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DIELECTRIC PROPERTIES OF ALUMINIUM POWDER–EPOXY RESIN COMPOSITES

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Abstract—The dielectric properties of aluminium powder–epoxy resin composites have been determined between 10 Hz and 800 kHz by measurements of the capacitance of a cell ending a coaxial waveguide in a short circuit. The aluminium concentration ranged from 0 to 80% by wt or 63.2% by vol. Study of the variations with frequency of ϵ_r' and ϵ_r'' at ambient temperature revealed two relaxation processes at 1 and 200 kHz. The Argand representation $\epsilon_r'' = \epsilon_r''(\epsilon_r')$ gave two Cole–Cole systems whatever the concentration, showing the non-conducting character of the composites although the threshold of physical contact between powder particles was reached at higher filler concentration. Such a result is due to the insulating layer of aluminium oxide which coats the granules of metal and prevents any conduction phenomenon other than percolation. A relationship between the static permittivity ϵ_s and the volume powder concentration is proposed.

INTRODUCTION

Thermosetting resins such as epoxy prepolymers are extensively used as structural adhesives because of their mechanical properties and strength of interaction with various substrates such as metals and glass, when in the crosslinked state. For some applications, electrically conductive adhesives are needed, where conductivity is achieved through additions of conductive powder such as carbon black, copper and aluminium derivatives at concentrations sufficient to build physical networks in which the phenomenon of electrical percolation takes place.

These composites also constitute excellent models for studying the interactions between condensed matter and electromagnetic radiation such as microwaves, since they contain at the same time conductive domains and dielectric organic material and that many formulations with increasing filler concentration are available. However, although they are more and more used for spatial applications where their dielectric or electrical behaviour has to be taken into account, it is not widely described in literature. Only the absorption at a given frequency is reported and no analysis can be made. Recently a programme to remedy this lack of knowledge has been started [1] for epoxy prepolymers over a large frequency range with future extension to solid state.

In the present work, a study of the dielectric behaviour of aluminium powder–epoxy resin crosslinked composites between 10 Hz and 800 kHz is reported and a law of absorption vs filler concentration is proposed.

EXPERIMENTAL

The polymeric matrix is obtained from an epoxy resin of DGEBA type (Lopox 200 from CDF Chimie) with a polymerization index $n \cong 0.1$, cured with diaminodiphenylmethane (DDM) (Fluka—Ref. 32950) according to a procedure previously described [2, 3]: epoxy resin at 60° is poured on to fused DDM at 120° in stoichiometric proportions; the mixtures are stirred and the final compounds are transparent and light yellow. The fluid DGEBA–DDM prepolymers at 75° are mixed with aluminium powder at ambient temperature (Prolabo—Ref. 20 998 296) with spheroidal shape and particle size $< 40\,\mu$m (mean dia $\cong 20\,\mu$m) inside a vessel and strongly stirred; then the composite matter is degassed at 60° under vacuum before being divided into 20 g. samples stored inside Pyrex glass pillboxes. The samples are degassed again and stored at −30° until curing.

The crosslinking reactions of the preceding samples are promoted by microwave (2.45 GHz) treatment which has already been carried out for epoxy resins [2, 3], through dielectric loss due to dipolar relaxation of organic species. Additional loss resulting from conduction has to be added at the level of aluminium particles for our composites. More details will be given in following papers derived from a thesis [4].

The determination of the relative complex permittivity $\epsilon_r^* = \epsilon_r' - j\epsilon_r''$ is done by measuring at 24 ± 1° the capacitance of a cell ending a waveguide in a short circuit, where the samples (discs—dia 14.4 mm, thickness 1 mm) are placed between the two electrodes of the cell. This assembly is completed with a Rhode & Schwarz vector network analyser ZPVE 1 working between 10 Hz and 800 kHz. The measurements of ϵ_r' and ϵ_r'' as functions of frequency are automated and the reproducibility is ±5% for ϵ_r' and ±10% for ϵ_r''.

