Effect of Moisture Sorption on ac Properties of Glass–Epoxy Composites

K. DOUKKALI and Y. SEGUI, *Laboratoire de Génie Electrique (UA CNRS), Université Paul Sabatier, 118, Route de Narbonne, 31062 Toulouse Cedex, France*

Synopsis

Alternating current responses of fiberglass-reinforced epoxy composites have been studied as a function of frequency (10 Hz to 100 kHz) and temperature (−30 to 100°C). At higher water content, permanent defects are created presumably at the fiber–matrix interfaces as the temperature goes down to 0°C. These defects increase significantly the dielectric losses. A recovery of the initial state is possible under thermal annealing above the glass transition temperature of the epoxy resin.

INTRODUCTION

In several domains, composite materials have received increasing attention. Many works have been done mainly on their mechanical properties[1,2,5] because the introduction of fillers in polymeric matrix improves its mechanical behavior. Compared to this research area, relatively less attention has been paid to their electrical properties.[4,6] This work is concerned with the electrical behavior of glass-fiber-reinforced epoxy resin. There are at least two reasons to improve our knowledge in this field. The first one is that some situations in which this material is used involve an electric field applied to the composite, and then the knowledge of its response to this stress is a major requirement. This is, for example, the case of insulators in multilayer circuit boards. The second and more general reason is concerned with the search for nondestructive tests to check the quality of composite materials and if possible to find some warning indicating the presence of defects or microcracks that could later lead to a breakdown (mechanical or electrical).

These defects are often located at the interface between matrix and fillers and are very difficult to detect before a catastrophic failure. Electrical responses are believed powerful in giving this new insight because they can be very sensitive to a local change in electrical properties. Furthermore, they could be controlled to a large extent by interfacial phenomena. Microelectronics gives examples that support this last argument. Alternating current responses (C–V curves) of MOS (metal oxide semiconductor) structures are almost completely controlled not by the bulk properties of oxide and silicon but by the electronic behaviors at the interface between these two components.

In this work ac responses at frequencies between 100 Hz and 100 kHz have been recorded on epoxy–glass composites. Two composite dielectric responses may be detected depending on experimental conditions, especially the water content of samples. Temperature was found to be a good parameter to emphasize

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the effect of water on dielectric responses, and finally it was shown that the clusters of water molecules at the interface between the epoxy matrix and glass fibers can induce defects when the temperature is lowered to 0°C. Dielectric losses measurements are able to display the presence of these defects.

EXPERIMENTAL

The samples used in this study were prepared from preimpregnated woven -satin 8-. The base resin was epoxy 1452 from Ciba-Geigy. We have used a thickness of 1 mm, the minimum that the manufacturing mode would permit.[1,2]

Composite samples are usually stored in a dry environment at 4°C. Prior to each measurement, the sample is cured for 16 h at 80°C. The two faces are metallized with aluminum by evaporation under vacuum. The electrode diameter is about 2 cm.

For dielectric measurements, the samples were placed between identical polished stainless steel electrodes. The system was then introduced into a chamber which allowed the temperature to be varied from 600°C to −180°C. In the frequency range (100 Hz–100 kHz), a wide temperature range is unnecessary in the study of the glass-fiber reinforced composite. Our temperature range has therefore been limited to −40°C and 100°C.

Usually measurements are made from the higher temperature (100°C in our case) to the lower in steps of 10°C. The temperature was controlled to an accuracy of 0.1°C. Prior to each measurement, the samples were allowed to equilibrate between 15 and 20 min at each temperature.

The capacitance and the dissipation factors of the composites were measured by a General Radio type 1689 bridge operating over a frequency range from 100 Hz to 100 kHz. The complex permittivity of a dielectric is given by the well-known expression[5,6]

$$\epsilon^* = \epsilon' - j\epsilon''$$

For the electrode configuration used in this study, a parallel plate approximation could be assumed. With this assumption experimental values can be related to the dielectric constant (real part) and dielectric loss (imaginary part) by the simple equation

$$\epsilon' = \frac{d}{S\epsilon_0} C$$

$$t_g(\delta) = \frac{\epsilon''}{\epsilon'}$$

where d is the sample thickness, S is the area of the electrode, ϵ_0 is the dielectric constant of free space, C is the measured capacitance, and $t_g(\delta)$ is the dissipation factor.

RESULTS AND DISCUSSIONS

Series of measurements were made on several samples in order to ensure the reproducibility of the dielectric response in the frequency and temperature ranges used. We have observed that the recorded responses fall into two categories by virtue of the characteristic shape as well as the magnitude of the dielectric loss $\epsilon''(\omega)$. The first category will be classified as normal behavior and the second as abnormal behavior.

Normal Behavior

In an attempt to further define the nature of the relaxation processes occurring in these systems, the dielectric constant and loss were examined as a function of frequency at various temperatures (Figs. 1 and 2). We have not presented all the curves at each temperature for ease of presentation. We note that the dielectric constant remains nearly the same in this frequency range, whereas for a range of temperatures between 55 and −40°C a change of about 15% in the dielectric constant can be observed. Dielectric loss in this zone indicates the existence of a relaxation. The plot of dielectric loss as a function of temperature at a fixed frequency shows a widely distributed loss peak (Fig. 3). For example, the loss peak was centered at −18.5°C for measurements made at 10 kHz, and the activation energy calculated from the Arrhenius plot was $E_0 = 0.48$ eV (Fig. 4).

