Eur. Polym. J. Vol. 24, No. 7, pp. 633–638, 1988
Printed in Great Britain.

0014-3057/88 \$3.00 + 0.00

DIELECTRIC PROPERTIES OF COPPER POWDER–EPOXY RESIN COMPOSITES

YVES BAZIARD,[1] SYLVIE BRETON,[2] SERGE TOUTAIN[2] and ALBERT GOURDENNE[1]

[1]Laboratoire de Physico-Chimie des Hauts Polymères, Ecole Nationale Supérieure de Chimie de Toulouse, 118 route de Narbonne, 31077 Toulouse Cedex, France

[2]Laboratoire d'Electronique Physique, Ecole Nationale Supérieure des Télécommunications de Bretagne, B.P. 832, 29285 Brest Cedex, France

(*Received* 14 *September* 1987)

Abstract—The dielectric properties of copper powder–epoxy resin composites have been determined between 10 Hz and 800 kHz through measurements of the capacitance of a cell ending a coaxial waveguide in a short circuit. The copper concentration ranged from 0 to 70% by wt or 23.2% by vol. The study of the variations with the filler content of the real and complex relative permittivities ϵ_r' and ϵ_r'' show that the two relaxation processes of Cole–Cole type operate in the 1 and 200 kHz regions, at least as long as the weight percentage does not exceed 50. Beyond this value, the circle arc which is observed at low frequency in the Argand diagrams, starts being distorted into exponential segments and, although the percolation threshold is never reached within the filler concentration range in this work, the dependence of ϵ_r' and ϵ_r'' on the amount of copper at 10 and 50 Hz can be described according to an electrical percolation law.

INTRODUCTION

In previous work [1], data on the dielectric properties of aluminium powder–epoxy resin composites between 10 Hz and 800 kHz were presented. When the filler concentration was increased from 0 to 80% by wt or 63.2% by vol, the real and complex permittivities ϵ_r' and ϵ_r'' monotonously increased and no electrical percolation threshold was detected although the metallic granules were in physical contact at high aluminium contents. Such a situation which confers dielectric behaviour on the materials is due to the fact that the filler particles were coated with an insulating alumina layer which prevents any electronic conduction between metallic granules forming a continuous network. For heterophase systems, the metallic powder–epoxy matrix should be an electrical conductor when the filler is poorly or not oxidized, as in the case of copper powder–epoxy resin composites as reported here.

EXPERIMENTAL

The epoxy matrix was obtained by stoichiometric mixing of an epoxy resin of DGEBA type (Lopox 200 from CDF Chimie) with a polymerization index of 0.1 with diaminodiphenylmethane (DDM) (Fluka—reference: 32950) according to a procedure previously described [1]. The polymeric material before crosslinking was filled with copper powder (Ventron GMBH—Alfa catalogue reference: 94) of low particle size ($\phi_i < 10\,\mu$m) and purity grade 98%. The preparation under microwaves of the final products and their cutting into discs (dia, 14.4 mm; thickness, 1 mm), for dielectric characterization in the 10 Hz–800 kHz range through a Rhode & Schwarz vector analyzer, were carried out as for aluminium powder–epoxy resin structures [1]. All measurements of the real and complex permittivities ϵ_r' and ϵ_r'' were made at 24° ± 1°.

RESULTS AND DISCUSSION

The frequency dependence of ϵ_r' and ϵ_r'' of the composites when the metal concentration had values of 0, 30, 50, 60, 66 and 70% by wt, is shown in Fig. 1. The DGEBA–DDM matrix used as reference exhibits the two relaxation processes (Fig. 1a) of Cole–Cole type which were attributed in the preceding study on aluminium powder–epoxy resin materials [1], centred at 200 kHz (Process I) and 2 kHz (Process II), and due respectively to the dipolar relaxation of hydroxyl groups on the one hand and to a Maxwell–Wagner–Sillars (MWS) [2–4] resulting from the lacunar structure with microvoids of the glassy epoxy network on the other. The dispersion of the data which is mainly noted at the level of the MWS relaxation in the Argand representation (Fig. 2a) could arise from the macroscopic heterogeneity of the polymeric matrix. The two processes did not occur when a soft silicone network RTV 141 (Rhône–Poulenc Industries) was used instead of the DGEBA–DDM association, because no significant amount of hydroxyl was present and the crosslinked silicone resin which is rather soft and rubbery does not present any MWS relaxation [5].

