

Dielectric Properties of an Epoxy Resin and Its Composite II. Solvent Effects on Dipole Relaxation

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Synopsis

Dipole relaxation dielectric loss behavior of a fiberglass-epoxy composite has been studied following submersion in polar and nonpolar organic solvents as well as in acidic and basic aqueous solutions. Certain adsorbed organic solvents, such as 1,2-dichloroethane, had little influence on the epoxy relaxation behavior. Other solvents, including chloroform, increased the composite relaxation intensity and shifted the temperature-frequency region over which the relaxation occurred. Both the amount of solvent uptake and the degree of interaction of solvent molecules with epoxy polar functional groups appear to control the amount of relaxation behavior perturbation. Arrhenius activation energies for relaxation were lowered by solvent uptake from the dry composite value of 18 kcal/M to between 6 and 16 kcal/M, depending on the solvent adsorbed. Submersion in methanol and chloroform sharply increased the direct current conductivity of the composite. Two molar acidic and basic solutions had little influence on composite dipole relaxation behavior other than the well known behavior associated with moisture uptake.

INTRODUCTION

In a previous paper,¹ the dipole relaxation dielectric loss behavior of the epoxy resin utilized in the present work was examined. The results, in agreement with parallel studies on similar systems,² suggested a dual-phase nature of moisture within the resin matrix. At lower moisture concentrations (< 1.4%) a hydrogen bonded or otherwise strongly adsorbed moisture phase was preferentially formed. By relaxing in phase with the polar epoxy groups, this moisture altered the intensity and shifted the frequency-temperature domain over which relaxation losses appeared. At higher moisture concentrations (> 1.4%) the appearance of a second dielectric loss peak indicated that a colloidal or weakly bound moisture phase, perhaps filling voids in the resin matrix,² was formed. The kinetics and modes of aqueous solvent adsorption in epoxy systems have been described by several authors,³⁻⁵ but no literature has appeared concerning the uptake of organic solvents.

Exposure of a solid surface within a porous matrix to a liquid or a gas will generally result in formation of an adsorbed phase which significantly alters the interfacial electronic properties. Generally, highly polar adsorbed phases such as HCl, NH₃, and H₂O will form more substantial adsorbed layers, especially at polar surfaces. Strongly adsorbed phases, including acetone at SiO₂,⁶ often undergo a loss of dipole activity and usually show permittivities far below bulk values.

Nonpolar molecules tend to form less substantial adsorbed layers, but may exist to a much greater extent within a matrix as a nonadsorbed diluent. In the case of a completely nonadsorbed diluent phase, the total permittivity of the matrix should equal that of the adsorbate plus that of the bulk adsorbent weight. The influence of adsorbed and diluent phases on dielectric properties of polymers have been studied extensively,^{7,8} but no comprehensive classification of solvent effects on either α or β relaxation properties has been established.

Fiberglass-epoxy composites are widely used throughout the electronics industry as insulators between adjacent planes of multilayer printed circuit boards. During processing, a circuit board epoxy is typically exposed to several organic solvents including formaldehyde, methanol, and chlorinated hydrocarbon mixtures as well as strongly acidic and basic aqueous solutions. The influence of such exposures upon composite integrity and insulation quality is of obvious importance in choosing appropriate circuit board manufacturing processes.

Several processes,¹ including direct current conduction, long-chain dipolar relaxation, interfacial polarization, and side group dipolar relaxation influence the overall dielectric response of an epoxy composite. The present study was undertaken both to further our fundamental understanding of epoxy dielectric properties, especially in the presence of adsorbed moisture, as well as to establish general guidelines regarding epoxy exposure to various solvents. In this paper, the behavior of side group dipolar relaxation and DC conduction of a dicyandiamide-epoxy resin formulation occurring upon exposure to polar organic solvents, nonpolar diluents, and acidic and basic aqueous solutions are presented.