A brief review of the literature on dielectric responses of epoxy resin and its composites,[3-5] shows that the same relaxation was exhibited in these materials. However, since the relaxation process in the present system was found to be fairly independent of the presence of reinforcement, it was assumed that the intensity of the relaxation peak in the composite depends on the volume fraction of the resin.

According to the works already published, this relaxation was associated with polar side groups or segmental motion like the glyceryl units in the epoxy resin.[3,6-8]

$$-O-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-$$

At high temperature, dielectric constant and dielectric loss (Fig. 5) increase rapidly with increasing temperature from 80°C. Two interpretations may be advanced to explain this behavior.

First, from 80°C the increase of dielectric constant and loss can be associated with glass transition of the composite, which results in the orientation of larger segments of molecular chain. This transition concerns particularly the epoxy resin, which generally has a glass transition temperature at about 100°C.[9-12]

Second, a charge transport, in particular ionic, is allowed by increasing temperature.[6] The phenomenon of charge transport can be sensitive to temperature both by thermally activated processes or by the motion of the molecular chain, which enhances carrier motion. This leads to an interfacial polarization. The simultaneous increase of dielectric constant and loss is in agreement with Maxwell–Wagner theory, which is usually accepted for the interpretation of the interfacial polarization.

Abnormal Behavior

The second behavior of the composite samples, which we refer to as abnormal, was observed at low temperature on incured samples.

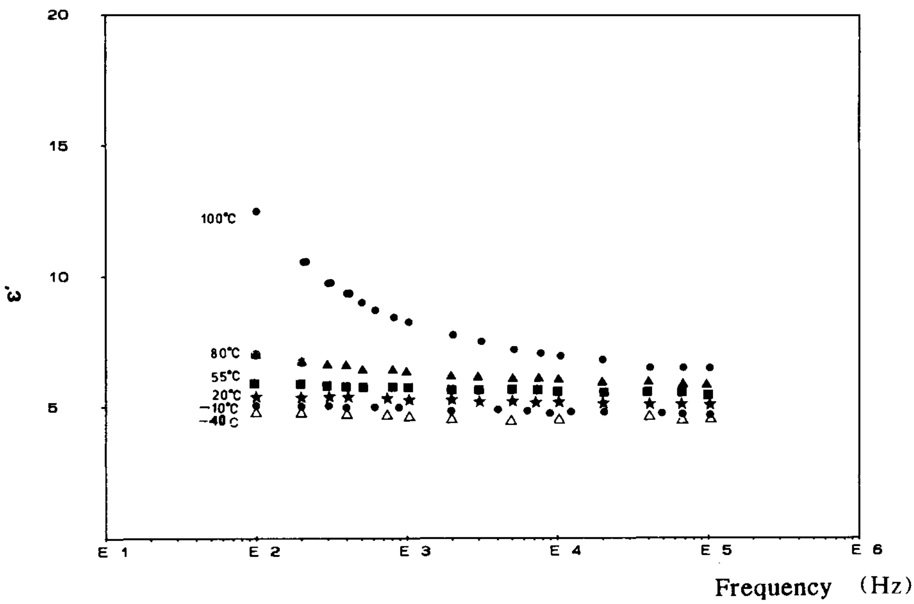

Fig. 1. Dielectric constant as a function of frequency at various temperatures: (●) 100°C, (▲) 80°C, (■) 55°C, (○) −10°C, (△) −40°C.

During measurement at low temperature, we observed an increase in dielectric loss as the temperature decreased (Fig. 6), whereas the dielectric constant maintained the same feature as in the normal samples (Fig. 7). Figure 8 shows

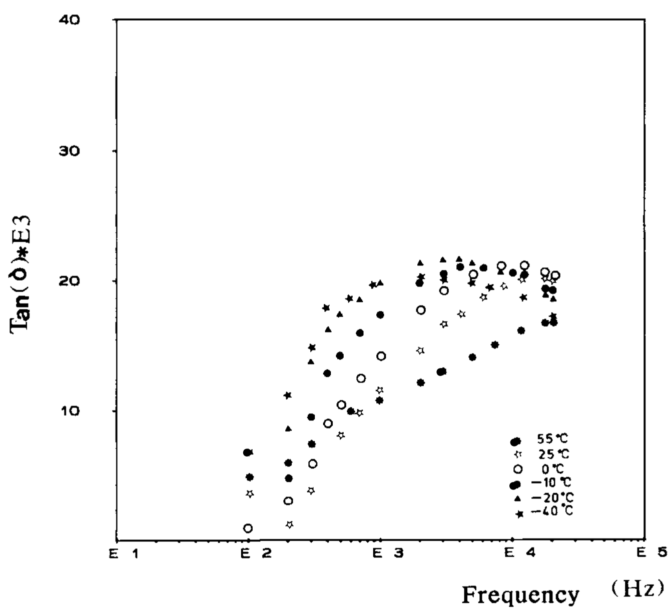

Fig. 2. Dielectric loss [$t_g\delta$] as a function of frequency at various temperatures: (*) 55°C, (☆) 20°C, (○) 0°C, (•) −10°C, (▲) −20°C, (★) −40°C.