The relaxation spectra of the composites are very sensitive to the amount of copper (Figs 1 and 2). At first, both relaxation processes (I and II) are detectable up to the filler concentration of 60% by wt; beyond this value, the distortion of the low frequency circle arc in the Argand plot becomes significant, unlike the case of aluminium powder–epoxy composites which behave as dielectrics, whereas the circle arc of hydroxyls (Process I) is maintained up to 66%. Nevertheless, this is completely hidden for 70% by the low frequency contribution which resumes the whole curve $\epsilon_r'' = \epsilon_r''(\epsilon_r')$ to an exponential segment

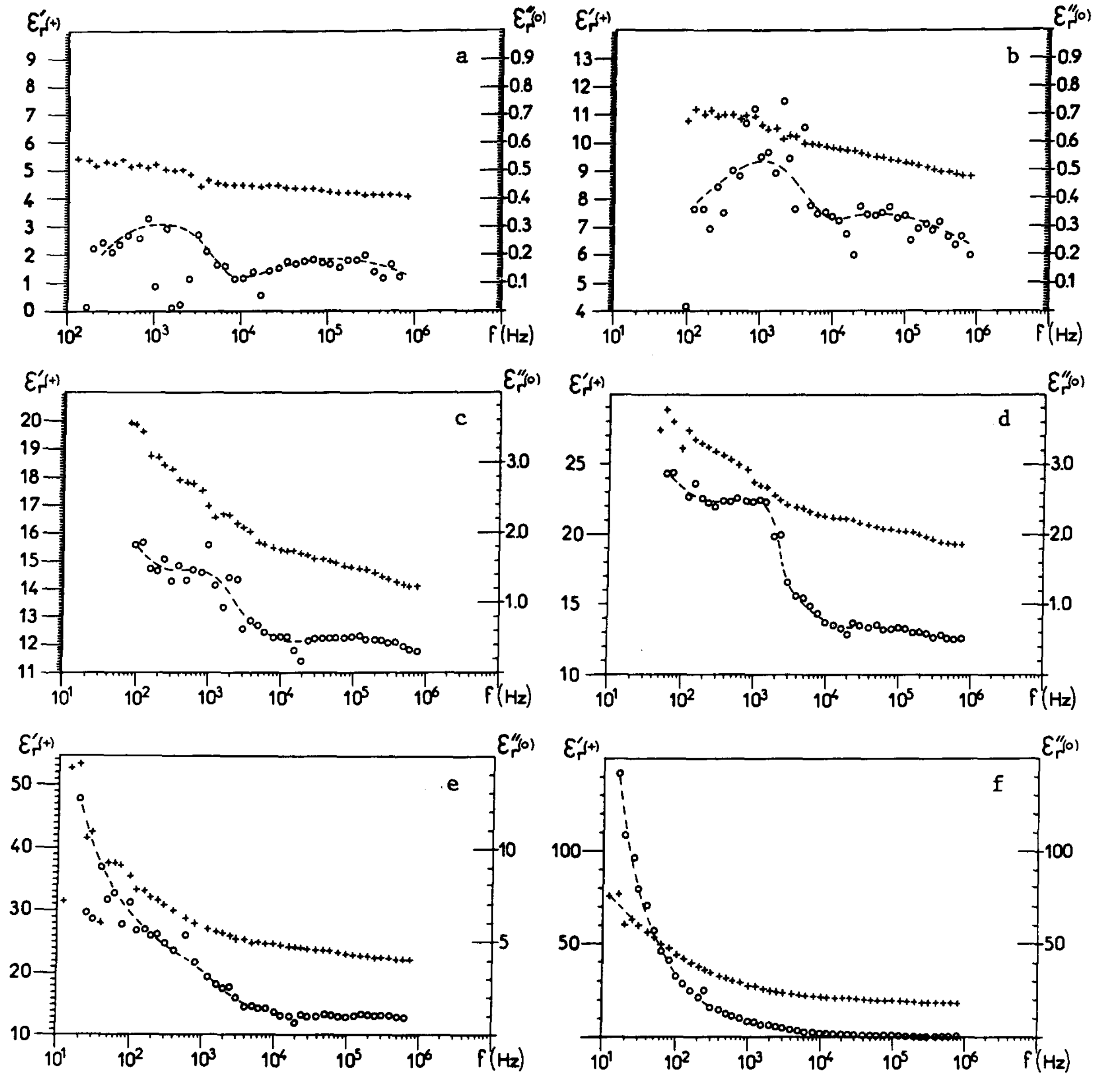

Fig. 1. Dielectric relaxation spectra of copper powder–epoxy resin composites at various filler concentrations (% by wt): (a) 0%; (b) 30%; (c) 50%; (d) 60%; (e) 66%; (f) 70%.

(Fig. 2f) as expected from the shape of the corresponding relaxation spectra (Fig. 1f). Moreover, the relaxation frequencies (f_0) of Processes I and II are more or less sensitive to the amount of copper. Table 1 gives an average value $f_0 = 180 \pm 18$ kHz for Process I instead of 200 ± 29 kHz for aluminium as filler [1]. This variation could indicate possible interaction between the —OH functions and the metallic particles which would increase the polarity of the hydroxyls and consequently induce a shift towards low frequencies. In the case of aluminium, such a phenomenon would not be observed because the granules are coated with insulating alumina. However this variation, when copper is added, could also be due to the low frequency contribution of copper which is not negligible at a concentration of 30% by wt or 5.3% by vol. An attempt of deconvolution of both peaks does not settle the doubt because of the lack of precision in the experimental data. The frequency of Process II is shifted as soon as copper is added, from 2 to 1 kHz, up to 63% (Table 1), whereas for aluminium the shift is progressive [1]. By analogy, as observed for aluminium–epoxy resins composites, the low frequency relaxation process could be attributed to an MWS effect due to copper particles, superposed on that of the epoxy network. The fact that its relaxation frequency is stabilized at 1 kHz suggests its existence, since it should be independent on the amount of copper, contrary to its peak intensity. Actually, the MWS effects due to aluminium [1] and copper could not be compared because their external chemical structures are not

