Rubber-modified epoxy resins: 2. Dielectric and ultrasonic relaxation studies

John Daly* **and Richard A. Pethrick**
Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, Glasgow G1 1XL, UK
(*Received* 1 *February* 1980)

Dielectric and ultrasonic relaxation measurements are reported on a series of rubber-modified epoxy resins over a temperature range from 190 to 423K. The resins were prepared by the reaction of the diglycidyl ether of bisphenol A with a chain-extender formed from carboxyl-terminated acrylonitrile–butadiene copolymer and cured with either triethylene tetramine or diethylene glycol bis-propyl amine. At low temperature, a dielectric relaxation was detected which was also active ultrasonically and can be associated with molecular motion of the acrylonitrile–butadiene chain extender. Changes in the concentration of the rubbery phase and type of curing agent used have marked effects on both the activation energy for molecular relaxation and in the breadth of the relaxation curves. Extensive studies of the dielectric properties at higher temperatures failed to reveal a resolvable relaxation associated with either of the higher temperature transitions observed using equilibrium measurements. Electrical conductivity, permittivity and acoustic velocity measurements performed as a function of temperature, however, indicate the existence of a change in slope at approximately the value of the glass transition of the epoxy phase. A further change in slope at approximately the temperature of the highest temperature transition was detected. The observed relaxation properties are compatible with the resins being phase-separated at low rubber concentrations and changing to a semicontinuous interpenetrating network structure at higher rubber concentrations.

INTRODUCTION

The pseudo-equilibrium properties of a series of rubber modified epoxy resins have been reported[1]. Three transitions were detected: the lowest temperature process, ascribed tentatively to the onset of motion in the acrylonitrile–butadiene phase; the mid-temperature process, associated with motion of the epoxy phase; and the highest temperature transition, ascribed to either motion of an acrylonitrile–butadiene–epoxy interface or chemical crosslinked regions produced during the curing process. A study of positron annihilation[2] in these resins supports the assignment of the two lower temperature transitions and indicates that the higher temperature transition is probably associated with the mixed interface. The morphology of these materials as detected by electron microscopy[1,3] was found to be composed of a dispersion of rubbery occlusions in a continuous epoxy phase. The curing agent, triethylene tetramine (TETA) appears to produce a three-dimensional network structure, whereas diethylene glycol bis-propyl amine (DGBP) generates a more regular, less crosslinked structure. In this paper, dielectric and ultrasonic relaxation measurements are presented and their interpretation in terms of molecular motion in these materials discussed.

EXPERIMENTAL

Preparation of materials

The synthesis of the rubber-modified epoxy resins has been described elsewhere[4–6]. The characteristics of the resins and their thermal histories are summarized in *Table* 1. The amount of curing agent used was determined by the epoxide value[7,8], which involves reaction of the epoxide group with a quaternary salt to form the halohydrin ion which is in turn titrated with perchloric acid.

Dielectric measurements

The real and imaginary parts of the dielectric permittivity were measured over a frequency range of 100 Hz to 10 MHz using a combination of Scheiber, Wayne Kerr (B224), General Radio (1621) and High Frequency Bridges (B602)[9]. Measurements were performed using a two-terminal cell designed for total immersion and employing quartz insulators and nitrogen flushing to exclude moisture. Additional drying agent was added to the cell in open containers in the form of phosphorus pentoxide.

Analysis of data. The characteristic frequency associated with dipolar relaxation was obtained by fitting a Cole–Cole distribution function to the observed dispersion curves:[10]

$$\frac{\varepsilon'(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\frac{1+(\omega\tau)^{(1-\alpha)}\sin(\pi\alpha/2)}{1+(\omega\tau)^{2(1-\alpha)}+2(\omega\tau)^{(1-\alpha)}\sin(\pi\alpha/2)}$$
$$\frac{\varepsilon''(\omega)}{\varepsilon_0-\varepsilon_\infty}=\frac{(\omega\tau)^{(1-\alpha)}\cos(\pi\alpha/2)}{1+(\omega\tau)^{2(1-\alpha)}+2(\omega\tau)^{(1-\alpha)}\sin(\pi\alpha/2)} \quad (1)$$

where ε_0 and ε_∞ are respectively the low and high frequency limiting values of the dielectric permittivity; τ is the characteristic time of the relaxation process and $(1-\alpha)$ is the distribution parameter. The analysis was undertaken using a PDP11/E10 computer equipped with a

---

* Present address: Wolfson Applied Electrostatics Unit, Department of Electrical Engineering, University of Southampton, Southampton, Hants, UK

