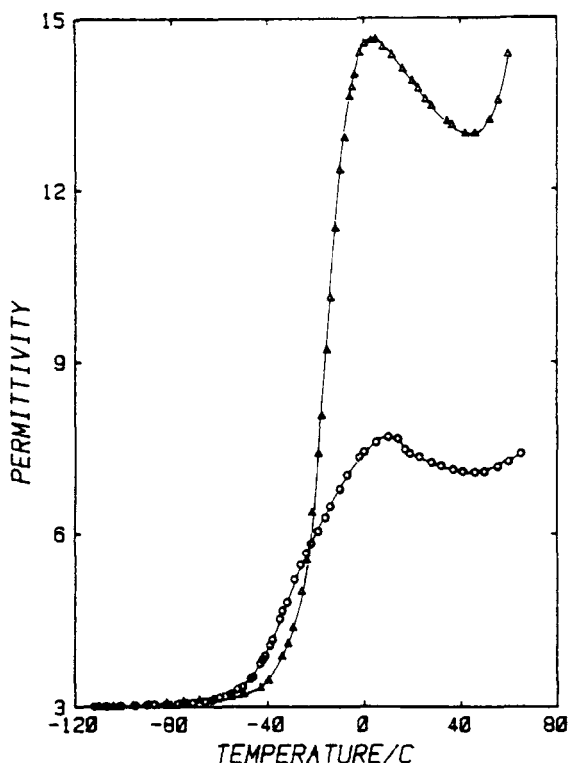
Fig. 4. Dielectric permittivity vs temperature for neat rubber. (○) amine-terminated (ATBN); (△) nonreactive.

DISCUSSION

Since the hardener used in this work was a cycloaliphatic secondary amine, the nitrogen atom could not act as a trifunctional crosslink point as it does in conventional primary amines. Upon mixing, a tertiary amine readily forms that can promote setting by catalyzing etherification reactions. Such reactions are sluggish and provide a long pot-life (at room temperature it takes many hours for gelation or vitrification to occur). The equilibrium shear modulus was used to estimate the molar mass among crosslink points (Mc = $\phi \delta RT/G$). For the neat resin, cured at 60°C, Mc was close to 0.5 kg, which assuming $\phi \sim 1$,[8,9] suggests a relatively tight network structure based on ether linkages.

Quite often high temperatures of cure are needed for developing epoxies characterized by high heat distortion temperature (HDT), yield strength, and hardness; this is not true for piperidine. Figure 1 shows that the high temperature peak, associated with Tg, moves to the left with increasing Tcure, in a way that parallels the decrease in HDT.[6] To account for this effect it was suggested[10] that some of the hardener could evaporate at high temperature (the boiling point of piperidine is 106°C). To check this point a mixture of degassed resin and piperidine was cured at 115°C for 6 hours and only a negligible weight loss (~ 1% of the hardener) was observed. The modifications
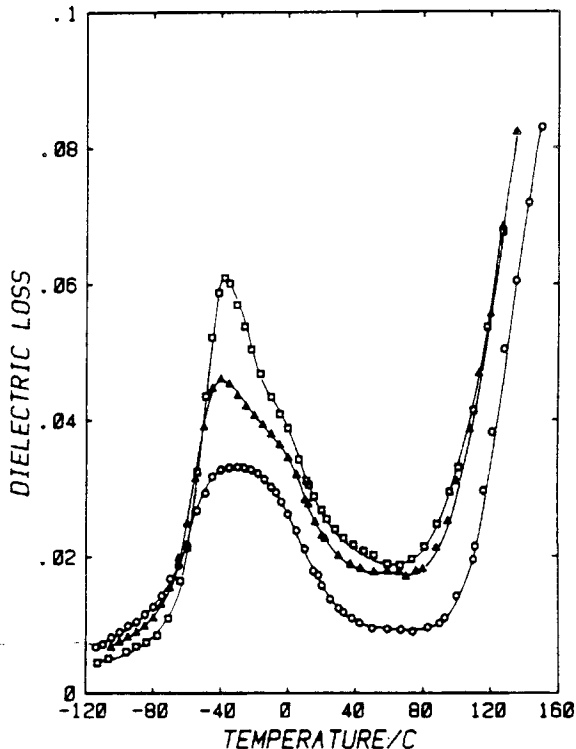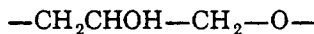
Fig. 5.   Loss factor vs temperature for blends of different ATBN content (% by wt): (○) 10%; (△) 30%; (□) 50%.