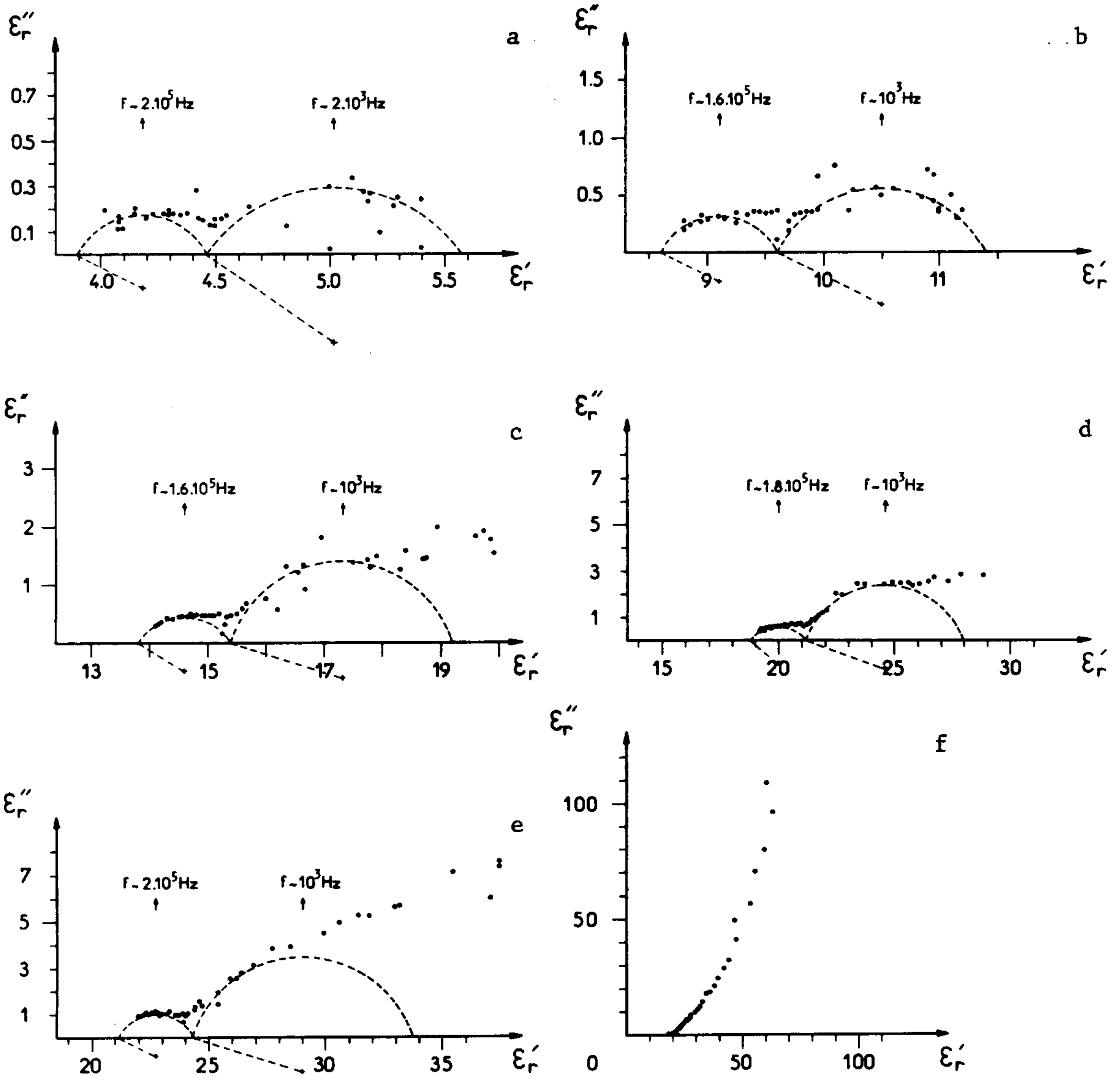

Fig. 2. Argand representations for copper powder–epoxy resin composites at filler concentrations (% by wt): (a) 0%; (b) 30%; (c) 50%; (d) 60%; (e) 66%; (f) 70%.

similar: the first is oxidized (the aluminium granules are coated with alumina and are not in direct contact with the organic matrix) and the second is not, as shown in Figs 1f and 2f corresponding to a filler content of 70% by wt or 23.2% by vol, which indicate that an insulator-to-conductor transition will occur because of the progressive formation of a physical network which makes possible the electrical percolation and which will be described later.

Table 1. Copper concentration dependence of the relaxation frequencies (Processes I and II)

% by wt Cu	f_0 (kHz) (Process I)	Mean f_0 (kHz) (Process I)	f_0 (kHz) (Process II)
0	200	180 ± 18	2.0
20	160		1.0
30	160		1.0
40	200		1.0
50	160		1.0
60	180		1.0
63	200		1.0
66	200		1.0
70	—		—

Before analysing the variations with the copper concentration of ϵ_r' and ϵ_r'' at a given frequency, the morphology of the composites has to be shown. Figure 3 presents three macroscopic structures for three filler contents viz. 20, 50 and 70% by wt or 3.1, 11.5 and 23.2% by vol, analysed through optical microscopy ($G = 800$). For both structures, all copper particles (white blobs) are separated; if they form a few aggregates, these are still isolated. At 70% by wt, local physical contacts appear but they are insufficient to build a continuous metallic network through the polymeric matrix.