EXPERIMENTAL

Capacitance and dielectric loss were measured and recorded from 400 Hz to 1 MHz using an impedance analyzer interfaced with a standard lab computer. Measurements were made using an AC amplitude of 1.0 V RMS as described previously.¹

Measurements were generally made at 10°C intervals from -100 to 40°C in a temperature control chamber. Samples were allowed to equilibrate at each temperature for 15 minutes prior to dielectric measurements. Measurements were performed on fiberglass-epoxy composite samples with a uniform thickness of 0.3 mm. The samples were firmly held between identical polished aluminum electrodes of 25 cm² area. The resin used was a typical dicyandiamide-epoxy formulation⁹ which was cured at 180°C for 90 min.

Samples were prepared by submersion at 20°C in desired reagent-grade solvents or aqueous 2 M HCl or NaOH solutions for 48 h. The 48-h submersion period was chosen as a time which allowed close approach to equilibrium solvent uptake, but did not result in substantial epoxy degradation by the solvents. All samples were dried at 100°C for 100 hrs prior to solvent submersion. Sample weights were measured prior to submersion, immediately following submersion, and following drying of adsorbed solvent at 130°C. Reported solvent uptake weights were determined by the difference between the final dried weight and that immediately following solvent uptake.

RESULTS AND DISCUSSION

A typical temperature domain dielectric loss spectrum of the glass-epoxy composite dried at 130° for 100 hours is shown in Figure 1. The Arrhenius activation energy of this single, widely distributed β relaxation loss peak is 18.1 kcal/M.¹ This loss behavior is interpreted as a manifestation of epoxy polar functional group dipole relaxation in the applied AC electric field. No additional features were observed in the dry composite loss spectrum between -180 and 100°C.¹

Composite temperature and frequency domain dielectric loss spectra are shown in Figures 2(a) and (b) following a weight gain of 0.94% nitrobenzene. The general characteristics of the loss spectrum were not strongly perturbed by adsorption of nitrobenzene, with the β loss peak remaining very widely distributed in the temperature domain and unresolved in the frequency domain. The integrated loss intensity between high temperature-low frequency and low temperature-high frequency measurements decreased slightly compared to that observed in dry composite, and no additional loss peaks were observed. The Arrhenius activation energy of 16.1 kcal/M determined from temperature domain data is slightly lower than the 18.3 value determined for the dry composite.

Nitrobenzene did not contribute to the total composite capacitance, and no additional loss peaks were observed over the temperature-frequency domain studied. If the nitrobenzene were present as a bulk phase within the composite, then a simple calculation based on additive permittivities yields approximately a 10% increase in total capacitance for 20°C-1 KHz measurement. The absence of such an increase, as well as the slight decrease in integrated loss intensity, suggests that nitrobenzene is present as a strongly adsorbed phase which does not relax in phase with polar epoxy side groups and may actually inhibit their β relaxation process. Such behavior could

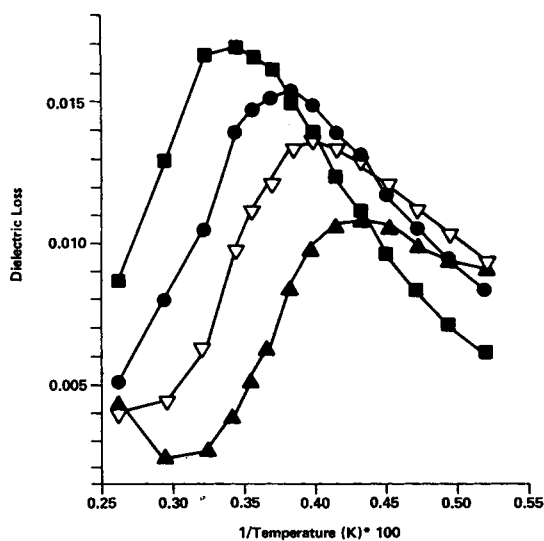


Fig. 1. Temperature domain dielectric loss spectrum of a composite sample dried at 130°C for 100 hrs: (■) 1000 kHz; (●) 100 KHz; (▽) 10 KHz; (▲) 0.4 KHz.

