Effect of a Filler on the Dielectric Properties of an Epoxy Resin

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Synopsis

The effect of aluminum hydroxide upon the dielectric properties of an epoxy resin has been studied in a wide frequency and temperature range. An interfacial polarization effect, known as the Maxwell–Wagner–Sillars polarization, is evidenced for the filled resin, which shows a higher permittivity, a higher dielectric loss, and a β transition with a larger relaxation time. The glass transition temperature is, on the contrary, mostly unaffected by the presence of the filler.

INTRODUCTION

Epoxy resins, like many other polymers employed as electric insulators, are often filled with inorganic materials in order to achieve an improvement either in the processing or in some properties, particularly mechanical and electric.[1] More particularly, aluminum hydroxyde is widely used as a filler in epoxy resins, both allowing good control of the viscosity and therefore better moldability and improving the antitracking properties and the flame resistance.[1,2]

On the contrary, other properties of the polymer matrix can be changed negatively: for instance, a slight worsening of the dielectric characteristics can occur.

In this work the effect of the aluminum hydroxyde upon the dielectric properties of an epoxy resin has been studied in a wide frequency and temperature range. Changes in the dielectric properties have been correlated with the structural modifications due to the presence of the filler.

EXPERIMENTAL

The polymer used in this work was a cycloaliphatic epoxy resin mixture made out of Lekuterm X100 and Lekuterm KV 6552, cured with Lekuterm H; Desmorapid DB was employed as a catalyst. Both the resins and the catalyst are commercial products from Bayer.

The resin was filled with aluminum hydroxide, Baco FRF. The concentration of the filler was 60% w/w. The filler had a spherical shape with a mean dimension of 11 μ.

Dielectric tests were performed with an AC GenRad, Model 1620A, Capacitance Measuring Assembly.

Samples approximately 0.1 cm thick were held in a modified three-terminal Tettex cell, Model 2904.
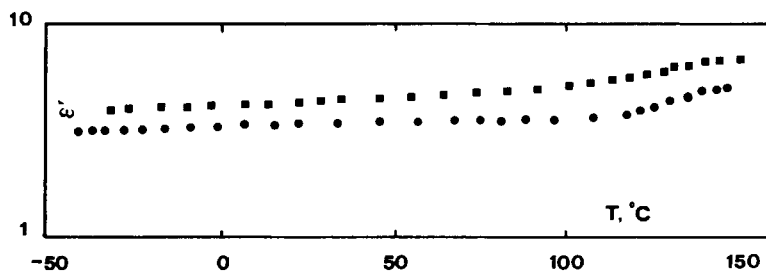
Fig. 1. The dielectric constant as a function of temperature at 1 kHz.

In order to avoid any influence of moisture, the samples were stored in a vacuum desiccator in presence of silica gel for at least 3 days before the tests. These were also carried out in a moisture-free atmosphere by means of silica gel and under vacuum.

The frequencies considered in the experiments were 60, 100, 200, 400, 1000, 2000, and 10,000 Hz; the temperature was varied in the range −40–160°C. The low temperatures were obtained by means of liquid nitrogen poured into the cell, which was then heated at a rate of about 1°C/min.

DC conductivity measurements were performed as a function of time with aid of a teraohmmeter Hewlett-Packard, Model 4329A, and of the same three electrodes cell. These tests were performed at 30°C.

RESULTS AND DISCUSSION

The dielectric properties, permittivity, dissipation factor, and dielectric loss, of both the unfilled and the filled systems, are reported in Figures 1–3 as a function of temperature at 1 kHz.
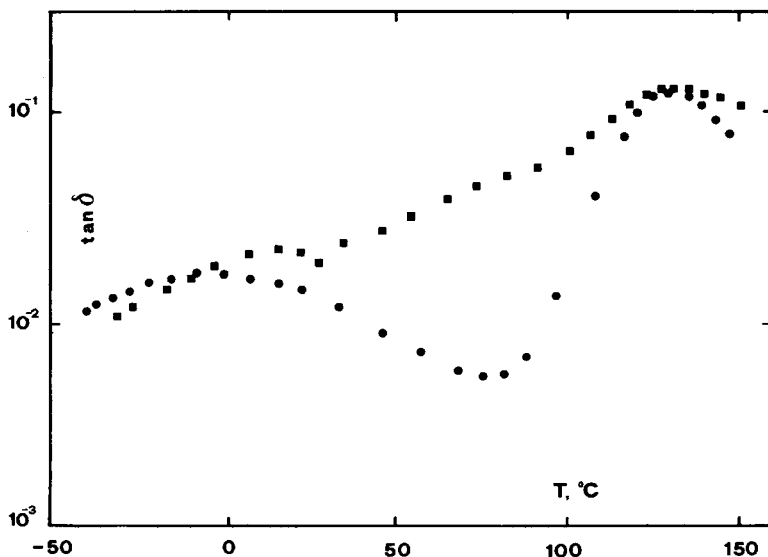

