Dielectric Studies of Water in Epoxy Resins

IAN D. MAXWELL* and RICHARD A. PETHRICK, *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland*

Synopsis

Dielectric measurements are reported on amine-cured epoxy resin samples over a frequency range from 200 Hz to 200 kHz and a temperature range from −60°C to 70°C as a function of molecular weight of the diglycidyl ether and water content. The effects of change of the molecular weight of the diglycidyl ether on the dielectric relaxation are small in comparison with the changes observed on the introduction of water into the matrix. Analysis of the data indicates the presence of cluster—free and bound—molecularly dispersed water. The former are presumed to be found in voids and cavities which arise in curing powder samples. The conductivity of the water-doped samples reflects the mobility of the water and is compared with the predictions of theories for amorphous materials.

INTRODUCTION

Epoxy resins are extensively used as coatings for various metallic structures.[1] As such, the flexibility of the coating, its adhesion to the substrate, and its impervious qualities to water are critical in determining the long time usefulness of these materials. Studies have been reported[2] of the variation of the dielectric properties as a function of the extent of cure and have been shown to indicate the rate at which the matrix progresses to its gel point. Because it is essentially a nondestructive test method, dielectric constant measurements have been widely employed to follow cure *in situ*, and the effects of various hardeners—composition, functionality, concentration, as well as curing conditions—time and temperature—have been reported.[3] The effects of fillers[4] and rubber additives[5] have also been reported.

In the pure epoxy system two relaxations have been identified,[6,7] a high temperature alpha process (α) usually associated with the glass transition process (T_g) and a lower temperature beta process (β). During the cure process the dielectric loss maximum increases in height and shifts to a higher temperature for both the α and β processes. Variation of the resin and curing agent effects the temperature of the α maximum associated with the T_g process but does not significantly influence the position of the β process,[3,8–10] this latter process being associated with relaxation of the glyceryl unit, —O—CH_2—CH(OH)—CH_2—. This assignment is supported by the observed variation in the amplitude of the relaxation with change in ratio of curing agent to resin.[11,12]

A shortage of amine causes a decrease in the peak height and a shift to lower temperature,[13] whereas excess curing agent has little effect. The majority of

* Present address: Redland Technology Ltd., P.O. Box 7, Graylands, Horsham, West Sussex, England.

Journal of Applied Polymer Science, Vol. 28, 2363–2379 (1983)
© 1983 John Wiley & Sons, Inc.
CCC 0021-8995/83/072363-17$02.70

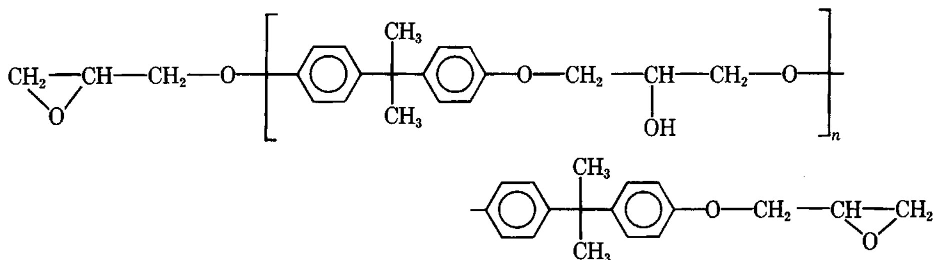
the studies on this relaxation process have been obtained using dynamic mechanical methods. The toughness or impact strength of the coatings may be associated with the position of the β relaxation.[9] The effects of crosslink density on the mechanical properties have been discussed by Schteinberg.[14] It is observed that a correlation exists between the observed variation and the size of the relaxing kinetic unit and the extent of interaction between molecules due to changes in the pendant hydroxyl concentration. The dielectric method is ideal for monitoring such effects and part of this study is concerned with an exploration of the effects of change of the resin on the properties of the cured material.

Permeation of water into epoxy resin films and also the effects which this has on the molecular relaxation are of interest in the discussion of the ultimate life of an epoxy coating. The second part of the study is concerned with this problem.

EXPERIMENTAL

Epoxy Resins and Curing Agents

The epoxy resins used in this study were of the diglycidyl ether of bisphenol A structure, with n having values between 0 and 4:



The base resins were obtained from Ciba Geigy, British Petroleum, and Shell Chemicals and were used without further purification. The codes and details of the epoxy resins used in this study are summarized in Table I. The curing agent used in these studies was imidazole, which is a catalytic curing agent. Only the first of the series is liquid at room temperature. The higher molecular weight resin required preprocessing for an effective cure to be achieved. The resin was firstly ball milled for 5–6 h and then sieved so as to produce a powder of particle size less than 50 μm. The powder was then mixed with an appropriate amount of imidazole. The curative was added in stoichiometric quantities calculated on the basis of one N—H group per epoxide ring. The powder was then heated until it was fluid and physically stirred to ensure cure occurring. The resultant

TABLE I
Characteristics of Epoxy Resins

Code	Source	Value of n	Molecular weight[a] M_N
MY750	Ciba Geigy	0	352
Epikote 1004	Shell Chemicals	3	1292
Epikote 2057	Shell Chemicals	4	1674

[a] Obtained from the epoxy equivalent value for the resin.

mixture was then ball milled for 5–6 h and once more sieved to yield a powder of less than 50 μm size. The resultant powder was then used to prepare the samples. The powder was pressed between aluminium foils for 1 min at 500 psi. This produced a stable disc which was subsequently cured at 145°C for 30 min and post-cured at 150°C for 1 h. The process of post-cure was usually carried out with pressure applied except in one of the samples where the cure was performed without application of pressure. This process leads to a fully cured material[15] as assessed on the basis of the disappearance of the epoxide group infrared absorption at 930 cm^{-1}.