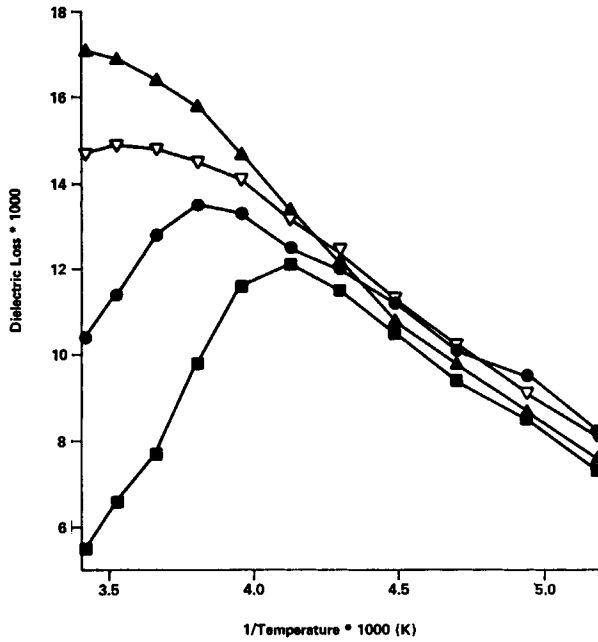


Fig. 2a. Temperature domain dielectric loss spectra of composite containing 0.94 wt% nitrobenzene: (▲) 1000 KHz; (▽) 100 KHz; (●) 1 KHz; (■) 0.4 KHz.

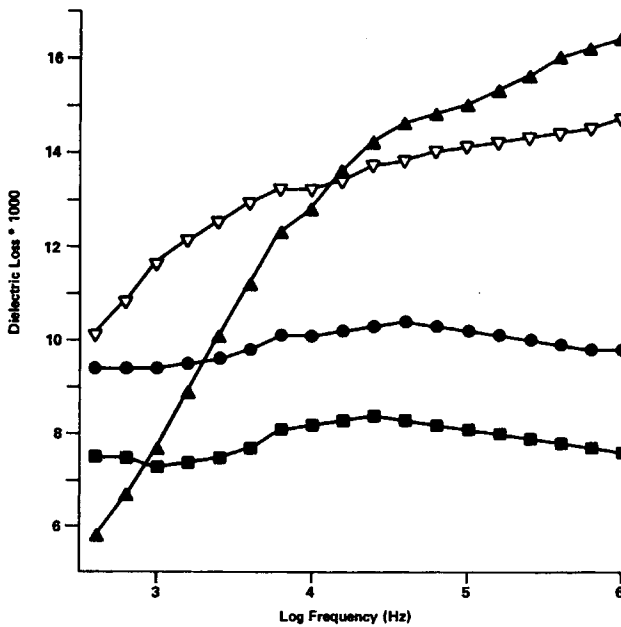


Fig. 2b. Frequency domain dielectric loss spectra of composite containing 0.94 wt% nitrobenzene: (▲) 0°C; (▽) -20°C; (●) -60°C; (■) -80°C.