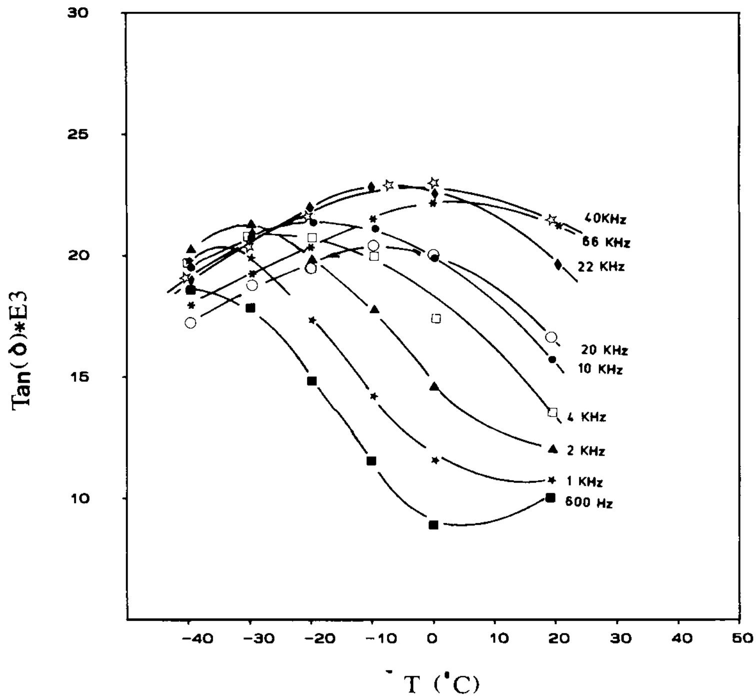

Fig. 3. Dielectric loss $[t_g\delta]$ as a function of temperatures at a fixed frequency: (■) 600 Hz, (★) 1 kHz, (▲) 2 kHz, (□) 4 kHz, (•) 10 kHz, (○) 20 kHz, (♦) 22 kHz, (☆) 40 kHz, (*) 66 kHz.

the dielectric loss for the abnormal behavior at 2 kHz during a cycle of temperature between −30 and 100°C; the increase of dielectric loss appeared especially from 0°C[13] and sometimes at lower temperatures. This phase of the

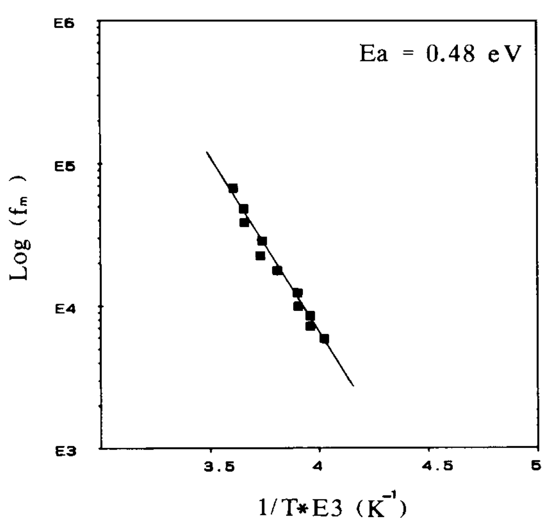

Fig. 4. Arrhenius plots of the dielectric loss maxima f_{max} obtained from Fig. 3.

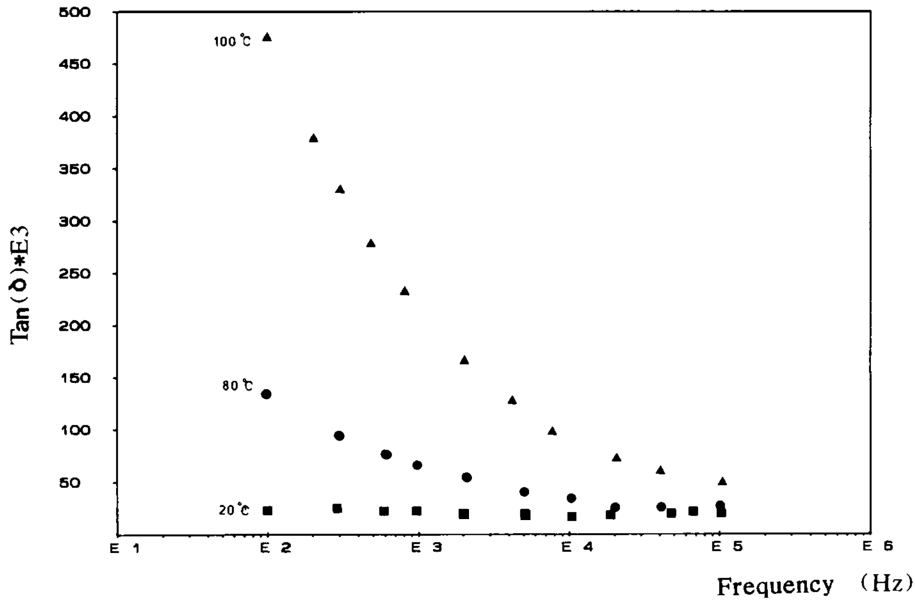

Fig. 5. Dielectric loss as a function of frequency at temperatures of 100, 80, and 20°C.

dielectric behavior is represented between points A and B. When the samples were reheated from −30°C to room temperatures, the increase in temperature was accompanied by two processes:

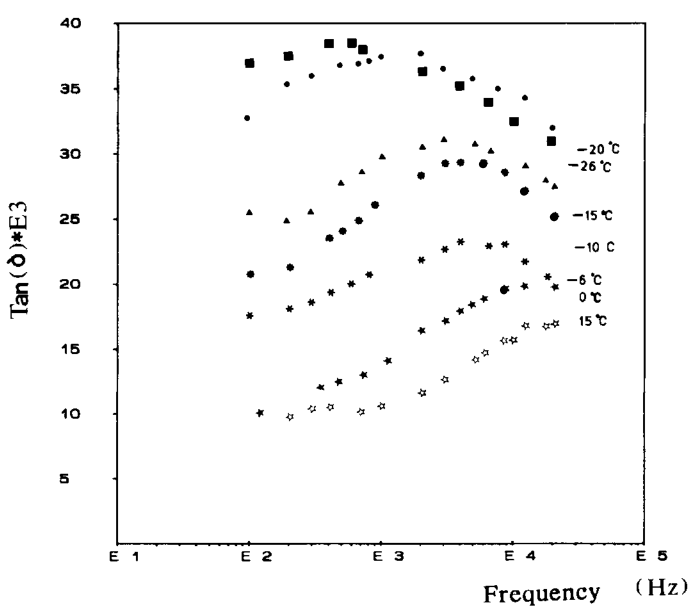

Fig. 6. Dielectric loss as a function of frequency at several temperatures for abnormal behavior: (☆) 15°C, (★) 0°C, (°) −6°C, (°) −10°C, (▲) −15°C, (•) −20°C, (■) −26°C.

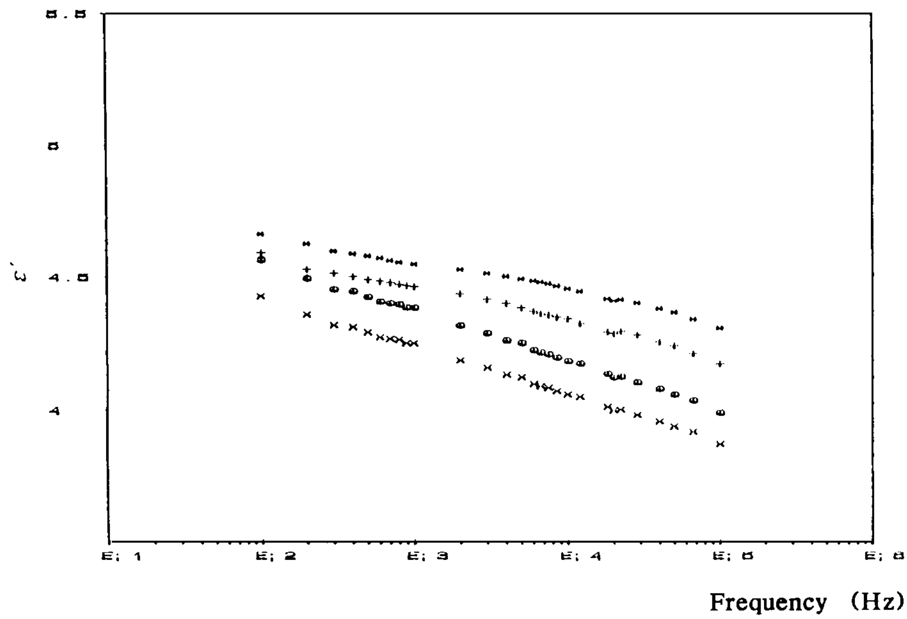

Fig. 7. Dielectric constant as a function of frequency at several temperatures for abnormal behavior: (⋈) 20°C, (+) 0°C, (Φ) −20°C, (×) −30°C.

1. The magnitude of the loss level remained the same at low temperatures and did not follow the same path during increasing as during decreasing temperature (the return trajectory from point *B* to point *C* is different from the path taken from point *A* to point *B*).

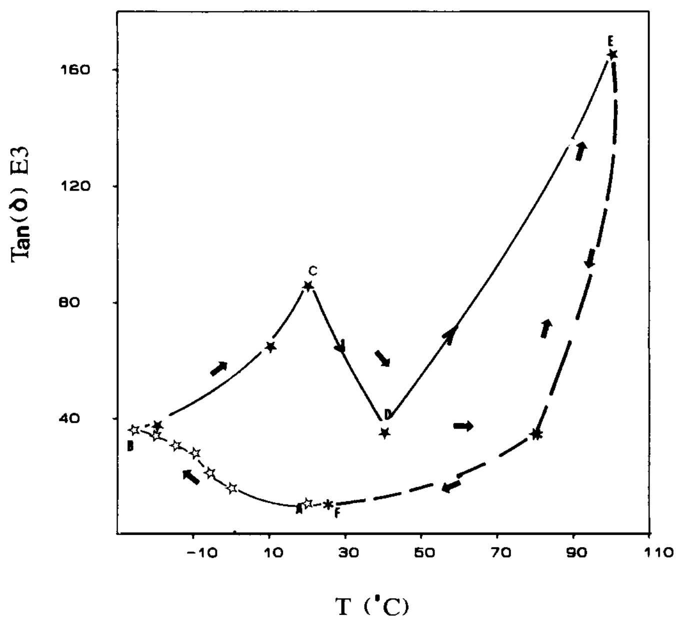

Fig. 8. Dielectric loss at 2 kHz for abnormal behavior (from 20 to −30°C and from −30 to 100°C).