The void content of the samples studied in this paper were determined using density measurements and optical micrography. The variation of the density and the void distribution during the cure of a powder epoxy resin has been discussed previously[15] by the authors and will not be repeated here.

Dielectric Measurements

Fixed Frequency—Variable Temperature. Dielectric measurements were performed as a function of temperature at 1 kHz using a Teradyne, automatically balancing capacitance resistance bridge. The samples were initially cooled and the data were collected on the heating cycle. The temperature of a thermocouple imbedded in the sample and one in close proximity to the sample allowed the thermal lag in the system to be measured. The temperature was recorded using a Digitron Thermometer 3750K, which had previously been calibrated at the melting and boiling points of water.

Variable-Frequency Measurements. These measurements were performed using a General Radio Type 1416A bridge operating over a frequency range from 200 Hz to 200 kHz, combined with a Rhode and Schwartz Indicating Amplifier UBM and a Rockland Programmable Frequency Synthesizer 5100. The cell used in this study was totally immersed in a "statim" low temperature bath and, the temperature was controlled with a precision of ±0.1K. This allowed temperatures down to −60°C to be reached. Lower temperatures were obtained by the addition of Drycold to a methanol bath, measurements being taken when an approximately constant temperature had been achieved. Temperatures above 283K were obtained using a water bath fitted with a Julabo Paratherm II, and allowed temperatures up to 75°C to be achieved. The dielectric cell used in these studies was sealed inside a heavy brass container, the temperature being controlled externally, and the humidity controlled using either saturated salt solutions or drying agents where appropriate. The water was absorbed by the sample placed in a dessicator containing salt solutions or a container of water. The dry samples were obtained by heating at 100°C for 24 h in a vacuum oven. The water uptake quoted for the wet samples was determined by taking the difference in weight between the equilibrated and dry samples. The weight of the samples were determined after the dielectric studies to check that there had been neither a gain nor a loss of weight. The values of water content quoted in this paper were the mean of the initial and final values.

The dielectric cell used in this study was a standard Wayne Kerr three terminal cell, the electrodes being constructed from polished stainless steel and the insulators are quartz. Contact between the sample and the electrodes was made using carbon electrodes.

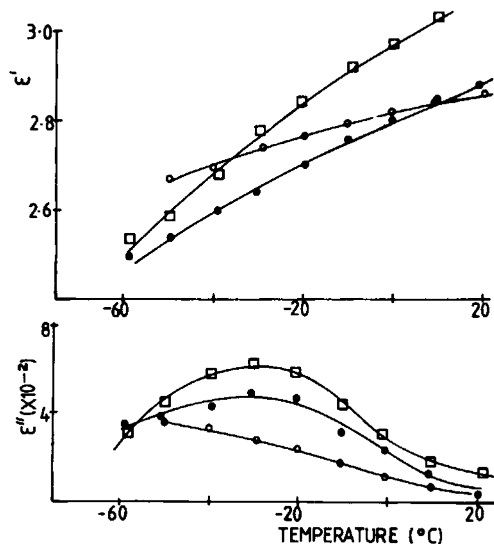


Fig. 1. Dielectric permittivity vs. temperature at 1 kHz for 1004/Imid: (○) 0% H_2O; (●) 1.52% H_2O; (□) 2.35% H_2O.

RESULTS

Fixed-Frequency Dielectric Measurements

The variable temperature fixed frequency data for the epoxy resins studied in this paper are summarized in Figures 1–3. The dielectric permittivity and loss indicate the existence of a broad relaxation feature spanning the temperature range −60°C to −40°C in the dry samples. This relaxation feature correlates

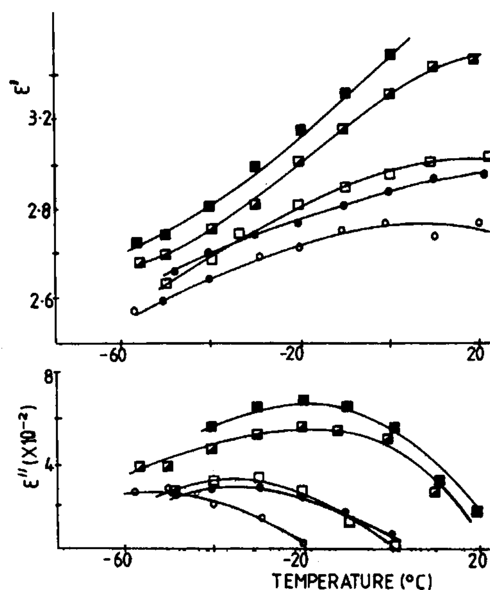


Fig. 2. Dielectric permittivity vs. temperature at 1 kHz for 2057/Imid: (○) 0% H_2O; (●) 0.11% H_2O; (□) 0.57% H_2O; (□) 1.44% H_2O; (■) 2.1% H_2O.

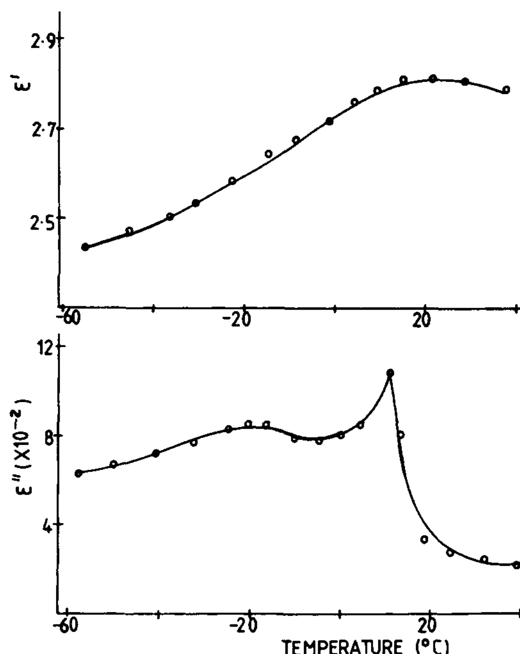


Fig. 3. Dielectric permittivity vs. temperature at 1 kHz for 1004/Imid containing 0.51% H_2O. This sample was cured without application of pressure and contained visible voids.