0032–3861/81/010037–06$02.00

Table 1 Composition of resins studied

Code		Composition DGEBA (phr)	CTBN (phr)	Mole fraction or rubber	Curing agent (phr)		Cure cycle
10%	+ TETA	100	10	0.0909	TETA	8	I
12½%	+ TETA	100	12½	0.1111	TETA	8	I
15%	+ TETA	100	15	0.1304	TETA	8	I
47%	+ TETA	100	47	0.3197	TETA	8	I
100/51%	+ TETA	51.7	100	0.6592	TETA	1.5	II
10%	+ DGBP	100	10	0.0909	DGBP	19	I
12½%	+ DGBP	100	12½	0.1111	DGBP	19	I
15%	+ DGBP	100	15	0.1304	DGBP	19	I
51.4%	+ DGBP	100	51.4	0.3397	DGBP	19	I
100/45%	+ DGBP	45	100	0.6896	DGBP	3.5	II

Cure cycle I: (a) preheat components to 333K; (b) add curing agent; (c) finish cure overnight at ambient. II: (a) and (b) the same as I; (c) finish cure overnight at 373K

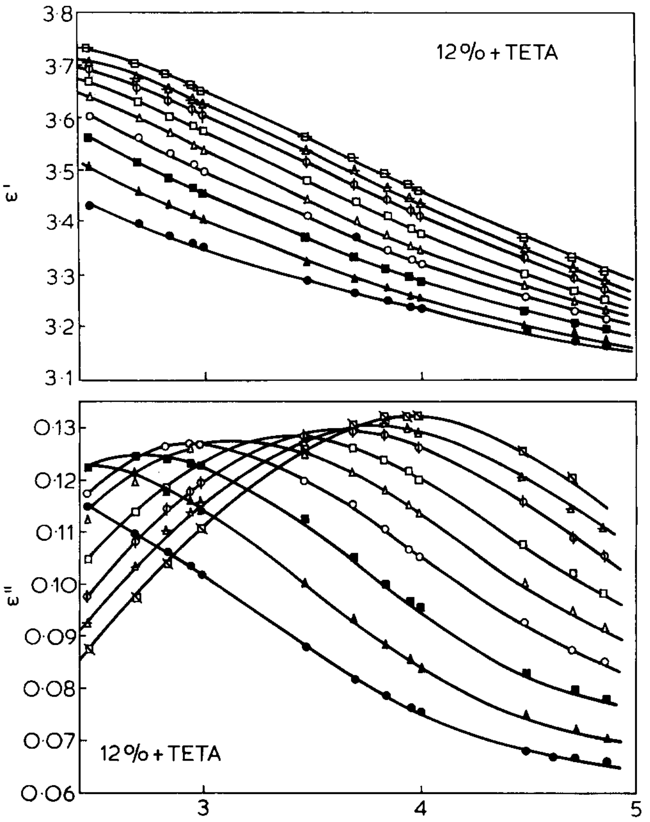

Figure 1 Low temperature dielectric relaxation curves for 12% + TETA resin. ●, 220.7K; ▲, 229.5K; ■, 231.6K; ○, 234.5K; △, 236.5K; □, 238.3K; ⦶, 240.5K; ⍋, 242.0K; ⊟, 244.0K

visual display, the fit was tested using a least-squares minimization procedure.

D.c. measurements

Current discharge methods[11-13] were applied to the study of these resins; however, no resolvable low frequency loss process was detected. The changes in conductivity as a function of temperature were determined from current charging and discharge data.

Ultrasonic absorption and velocity measurements

The attenuation and velocity data were obtained using an immersion technique[14,15]: the liquids used were either methanol or propanol for low temperatures (below 283K) and water above 273K. The attenuation was obtained from a comparison of the amplitude of the received signal with and without the sample. Correction was made for the effects of reflection in the determination of the acoustic absorption. The velocity was determined using the critical angle approach.

Table 2 Analysis of dielectric relaxation data for two resins, Cole–Cole fit

Temperature (K)	ϵ_0	ϵ_∞	$1-\alpha$	τ (s)
0.091 Mol fraction of rubber + TETA				
227.7	3.85	2.65	0.27	1.05×10^{-4}
232.0	3.90	2.70	0.27	1.2×10^{-4}
236.1	3.95	2.70	0.27	1.0×10^{-4}
237.8	3.95	2.70	0.27	0.9×10^{-4}
239.8	4.00	2.70	0.27	0.65×10^{-4}
241.8	4.00	2.70	0.27	0.35×10^{-4}
244.4	4.00	2.65	0.27	0.25×10^{-4}
0.66 Mol fraction of rubber + TETA				
246.2	5.8	2.65	0.46	1.57×10^{-4}
248.4	5.88	2.65	0.46	1.28×10^{-4}
250.5	6.02	2.65	0.46	0.96×10^{-4}
252.5	6.20	2.65	0.46	0.71×10^{-4}
254.2	6.28	2.67	0.46	0.52×10^{-4}
256.3	6.50	2.90	0.46	0.55×10^{-4}

