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Dielectric study of hollow microsphere composites

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Composites of epoxy resins filled with hollow microspheres of ceramics, glass and polymer were studied in an attempt to produce a material of low dielectric constant. The accumulation of interfacial water was tested for exposures to 85% humidity at 85 °C for periods of up to 1000 h. Water absorption was monitored by gravimetry and dielectric measurements. With all but one type of microsphere, a dramatic increase of the dielectric constant developed after durations of exposure which were of the order of the Fickian diffusion time of samples of unfilled resin. Unfilled samples, on the other hand, did not exhibit this behaviour. Impedance spectroscopy carried out at frequencies of up to 1 GHz gave evidence for two distinct modes of ionic conduction: about the spheres and across the bulk of the sample. Microspheres of acrylonitrile–vinylidene chloride copolymer in amine-cured epoxy resins did, however, remain stable and therefore yielded a reliably low dielectric constant.

1. Introduction

Materials of low dielectric constant with a good reliability with respect to moisture are required in several advanced applications in digital electronics [1]. They can enter also in the fabrication of radar-absorbing materials [2].

The possibility of lowering the dielectric constant of thermosets by admixing hollow spheres is of interest as an economical way of achieving low dielectric constants compared to using expensive D-glass or Teflon fibres instead of E-glass. This approach has been examined by other workers: workers at Dow Chemicals [3] used glass hollow spheres in Kevlar-reinforced thermoset. The glass spheres were shown to induce a Maxwell–Wagner effect at temperatures of 140–230 °C, due to the conduction in the glass at these temperatures; Toray Industries [4] claimed for the use of any type of hollow spheres (SiO_2, Al_2O_3, ZrO_2, glass, phenolic, carbonaceous materials) to lower the dielectric constant of printed wiring boards; Sumitomo Bakelite [5] patented the use of glass hollow spheres in epoxy resins for potting semiconductor devices; Junkosha Co. [6] used hollow spheres of a copolymer of acrylonitrile–vinylidene chloride in a polyester matrix.

We probed the effectiveness of a variety of hollow microspheres in reducing the dielectric constant of a thermoset composite and tested their resistance to moisture.

2. Experimental procedure

2.1. Samples

Seven types of hollow microspheres were considered (Table I). The D-type spheres are phenolic microspheres and the E-type ones are made of a copolymer of acrylonitrile–vinylidene chloride. The density of the microspheres was measured in our laboratories, except in the case of organic microspheres for which the manufacturers data were used.

Most samples were prepared with the resin labelled SA5, an anhydride-cured bisphenol F epoxy resin (Table II). The E-type microspheres were seen to dissolve in anhydride hardeners. Consequently, two epoxy systems with amine hardeners were tested, labelled SAM2 and SAM4. It was found that the E-type microspheres did not dissolve in these epoxy systems. Mixed with uncured resins, they could also be kept under vacuum at 100 °C without bursting.

The samples were prepared by gradually adding the amount of filler which was to yield a set value of the volume content, as deduced from the densities listed in Table I. The mixture was stirred manually and degassed under vacuum prior to casting in moulds. The moulds were rotated about a horizontal axis perpendicular to the mould in order to minimize sedimentation (floating). The volume content of filler of the

TABLE I Microspheres

Type	Manufacturer	Grade	Density ($g\,cm^{-3}$)
Ceramics	A	–	0.78
	B	–	0.87
Glass	C	CX	0.28
	C	CY	0.22
	C	CZ	0.24
Organic	D	–	0.1
	E	–	0.036

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TABLE II Volume content of filler

Sample	Nominal vol. %	Measured vol. %	Resin
A/H	57	52	SA5
A/B	57	52	SA5
B/B	54	54	SA5
B/H	54	62	SA5
CX/0	50	54	SA5
CX/1	40	40	SA5
CY/1	40	41	SA5
CZ/1	40	37	SA5
CZ/S	–	57	SA5
D/1	55	48	SA5
D/3	55	50	SA5
D/7	48	50	SA5
D/6	32	40	SA5
E/1	40	44	SAM4
E/2	40	43	SAM4
E/4	40	45	SAM4
E/5	40	40	SAM2