closely with the position of the beta relaxation reported previously using dynamic mechanical measurements.[8–10] The introduction of water leads to a marked increase in the amplitude of the dielectric increment and a shift of the loss peak to higher temperatures. In certain of the samples a feature is observed at around 10°C, which is believed to be associated with the presence of adsorbed water in voids (Fig. 3). Heating the sample leads to recovery of the dielectric properties of the dry sample; reabsorption of water leads to similar changes in amplitude of the broad peak. However, the amplitude of the peak at 10°C varied markedly from sample to sample. The intensity of this peak is also sensitive to the pressure used in curing the samples and reflects the ability of the sample to degas during cure. The effects of water appear to be relatively insensitive to the molecular weight of the resin used; however, small differences are observed.

Frequency-Dependent Dielectric Measurements

In an attempt to further define the nature of the relaxation processes occurring in these systems, the dielectric permittivity and loss were explored as a function of frequency at various temperatures (Figs. 4 and 5). The observed relaxation is very broad extending over several decades of frequency. The effects of change in the molecular weight are small, though significant [Figs. 1(b) and 2(b)].

Analysis of the Data

In an attempt to identify the contribution to the dielectric loss due to added water, the Cole–Cole method of data presentation was adopted (Figs. 6 and 7). The plot of ϵ' versus ϵ'' is semicircular for an ideal relaxation process. In the

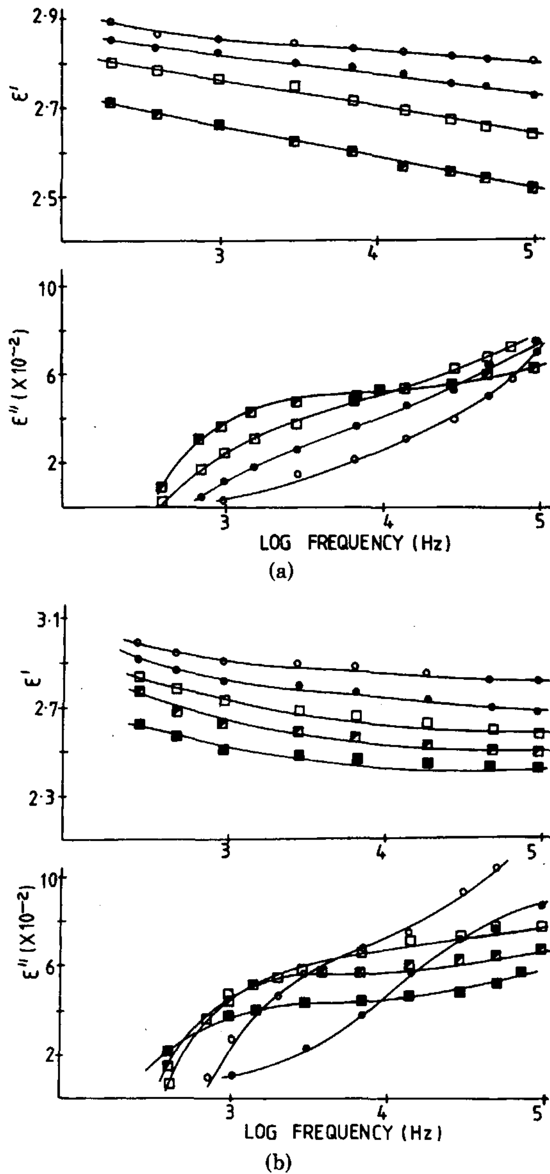


Fig. 4. Frequency dependence of the dielectric permittivity of 1004/Imid: (a) 0% H_2O: (○) 20°C; (●) 0°C; (□) −20°C; (◩) −50°C. (b) 1.52% H_2O: (○) 20°C; (●) 0°C; (□) −20°C; (◩) −40°C; (■) −60°C.

systems studied here we observe two overlapping semicircles in the case of resins containing additional water in comparison to the single semicircle for systems without added water. The additional processes can therefore be identified. In an attempt to clarify the contribution of the added water to the overall relaxation, different plots were constructed. The dielectric parameters for the dry sample were subtracted from those of the wet samples and the residual presented using the Cole–Cole approach (Figs. 8 and 9). The expected semicircular plots are obtained. These water molecules are strongly interacting with the resin matrix