RESULTS AND DISCUSSION

Dielectric relaxation

Low temperature process. A distinct relaxation process was observed in the frequency range 10^2 to 10^5 Hz in the temperature range 220 to 246 (*Figure 1*). The data was analysed in terms of the Cole–Cole distribution function and the results are presented in *Table* 2. A plot of the amplitude of $\varepsilon''_{\max}$ normalized to 243K for various resins (*Figure 2*) indicates a linear variation with mol fraction of rubber, the DGBP cure giving a slightly higher slope than the TETA cure. This trend is consistent with the DGBP, introducing additional dipoles into the rubbery phase, and hence leading to an increase in the effective amplitude of the relaxation process.

The 'effective' dipole moment μ_0 associated with the relaxation can be calculated using the Fröhlich equation[16]:

$$\frac{(\varepsilon_0-n^2)(2\varepsilon_0+n^2)}{\varepsilon_0(n^2+2)^2}=\frac{4\pi N}{9}\frac{g\mu_0^2}{kTV\varepsilon} \qquad (2)$$

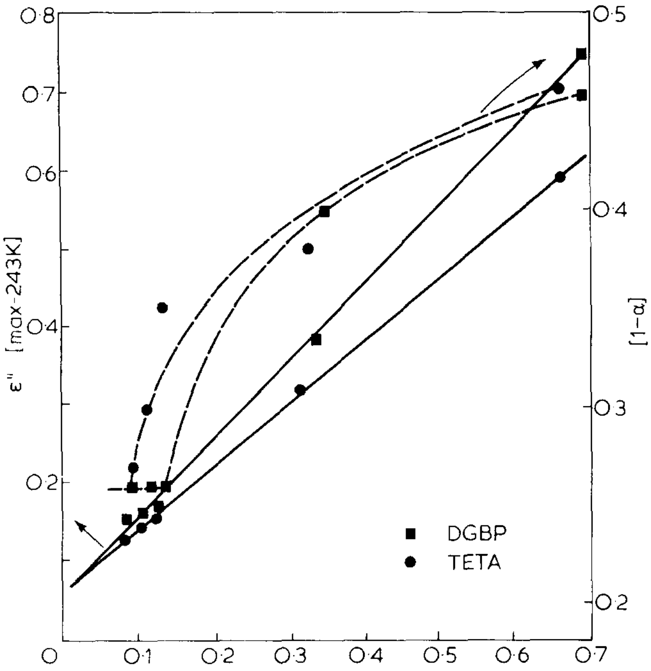

Figure 2 Variation of ε''_{max} normalized to 243K and the distribution parameter as a function of mol fraction of rubber

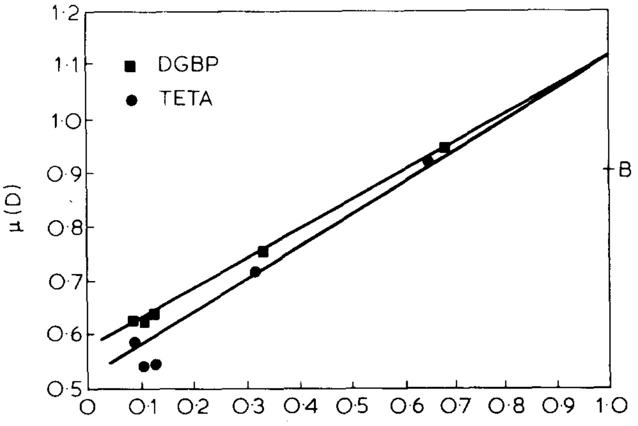

Figure 3 Variation of the effective dipole moment μ(D) with mol fraction of rubber: ■, DGBP cure; ●, TETA cure

where k and T have their usual meanings and n is the refractive index, with ε the permittivity of free space. The values obtained are presented diagramatically as a function of mol fraction of rubber in *Figure* 3. The value of B on the axis corresponds to the effective dipole moment of butadiene in a block copolymer, and was determined from studies of styrene–butadiene–styrene block copolymer[17]. The extrapolated curve has a much higher intercept than that for the butadiene–styrene copolymer as would be expected from the random nature of the acrylonitrile–butadiene block copolymer[17]. The 'effective' dipole is consistent with the hypothesis that the relaxing entity is a combination of butadiene–acrylonitrile and the carboxyl linking group.