Fig. 2. The dissipation factor as a function of temperature at 1 kHz.
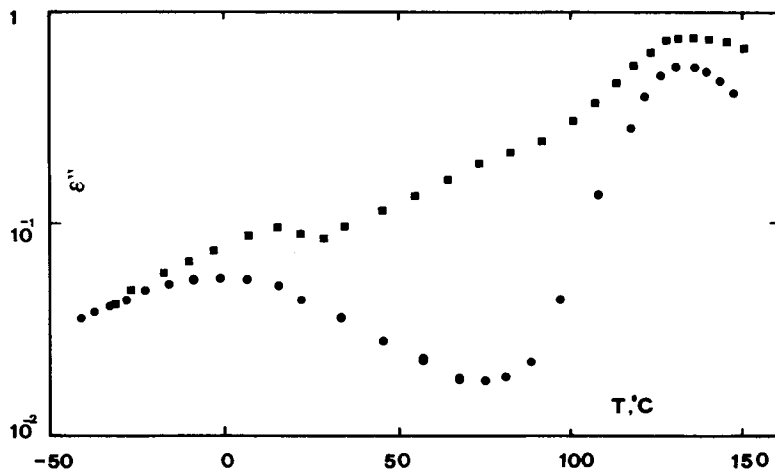
Fig. 3. The dielectric loss as a function of temperature at 1 kHz.

The dielectric constant of the filled polymer is larger than that of the pure resin in the whole temperature range. The behavior as a function of the temperature is, however, for both very similar, with a small gradual increase of ϵ', increasing T.

The tan δ and the ϵ'' curves are, on the contrary, very different. The values are indeed similar at low temperatures but then, while the curve for the filled resin goes up quickly, showing a very small maximum at about 15°C, and goes further to a second maximum, the curve relative to the unfilled resin shows a rather important maximum approximately at −5°C, then decreases reaching a deep minimum at 75°C, and finally goes up to a second maximum. It can be noted that while the first maximum occurs for the filled resin at a significantly higher temperature, the second maximum is approximately at the same temperature for both the unfilled and the filled resins.

Figure 4 further shows dielectric loss values taken at 30°C as a function of the frequency. The data in the low frequency region [Fig. 4(a)] originate from the DC conductivity measurements and have been evaluated by applying Hamon's method.[3] They show a large difference in the values of the filled and the unfilled resin, those of the former being always larger. The difference, however, decreases, increasing the frequency [Fig. 4(b)].

All these features can be explained on the basis of the heterogeneity of the filled epoxy resin. The accumulation of the electric charges at the interface of the two materials having different permittivity and conductivity (the epoxy resin and the aluminum hydroxyde) gives rise to the polarization effect known as the Maxwell–Wagner–Sillars (MWS) polarization.[4] As a result of such an effect, the filled resin shows a higher permittivity and a higher dielectric loss and, moreover, a transition with a relaxation time larger than that due to a typical dipole orientation, as in the pure resin.