Sample CZ/S was not rotated and the plate exhibited clear resin at the bottom. The sample was cut in the top part of the plate, where the microspheres had floated before cure.

finished composite was again deduced from the densities of the sample, the resin and the filler. Good agreement between the nominal and measured volume contents indicate minimal sedimentation or air bubbles in the samples, as shown in Table II. The analysis of the dielectric constant of the composites indicated also that air bubbles did not play a significant role.

2.2. High-frequency impedance measurements

A high-frequency probe head (Fig. 1) was developed in order to measure at frequencies of 1–1000 MHz the samples which were used with a commercial apparatus for measurements at lower frequencies (DETA of Polymer Laboratories Ltd). It is, in essence, a segment of coaxial transmission line in which the inner diameter increases from that of the connector to the size of the electrode on the samples. The outer diameter increases proportionally so that the characteristic impedance of the line remains equal to 50 Ω. The sample terminates the transmission line. The probe head is connected to the terminal of an impedance meter (Hewlett Packard HP4191A). The effect of the length of the coaxial line between the connector of the meter and the sample is simply subtracted out by the instrument itself. The stray fields at the edge of the inner conductor were accounted for by the following procedure. A series of measurements with samples of several thicknesses and dielectric constants revealed that the distortion of the field at the end of the inner conductor can be accounted for by assuming that the end cross-section of the inner conductor is 7% larger than its actual size. Furthermore, the standard formula was used for the correction of stray fields as the edge of a planar circular electrode [7].

The entire probe head was gold plated. The grounding of the piston-type back was established by 50 spring-loaded gold-plated pins pressed against the side wall of the coaxial cell. Measurements of the dielectric constant of materials in the form of plates of 3 cm side, 1–3 mm thick, were measured with a precision of 5%. Dielectric losses greater than 0.005 could be detected reliably.

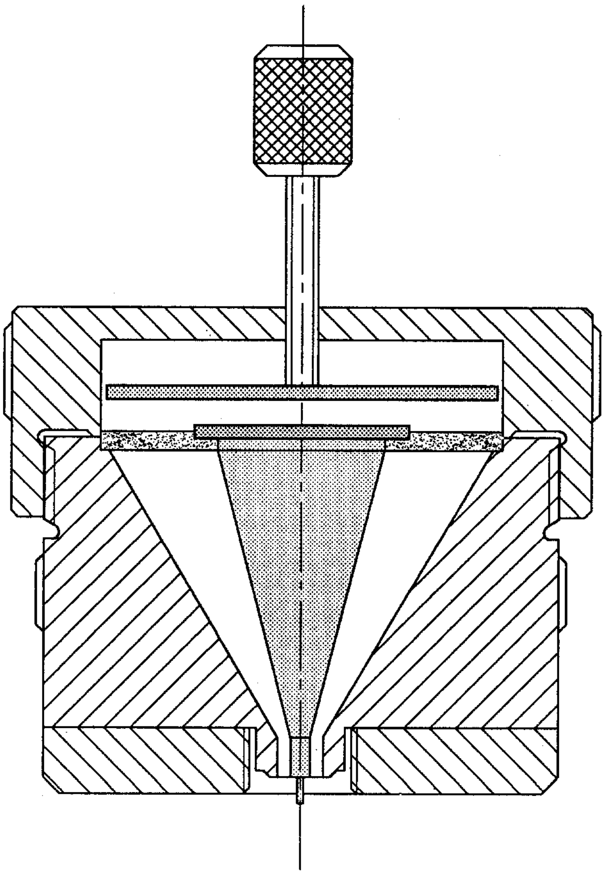

Figure 1 Coaxial probe head used to measure dielectric constant and loss in the frequency range 1–1000 MHz. The sample lies at the end of the inner conical conductor and is pressed with the grounded piston. The wide-top element is unscrewed to access the sample held in place by small spacers.