RESULTS AND DISCUSSION

The frequency dependence of ϵ_r' and ϵ_r'' for crosslinked DGEBA–DDM resin is shown in Fig. 1a. When the frequency increases, ϵ_r' decreases slowly from 5.5 at 100 Hz to 4.0 at 800 kHz, whereas the ϵ_r'' curve has two peaks in 1 and 200 kHz regions, the first being more marked $\epsilon_r'' \cong 3.0$ instead of 0.18. The Argand representation in the complex plane of

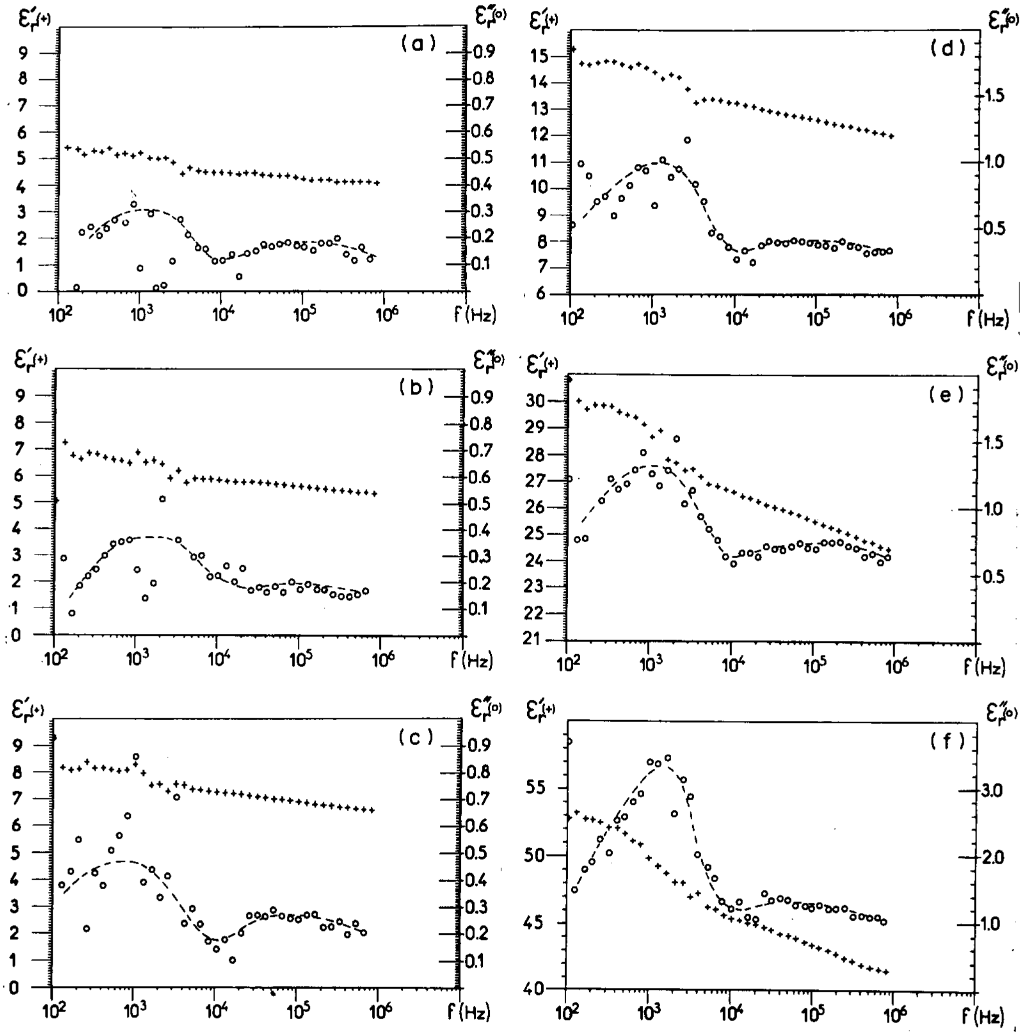
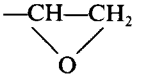
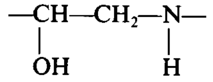


Fig. 1. Dielectric relaxation spectra of aluminium powder–epoxy resin composites at various filler concentrations (% by wt): (a) 0; (b) 10; (c) 20; (d) 40; (e) 60; (f) 80.