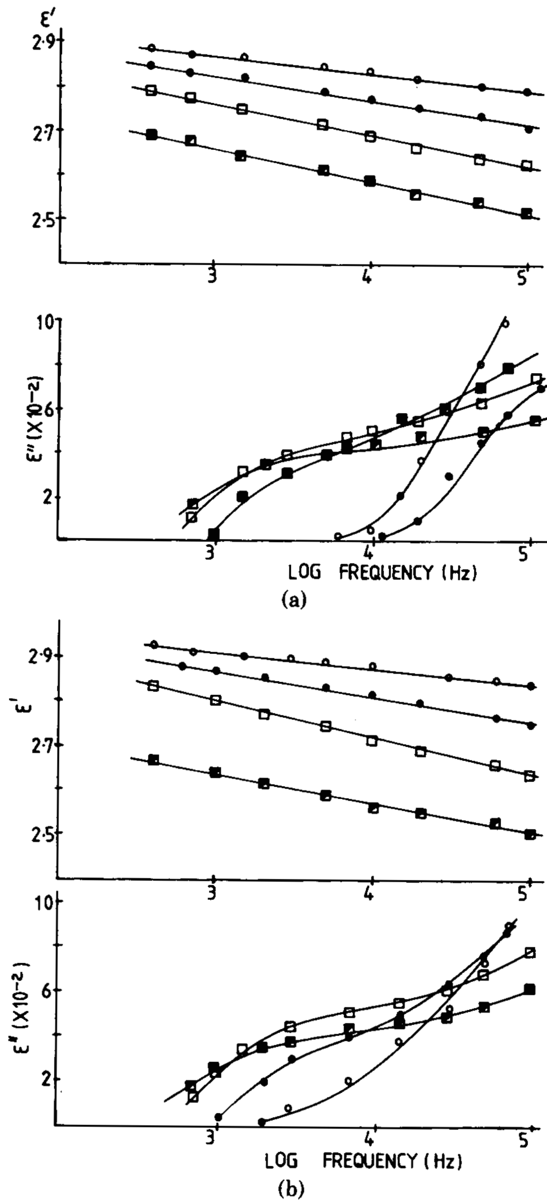


Fig. 5. Frequency dependence of the dielectric permittivity of 2057/Imid: (a) 0% H_2O: (○) 20°C; (●) 0°C; (□) −20°C; (◩) −50°C. (b) 0.57% H_2O: (○) 20°C; (●) 0°C; (□) −20°C; (◩) −50°C. (c) 1.44% H_2O: (○) 20°C; (●) 0°C; (□) −20°C; (■) − 40°C; (◩) −60°C. (d) 2.1% H_2O: (○) 20°C; (●) 0°C; (□) −20°C; (◩) −40°C; (■) −60°C.

and are probably hydrogen bonded to the hydroxyl group of the glycidyl segment of the resin.

The conductivity $\sigma(\omega)$ of the epoxy resin matrix as a function of frequency is shown in Figures 10 and 11. The log–log plot shows that a linear dependence over a large frequency range is observed. Charge conduction in amorphous solids can be described by a single law of the form

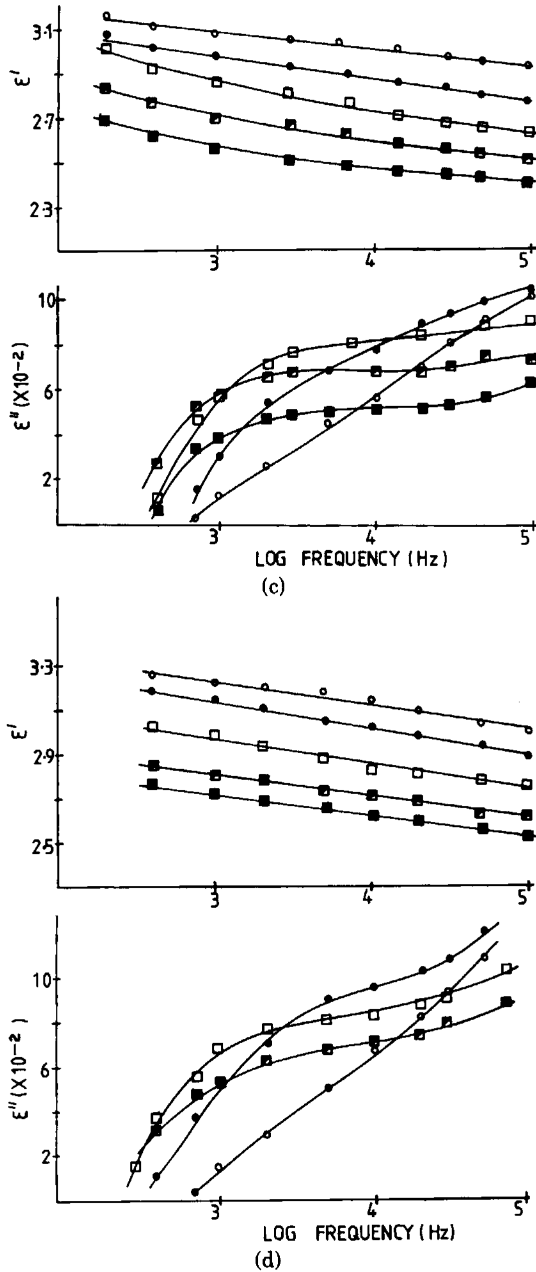


Fig. 5. (*Continued from the previous page.*)

$$\sigma(\omega) = A(T)\omega^{n(T)} \tag{1}$$

where $A(T)$ and $n(T)$ are weakly temperature-dependent parameters and are characteristic of the mode of conduction. For many amorphous solids, e.g., organic polymers, silicon, and aluminium oxides, it has been found that n has a value in the range 1.1–0.5 and is frequency less than unity.[16–19] The analysis of the epoxy resins is presented in Table II.

TABLE II
Variation of Mode of Conduction (n) with Temperature and Water Content for Epikote/Imidazole Systems

	n Value			
	1004/Imid		2057/Imid	
Temp	0% H_2O	2.35% H_2O	0% H_2O	2.1% H_2O
20°C	1.43	1.23	1.88	1.37
0°C	1.32	1.16	1.59	1.17
−50°C	1.07	1.07	1.14	1.13

DISCUSSION

Relaxation in the Presence of Water

Comparison of the data presented in Figures 1 and 2 indicates a weak molecular weight dependence. This appears to suggest that, although there will be significant differences in the number of pendant OH groups, as the resin is changed the nature of the environment and hence the effective g factor tends to minimize these effects. The g factor is a multiplying factor which reflects the restrictions on the reorientational motion of the water molecule as a consequence of being bound to other water molecules or to the polymer matrix. Similarly, although there are differences between the various resins studied, these are considerably smaller than the overall effect of water addition. It is also clear that water can exist in epoxy resins in at least two types of environment. Karasz and Moy[20] have discussed the effects of sorbed water on the hydrogen-bonded