Consider now the dependence of ϵ_r' and ϵ_r'' on the amount of metal. It is obvious that the absorption

Table 2. Copper concentration dependence of ϵ_s, ϵ_∞ and $(\epsilon_s - \epsilon_\infty)$ for both relaxation processes (I and II)

% by wt Cu	Vol % Cu	ϵ_s (I)	ϵ_∞ (I)	$(\epsilon_s - \epsilon_\infty)$ (I)	ϵ_s (II)	ϵ_∞ (II)	$(\epsilon_s - \epsilon_\infty)$ (II)
0	0	4.47	3.89	0.58	5.58	4.47	1.11
20	3.1	6.09	5.41	0.68	7.60	6.09	1.51
30	5.3	9.60	8.60	1.00	11.41	9.60	1.81
40	8.0	10.62	9.56	1.06	13.58	10.62	2.96
50	11.5	15.40	13.80	1.60	19.20	15.40	3.80
60	16.3	21.20	18.80	2.40	28.00	21.20	6.80
63	18.1	22.50	19.50	3.00	29.50	22.50	7.00
66	20.1	24.30	21.10	3.20	33.80	24.30	9.50
70	23.2	—	—	—	—	—	—

does not stop increasing when the composites become richer and richer in metal, although the percentage of resin goes down and that consequently the intensity of Process I should be lowered. The only explanation of such a variation is that Process II, mainly due to copper, becomes more important and that it expends on the frequency axis. Moreover, at high filler concentrations and low frequencies, ϵ_r'' rises above ϵ_r' so that $\tan\delta = \epsilon_r''/\epsilon_r'$ exceeds unity. The increase of polarity of the composites can be appreciated through the difference between ϵ_s and ϵ_∞, respectively static and infinite permittivities extrapolated from