3. Dielectric constant of dried samples

3.1. Results

The samples were dried for 6 days in vacuum at 100 °C. The dielectric constant was measured at frequencies of 100 Hz–10 MHz. The frequency dependence is small and parallels the frequency dependence of the resin itself (Fig. 2).

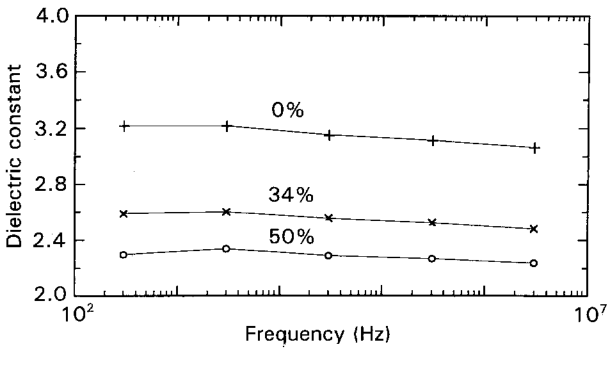

Figure 2 Dielectric constant of samples of epoxy resin (SA5) filled with phenolic hollow spheres (D). The parameter is the volume concentration of spheres. The samples were measured after 3 days in vacuum at 100 °C.

TABLE III Prediction of the dielectric constant of a composite containing hollow spheres

Type	Sample	Properties of the filler					Properties of the composites			
		Density, crushed, ρ_f	Density, whole, ρ_B	Volume fraction of air, (vol %)	Dielectric constant		Dielectric constant of matrix, ε_m	(vol %) V_f	Dielectric constant of composite, ε_{exp}	Dielectric constant of model, ε_{HS}
					Shell (guess) ε_2	Filler (effective) ε_f				
Ceramics	A/H	0.78	2.53	0.69	9	2.9	3.2	52	2.9	3.0–3.0
	B/B							52	2.9	3.0–3.0
	B/B	0.83	2.54	0.67	9	3.0	3.2	54	3.0	3.1–3.1
	B/H							62	2.9	3.1–3.1
Glass	CZ/0	0.24	2.27	0.89	6	1.4	3.2	37	2.5	2.4–2.4
	CZ/S							57	2.1	2.0–2.1
	CX/0	0.28	2.21	0.87	6	1.4	3.2	54	2.3	2.1–2.1
	CX/1							40	2.5	2.3–2.4
	CY/1	0.22	2.37	0.91	6	1.3	3.2	41	2.3	2.2–2.3
Organic	D/1	1.41	0.10	0.93	4	1.1	3.2	34	2.6	2.6–2.9
	D/3							50	2.3	2.1–2.4
	E/1	1.37	0.0036	0.97	3.3	1.1	4.2	43	2.7	2.3–2.6
	E/5						3.7	40	2.5	2.2–2.4

The dielectric constants at 3 kHz of all of the samples are reported in Table III. At the right-hand side, under properties of the composite, the dielectric constant of the composites, ε_{exp}, is to be compared to that of the matrix, ε_m, for the given volume concentration of filler, V_f. In particular, it is found that the ceramics microspheres did not lower significantly the dielectric constant of the composites with respect to that of the resin. The purpose of the model presented in the next section is to show the relative importance of the design parameters of such composites: dielectric constant of the walls of the microspheres, their thickness, and the volume ratio of filler.

3.2. Discussion

A model is presented which can be used to predict the efficiency of microspheres as a means of obtaining low dielectric constants. The results of the model are compared with the experimental values in Table III.

The calculation of the dielectric constant of a composite made of hollow microspheres was carried out in three steps. First the polarizability of a hollow shell embedded in the resin was calculated. Then, the effective dielectric constant, ε_f, which would give rise, for a whole (homogeneous) sphere, to the same polarizability, was deduced. Finally, the upper and lower bounds of Hashin–Shtrikman were used in order to determine the dielectric constant of the composite.