$\epsilon_r'' = \epsilon_r''(\epsilon_r')$ (Fig. 2a) shows much better both transitions through circle arcs of the Cole–Cole type centred at 200 (Process I) and 2 kHz (Process II); the determination of these frequency values cannot be improved because of the relative dispersion of ϵ_r' and ϵ_r'' values due to structural heterogeneity of the epoxy network. Nevertheless, the attribution of the relaxation must be discussed. First, since the polymeric matrix stays in a glassy state, no local motion of short chain segments is expected. Now, as far as dipolar relaxation, it could be the result of polar entities such as residual amines —NH$_2$ and —NH—, epoxides



and hydroxyls formed from ring-opening of epoxides by amines



$$\begin{array}{ccc}\text{—CH—} & \text{CH}_2\text{—} & \text{N—}\\ | & & |\\ \text{OH} & & \text{H}\end{array}$$

and in larger amount than the other possible dipolar species. A contribution of —OH groups has to be considered. On the other hand, a Maxwell–Wagner–Sillars (MWS) effect [5–7] can also interfere at low frequencies, which deals with charge carriers appearing inside a heterogeneous medium consisting of phases with different dielectric permittivities as in the case of epoxy networks which present a lacunar structure with microspherical voids and consequently where two phases, air and polymeric matter, are associated. So, a possible explanation is as follows: Process I at high frequencies (200 kHz) is due to the dipolar relaxation of hydroxyl groups, and Process II at lower frequencies (2 kHz) to an MWS effect. A complementary study of the two processes is essential.

Processes I and II are still observed when one passes to aluminium powder–epoxy resin composites even up to 80% by wt, or 63.2% by vol (Fig. 1b–f), with respect to Cole–Cole type (Fig. 2b–f). But the Argand diagrams are better and better defined with increasing aluminium concentrations, i.e. when the composite matter becomes more heterogeneous as far as the spatial distribution of filler particules. More-