of network topology (crosslink density, concentrations of dangling ends, etc.) must therefore result from different reaction paths.

From a mechanical point of view the modifications of the network structure brought about by the temperature are very important. They can influence the plasticity of the resin, and therefore its fracture resistance. Indeed, it has been shown that the critical stress intensity factor, K_{IC}, steadily increases with increasing the temperature of cure in epoxy/piperidine formulations.[7]

The relaxation behavior in the glassy state was characterized by a fairly large β process (sometimes referred to as γ in the literature) and many studies have been devoted to identifying the nature of the kinetic units or to investigating the effects of stoichiometry and type of curing agents.[8,11-17] In summary, the relaxation has been attributed either to the hydroxyether group:

$$-CH_2CHOH-CH_2-O-$$

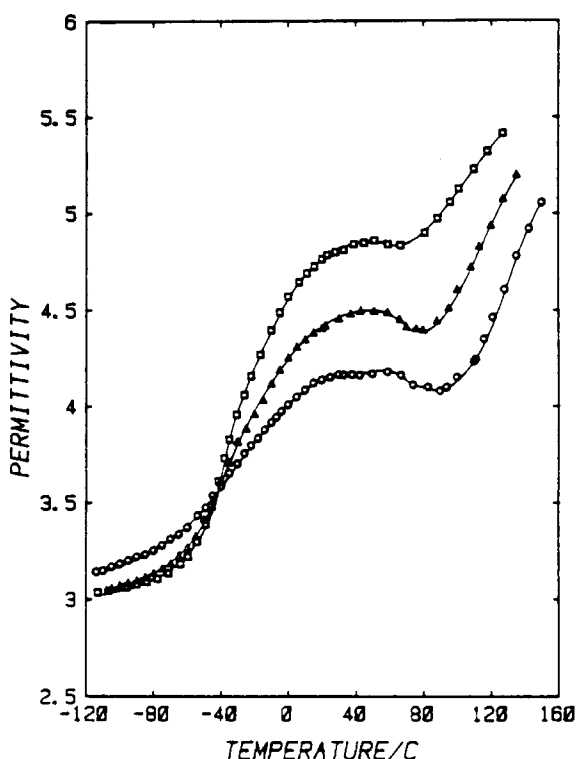or to the diphenylpropane unit:

$$-O-C_6H_4-C(CH_3)_2-C_6H_4-$$
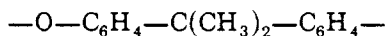
Fig. 6. Dielectric permittivity vs temperature for blends of different ATBN content (% by wt): (O) 10%; (△) 30%; (□) 50%.

Ochi et al.[17] have studied the mechanism in resins crosslinked with both primary diamines (hydroxyether linkages) and tertiary amines (ether linkages). They found that the intensity of the peak increased with increasing the conversion of the epoxide groups when setting was carried out with primary amines, since the concentration of hydroxyether units increased as crosslinking proceeded. On the contrary, in systems based on ether linkages, the intensity was independent of the extent of cure and, therefore, of crosslink density (at least above a certain level of conversion). The result that the intensity of the β relaxation in the present piperidine/DGEBA formulations was independent of cure temperature agrees with Ochi's conclusions.

When the ATBN was added to the resin, the α peak of the rubber superimposed on the β peak of the resin and it was not possible to verify whether or not the presence of rubber could modify the intensity and location on the temperature scale of the β process.