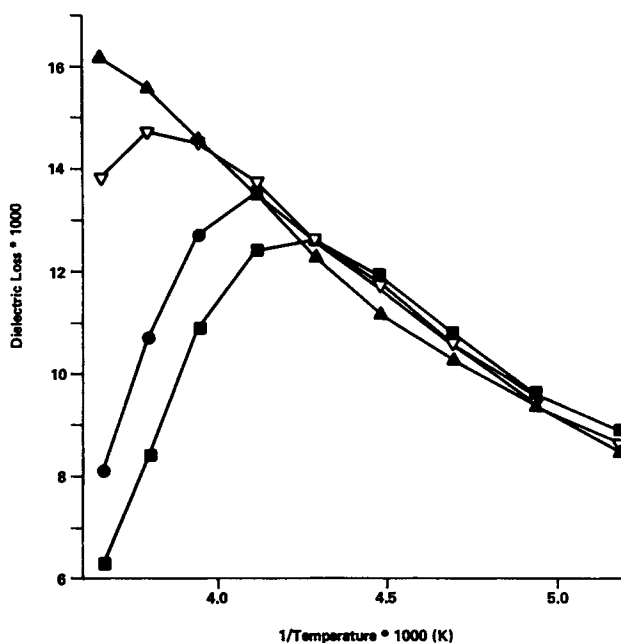


Fig. 3. Temperature domain dielectric loss spectra of composite following uptake of 2.96 wt% 1,2 dichloroethane: (▲) 100 KHz; (▽) 10 KHz; (●) 1 KHz; (■) 0.4 KHz.

result if the nitrobenzene adsorbs at sites other than polar functional groups, or could simply be the result of steric inhibition of nitrobenzene movement at polar epoxy sites. The observed behavior contrasts sharply with that of water which appeared to adsorb at, and relax in phase with, polar epoxy functional groups.¹

Figure 3 shows the temperature domain composite loss spectra following uptake of 2.96 wt% 1,2-dichloroethane. As in the case of nitrobenzene adsorption, the frequency domain loss spectra did not show well resolved features. The Arrhenius activation energy of 16.6 kcal/M determined from the temperature domain spectra is close to those for nitrobenzene adsorption. For dichloroethane adsorption, a 9% increase in composite capacitance is estimated from an additive permittivity calculation ($\epsilon = 10.4$, 2.96%). Since no increase in capacitance or integrated loss intensity was observed, it is again suggested that the adsorbed phase does not relax in phase with polar epoxy groups. The substantial mass or size of large, but moderately polar, molecules such as nitrobenzene and dichloroethane may preclude their participation in relaxation in phase with polar functional groups within the epoxy matrix.

Figures 4(a) and (b) show the temperature and frequency domain loss spectra following uptake of 0.78 wt% of the nonpolar solvent carbon tetrachloride. The temperature domain loss peaks are somewhat more well defined, show more intense maxima, and are of about equivalent integrated intensity to those observed for nitrobenzene and 1,2-dichloroethane adsorption. The Arrhenius activation energy of 15.2 kcal/M and the frequency factor of 10^{16} are somewhat lower than those previously discussed. The frequency domain spectra show broad but resolved loss peaks from which an Arrhenius activa-

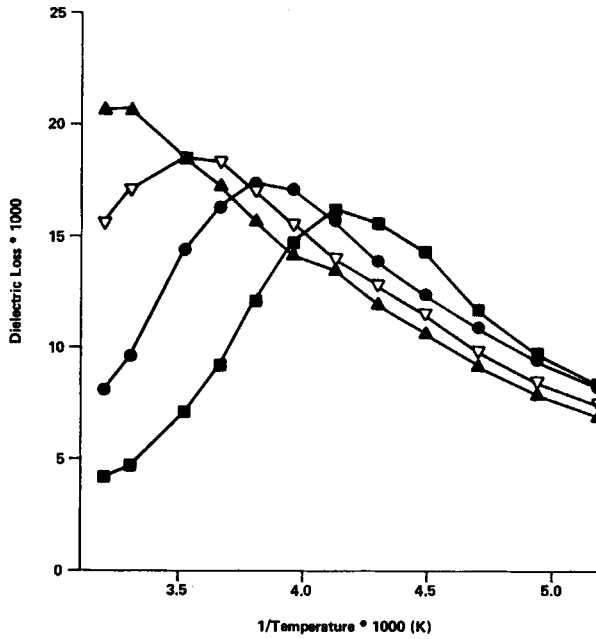


Fig. 4a. Temperature domain composite dielectric loss spectra following uptake of 0.78 wt% carbon tetrachloride: (▲) 100 KHz; (▽) 10 KHz; (●) 1 KHz; (■) 0.4 KHz.