The distribution parameter $(1-\alpha)$ indicates that as the composition of the resin is changed (*Figure* 2) so there are corresponding variations in the breadth of the relaxation. A value of $(1-\alpha)$ equal to one would correspond to an ideal relaxation, whereas a shift towards a value of 0.5 is usually associated with an increase in the cooperativity of the relaxation process. In the case of DGBP cure, a mole fraction-independent value of $(i-\alpha)$ is observed at low rubber fraction, whereas with the TETA cure the value of $(1-\alpha)$ increases continuously with increasing rubber fraction. The value of $(1-\alpha)$ increases for both systems as the percentage of rubber is further increased. Studies of the epoxy rubber modified resins with piperidine cures show that below 0.2 mol fraction, the rubber exists as distinct particulate phases. Above 0.2 mol fraction the rubber is continuously dispersed throughout the epoxy phase and forms an interpenetrating network structure. The observed variations in $(1-\alpha)$ and also the magnitude of the effective dipole moment are consistent with a similar morphological description being used for these materials. The variation of the parameter $(1-\alpha)$ is indicative of an increase in the cooperativity of the motion with the formation of a continuous phase structure.

Higher temperature processes. Although no distinct relaxation features can be identified at high temperatures (*Figure* 4) evidence for changes in the extent to which molecular motion occurs in these resins can be obtained from plots of G and ε' as a function of temperature (*Figure* 5). A plot of the bulk conductivity against temperature obtained from d.c. transient experiments exhibits a marked change in slope at a temperature which is close to that associated with the glass transition of the epoxy phase. A second marked increase in slope of the variation of ε'' against temperature (*Figure* 6) is observed at approximately 373K and corresponds closely to the highest temperature transition observed dilatometrically and using positron annhilation studies. This latter transition resembles closely the change in both ε' and ε'' observed for pure polyacrylonitrile[18]. No resolvable

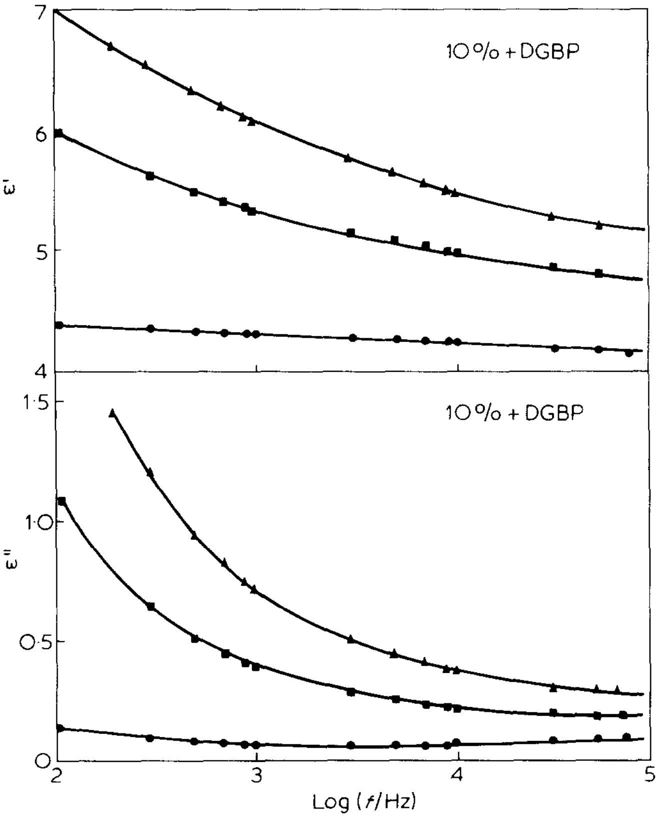

Figure 4 High temperature spectrum of 10% + DGBP resin ●, 302.2K; ■, 323K; ▲, 333.2K

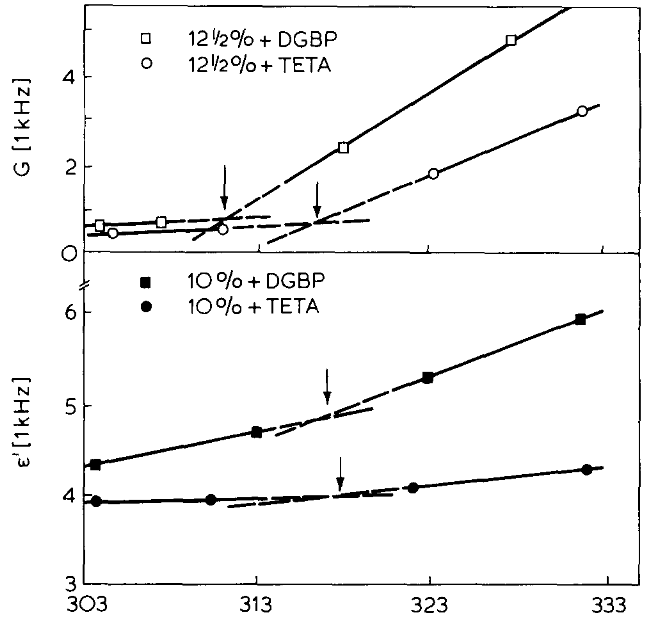

Figure 5 Variation of ϵ' and G at 1 kHz as a function of temperature for TETA and DGBP cured systems