2. An additional increase in loss between 0 and 20°C (represented by the point C).

An annealing at 40°C allowed samples to recover the loss level they had at −30°C (points D and B, respectively), and an annealing at a temperature higher than 80°C (point E) was necessary to recover the loss level in virgin samples (point F).

We are particularly interested in the abnormal behavior in order to understand it and to give an interpretation related to the change of the material structure. The abnormal behavior occurs below 0°C. It is suspected that moisture plays a major role in the observed phenomenon.

The first verification we did was to evaluate the water content in our composite samples. The amounts of water content for uncured samples were between 0.7 and 0.8% by weight. The measurements were made with the aid of a DuPont 902 moisture analyzer.

To confirm the effect of moisture on the observed behavior, the experimental process was repeated under vacuum conditions.

The samples were annealed at 80°C for 16 h and then kept at vacuum for 5 days. Indeed, this treatment has a notable effect. The moisture concentration was evaluated this time at lower than 0.01% by weight. Interestingly, the measurement at vacuum (Figs. 9 and 10) revealed a decrease of loss values with a good reversibility during thermal cycle between 100 and −30°C. The reproducibility of results from sample to sample was remarkable.

From published works and experimental results, the dielectric behavior of polymer, materials or composite polymer matrix was affected by the presence of water,[4,14] according to its distribution mode in the bulk material.[15,16]

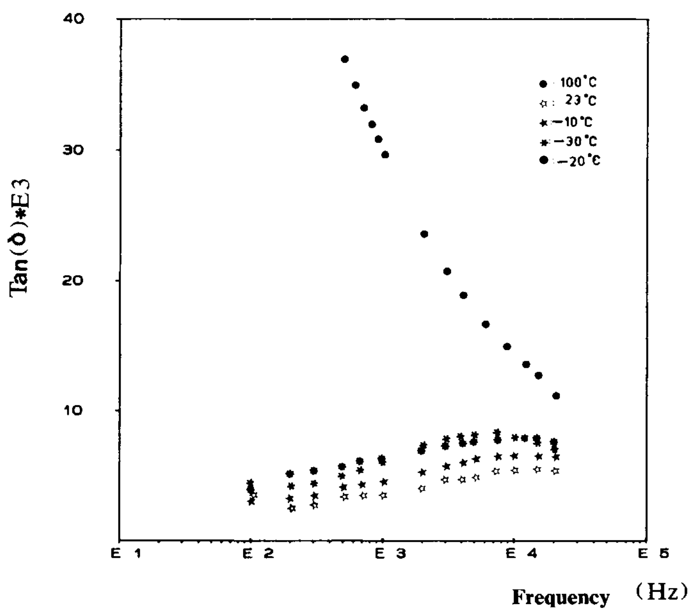

Fig. 9. Measurements made at vacuum. Dielectric loss as function of frequency at several temperatures: (●) 100°C, (☆) 23°C, (★) −10°C, (°) −20°C, (*) −30°C.

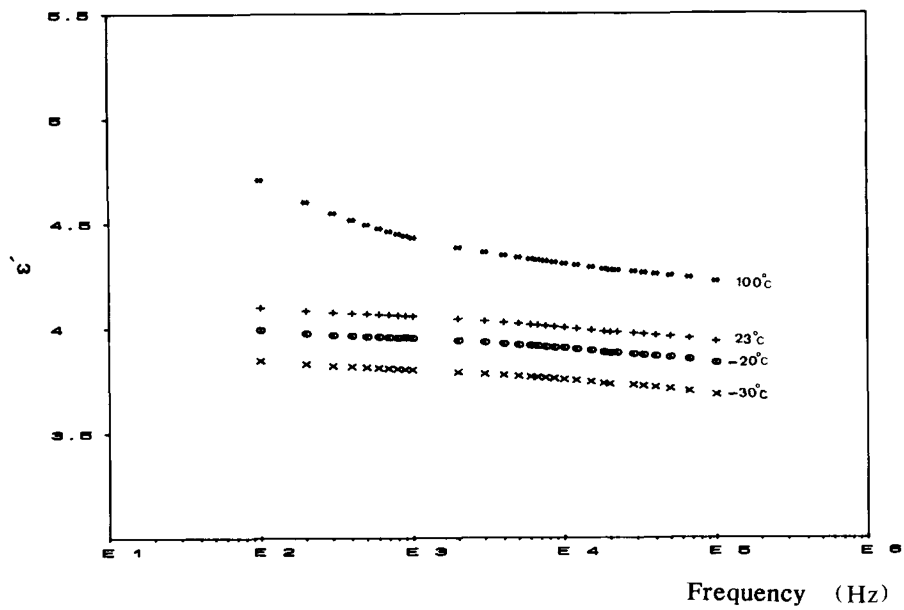

Fig. 10. Measurements made at vacuum. Dielectric constant as a function of frequency at various temperatures: (*) 100°C, (+) 23°C, (Ⓓ) −20°C, (×) −30°C.

We had noted that dielectric loss of the epoxy–glass composite increases with exposure time and temperature to a relative humidity (85% RH). The variations of the dielectric loss is represented in Fig. 11, where they obey Fick's law of diffusion.