3.2.1. Effective dielectric constant of the filler

The polarizability of a coated sphere is given by [8]

$$\alpha_{\text{shell}} = \frac{(\varepsilon_2 - \varepsilon_m)(\varepsilon_1 + 2\varepsilon_2) + f(\varepsilon_1 - \varepsilon_2)(\varepsilon_m + 2\varepsilon_2)}{(\varepsilon_2 + 2\varepsilon_m)(\varepsilon_1 + 2\varepsilon_2) + 2f(\varepsilon_2 - \varepsilon_m)(\varepsilon_1 - \varepsilon_2)}$$

where ε_1 is the core dielectric constant = 1 (air), ε_2 the shell dielectric constant, ε_m the matrix dielectric constant, and f the volume fraction of air. The polarizability of a homogeneous sphere of dielectric constant, ε_f, is

$$\alpha_{\text{homo}} = 3\frac{(\varepsilon_f - \varepsilon_m)}{(\varepsilon_f + 2\varepsilon_m)}$$

Typical values of ε_2 were used: 9 for the ceramics microspheres and 6 for the glass ones. The dielectric constant of the matrix, ε_m, was measured.

The volume fraction of air, f, is

$$f = (R_1/R_2)^3 \qquad (1)$$

where R_1 and R_2 are the inner and outer radii, respectively. It is deduced from the density of the microspheres measured before, ρ_f, and after, ρ_B, they were crushed in a mill of steel balls

$$f = 1 - (\rho_f/\rho_B) \qquad (2)$$

The parameter ε_f given in Table III can be considered as a quality factor of the filler, characterizing its ability to lower the dielectric constant.

3.2.2. Dielectric constant of the composites

A great number of models has been developed to predict the effective dielectric constant of composites. The upper and lower bounds of Hashin and Shtrikman give a narrow range of values in our case, because the dielectric constants of both components are of the same order of magnitude. The lower bound to the dielectric constant of a composite comprising spheres of dielectric constant ε_f, embedded in a medium of dielectric constant ε_m is given by [9]

$$\text{HS}(\varepsilon_f, \varepsilon_m, x_f, x_m) = \varepsilon_m + x_f \Big/ \left(\frac{1}{\varepsilon_f - \varepsilon_m} + \frac{x_m}{3\varepsilon_m}\right)$$

where x_f and x_m are the volume ratio of filler and matrix, respectively. The upper bound is HS $(\varepsilon_m, \varepsilon_f, x_m, x_f)$. The calculated upper and lower bounds are reported in the column ε_{HS} of Table III and can be compared with the experimental values, ε_{exp}. The volume fraction of filler, V_f, is the value deduced from the density of the samples, the resins and the fillers.

The uncertainty in this calculation is for the most part in the estimate of ε_f, the effective dielectric constant of the filler. The predicted values are within 12% of the measured ones. The prediction tends to be systematically too optimistic: the measured value is higher than the predicted one.

The ceramics microspheres do not reduce significantly the dielectric constant of the composite with respect to the neat resin because the shells are made of a material of fairly large dielectric constant, ε_2, and because the aspect ratio, f, is not particularly large. On the other hand, the glass spheres give better results because their aspect ratio is larger. The performance of E-type spheres arises from the high aspect ratio and the low dielectric constant of the shell material.

This model shows that it is not easy to lower the dielectric constant of a resin with ε in the range of 3–4 by adding a filler of hollow microspheres. Consider the following "best case". The microspheres are made of quartz, so $\varepsilon_2 = 3.7$, with a diameter of 50 μm and a wall thickness of 1 μm. A volume concentration of 50% is necessary in order to reach a dielectric constant of the composite of about 2.0 with resin $\varepsilon_m = 3.2$.