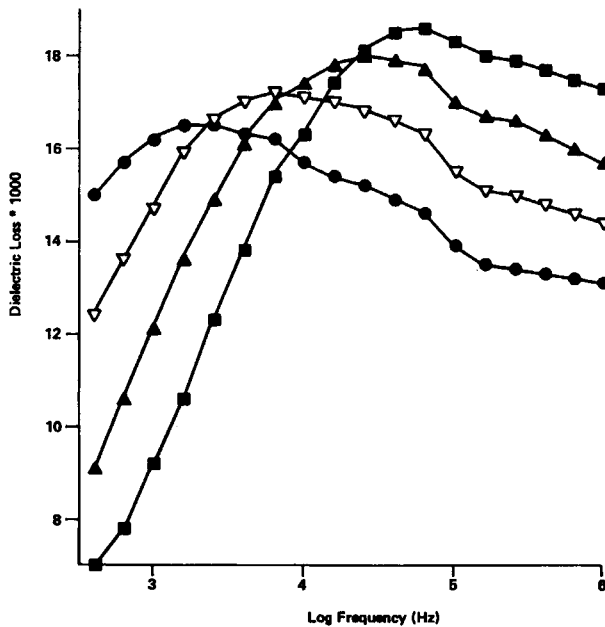


Fig. 4b. Frequency domain composite dielectric loss spectra following uptake of 0.78 wt% carbon tetrachloride: (■) 0°C; (▲) -10°C; (▽) -20°C; (●) -30°C.

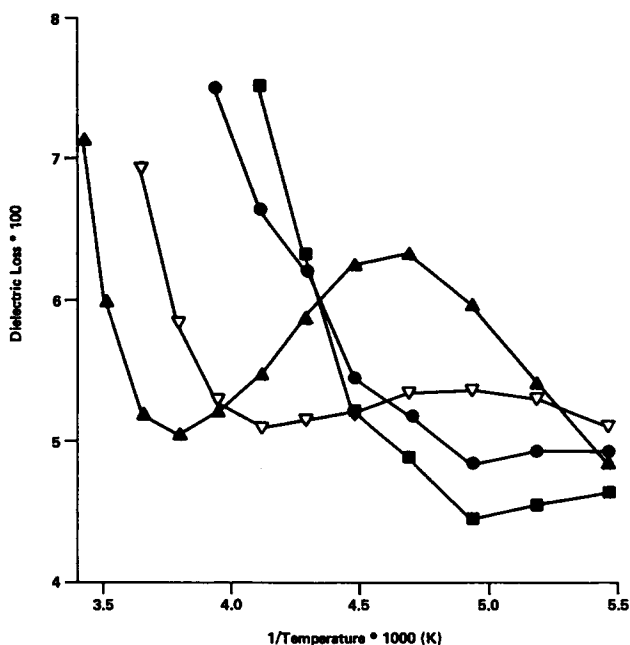


Fig. 5. Temperature domain dielectric loss spectrum of composite following uptake of 9.7 wt% methanol: (▲) 1000 KHz; (▽) 100 KHz; (●) 10 KHz; (■) 1 KHz.

tion energy of 15.0 kcal/M is determined. A total capacitance change of less than one percent is calculated assuming additive permittivities ($\epsilon = 2.24$, 0.78%), and no capacitance change was experimentally observed.

The sharper temperature domain loss peaks, the resolution of peaks in the frequency domain, and the lowered activation energy and frequency factor suggest that CCl_4 adsorption increases the effective homogeneity of epoxy polar functional groups and may plasticize the matrix. Nonpolar molecules often plasticize a polymer matrix in which they are adsorbed, but usually the result is a decrease in the temperature range over which temperature domain loss peaks appear. In the present case, solvent adsorption at nonpolar epoxy sites may increase the free volume for epoxy polar group relaxation, thus yielding more homogeneous relaxation sites.