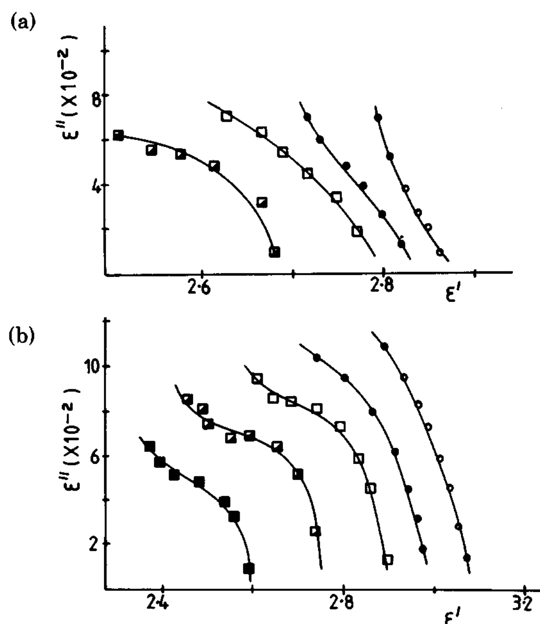


Fig. 6. Cole–Cole type plots for 1004/Imid: (a) 0% H_2O: (○) 20.8°C; (●) 0.2°C; (□) −20°C; (◪) −49.7°C. (b) 2.35% H_2O: (○) 21.5°C; (●) 0.4°C; (□) −20.2°C; (◪) −39.0°C; (■) −58.4°C.

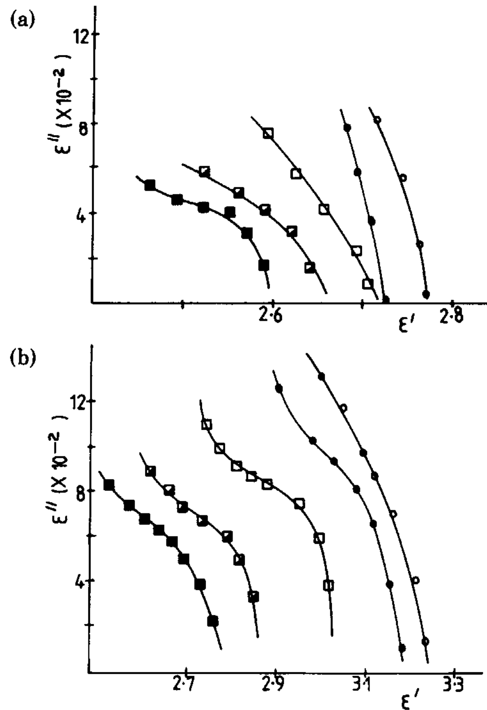


Fig. 7. Cole–Cole type plots for 2057/Imid: (a) 0% H_2O: (○) 19.7°C; (●) −0.9°C; (□) −20.2°C; (◪) −40.0°C; (■) −56.0°C. (b) 2.1% H_2O: (○) 19.1°C; (●) 0.5°C; (□) −20.3°C; (◪) −40.1°C; (■) −56.0°C.

epoxy matrix and shown using nmr and dsc that two types of processes can be identified. The first associated with "bound" and the second with "free" water. The variation of the loss at 0°C and also correlation of changes of void structure with the conditions of cure appear to indicate that the presence of free water can in part be associated with microscopic voids in the material. Bound water appears to be associated with water not possessing the normal tetrahedral structure and is probably associated with single or small numbers of water molecules interacting with the glycidyl segment.

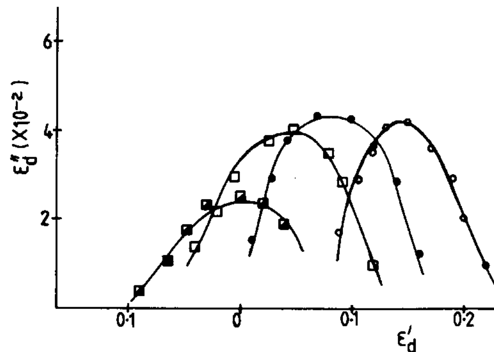


Fig. 8. Differential Cole–Cole plots for 1004/Imid for 2.35% H_2O at: (○) 21.5°C; (●) 0.6°C; (□) −20.3°C; (◪) −39.0°C.

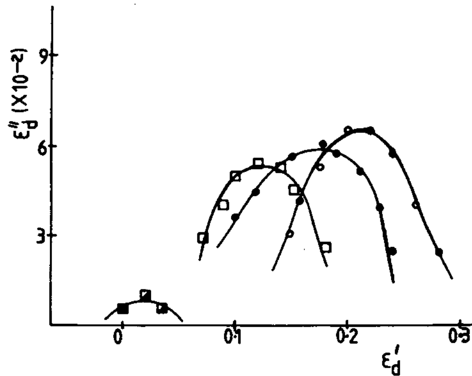


Fig. 9. Differential Cole–Cole plots for 2057/Imid for 2.1% H_2O at: (○) 19.1°C; (●) 0.5°C; (□) −20.3°C; (◪) −56.0°C.