The dielectric properties of the heterogeneous system have been shown[5] to obey the well-known Debye equations:

$$\epsilon'(\omega) = \bar{\epsilon}_\infty + \frac{\bar{\epsilon}_0 - \bar{\epsilon}_\infty}{1 + \omega^2 \bar{\tau}^2} \qquad (1)$$

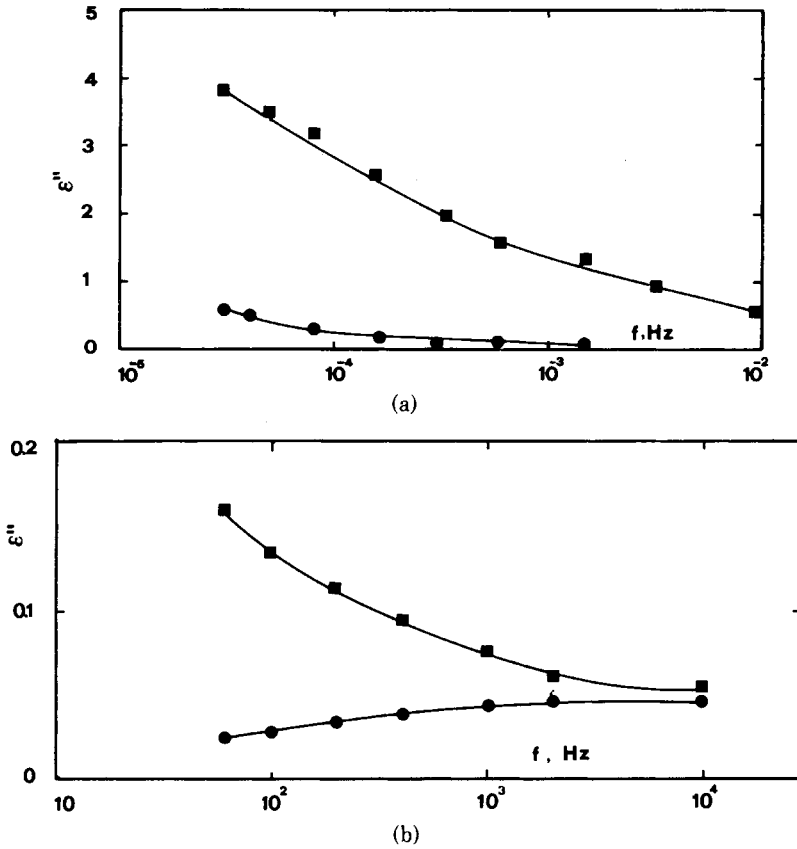LA MANTIA, SCHIFANI, AND ACIERNO

Fig. 4. The dielectric loss as a function of frequency at 30°C: (a) values from DC conductivity measurements; (b) directly measured data.

$$\epsilon''(\omega) = \frac{(\bar{\epsilon}_0 - \bar{\epsilon}_\infty)\omega\bar{\tau}}{1 + \omega^2\bar{\tau}^2} + \frac{\bar{\sigma}}{\omega} \qquad (2)$$