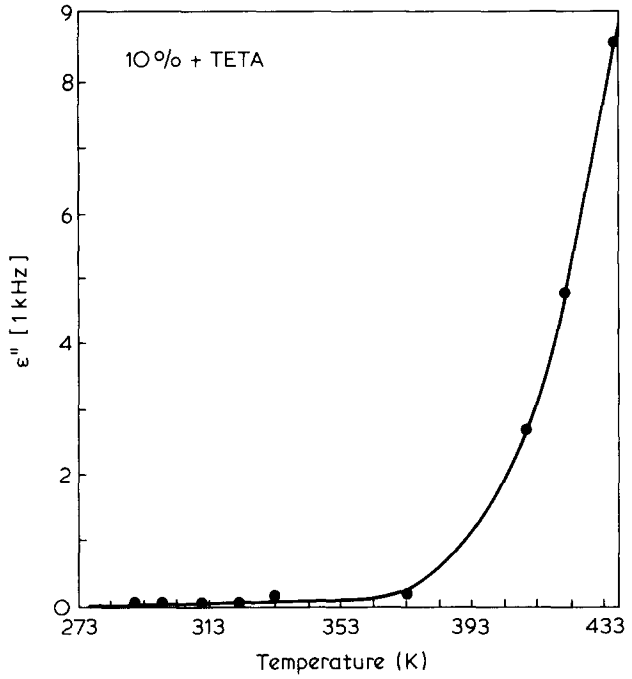

Figure 6 Variation of ϵ'' at 1 kHz as a function of temperature for 10% + TETA cure

dielectric relaxation feature can be distinguished in this polymer, the dielectric loss and permittivity exhibiting a marked increase with increasing temperature. This polymer is known to decompose forming charge carriers and although no colour changes were observed until above 406K, in the runs studied here it is possible that the carriers responsible for the observed affects are the residue of products generated during the polymerization reaction. It was also noted that on cooling the sample to low temperature there was no significant increase in the bulk conductivity of the sample. It would therefore be reasonable to suppose that the marked increase in conductivity observed can be associated with an increase in the mobility of the carriers. This hypothesis is consistent with the highest temperature transition being associated with the onset of motion of epoxy–acrylonitrile–butadiene interface.

Ultrasonic absorption and velocity measurements

A distinct maximum was observed in the ultrasonic absorption *versus* temperature plot of *Figure* 7, indicating a molecular relaxation process[19–21]. The linear de-