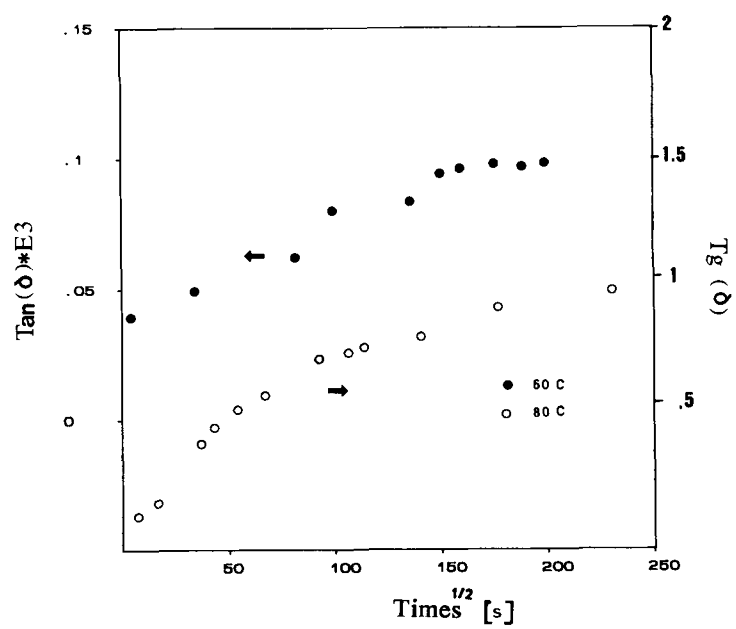

Fig. 11. Evolution of dielectric loss as a function of time at 10 kHz.

The interface between matrix and fillers is a rather ill-defined but extremely important part of the composite, which can easily allow the absorption of moisture. The amount of moisture content in the system causes cluster formation. The fact of decay temperature through 0°C allows the solidification of water clusters,[10,14] which increases the volume and induces mechanical stress on the glass–epoxy interface. This interface may be considered as the region where the matrix is bonded chemically or keyed mechanically to reinforcement.[2] Therefore, stress leads to delamination and microcracking in the bulk composite.[17] This is interpreted as an increase in dielectric loss at low temperature.

The additional increase in loss at about room temperature is believed to be associated with the presence of absorbed water within defects at the interface. This is a confirmation that the damage at one interface is caused by adsorped water. This defect persists and does not disappear until annealing at a temperature higher than 80°C. Electrically this is interpreted as a return to normal loss level at room temperature.

It should be remarked that DSC (differential scanning calorimeter) allows the detection of glass transition of our composite at about 86°C (Fig. 12). Hence, it can be seen in this particular case that delamination or microcracking can be eliminated since the polymer matrix can flow and allow a return to the initial state.

Defect Modeling in the Composite

Within the context of low-temperature abnormal behavior of the glass–epoxy composite, we have carried out an electrical modeling of this system. We have electrically represented the microcracks or delamination in such a way that they could explain an increase in the dielectric loss in the material.

To account for the increase in the dielectric loss at low temperatures (which we have associated with microcracks or delamination), we have advanced and hypothesis based essentially on the presence of accumulated moisture at glass–epoxy interfaces. Thus we introduce in the model the appropriate electrical representations of the different constituents: epoxy, glass, free water, ice, and microcraks, which are present in the whole system. A modeling of microcraks is necessary because the transition of water into ice, which is reversible, cannot explain the permanence in the high level of dielectric loss, and hence a consideration of the mechanical damage at the interface is necessary.

We consider the composite material as a combination of several layers of epoxy and glass. Each glass layer is held between two epoxy layers. The glass layer is 20 μm thick, whereas the epoxy is 180 μm thick.

Each glass or epoxy layer will be represented by a resistance in parallel with a capacitance, and the whole system will be treated as a combination of admittances in series. The admittance associated with each constituent is given (for the ith constituent) by