4. Water absorption

4.1. Basic experimental results

Water absorption at 85 °C and at 85% relative humidity was monitored by gravimetry. Its effect on the dielectric constant was studied in the samples containing glass and organic microspheres. The weight gain followed a regular course reminiscent of a fickian absorption (Fig. 3). On the other hand, the dielectric constant at low frequency changed drastically during this absorption process (Fig. 4). The dielectric constant in the final state had a strong frequency dependence, as discussed below. This effect has been observed in all composites, except those made with E-type microspheres. Its origin is discussed next. The case of E-type spheres is discussed last.

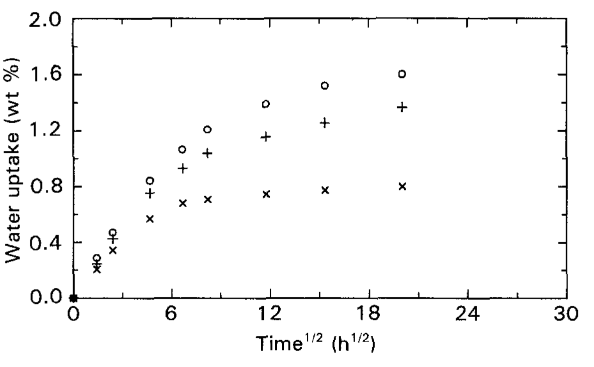

Figure 3 Water uptake as a function of exposure to 85% relative humidity at 85 °C. The samples contain 40 vol % glass microspheres. Their sizes are identical. (O) CX, (+) CZ, (×) CY.

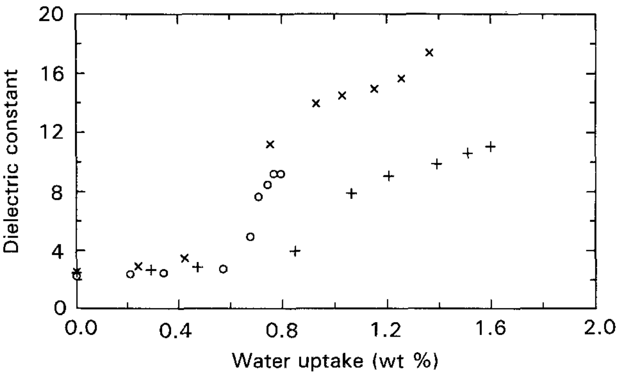

Figure 4 Dielectric constant at 3 kHz as a function of the water uptake reported in Fig. 3. (×) CZ, (O) CY, (+) CX.

4.2. Maxwell–Wagner effect

The absorbed water was found to result in an enormous frequency dependence and a low dielectric constant of the order of 10, much greater than expected with dipolar contributions only. This effect was observed in all samples containing glass (C) and phenolic microspheres (D). The data taken in the frequency range of 100 Hz–1000 MHz display two conspicuous features (Fig. 5): the divergence of the dielectric constant at low frequency and a high-frequency peak of the loss factor. The low-frequency behaviour was strongly dependent on the extent of water absorption at the surface of the sample, which could be varied by keeping the sample under vacuum in the measuring cell. The frequency at the maximum of the loss peak was measured as a function of temperature from + 25 °C to − 35 °C (Fig. 6). An Arrhenius plot of the