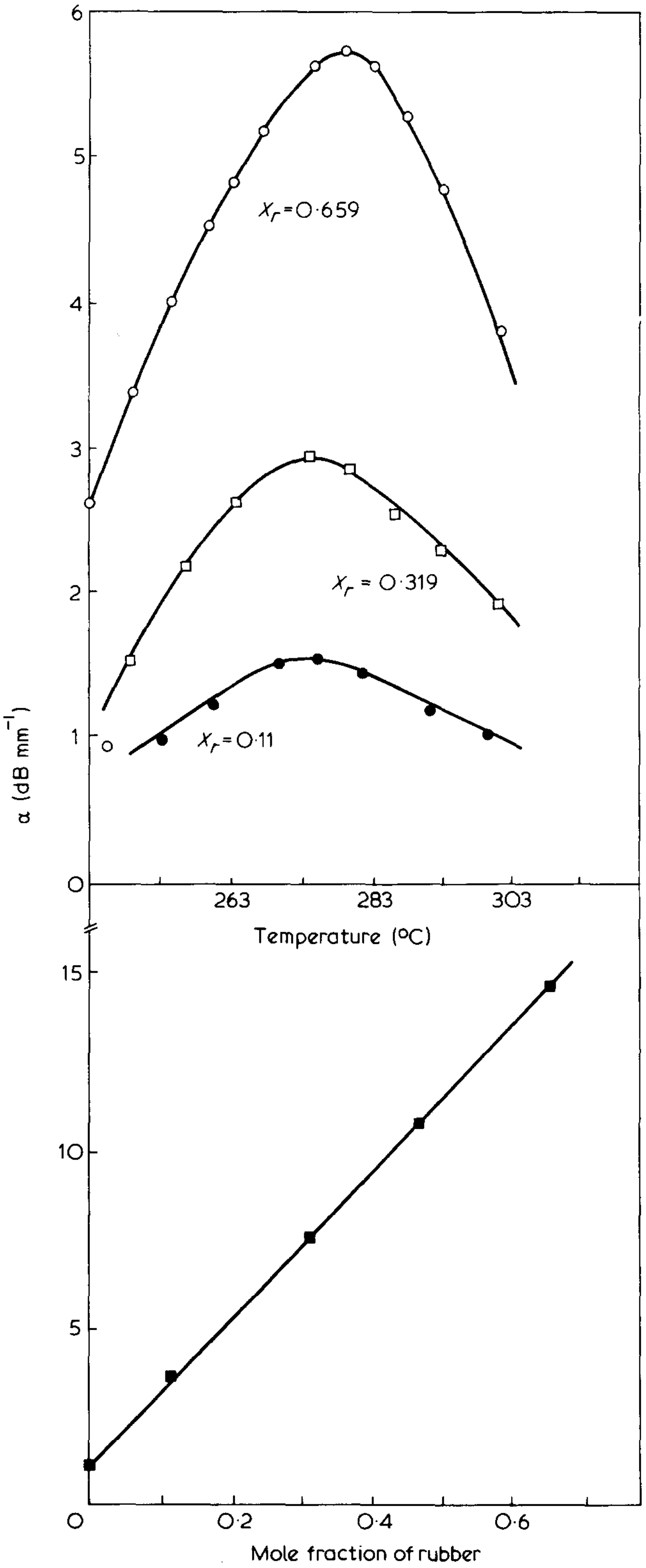

Figure 7 Temperature and composition variation of the ultrasonic absorption at 5 MHz for TETA cured systems

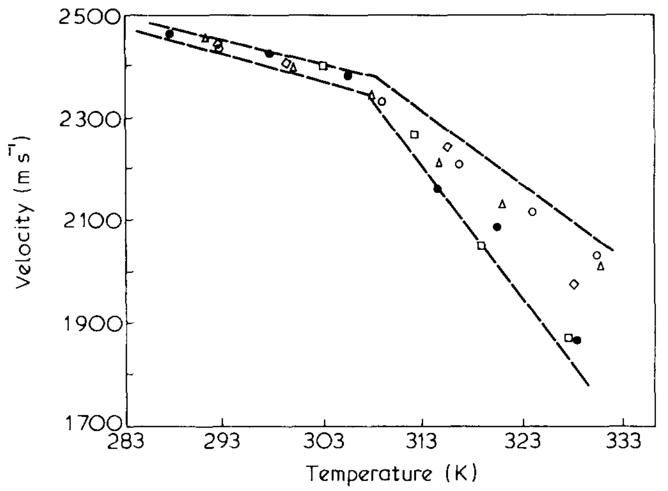

Figure 8 Variation of velocity against temperature for rubber-modified epoxy resins at 5 MHz. ●, 15% + glycol; □, 12½% 3 Glycol; ○, 10% + Glycol; ◇, 15% + TETA; △, 12½% + TETA

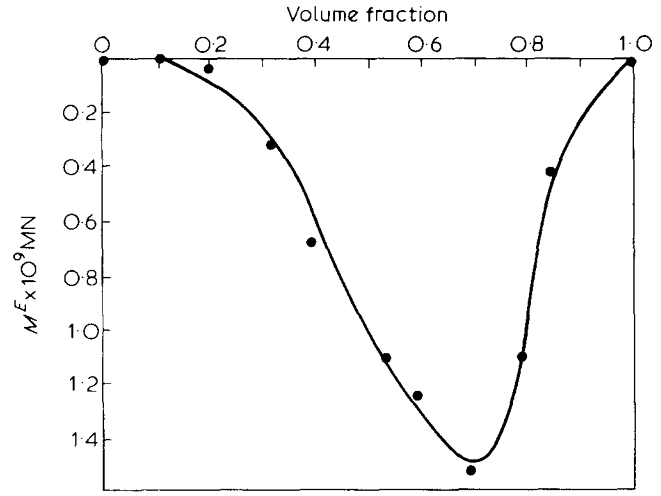

Figure 9 Variation of the excess of modulus *versus* mol fraction

pendence of the peak amplitude on the rubber content suggests that the molecular relaxation is associated with the motion of the acrylonitrile–butadiene block. The modulus of a polymer is known to drop markedly in the region of the glass transition[22]. Plots of two of the resins which had not been thermally annealed exhibited a stepwise change in the velocity *versus* temperature at approximately the expected T_g of the epoxy phase. On thermal annealing the step disappears. However, the presence of a transition is still evident as a change in the slope of the velocity *versus* temperature (*Figure* 8). The step jump observed in the unannealed samples may be attributed to the presence of stressed areas within the sample, which on raising the temperature above the glass transition are annealed out. The velocity of sound was found to be only slightly sensitive to the curing agent used, but is dominated by the variation with mol fraction of the rubbery phase (*Figure* 8).