$$Y_i = \frac{1}{R_i} + i\omega C_i$$

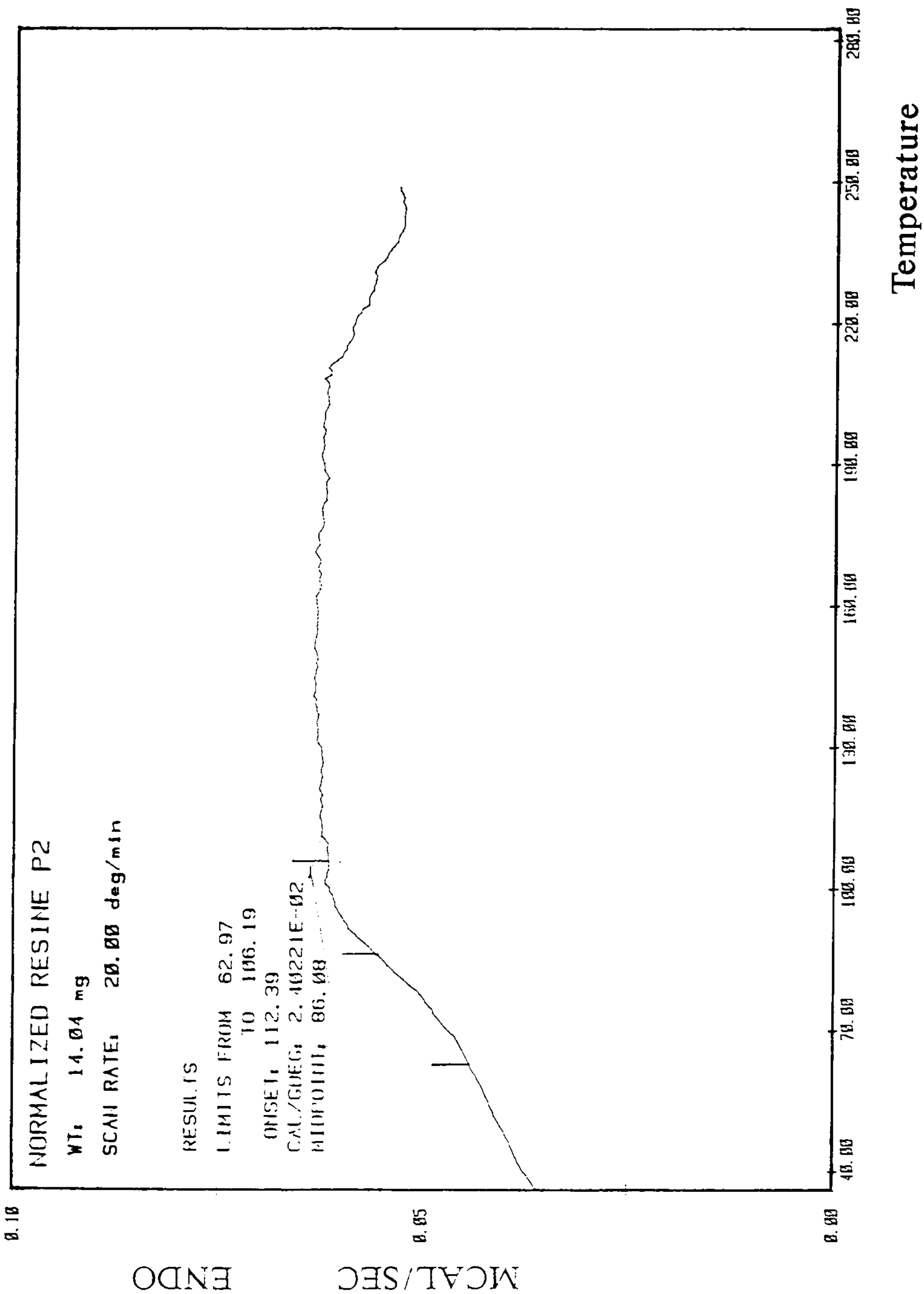

Fig. 12. Differential scanning calorimetry (DSC) of the composite (glass-fiber–epoxy resin).

This can also be written as a function of ϵ_i, σ_i, and d_i

$$Y_i = \frac{\sigma_i}{d_i} S + i \frac{\epsilon_0 \epsilon_i}{d_i} S$$

where S = area of the electrode
σ_i = conductivity of the samples
ϵ_i = dielectric constant of the samples
d_i = thickness of the samples

The total admittance of the system is of the form

$$Y = \frac{\prod^{n} Y_i}{\sum^{n} Y_i}$$

The total admittance of the system can also be obtained from the given values of σ, ϵ, and d for the whole system:

$$Y = \frac{\sigma_s}{d} + i\omega\epsilon_0(\epsilon' - i\epsilon'') \frac{s}{d}$$

The system can then be described by the Debye equations with permittivity limits given by:

$$\epsilon_s = \frac{d[\sum_i (d_i \epsilon_i / \sigma_i^2)]}{[\sum_j (d_i / \sigma_i^2)]}$$

$$\epsilon_\infty = \frac{d}{[\sum_i (d_i / \epsilon_i)]}$$

$$\sigma = \frac{d}{[\sum_i (d_i / \sigma_i)]}$$

From the conductivity and permittivity values of each constituent found in the literature,[18,19] the previous equations have enabled us to calculate the limiting values of permittivity ϵ_s and ϵ_∞.

We have observed that the measured values of the samples' permittivity range in the interval $[\epsilon_s, \epsilon_\infty]$ as calculated in Table I. This may be a satisfactory means of justifying our calculation procedure.

Figure 13 shows the theoretical curves of the dielectric loss as a function of frequency according to the composition of the composite system. Curve 1 shows the dielectric loss of the system when it is composed of glass and epoxy layers. Curve 2 shows the case of water layers introduced between glass and epoxy layers. Curve 3 shows the case of the frozen water layers introduced between glass and epoxy layers.

TABLE I
Calculations of ϵ_s, ϵ_∞, and σ of the Composite from Various Combinations of the Dielectric Response of Glass, Water, and Epoxy

σ_{glass} (Ω-m)	ϵ_{glass}	σ_{epoxy} (Ω-m)	ϵ_{epoxy}	σ_{H_2O} (Ω-m)	ϵ_{H_2O}	Calculations ϵ_s	ϵ_∞	σ (Ω-m)
10^{-15}	6.5	10^{-14}	4	—	—	18.82	4.12	5.81 10^{-15}
10^{-15}	6.5	10^{-13}	4	—	—	65.4	4.12	1.12 10^{-12}
10^{-15}	6.5	10^{-14}	4	10^{-4}	80	19.23	4.2	5.88 10^{-15}
10^{-15}	6.5	10^{-14}	4	10^{-6}	6	19.23	4.15	5.88 10^{-14}

The curves show clearly enough the influence of the presence of water or ice on maximum dielectric loss. A shift in this peak toward higher frequencies can be observed. However, this model cannot explain the irreversible increase in dielectric losses demonstrated experimentally in the lowering of temperature, since the water–ice transition is reversible.