A number of dynamic mechanical and viscoelastic studies have been performed on the effects of low molecular weight additives. Both antiplasticization and plasticization have been observed. Plasticization is associated with a reduction of the glass transition temperature (α process) and a subsequent decrease in modulus and yield strength of the polymer. Antiplasticization has the opposite

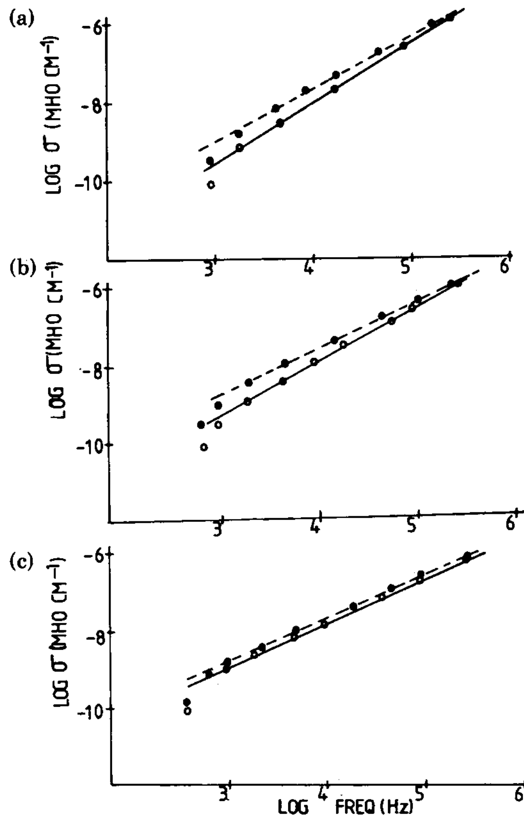


Fig. 10. Log of conductivity against frequency for 1004/Imid: (○) 0% H_2O; (●) 2.35% H_2O. (a) 20°C; (b) 0°C; (c) −50°C.

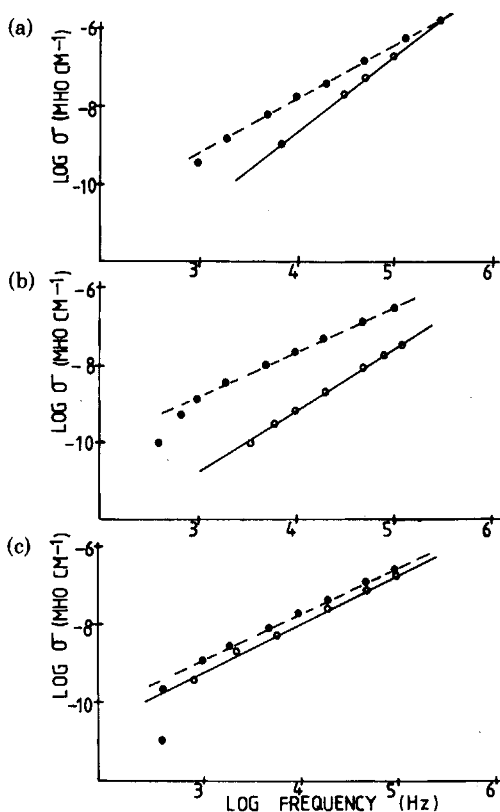


Fig. 11. Log of conductivity against frequency for 2057/Imid: (O) 0% H_2O; (●) 2.35% H_2O. (a) 20°C; (b) 0°C; (c) −50°C.

effect. Kumanotani and co-workers[21] have observed that chlorinated biphenyl is effective as a plasticizer for epoxy resins. They also observed that the plasticization effect was accompanied by decrease in the intensity of the β relaxation process. Water has also been observed to produce plasticization. Torsional braid measurements have indicated that in certain systems it is possible to detect two transitions: one associated with the β process and the other labeled T_{H_2O}. The reduction in the intensity of the β process is associated with water complexing with the glycidyl segments, and therefore segmental motion is inhibited by increasing the size of the relaxing unit.[22] This will certainly decrease the intensity of the transition but should also move it to higher temperature in accord with the greater thermal activation energy required for segmental motion.

The observed lowering of the T_g is explained in terms of a disruption of the strong hydrogen bonds in the cured network,[23] intermolecular bonds being replaced by epoxy water bonds. Diffusion studies have indicated that water molecules are bound to specific sites within the network which is consistent with the dielectric observations reported here.

Despite the differences in molecular weight and thus structure of the resin, the relaxation of the water containing resins are very similar. The H-bonded attachment of water must be presumably similar in all cases, which is consistent with the dominant interaction occurring via the glycidyl segment. The motion

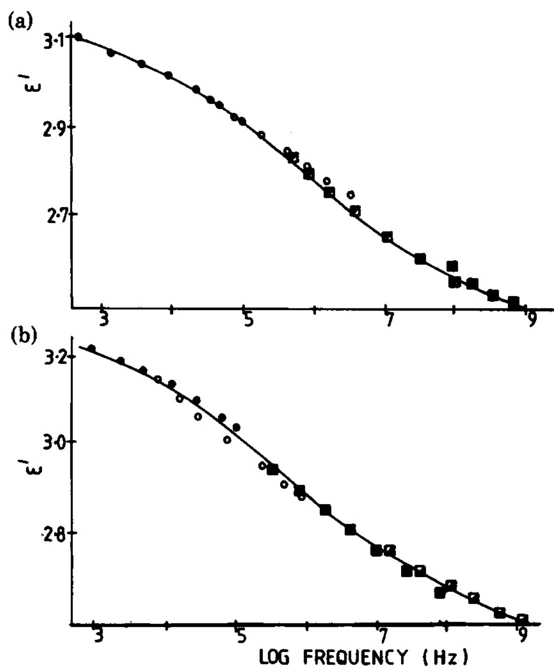


Fig. 12. Master plots for (a) 1004/Imid 2.35% and (b) 2057/Imid 2.1% H_2O. Temperatures as for Figures 8 and 9.

of this entity has been previously assigned to the relaxation and the interaction of water leads to a shift to higher temperature consistent with an antiplasticization effect. There is a minor change in ϵ' with molecular weight of the resin, and this parallels that previously reported for the changes observed using dynamic mechanical methods. Use of the WLF shift approximation leads to a normalized set of curves (Fig. 12). The time temperature superposition principle can be applied to these data and indicates that as shown from the breadth of the curves the process is highly cooperative and influenced by the free volume. This is surprising since it is usually the T_g relaxation which behaves in this manner. Using the shift data (Fig. 13), an activation energy can be obtained. Values of 30. kJ/mol are obtained, and these are similar in magnitude to the values predicted on the basis of the processes involving the breaking of H bonds.