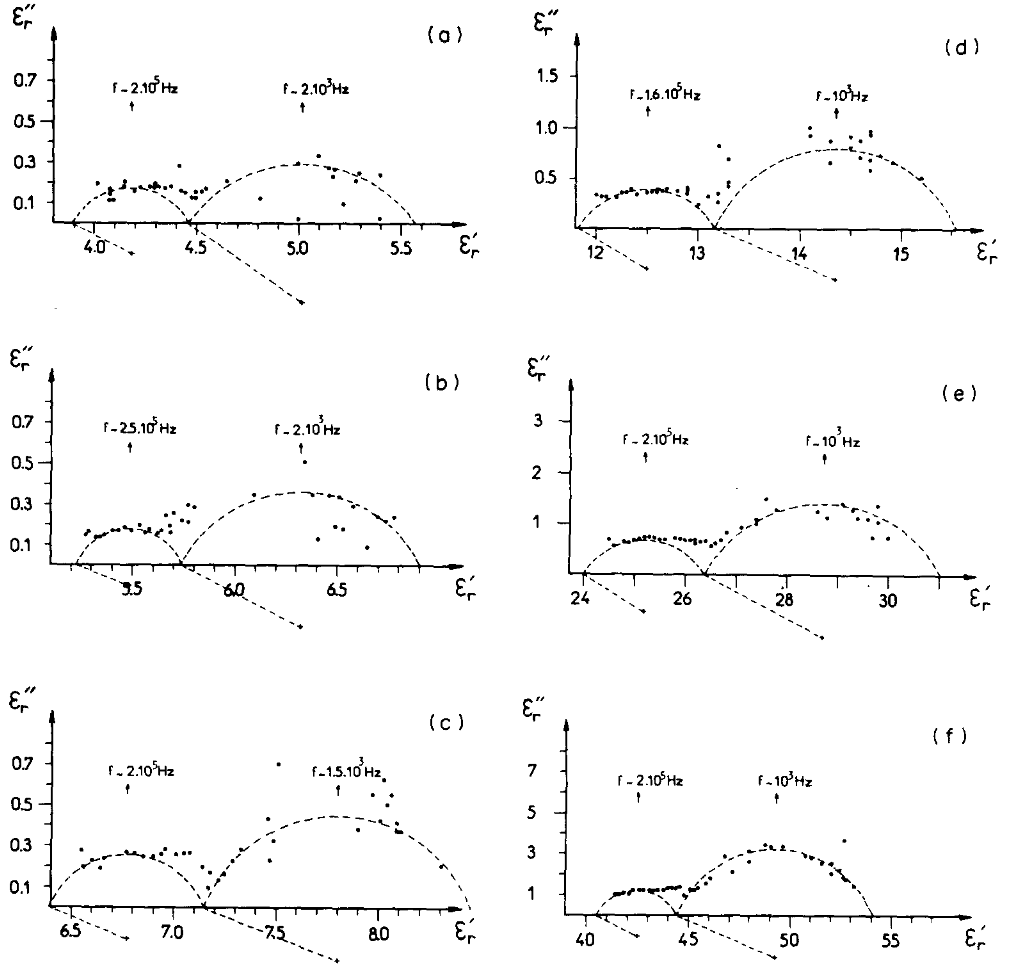


Fig. 2. Argand representations for aluminium powder–epoxy resin composites at various filler concentrations (% by wt): (a) 0; (b) 10; (c) 20; (d) 40; (e) 60; (f) 80.

over, it seems that the position in frequency is maintained for Process I at 200 kHz, whereas the situation is different for Process II: the abscissa of the maximum is shifted from 2 kHz towards low frequencies, viz. 1.5 and 1.0 kHz respectively for 20 and 80% by wt. The stability of the relaxation frequency of Process I means that no significant interaction between aluminium granules and the assumed relaxing hydroxyl species, which would have increased their polarity and decreased their relaxation frequency. Such a result is not surprising because the bonding between entities located in separated phases poorly involves short segments, i.e. separated hydroxyls do not interact by themselves. On the other hand, the fact that the frequency of Process II is sensitive to aluminium concentration indicates that another MWS effect, at the level of the interface metal–polymer, could be superimposed on the MWS effect existing in the matrix at the interface air–polymer.

The influence of the filler content on the dielectric behaviour of the composites is also apparent through the aluminium concentration dependence of the difference $(\epsilon_s - \epsilon_\infty)$, where ϵ_s is the static relative permittivity at zero frequency and ϵ_∞ is the relative permittivity at infinite frequency, ϵ_s and ϵ_∞ values being extrapolated from Cole–Cole plots. Indeed the quantity $(\epsilon_s - \epsilon_\infty)$ is a measure of polarity of the materials. Table 1 shows the values corresponding to Processes I and II of the aluminium powder–epoxy resin composites, which behave as dielectrics in spite of high metal concentrations. The variations with aluminium volume concentration of ϵ_r' at 200 kHz (relaxation frequency of Process I) and 1 kHz (relaxation frequency of Process II at high filler concentration) also emphasize the contribution of the metal which appears monotone (Fig. 3). The fact of taking the ϵ_r' values at 1 kHz at low aluminium levels does not introduce much error because of the oblate shape in the maximum region of the peak of Process II. On the other hand, ϵ_r' values at 1 kHz always remain above that determined at 200 kHz for a given composite. The same situation is encountered for ϵ_r'' as shown in Fig. 4. Moreover, when one passes from the pure resin to a composite with 80% by wt of aluminium, ϵ_r' and ϵ_r'' are multiplied by 10. As far as the evolution of the loss factor $t_g\delta = \epsilon_r''/\epsilon_r'$, the corresponding curves are less well defined and cannot be described by a simple law of variation. However, $t_g\delta$ takes values always lower than 0.08.

All the preceding results lead to the intermediate conclusion that no electrical conductor–insulator