Temperature domain composite loss behavior following uptake of 9.7 wt% methanol is shown in Figure 5. Intense but broad loss peaks appear at temperatures approximately 50° lower than in the dry composite. The temperature shift, as well as the large methanol uptake, indicate that the matrix is highly plasticized by the methanol. An Arrhenius activation energy of 12.5 kcal/M and a frequency factor of 10^{18} are calculated from the data. The sharply rising losses at higher temperatures are a manifestation of DC conduction through the MeOH-containing matrix. The activation energy for conduction is estimated from the separation of loss curves at $D = 0.1$ to be 15 kcal/M. As is often observed, the activation energy associated with DC conduction is very close to that of the β relaxation process. It is thought that this suggests that charge transfer and β relaxation involve a common physical process such as site to site movement of a pendant OH group.

The frequency domain spectra did not show well resolved peaks as a result of the sharply rising loss background associated with DC conduction.

Composite temperature and frequency domain loss spectra measured following uptake of 21 wt% chloroform are shown in Figures 6(a) and (b), respectively. Following chloroform uptake, the temperature domain spectra increased in total intensity by about one third; however, the peaks broadened somewhat compared to the dry composite. At higher temperatures, the sharply rising background reflects DC conductivity associated with the presence of chloroform within the epoxy matrix. The loss peaks which were resolved occurred over a distinctly different temperature range than those of the dry composite, and yield an activation energy of 5.8 kcal/M and a frequency factor of 10^{10} s^{-1} (Fig. 7).

The frequency domain spectrum shows well resolved loss peaks with considerably greater intensity than those of the dry composite. The Arrhenius plots constructed from temperature and frequency domain loss data for chloroform are shown in Figure 7. The plot also yields an activation energy of 6.3 kcal/M and a frequency factor of $\sim 10^{10} \text{ s}^{-1}$ for β relaxation frequency domain data. The case of chloroform uptake was unique in that a physically reasonable value for the frequency factor was obtained. This probably indicates that a linear Arrhenius extrapolation is possible over a very wide temperature range. Such behavior contrasts with the dry composite and may indicate that the epoxy has undergone glass-transition order-disorder changes during solvent uptake. These changes may act to lower the relaxation activation energy in a way that simulates higher temperatures in the dry composite. Arrhenius plot curvature¹⁰ upon extrapolation to infinite temperature (which is required by the unreasonably high frequency factors measured for composite samples) may be minimal in the highly plasticized matrix obtained at either higher temperature or following solvent uptake. An approximately 10% increase in capacitance associated with chloroform uptake agrees well with that calculated assuming an additive permittivity relationship ($\epsilon = 4.8, 21\%$).

A highly plasticized epoxy matrix in which most adsorbed chloroform is able to participate in the β relaxation process is indicated by the decreased activation energy and frequency factor, and the substantial measured capacitance increases.

For all cases of solvent submersion, the composite loss spectrum following solvent evaporation and drying were nearly identical to those of the initial dry composite. This is interpreted as an indication that little dissolution of polar functional groups or other disruption of matrix structures occurred during solvent submersion.