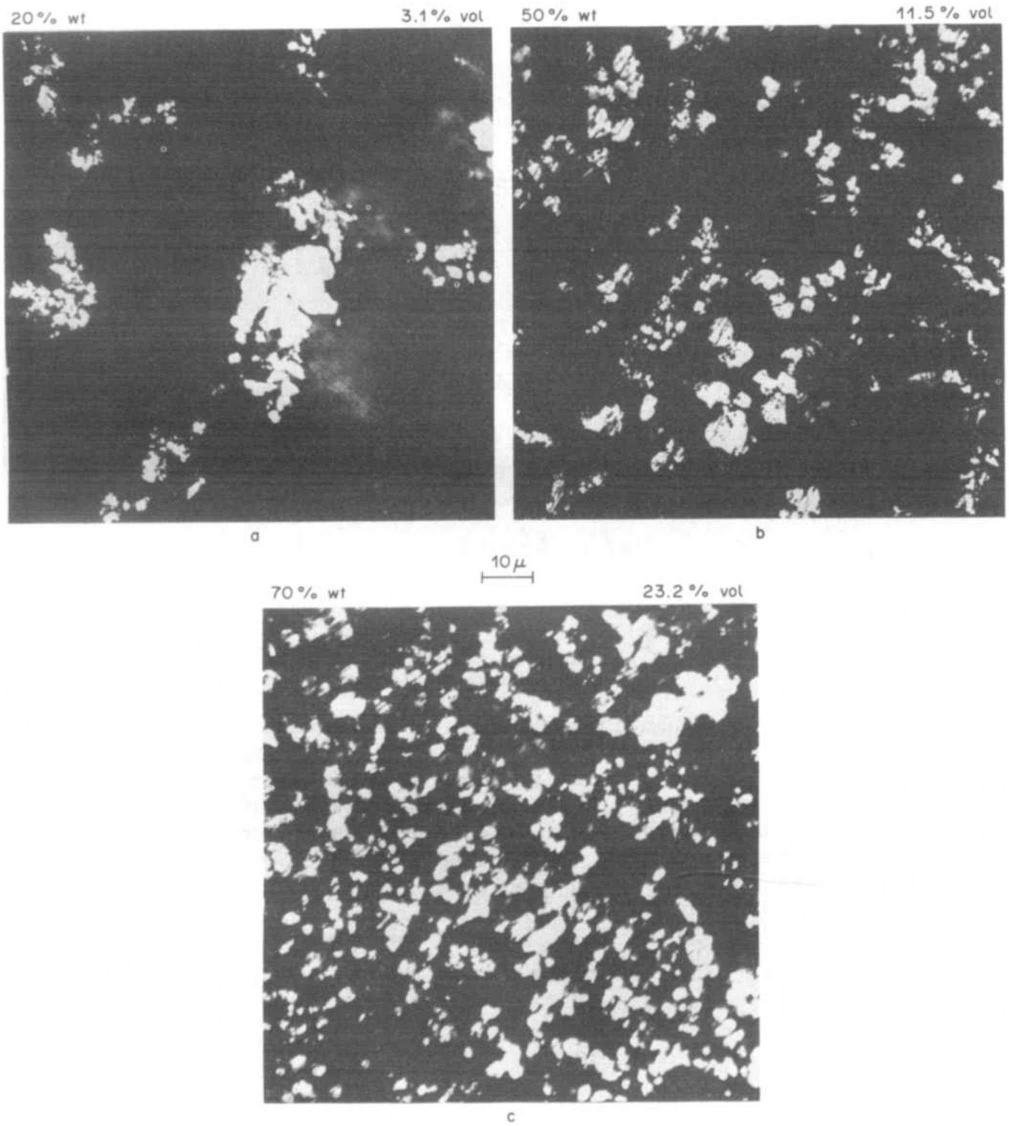

Fig. 3. Morphology of copper powder–epoxy resin composites at various filler concentration (% by wt or vol, respectively): (a) 20 or 3.1%; (b) 50 or 11.5%; (c) 70 or 23.2%.

Table 3. Copper concentration dependence of ϵ'_r, ϵ''_r and tan δ at given frequencies: (1), 1 kHz; (2), 100 Hz; (3), 50 Hz; (4), 16 Hz

% by wt Cu	Vol % Cu	ϵ'_{r1}	ϵ''_{r1}	tan δ_1	ϵ'_{r2}	ϵ''_{r2}	tan δ_2	ϵ'_{r3}	ϵ''_{r3}	tan δ_3	ϵ'_{r4}	ϵ''_{r4}	tan δ_4
0	0	5.00	0.29	0.058	5.40	—	—	—	—	—	—	—	
20	3.1	6.60	0.41	0.062	7.25	—	—	—	—	—	—	—	
30	5.3	10.60	0.55	0.052	11.20	0.36	0.032	—	—	—	—	—	
40	8.0	11.55	1.07	0.093	13.10	1.25	0.095	—	—	—	—	—	
50	11.5	16.95	1.81	0.107	19.80	1.78	0.090	18.95	1.99	0.105	—	—	
60	16.3	23.75	2.41	0.101	27.50	—	—	27.30	—	—	—	—	
63	18.1	25.00	2.67	0.107	30.20	2.44	0.081	30.30	2.64	0.087	42.4	—	
66	20.1	27.00	3.81	0.141	35.50	7.12	0.200	37.50	7.34	0.196	52.6	25.1	0.477
70	23.2	28.00	8.73	0.311	44.00	32.50	0.739	53.50	56.70	1.060	76.8	141.0	1.836

Cole–Cole plots, at least when these operate. Table 2 collects all data concerning Processes I and II and especially shows that the quantity ($\epsilon_s - \epsilon_\infty$) is raised in both relaxations, the effect being more marked, as expected, for the low frequency process.