However, since the β process in the present systems was found to be fairly independent of network topology, it was assumed that the intensity of the β peak in the blends only depends on the volume fraction of the resin.

The addition of reactive rubbers has profound effects on the morphology and physical properties of epoxy resins. The solubility parameter of ATBN is close to that of the epoxy prepolymer so that a homogeneous system forms at
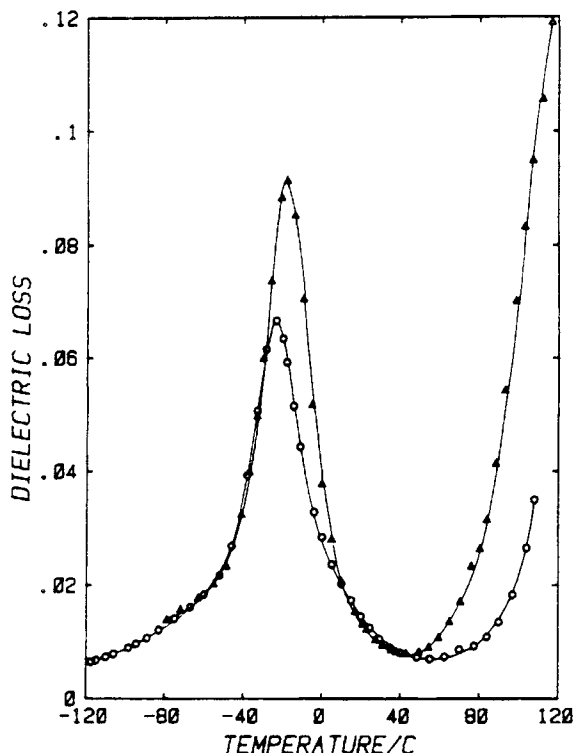
Fig. 7.   Loss factor vs temperature for Hycar 1312/Epoxy blends (% by wt): (○) 10%; (△) 20%.

sufficiently high temperature.[18] However, as setting takes place, the solubility parameters no longer match and phase separation occurs. At low rubber contents (5 to 15%), the resin constitutes the continuous phase and the rubber is dispersed in the form of spherical droplets, whose diameter strongly depends on cure temperature (Figs. 9 and 10). The two phases are not made of pure components; some epoxy dissolves into the rubber particles and some rubber remains in the crosslinked matrix. The rubber left in the matrix is expected to play a role in the plastic processes that control the toughness of modified epoxies.

The ATBN molecules carry two terminal groups, generated by reacting a CTBN rubber with N-(2-aminoethyl)piperazine,[19] so that it can react with the resin, particularly at high temperature. This allows the formation of high molecular weight copolymers within the particles with the result of increasing their tear energy. The reason for adding reactive rubbers to epoxies is that of limiting their brittleness, and soft particles characterized by high tear energy perform better;[20] indeed, nonreactive rubbers have little or no effect.