where $\bar{\epsilon}_0$ and $\bar{\epsilon}_\infty$ are the static and dynamic permittivity of the system, $\bar{\tau}$ is the relaxation time, and $\bar{\sigma}$ is the conductivity. Equation (2) shows that the dielectric
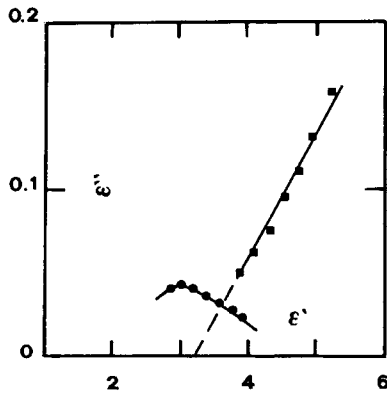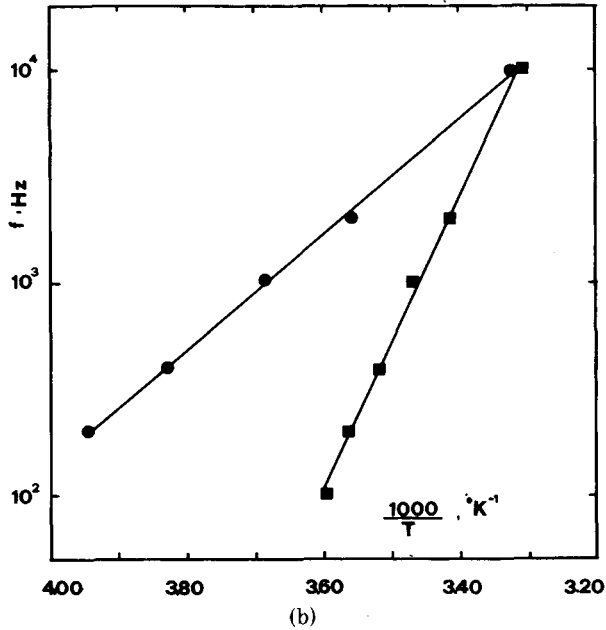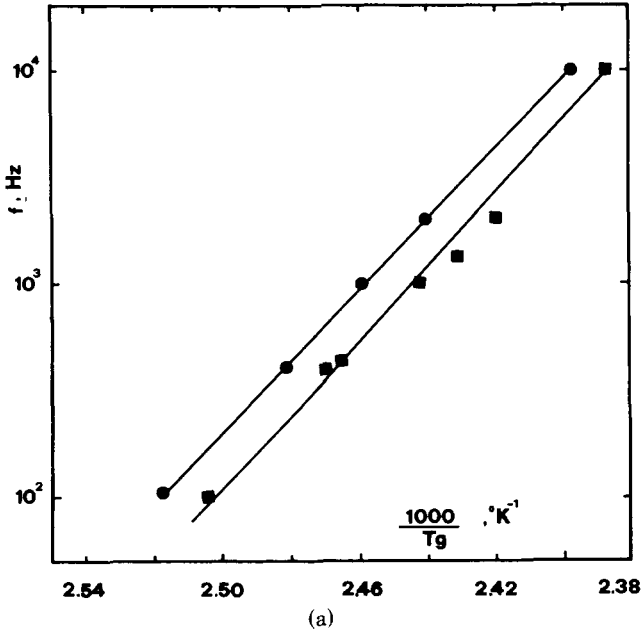

Fig. 5. The Cole–Cole plot.

Fig. 6. A frequency–temperature map: (a) for the α transition (glass transition); (b) for the β transition.

loss ϵ'' decreases quickly with increasing frequency at low frequencies, as also seen experimentally and reported above. This is due to the term $\bar{\sigma}/\omega$. Furthermore, from eq. (1), one expects for heterogeneous systems value larger than those of the homogeneous ones: this is because both $\bar{\epsilon}_\infty$ and ($\bar{\epsilon}_0 - \bar{\epsilon}_\infty$) are larger than the corresponding values of the homogeneous system ϵ_∞ and ($\epsilon_0 - \epsilon_\infty$). This

is confirmed, although the exact values cannot be taken, by the Cole–Cole plot reported in Figure 5. Following Refs. 5–7, the unrelaxed permittivity of the filled resin $\bar{\epsilon}_\infty$ has been calculated through the Hanai–Bruggeman equation valid for concentrated dispersion:

$$\frac{\bar{\epsilon}_\infty - \epsilon'_f}{\epsilon'_p - \epsilon'_f} \left(\frac{\epsilon'_p}{\bar{\epsilon}_\infty}\right)^{1/3} = 1 - v_2 \tag{3}$$

where ϵ'_p and ϵ'_f are the dielectric constant fo the resin and of the filler, respectively, and v_2 is the volume fraction of the dispersed component. The theoretical equation gives a value of 3.15 while the experimentally found value (Fig. 5) is 3.25. The very good comparison confirms the occurrence of the MWS polarization in this system.

Let us finally go back to consider the transition points evinced in the ϵ''–T plots. The maximum at high temperature, which has been already correlated to the glass transition temperature,[8] is only slightly influenced by the presence of the aluminum hydroxyde: this is in fact better seen in Figure 6(a), i.e., a typical frequency–temperature map. And, indeed, one sees that only a slight difference exists between the glass temperature of the two materials and, moreover, that the activation energy is almost the same. On the contrary, the maximum at lower temperature in the ϵ''–T plot is strongly dependent on the inorganic filler. Figure 6(b) shows that such a transition temperature T_β is larger for the filled resin and that also the activation energy is noticeably different.

A possible explanation of the different behavior in the two transitions is that T_g depends only on the motions of large parts of the macromolecules in the amorphous phase, which are certainly similar and perhaps only hindered by the filler, while the T_β is caused by the motions of small polar groups strongly influenced by the mentioned polarization effect due to the inorganic filler.

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