Defects such as microcracks or delamination can produce sites or charges giving rise to a conduction process in the material. Hence, they can be conveniently represented in the model by a resistance in parallel in the *RC* circuit of the epoxy layer.

The theoretical curves obtained in this case are shown in Figure 14. Curves 1 and 2 represent, respectively, the dielectric response of the glass–epoxy system without (1) and with (2) defects. These curves show that the presence of defects in the epoxy–glass composite causes an increase in the dielectric losses, which are now irreversible owing to the presence of defects in the material. It should be noted that the increase in losses will be eliminated only with an elimination

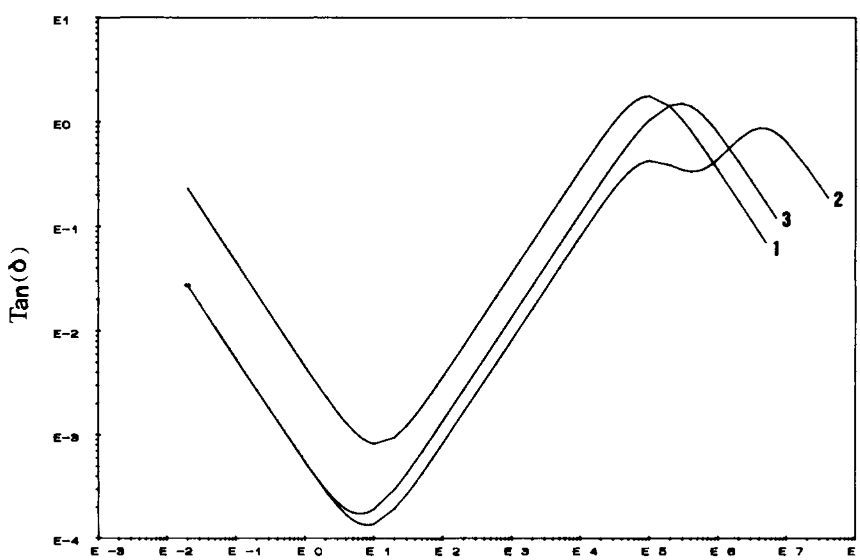

Fig. 13. Dielectric loss as a function of frequency: (1) epoxy–glass, (2) epoxy–water–glass, and (3) epoxy–ice–glass.

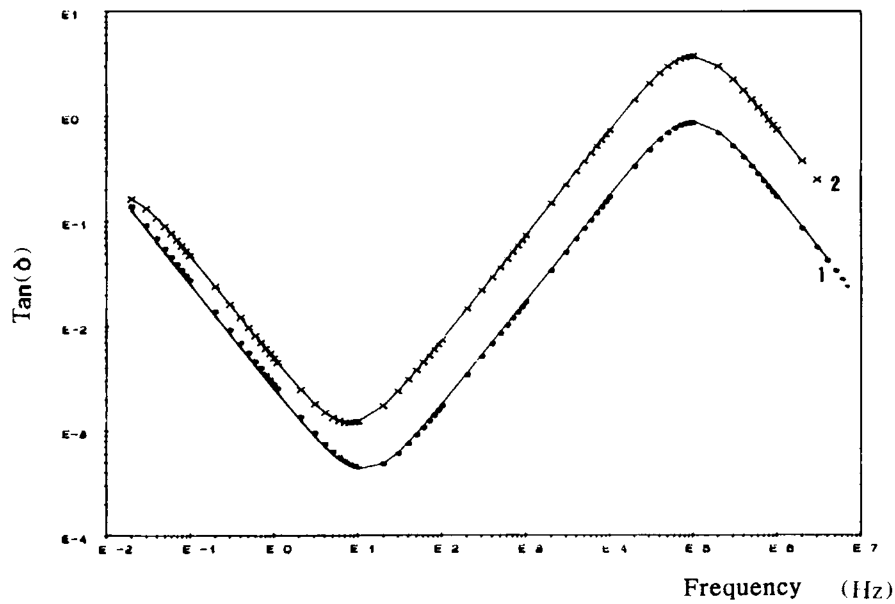

Fig. 14. Dielectric loss as a function of frequency: (1) epoxy–glass and (2) epoxy–glass + cracks.

of the defects. The calculated curves of dielectric losses obtained from this model are in good agreement with the increase of experimentally observed dielectric losses, when the temperature goes down to 0°C, generating defects by freezing out the absorbed water.

Moreover, this model can give the variation of permittivity with frequency. In good agreement with experimental results, ϵ' is nearly constant in the frequency range 10 Hz to 100 kHz, which is the domain experimentally checked.

CONCLUSION

The study of dielectric responses of glass-fiber-reinforced epoxy resins has suggested two kinds of behavior. At low moisture content and in the range of frequency and temperature presented in this work, the dielectric response is controlled by the epoxy matrix. Dipolar relaxation involving polar side groups or segmental motion takes place.

At higher moisture content (0.8%) and low temperature, water clusters induce microcracks that in turn contribute to the dielectric losses. A recovery from these defects is possible by thermal annealing above the glass transition temperature of the epoxy resin.

If our interpretation is correct, this work would give evidence that dielectric measurement could provide a nondestructive test of the quality of the interface between a polymeric matrix and mineral fillers.

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