Conductivity Data

The variation in the exponent of eq. (1) reflects the changes in the nature of the conduction process with change in temperature. As the temperature is lowered the value of n tends to 1.1, which is the upper limit of the range for eq. (1). The high n values show an ω^2 dependence of conductivity, where the conduction process is occurring at frequencies slightly greater than the observation frequency. Thus a free carrier conduction model is not operative in the low temperature regions of low water content epoxies. As the water content is increased and the temperature increased, the value of n changes as processes are activated and conduction becomes a free carrier process. Values of $n = 1$ have

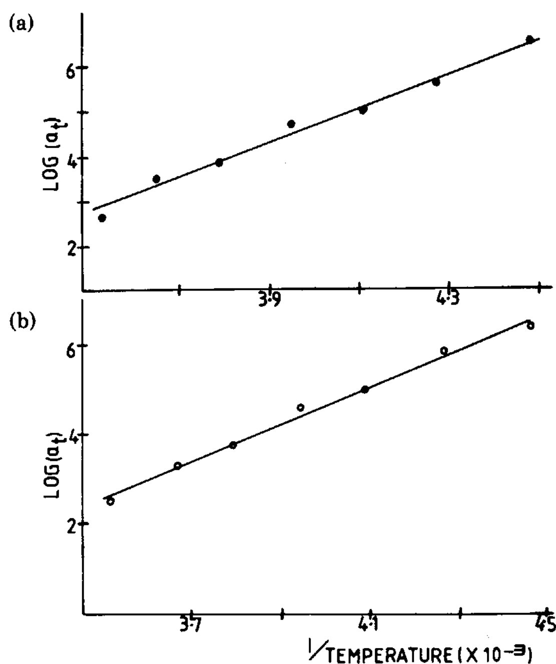


Fig. 13. Plots of shift factors for (a) 1004/Imid 2.35% H_2O and (b) 2057/Imid 2.1% H_2O.

been observed in selenium[24] and associated with a loss peak due to the ac conductivity.

High-Frequency Limiting Permittivity Data

The observed increase of ϵ'_∞ derived from the Cole–Cole plots (Fig. 14) with increasing water content is consistent with the water molecules increasing the atom density of the sample, hence filling molecular size cavities. The general decrease of ϵ'_∞ value with temperature for water-containing materials is consistent with the loss of a high frequency component to the dielectric permittivity. The dielectric relaxation of pure water is known to occur in the GHz region and implies therefore that the epoxy contains voids of sufficient dimensions to allow waterlike clusters to exist. The break at approximately 233K is consistent with the relaxation being frozen out and reflects a change in the Kirkwood correlation factor. Local forces between molecules in water are very large so that g, which reflects the constraints on free reorientation, also may become large. As a consequence, value of g of the order of 2.65 can be observed in water, this value being changed by the effects of the epoxy matrix on the free form rotation of the water molecules.

A plot of ϵ' vs. H_2O content at 1 kHz shows a linear dependence of ϵ' with increasing water content (Fig. 15). The observation that the slope of the plots are approximately independent of temperature down to −35°C is consistent with the idea that the water molecules are interacting with the epoxy resin matrix rather than with one another. The break in the curve at −35°C is indicative of the cessation of motion of the water molecules. The scatter in the data does not allow a precise g value to be calculated. An interpolation of the data to 100%

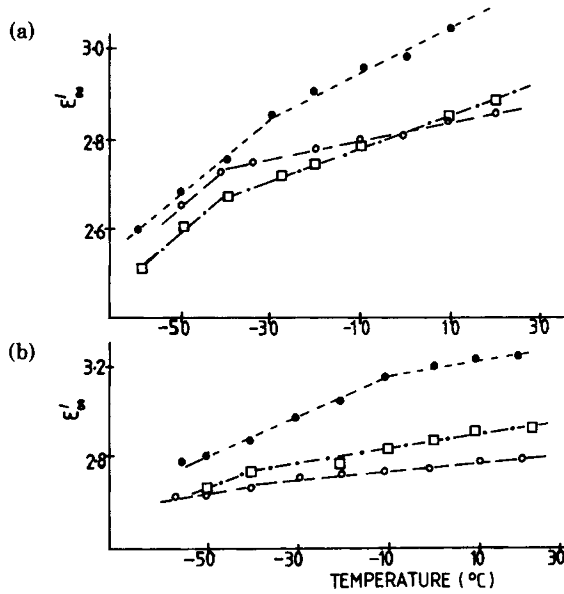


Fig. 14. Plots of high frequency limiting permittivity for (a) 1004/Imid: (O) 0% H_2O: (□) 1.52 %H_2O: (●) 2.35% H_2O. (b) 2057/Imid: (O) 0% H_2O; (□) 0.57% H_2O; (●) 2.1% H_2O.