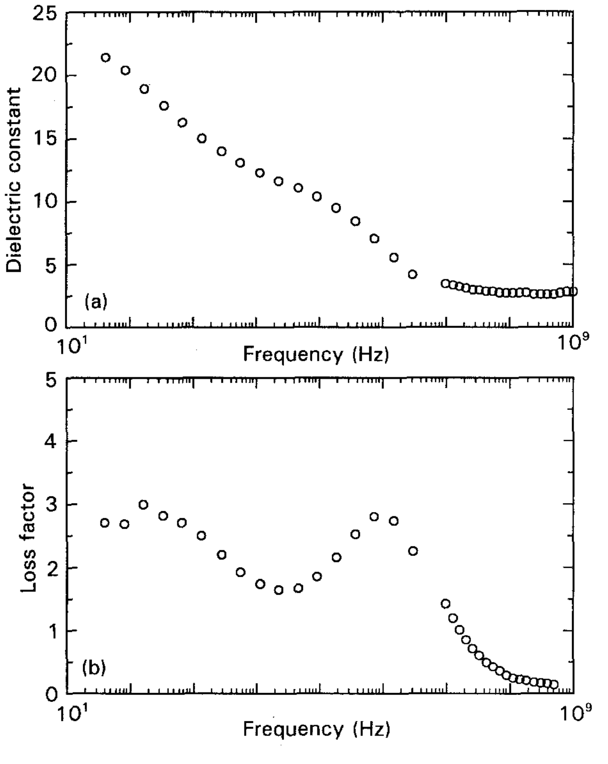

Figure 5 (a) Dielectric constant and (b) loss factor of a composite of glass spheres (CZ) with a water uptake of 1.5%. The samples were kept 1 h in vacuum prior to the measurement.

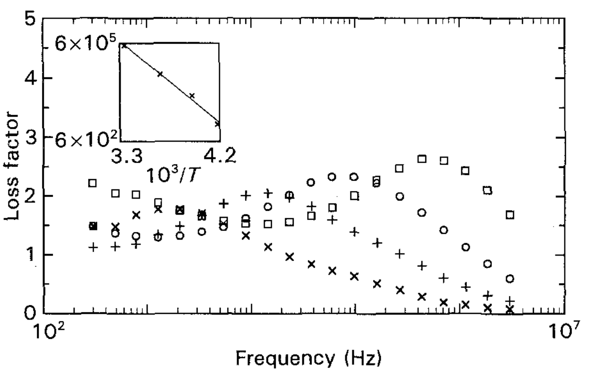

Figure 6 Dielectric loss peak at several temperatures: (□) 26 °C, (○) 0 °C, (+) − 20 °C, (×) − 34 °C (sample of Fig. 5). Inset: Arrhenius plot of the frequency at the peak.

frequency at the peak as a function of temperature yielded an activation energy of 13 kcal mol^{-1} and a pre-exponential factor of about 10^{15} Hz. In comparison, typical values for the diffusion of water in materials such as epoxy resins [10], starch [11] or cellulose [12] are of the order of 6–8 kcal mol^{-1}. The rather large diffusion energy which was found rules out ionic conduction in microcracks at the interface between the filler and the matrix, where water and ions could move freely.

The overall dielectric behaviour (Fig. 5) can be accounted for with a simple model. Conduction of impurity ions in the presence of absorbed water is assumed. It gives rise to a Maxwell–Wagner effect at the interface and to an ionic conduction throughout the sample because the volume content of filler is above the percolation threshold. The drying of the surface, on the other hand, results in a blocking layer. The Maxwell–Wagner formula for the dielectric constant of spheres of conductivity σ, dielectric constant ε_f, dispersed at a volume concentration, Q, in a matrix of dielectric constant, ε_m, can be written in the Debye form [13]

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \qquad (3)$$

with

$$\varepsilon_s = \varepsilon_m \frac{(1 + 2Q)}{(1 - Q)} \qquad (4a)$$

$$\tau = \frac{(2\varepsilon_m + \varepsilon_f)\varepsilon_0}{\sigma} \qquad (4b)$$

$$\varepsilon_\infty = \varepsilon_m \left[1 + \frac{3Q(\varepsilon_m - \varepsilon_f)}{(2\varepsilon_m + \varepsilon_f)}\right] \qquad (4c)$$

where ε_0 is the vacuum permittivity, ω the applied frequency.