A strong indication of the presence of some epoxy resin in the soft phase is given by the fact that its total volume has been found to be greater than the volume of the added rubber.[7] On the other hand, the reactions between epoxy prepolymer and reactive rubber which occur before phase separation, particularly at high temperature, have the effect of increasing the compatibility between the two components and can lead to incomplete precipitation.
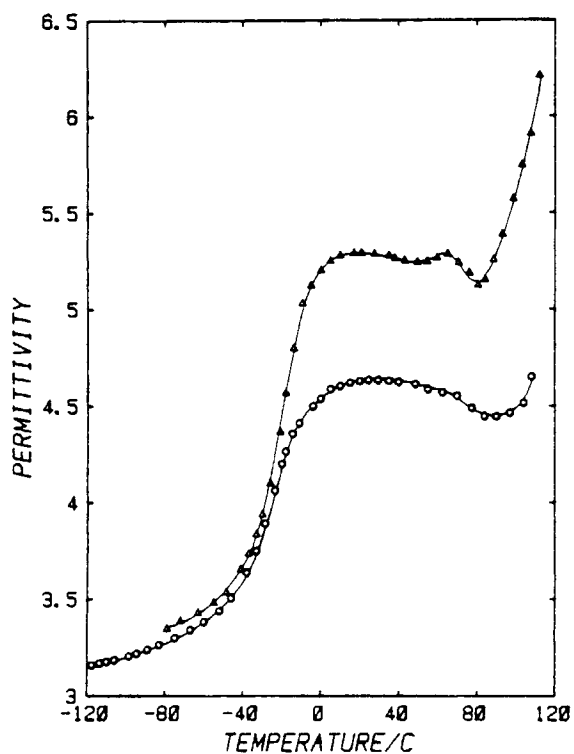
Fig. 8.   Dielectric permittivity vs temperature for Hycar 1312/Epoxy blends (% by wt): (O) 10%; (△) 20%.
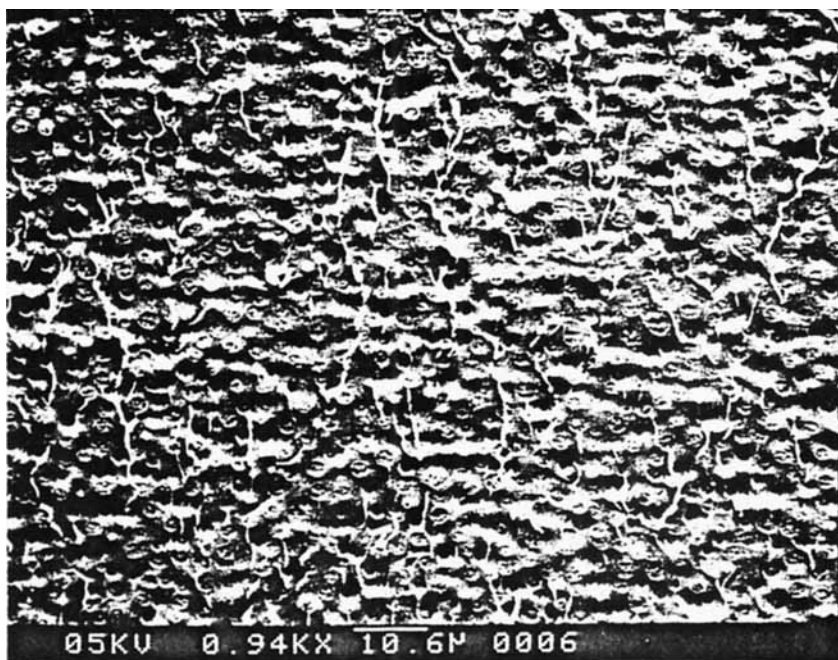

Fig. 9.   SEM micrograph of a 10% ATBN blend cured at 60°C.
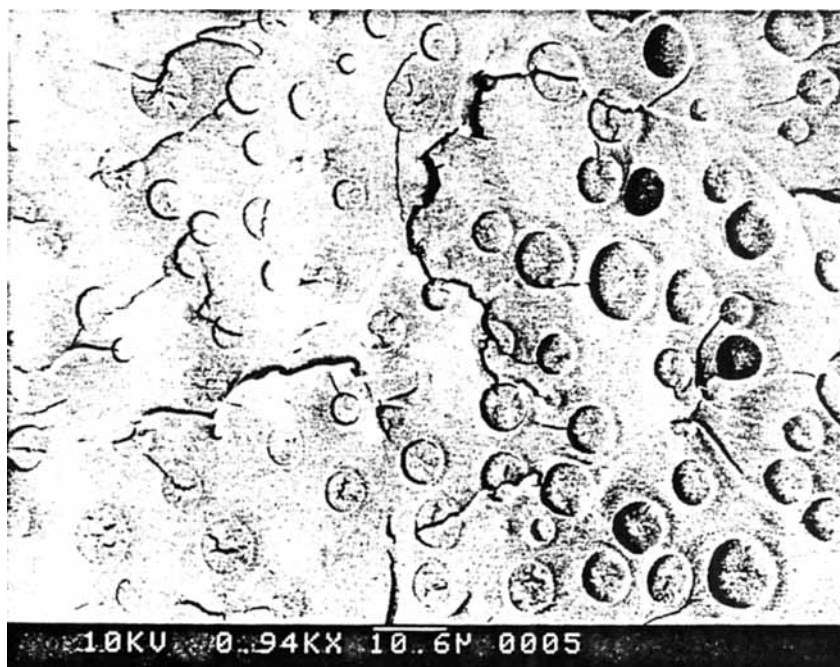
Fig. 10.   SEM micrograph of a 10% ATBN blend cured at 140°C.