Submersion of composite for 48 hours in 2M HCl and saturated NaOH solutions resulted in increased β relaxation loss intensity and improved loss peak definition. The changes, however, can be entirely attributed to the amount of moisture taken up by the composite,¹ rather than to an epoxy chemical change. The frequency domain loss spectrum measured following submersion in HCl is shown in Figure 8. The moisture uptake of 1.13% as well as the loss spectrum were nearly identical to that obtained following submersion in pure water.¹ A moisture uptake of 0.92% resulted from submersion in a saturated NaOH solution, and the loss intensity was consistent with the mass of water uptake. The decreased moisture uptake following submersion in the

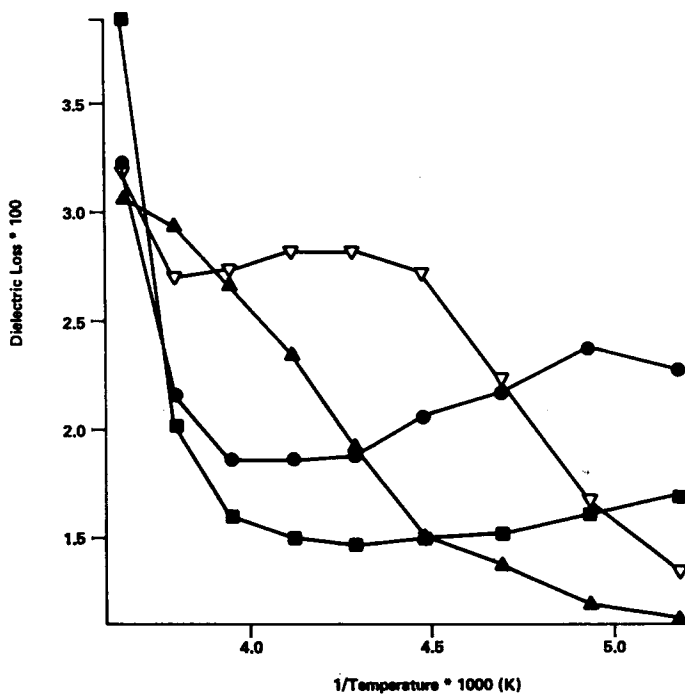


Fig. 6a. Temperature domain composite dielectric loss spectra following uptake of 21 wt% chloroform: (▲) 1000 KHz; (▽) 100 KHz; (●) 10 KHz; (■) 1 KHz.

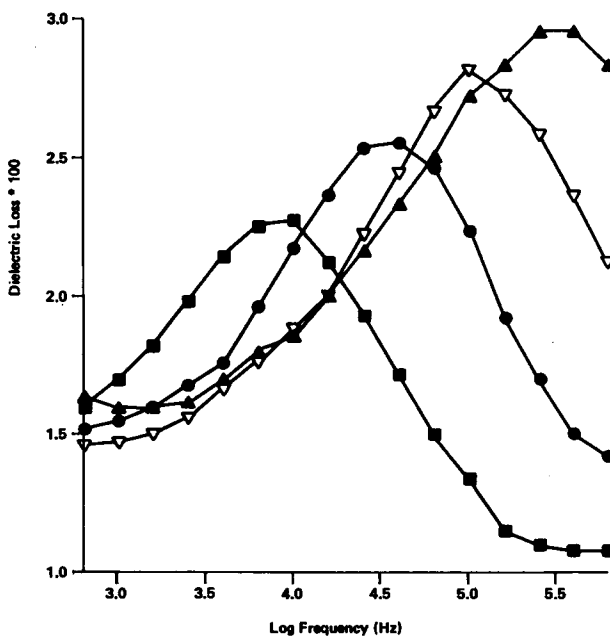


Fig. 6b. Frequency domain composite dielectric loss spectra following uptake of 21 wt% chloroform: (▲) 1000 KHz; (▽) 100 KHz; (●) 10 KHz; (■) 1 KHz.