The dielectric constant, ε_f, of the filler was taken from the calculation of the effective dielectric constant of the hollow spheres. The loss peak is at $\omega\tau = 1$. Thus, the conductivity of the filler can be deduced from the data to be about 7×10^{-6} S cm^{-1}. This is a typical value, for example for an antistatic material based on hydrophilic antistatic agents. If conduction about the spheres is taking place, then a bulk conductivity must also be assumed. If water is depleted at the surface of the sample, the surface is purely dielectric. The simplest equivalent circuit is a capacitance in series with the parallel combination of the capacitance and a resistance which are determined by the geometry of the sample, the bulk conductivity and the effective dielectric constant given by the Maxwell–Wagner formula. Two parameters must be adjusted: the thickness of the blocking layer and the bulk conductivity of the core. A rough fit to the data was obtained with reasonable values of the thickness (0.5 mm) and the bulk conductivity (5×10^{-9} S cm^{-1}). It is typical for the conduction of a composite above percolation to be 1000 times less than the intrinsic conductivity of the filler [14].

4.3. Dipolar effects

The increase of the dielectric constant due to the presence of the water dipoles in polymeric films has been studied by several groups [15, 16, 17]. These authors found that the static dielectric constant increases linearly with the percentage of absorbed water according to

$$\varepsilon(m) - \varepsilon(0) = 4.0[\varepsilon(0) + 2]^2 \phi\rho m/T \qquad (5)$$

where m is the percentage of absorbed water (wt %), $\varepsilon(m)$ the dielectric constant with m % water, ρ the resin density, T the temperature (K), and ϕ is an experimental factor representing the relative polarizability of a water molecule in the resin with respect to its free state. Assuming the maximum value for $\phi(\phi = 1)$, the increase of the dielectric constant of a resin of $\varepsilon(0) = 3.0$ is 0.4 at room temperature when 1% of water is absorbed ($\rho = 1.2$). Hence the increase of the dielectric constant at 3 kHz to as much as 15 as observed with glass and phenolic microspheres, cannot be of dipolar origin.

On the other hand, composites of type E microspheres are only mildly affected by water absorption. No dispersion of the dielectric constant develops under the influence of water absorption even after 500 h exposure to 85% relative humidity at 85 °C. The dielectric constant increases linearly with the amount of absorbed water (Fig. 7), as predicted by the dipolar

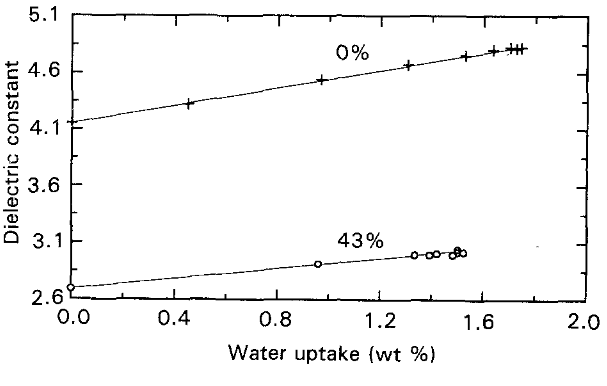

Figure 7 Dielectric constant of amine-cured epoxy resin (SAM4) as a function of the amount of water absorbed at 85% relative humidity, 85 °C. Upper curve, neat resin (SAM4); lower curve, resin with 43 vol % microspheres of type E.

model. The data for the sample of neat resin yield $\phi = 0.8$, which is a typical result [16]. This value of the relative polarizability accounts for the increase of the dielectric constant of the composite of E-type spheres with water uptake.

5. Conclusion

Our evaluation of hollow microspheres can be summarized as follows.

1. Ceramic microspheres did not lower the dielectric constant significantly. The walls of the spheres were not thin enough, compared to their radii, for the low dielectric constant of the air contained in them to offset the large dielectric constant of the ceramic walls.

2. Glass and phenolic microspheres did lower the dielectric constant. However, water absorption induced conduction around the spheres and consequently deteriorated the dielectric properties of the composite completely.

3. The E-type microsphere satisfied both requirements of low and water-resistant dielectric constant. However, the E-type microspheres could not be processed as freely as the phenolic or the glass spheres. In particular, they dissolved in anhydride hardeners.

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