Measuring the volume fraction of the segregated phase by means of image analysis of fracture surfaces was, therefore, of no help in establishing whether or not a certain amount of ATBN remained molecularly dissolved as a part of the crosslinked matrix. The study of the dynamic mechanical properties failed, too. The location of the α peak of the rubber on the temperature axis was unaffected by the cure temperature and its intensity could not be used to estimate the amount of precipitated rubber. In fact, in toughened polymers, the size of the α peak depends on the total amount of the soft phase, which is greater than the volume of the added rubber.[21] Moreover, the Q^{-1}/T curve of the pure rubber (it is liquid) was unknown.

' On the contrary, the dielectric loss factor of neat ATBN could be easily obtained and a more detailed analysis was carried out. To this end it is useful to consider the rubber/epoxy composite as a multilayer structure to which an external stimulus is applied normal or parallel to the layers. In the case of dielectric properties this corresponds to the well known series and parallel models.

It can be easily shown that these two extreme cases are analytically represented as:

$$Q = \phi_1 Q_1 + (1 - \phi_1)Q_2 \tag{1}$$

$$1/Q = \phi_1/Q_1 + (1 - \phi_1)/Q_2 \tag{2}$$

where Q is a generic physical quantity.
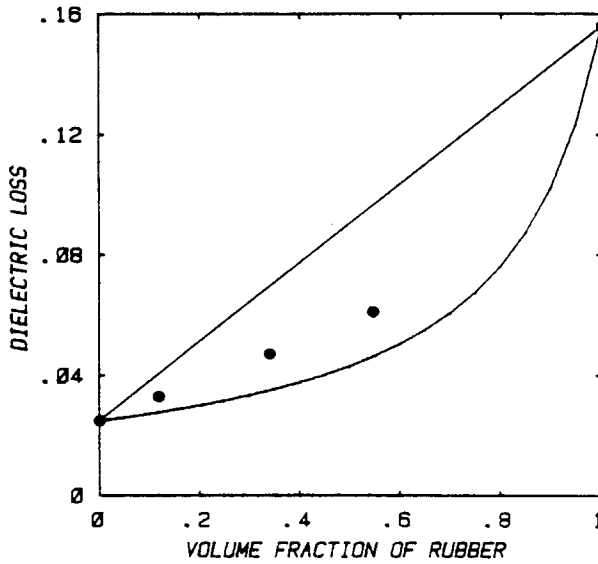
Fig. 11. Loss factor of ATBN blends vs rubber content (T = −38°C).