The alteration of low frequency Cole–Cole plots with the metal concentration, which is not observed for aluminium powder–epoxy resin composites [1], indicates the formation of a new structured organization of the particles embedded in the epoxy matrix with a tendency to aggregation on a large scale as shown in Fig. 3e. The study of the variations of ϵ'_r and ϵ''_r at a given frequency (1000, 100, 50 and 16 Hz) shows the progressive change of dielectric behaviour with metallic content. All values are collected in Table 3, where some data are missing because of the weakness of the corresponding parameters. All values at 70% by wt and for 50 and 16 Hz have not been taken into account from the dielectric point of view since they lead to tan δ values above unity (tan $\delta_3 = 1.060$ and tan $\delta_4 = 1.836$); then the composite should be considered rather as an intermediate between a dielectric material and a conductor. The volume copper concentration dependence of ϵ'_r, ϵ''_r and tan δ at the four frequencies is shown in Figs 4 and 5 where the intensity jump occurs after 18.3% by vol or 63% by wt. Obviously, the composite at 70% by wt cannot be a conducting material because its morphology does not reveal any continuous conductive metallic network (Fig. 3e). However, the strong filler concentration dependence of ϵ'_r at low frequencies can be interpreted by resorting to a percolation law, proposed for conductor–dielectric medium mixtures [6, 7], when the percolation threshold x_c is reached at lower values x_2, and the frequency f tends to zero:

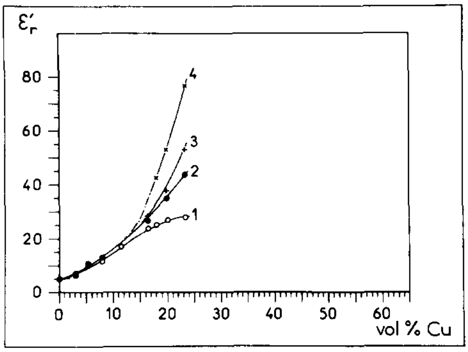

Fig. 4. Copper volume concentration dependence of ϵ'_r at given frequencies: (1) $f = 1$ kHZ; (2) $f = 100$ Hz; (3) $f = 50$ Hz; (4) $f = 16$ Hz.

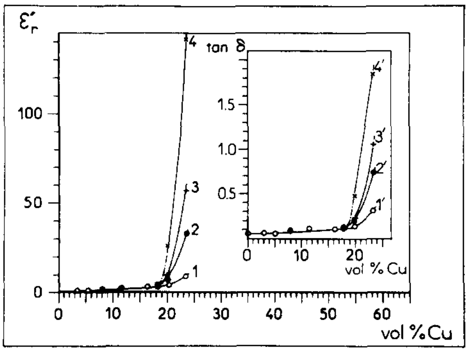

Fig. 5. Copper volume concentration dependence of ϵ''_r and tan δ at given frequency. $f = 1$ kHz: (1) ϵ''_r; (1') tan δ. $f = 100$ Hz: (2) ϵ''_r; (2') tan δ. $f = 50$ Hz: (3) ϵ''_r; (3') tan δ. $f = 16$ Hz: (4) ϵ''_r; (4') tan δ.

Table 4. Values of ϵ'_r of composites at 50 (ϵ'_{r50}) and 10 Hz (ϵ'_{r10})

% by wt Cu	x_2	ϵ'_{r50}	ϵ'_{r10}
50	0.115	18.95	21.10
60	0.163	27.30	31.50
63	0.181	30.30	38.00
66	0.201	37.50	47.30
70	0.232	53.50	78.50

$$\epsilon'_r = \epsilon'_{r1}(x_c - x_2)^{-s},$$

where ϵ'_{r1} is the real permittivity of the dielectric medium, i.e. the epoxy matrix, and s a critical exponent. This relation implies linearity in the plot of $\log \epsilon'_r$ vs $\log(x_c - x_2/x_c)$ within the volume copper concentration interval just below the critical threshold where the percolation transition occurs. For the present work, graphical treatment of the data collected in Table 4 where ϵ' values are extrapolated from the curves $\log \epsilon'_r = g\ (\log f)$ at 50 and 10 Hz, leads to two logarithmic percolation curves (Fig. 6) with wide straight segments predicted by the percolation law at zero frequency which is nevertheless proved at the chosen frequencies, at least beyond $x_2 = 0.163$. Two different pairs of values (x_c; s) are obtained according to the frequency:

$$f = 50\ \text{Hz} - x_c = 0.275 \pm 0.010; \quad s = 0.73 \pm 0.09;$$

$$f = 10\ \text{Hz} - x_c = 0.270 \pm 0.010; \quad s = 0.86 \pm 0.06.$$

These values of the critical exponent s have to be compared with those obtained through measure-