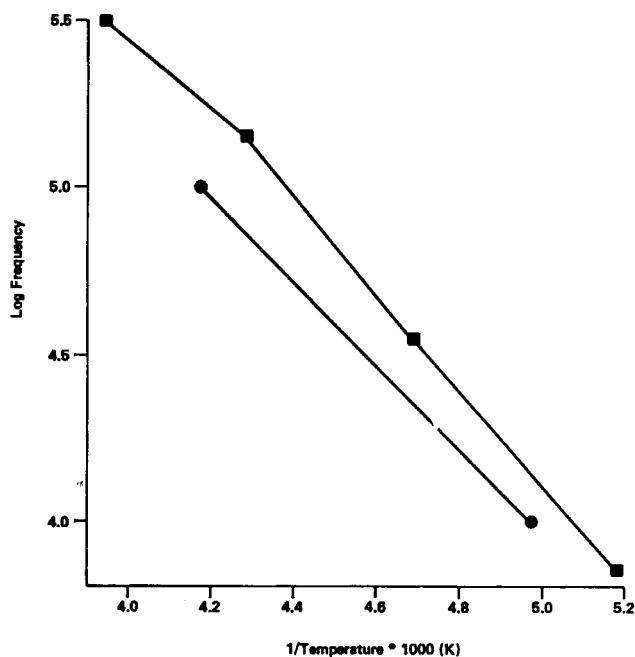


Fig. 7. Arrhenius plots constructed from the temperature and frequency domain data of Figure 6 for composite samples containing 21 wt% chloroform: (●) Temperature Domain Data; (■) Frequency Domain Data.

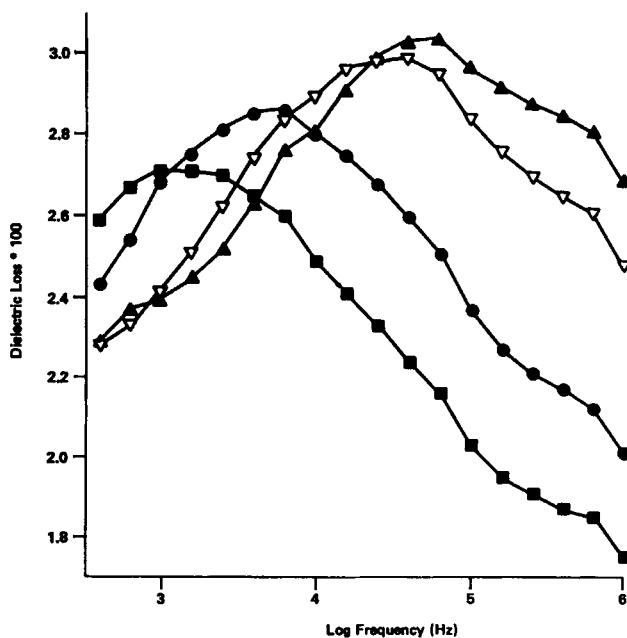


Fig. 8. Temperature domain dielectric loss spectra of composite samples undergoing a 1.13 wt% gain following submersion in 2 M HCl: (■) -30°C ; (●) -20°C ; (▽) 0°C ; (▲) 10°C .

saturated NaOH solution presumably resulted from the lower water activity in this system. Changes in the loss spectrum were reversible upon drying, suggesting little or no change in the polar functional group characteristics occurred during submersion.

Submersion in a concentrated HCl solution resulted in a 1.39% weight gain and a relatively highly conductive epoxy matrix. In this case, the concentration of protonated functional groups or free acid apparently became large enough to allow a proton hopping or a migration charge transfer mechanism.

CONCLUSION

The dielectric loss behavior of a dicyandiamide-epoxy based composite was examined following adsorption of several organic solvents. Dielectric loss behavior following solvent uptake showed that solvent participation in epoxy polar group relaxation, and presumably the degree of interaction between adsorbed solvent and epoxy polar groups depends strongly on the solvent adsorbed. Interactions were weaker for all solvents studied than those involved in moisture adsorption. Some solvents, including methanol and chloroform, strongly reduced the composite direct current resistance and distinctly lowered the Arrhenius relaxation activation energy. Others, such as carbon tetrachloride, improved loss peak definition probably as a result of increased epoxy polar group homogeneity. Composite dielectric behavior following evaporation/drying of each of the adsorbed organic solvents was not detectably different than that of the original dry composite.

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