The modulus of the resins can be calculated using the relationship:

$$M = 1/v^2\rho \qquad (3)$$

where M is the modulus, v is the velocity and ρ is the density. The effects of variation of the rubbery phase can best be described by calculating the excess functions:

$$M_{\text{excess}} = M_{\text{obs}} - (M_{\text{epoxy}}V_{\text{epoxy}} + M_{\text{rubber}}V_{\text{rubber}}) \qquad (4)$$

where M_{epoxy} and M_{rubber} are respectively the moduli of the rubber (acrylonitrile–butadiene) and the epoxy phases; and V_{epoxy} and V_{rubber} are respectively the volume fractions of the epoxy and rubber phases. The plots using equation (4) show a distinct minimum at approximately 0.7 volume fraction of rubber (*Figure* 9). A possible explanation for the observed changes is that the almost ideal value for low volume fractions is indicative of the material behaving as a simple composite. Increasing the rubber content will lead to a change of the dominant morphology from one of rubbery occlusions dispersed in a continuous epoxy phase to an interpenetrating network structure and ultimately to epoxy occlusions dispersed in an almost continuous rubber phase. The more mobile acrylonitrile–butadiene chains will destabilize the epoxy network and hence the material will appear more rubbery. However further increase in the rubber content leads to an increase in the modulus consistent with the effect of the acrylonitrile dipoles stabilizing the rubbery matrix. In the high rubber content materials the epoxy will be the minor phase and may be expected to tend to form occlusions within the rubbery phase – the reverse of the morphology observed at low rubber concentrations.

Effects of curing agent on the molecular relaxation spectrum

The Cole–Cole form of the distribution equation was capable of fitting the dielectric relaxation (*Table* 3). This equation describes the situation where the spectrum can be attributed to a single molecular process but with a distribution of activation energies. This is a reasonable hypothesis for these systems since the rubber phase at low concentrations will be in the form of occlusions and hence the average environment associated with each chain will be similar. The correspondence between the values of $(1-\alpha)$ observed for low rubber content resins cured with TETA and DGBP is consistent with this hypothesis (*Figure* 3). Increasing the rubber content leads to a marked change in the distribution parameter consistent with the formation of a more interpenetrating network structure and the appearance of a more cooperative molecular relaxation process.

Table 3 Distribution parameters and activation energy for resins

Code		Mol fraction of rubber	Distribution parameter $(1-\alpha)$	Activation energy (kJ mol^{-1})
10%	+ TETA	0.09	0.27	40.3
12½%	+ TETA	0.11	0.30	42.5
15%	+ TETA	0.13	0.35	46.1
47/100	+ TETA	0.32	0.38	75.2
100/51	+ TETA	0.66	0.46	48.3
10%	+ DGBP	0.09	0.26	41.7
12½%	+ DGBP	0.11	0.26	37.0
15%	+ DGBP	0.13	0.26	43.6
51.4/100	+ DGBP	0.34	0.40	63.8
100/45	+ DGBP	0.65	0.46	58.8