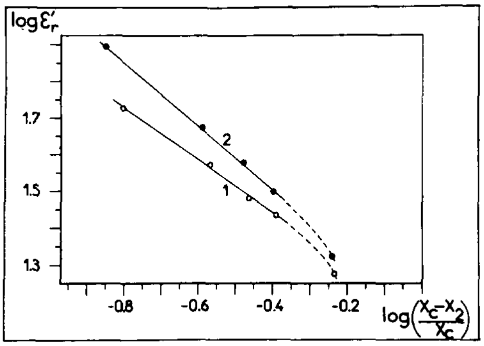

Fig. 6. Determination of the critical copper volume fraction x_c and exponent s: representation of log ϵ_r' as a function of log $(x_c - x_2/x_c)$ at given frequencies: (1) $f = 50$ Hz; (2) $f = 10$ Hz.

ments of dielectric constants for crystalline potassium chloride–silver powder ($\phi_i \approx 200$ Å) composites [8] and glass powder–silvery glass powder ($\phi_i \approx 40\ \mu$m) mixtures [9], respectively $s = 0.73 \pm 0.07$ and $s = 0.65 \pm 0.10$. The critical percolation threshold x_c is 0.275 ± 0.010 (or 74.5% by wt) at 50 Hz and 0.270 ± 0.010 (or 74.1% by wt) at 10 Hz, whereas it is 0.21 for the preceding composite and 0.26 for the mixtures with glass powders. The difference between these critical concentrations is not surprising, since they depend on various parameters such as the granular nature of the filler, the shape of the particles and the quality of physical contact between the granules. Note that the average copper particle size in this work is $< 10\ \mu$m.

All these calculations demonstrate that the copper powder–epoxy resin composites are able to go through an electrical percolation transition when the volume copper concentration exceeds 0.27 (or 74.1% by wt). The preparation of composites of such a composition or higher concentration cannot be carried out by the mixing techniques used in this study; other techniques as extrusion, are required in these cases.

CONCLUSION

The previous study shows that the copper powder–epoxy resin composites behave as dielectrics between 10 Hz and 800 kHz with high loss depending on the metallic content as long as the electrical percolation threshold is not reached. Two relaxation processes of Cole–Cole type operate within that frequency domain, respectively attributed to an MWS effect at low frequencies in the 1 kHz region and to a dipolar relaxation of hydroxyl side-groups of the matrix at higher frequencies around 200 kHz. However, more work is needed for confirmation. The time dependence of the frequencies and intensities of relaxation maxima need careful consideration. When the copper concentration is considerably increased beyond 16.3% by vol or 60% by wt, the composites are intermediate between dielectrics and conductors and their behaviour can be described according to a classical law of electrical percolation with a threshold of 27% by vol or near 74% by wt, which is never exceeded in the present work, the mixing techniques not being suitable because of the high viscosity of filler–epoxy prepolymer systems. A study in progress indicates that the percolation transition can be easily undergone when the epoxy resin is replaced by a silicone thermoset; on the other hand, it confirms our results on percolation since this matrix presents no perturbating specific absorptions.

REFERENCES

1. Y. Baziard, S. Breton, S. Toutain and A. Gourdenne. *Eur. Polym. J.* **24**, 521 (1988).
2. J. C. Maxwell. *Electricity and Magnetism*, Vol. 1, p. 452. Clarendon Press, Oxford (1892).
3. K. W. Wagner. *Arch. Elektrotech.* **2**, 378 (1914).
4. R. W. Sillars. *Proc. R. Soc. Lond.* **A169**, 66 (1939).
5. S. Breton, Y. Baziard, S. Toutain and A. Gourdenne. *European Polymer Federation First Meeting: Joint Symposium on Polymers for Electronics*, Lyon (1987).
6. S. Kirkpatrick. *Rev. mod. Phys.* **45(4)**, 574 (1983).
7. A. L. Efros and B. I. Shklovskii. *Physica Status Solidi*, **676(2)**, 475 (1976).
8. D. M. Grannan, J. C. Garland and D. B. Tanner. *Phys. Rev. Lett.* **46(5)**, 375 (1981).
9. J. M. Laugier. Thesis 3rd Cycle, Université de Provence, France (1982).