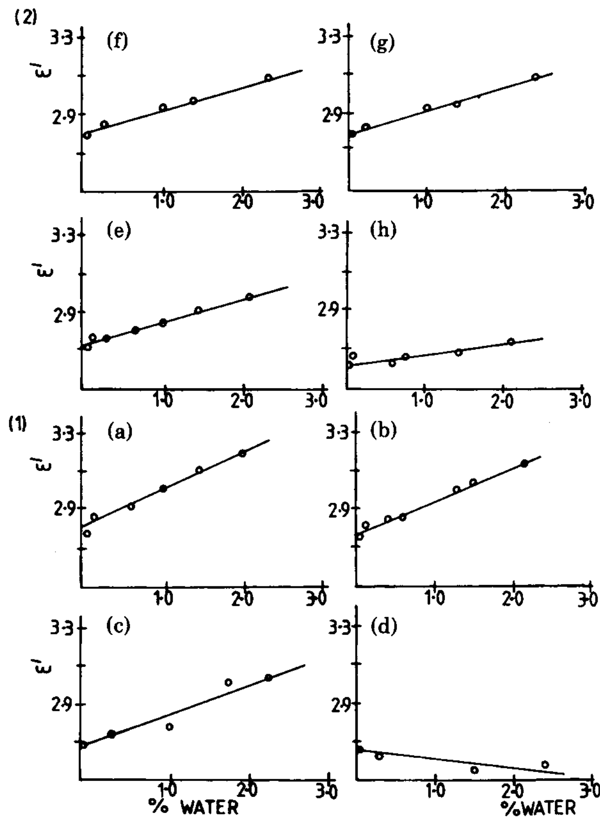


Fig. 15. Variation of permittivity with water content for (1) 1004/Imid: (a) 20°C; (b) 0°C; (c) −20°C; (d) −50°C. (2) 2057/Imid: (e) 20°C; (f) 0°C; (g) −20°C; (h) −50°C.

water should give a value of 80.13 for free water. A lower value is obtained which implies that the g factor is different from that in tetrahedral water.

The studies described above are subject to some uncertainty as a consequence of nonreproducibility of data. For instance, the void content changes from sample to sample, and hence the effects of water content are also variable. Further, although the data on samples in which water had been adsorbed was nominally reproducible, an exact match of data after a drying and rehydrating cycle was rarely observed. However, the conclusions drawn appear completely general for these epoxy resin systems.

CONCLUSIONS

It is observed that water can exist in two forms: bond water molecularly dispersed throughout the epoxy matrix and free water which probably resides in, or is adsorbed onto the surface of, the cavities within the matrix. The activation energy for the relaxation has a value which is close to that predicted on the basis of H-bonded breaking and reflects the nature of the process which involves both rotation of the glycidyl unit and the breaking and making of H bonds. The conductivity behavior reflects changes in the probability of charge hopping between trap sites as a consequence of changes in the mobility of water molecules in the epoxy matrix.

One of us (I. D. M.) wishes to thank the SERC for a CASE award and the support of British Gas Corporation for the period during which this research was undertaken.

References

1. W. G. Potter, *Epoxide Resins*, Iliffe Books, London, 1970.
2. J. Delmonte, *J. Appl. Polym. Sci.*, **2**, 108 (1959).
3. Y. M. Blyakhman, T. I. Bonsova, and T. S. M. Levitskaya, *Polym. Sci. USSR*, **A12**, 1756 (1970).
4. T. Tanaka, S. Hayaki, and K. Shibayama, *J. Appl. Phys.*, **48**, 3478 (1977).
5. J. Daly and R. A. Pethrick, *Polymer*, **22**, 37 (1981).
6. V. Adamec, *J. Polym. Sci., A1*, **10**, 1277 (1972).
7. J. G. Williams, *J. Appl. Polym. Sci.*, **23**, 3433 (1979).
8. L. A. O'Neill and C. P. Cole, *J. Appl. Chem. London*, **6**, 356 (1956).
9. C. A. May and Y. Tanaka, Eds., *Epoxy Resins, Chemistry and Technology*, Marcel Dekker, New York, 1973.
10. Ye M. Blyakhman, T. I. Borisova and T. S. M. Levitskaya, *Polym. Sci. USSR*, **A12**, 2602 (1970).
11. G. A. Pogany, *Polymer*, **11**, 66 (1970).
12. R. G. C. Arridge and J. E. Speake, *Polymer*, **13**, 443 (1972).
13. T. Hirai and D. E. Kline, *J. Appl. Polym. Sci.*, **16**, 3145 (1972); **17**, 31 (1973).
14. V. G. Schteinberg, A. L. Yefremara, and B. A. Rozenberg, *Polym. Sci. USSR*, **21**, 1381 (1980).
15. I. D. Maxwell, L. Bunton, and R. A. Pethrick, *J. Appl. Polym. Sci.*, **27**, 4284 (1982).
16. T. J. Lewis, *Spec. Periodical Reports*, *Dielectric and Molecular Processes*, M. M. Davis, Ed., Chem. Soc., London, 1977, Vol. 3.
17. H. W. Soeb, G. M. Young, P. A. Quickenden, and A. Suggett, *Ber Bunsenges. Phys. Chem.*, **75**, 1155 (1971).
18. F. Argall and A. K. Jonscher, *Thin Solid Films*, **2**, 185 (1968).
19. D. J. Crofton and R. A. Pethrick, *Polymer*, **22**, 1048 (1981).
20. F. E. Karasz and P. Moy, *ACS Symposium Resins for Aerospace*, Am. Chem. Soc., Washington, D.C., 1980, Chap. 30.

21. J. Kumanotoni, N. Hata, and R. Yamuchi, *J. Appl. Polym. Sci.*, **17**, 2173 (1973).
22. K. Gilham and C. A. McPherson, "Characterization of Thermosetting Epoxy Resins Using a Torsional Pendulum Effect of Environment," Proc. 32nd Ann. Tech. Conf. Reinf. Plastics/Composites Inst. SPI, 1977.
23. J. Vanderschueren and A. Linkens, *J. Electrostat.*, **3**, 155 (1977).
24. A. I. Lakatos and M. Abkowitz, *Phys. Rev. B*, **3**, 1791 (1971).

Received August 5, 1982
Accepted February 7, 1983