Equations (1) and (2) constitute the lower and upper bounds for real systems and are often obeyed at extreme volume fractions, that is, when ϕ_1 approaches 0 or 1. Intermediate compositions fall somewhere in between. Though more complex relationships have been proposed to represent dielectric data, for instance the logarithmic or the Maxwell's mixture laws,[22] the use of bounds 1 and 2 is sufficient for this discussion.
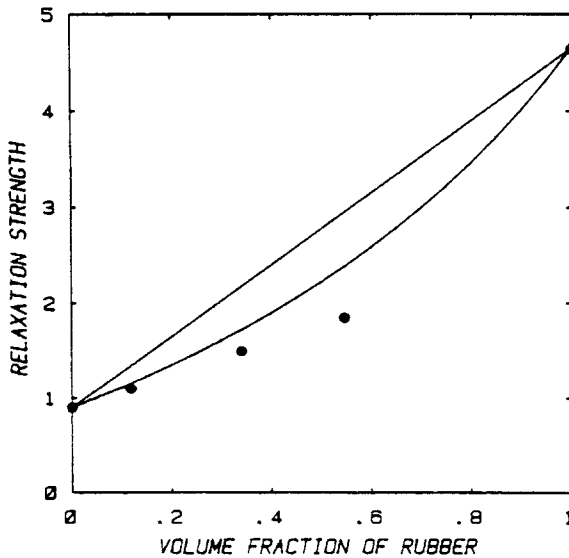

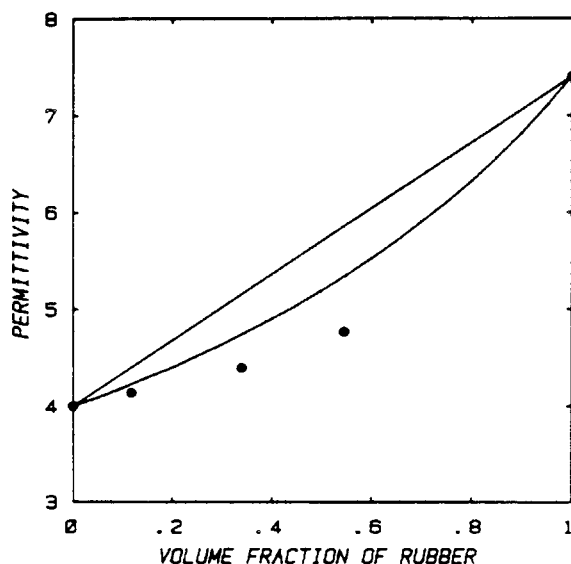Fig. 12. Relaxation strength vs rubber content for ATBN blends.

Fig. 13.   Dielectric permittivity vs rubber content for ATBN blends (T = 20°C).

Values of loss factor, taken from Figure 3 at T = −38°C, are plotted vs. rubber content in Figure 11; they lie well below the line of simple additivity. However, a single value of tan(δ), taken at a certain temperature, is likely not to represent the relaxation behavior of the system, particularly if the individual components can strongly interact. It was therefore preferred to use the relaxation strength, $\Delta\epsilon'$—the rise of ϵ' from the unrelaxed (T = −120°C) to the relaxed state (T = 50°C)—since it represents an integral quantity (Fig. 12). A similar plot in Figure 13 represents permittivity data.

All the experimental values fell below the lower bound and this, from a phenomenological point of view, can be accounted for by admitting that the amount of effective (dielectrically active) rubber is smaller than the nominal value. It is worth noting that measurements of the increase in specific heat at the glass transition of the rubber led to the same conclusion (Fig. 14). $\Delta C p$ is an intensive quantity, like specific volume, and a linear dependence was therefore expected. This is an interesting point since a linear dependence of $\Delta\epsilon'$ on ϕ_1 and can be obtained only if ϵ' is also linearly dependent on ϕ_1.

It is apparent from the experimental results that the relaxation activity of the ATBN in the α region is somehow depressed when it is embedded into the rigid matrix; two hypotheses can be made to explain this behavior. (1) The long range mobility of the rubber molecules is reduced, no matter how the rubber is distributed in the blend. (2) The molecular mobility is largely affected by being the molecules within the soft phase (rubber with rubber) or part of the more rigid matrix. Precipitated rubber should experience a minimum hindrance and be substantially indistinguishable from the pure component.