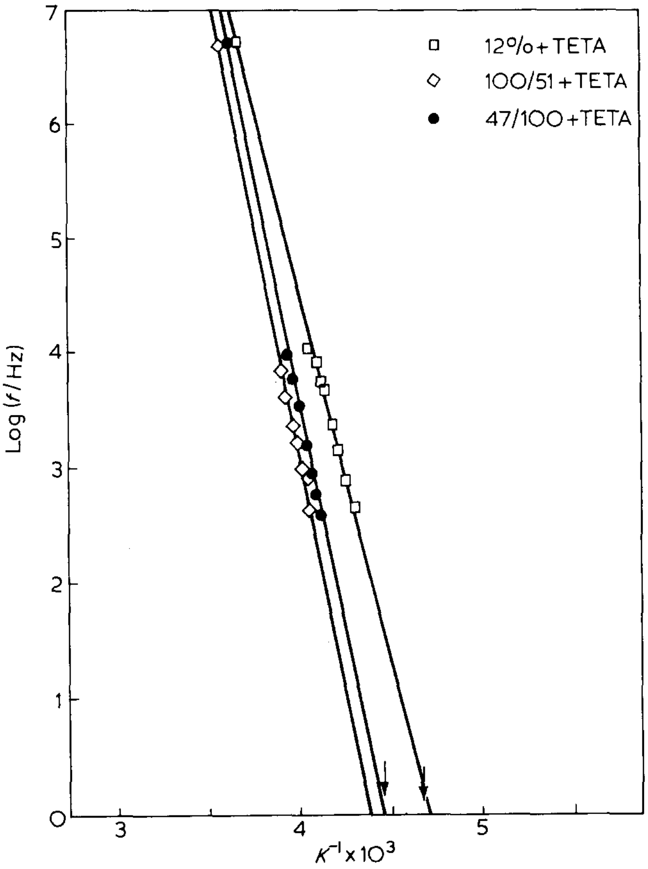

Figure 10 Activation energy plots for rubber-modified epoxy resins

Activation energies of the resins

Using a combination of dielectric and acoustic data it is possible to cover a frequency range of 10^2 to 10^7 Hz. *Figure* 10 illustrates the behaviour of TETA cured materials. Although the range of samples studied was limited it is possible from the derived activation energies in *Table* 3, to infer that there is an increase in the activation energy with increasing rubber content up to a certain value and then a decrease. The number of samples studied in this high rubber regime limits the interpretation. However, it may be proposed that the observed increase is a manifestation of the increased degree of interpenetration of the epoxy and rubbery phases. At high rubber contents the epoxy will now become the occluded phase and this will be reflected in a decrease in the activation energy. This interpretation of the data is consistent with the changes observed in the ultrasonic velocity and is in agreement with the observations of the dependence of the dynamic mechanical properties[3,23], of the resins on rubber content.

CONCLUSIONS

The dynamic data presented in this paper support the effects of morphology on the mobility of the rubbery chains and further indicate how the change in curing agent can markedly influence the behaviour of certain properties yet have little effect on others. The apparent linear dependence of the relaxation frequency on the reciprocal temperature indicates that the relaxation is most probably a simple thermally-activated process rather than a free volume-controlled process.

ACKNOWLEDGEMENTS

J.D. wishes to acknowledge receipt of financial support from the Procurement Executive, Ministry of Defence, for part of the period during which this study was performed.

REFERENCES

1 Daly, J., Fuller, P., Cunliffe, A. V., Datta, P. K. and Pethrick, R. A. *Polymer* 1980, **21**, 000

2 Mogenson, O. E., Jacobsen, F. and Pethrick, R. A. *Polymer* 1979, **20**, 1034

3 Kaloglou, N. K. and Williams, H. L. *J. Appl. Polym. Sci.* 1973, **17**, 1377

4 Cunliffe, A. V., Huglin, M. B., Pearch, P. J. and Richards, D. H. *Polymer* 1975, **16**, 654

5 Paul, N. C., Richards, D. H. and Thompson, D. *Polymer* 1977, **18**, 945

6 Paul, N. C., Richards, D. H. and Thompson, D. *Polymer* 1977, **18**, 951

7 Jay, R. R. *Anal. Chem.* 1964, **36**, 667

8 Dijkstra, R. and Dahmen, E. A. M. *Anal. Chem. Acta.* 1964, **31**, 38

9 Vaughan, W. E. 'Dielectric Properties and Molecular Behaviour' Van Nostrand Reinhold, London, New York, 1969, p. 108

10 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1949, **9**, 341

11 Wagner, K. W. *Arch. Electrotechn.* 1914, **2**, 371

12 Van Beek, L. K. H. 'Progress in Dielectrics' (Eds. J. B. Birks and J. Hart) Heywood, London, 1967, Vol. 7, p. 69

13 Van Beek, L. K. H. *Arch. Sci. Genere Bull. Colloque Ampere* 1962, 229

14 Gilbert, A. S., Pethrick, R. A. and Phillips, D. W. *J. Appl. Polym. Sci.* 1977, **21**, 139

15 Waterman, H. A. *Kolloid Z.* 1963, **192**, 1

16 Frohlich, H. 'Theory of Dielectrics' Oxford University Press, 1949

17 North, A. M., Pethrick, R. A. and Wilson, A. D. *Polymer* 1978, **19**, 913

18 Ishida, Y., Amano, O. and Takayanagi, M. *Kolloid Z.* 1960, **172**, 129

19 Arnold, N. D. and Guenther, A. H. *J. Appl. Polym. Sci.* 1966, **10** 731

20 Protzman, T. F. *J. Appl. Phys.* 1949, **20**, 627

21 Assay, J. R. and Guenther, A. H. *J. Appl. Polym. Sci.* 1966, **11**, 1087

22 Neilsen, L. E. 'Mechanical Properties of Polymers and Composites', Marcel Dekker, New York, 1974, Vol. 2, p. 293

23 Geiszler, W. A., Koutsky, J. A. and Di Benedetto, A. T. *J. Appl. Polym. Sci.* 1970, **14**, 89