A way to distinguish between these two possibilities is to minimize the extent of copolymerization. This was achieved with the nonfunctionalized rubber that could not react with the resin. It was, in fact, argued that the
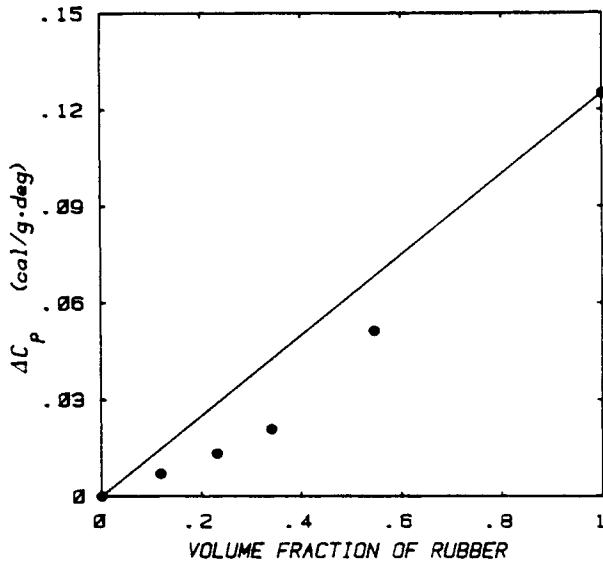
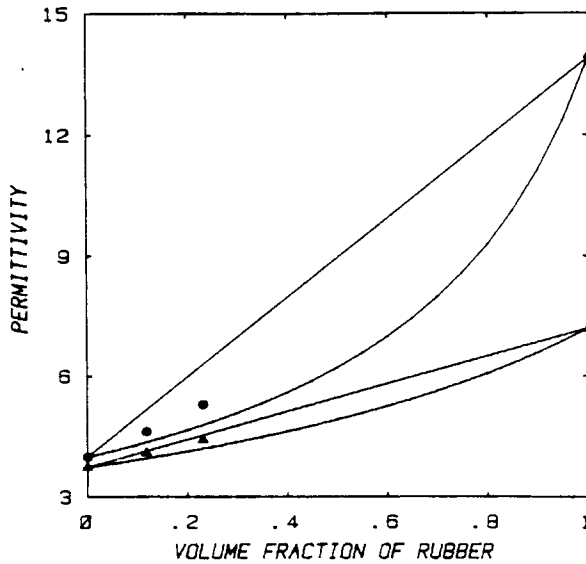Fig. 14.   Increase in specific heat at Tg vs rubber content for ATBN bends.

Fig. 15.   Dielectric permittivity of nonreactive rubber/epoxy blends vs rubber content: (▲) T = -20°C; (●) T = 20°C.

formation of copolymers would promote the compatibility between rubber and resin. As shown in Figure 15, the permittivity data of these blends fell between the bounds.

The relevant point, however, is that irrespective of which bound better represents the data, the dielectric activity was higher than it was with ATBN and this strongly supports the second hypothesis.

It has to be pointed out that the term compatible has, in the present case, a particular meaning. A popular test for compatibility is that of looking at the shift of the main transitions of the pure components. All the techniques used in this work indicated that the T_g's were independent of composition, so that resin and rubber are to be regarded as truly incompatible. What is of interest here is the degree of dispersion of the rubber. As a result of incompatibility, there is, when the system is still fluid, a tendency for the rubber to migrate and coalesce in relatively large particles in order to minimize the surface energy. It is then conceivable that only mobile molecules can be involved in the long-range movements required for coalescence. Molecules that, by copolymerization, are being incorporated into the growing network are unlikely to participate, at least massively, in phase separation. They remain molecularly dissolved into the glassy matrix, although the degree of segmental miscibility remains very low or nil. This type of rubber, somehow hidden within the matrix, is thought to be responsible for the reduction in dielectric activity in the α region. The presence of rubber in the matrix is expected to alter the network topology and, indeed, differential scanning calorimetry (DSC) measurements[6] showed that the main transition of the matrix broadens, on the low temperature side, as the ATBN content increases.

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