Table 1. Aluminium powder concentration dependence of ϵ_s, ϵ_∞ and $(\epsilon_s - \epsilon_\infty)$ for Processes I and II

wt % Al	vol. % Al	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
5	2.2	5.08	4.52	0.56	6.12	5.08	1.04
10	4.5	5.73	5.10	0.63	6.89	5.73	1.16
20	9.7	7.15	6.39	0.76	8.45	7.15	1.30
30	15.5	7.78	7.00	0.78	10.02	7.78	2.24
40	22.2	13.16	11.83	1.33	15.56	13.16	2.40
45	26.0	14.48	13.00	1.48	17.15	14.48	2.67
50	30.0	18.85	17.15	1.70	22.70	18.85	3.85
55	34.4	21.65	19.75	1.90	25.95	21.65	4.30
60	39.2	26.40	24.00	2.40	31.05	26.40	4.65
65	44.4	29.10	26.65	2.45	33.70	29.10	4.60
70	50.0	36.65	34.00	2.65	42.80	36.65	6.15
75	56.3	37.40	34.60	2.80	43.60	37.40	6.20
80	63.2	44.40	40.50	3.90	54.20	44.40	9.80

transition is observed inside the series of aluminium–epoxy composites, and that consequently no percolation phenomenon takes place within the filler concentration range, although at high concentrations, as seen in Fig. 5 [which presents the morphology analysed through optical microscopy ($G = 800$) of various composite materials] possible physical networks are formed from powder granules in contact and that electrical percolation should be expected [8]. The only explanation of such a situation is that aluminium particles are coated with a layer of insulating alumina due to oxidation of the metal which prevents electronic conduction between the particles.

The non-conducting character of the composites can be turned to account for describing the filler concentration dependence of their dielectric behaviour by using the mixing law proposed by Lichtenecker [9] for a system consisting of a phase dispersed in another continuous one which expresses the static permittivity ϵ_s of such a composite as a function of the static permittivities ϵ_{s1} and ϵ_{s2} of the matrix (1) and the filler (2):

$$\log \epsilon_s = x_1 \cdot \log \epsilon_{s1} + x_2 \cdot \log \epsilon_{s2},$$

where x_1 and x_2 are the corresponding volume fractions of the two phases. The application of this law implies the determination of the constant parameter ϵ_{s2} of the metallic compounds. The extrapolation from Cole–Cole plots of the various aluminium–epoxy composites with $0 < x_2 < 0.50$, provides an average value $\epsilon_{s2} = 404$, instead of infinity as expected for a metal. The experimental variations with x_2 of ϵ_s are represented in Fig. 6 by solid circles. Curve a (---) corresponds to Lichtenecker's law [9] with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} = 404$. Curve b is obtained from an empirical formula proposed in this work (Table 2): $\epsilon_s = \epsilon_{s1}(1 + x_2)^5$ and includes now the experimental point up to $x_2 = 0.50$. This law has to be compared to that found by Paipetis *et al.* [10] which gives the electric susceptibility vs $(1 + x_2)^{4.42}$ for $0 < x_2 < 0.30$, measured at 1.8 MHz for aluminium powder–epoxy resin systems. Simulations (Table 2) based on effective medium laws also lead to partial overlapping with the experimental points (Fig. 6).

Bruggeman's formula [*11*]: $\epsilon_s = \epsilon_{s1}/(1 - x_2)^3$ with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} \rightarrow \infty$.

Bottcher's formula [*12*]: $\epsilon_s = \epsilon_{s1}/(1 - 3x_2)$ with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} \rightarrow \infty$.

The curve derived from Bruggeman's law gives the better fitting. Anyway, these laws should not be considered since ϵ_{s2} is supposed to be infinite.

CONCLUSION

The results on dielectric properties between 100 Hz and 800 kHz, just presented, show that the alumi-

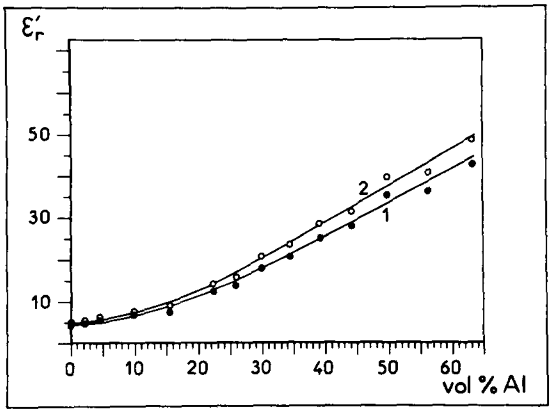


Fig. 3. Aluminium volume concentration dependence of ϵ'_r at a given frequency: (1) $f = 200$ kHz; (2) $f = 1$ kHz.

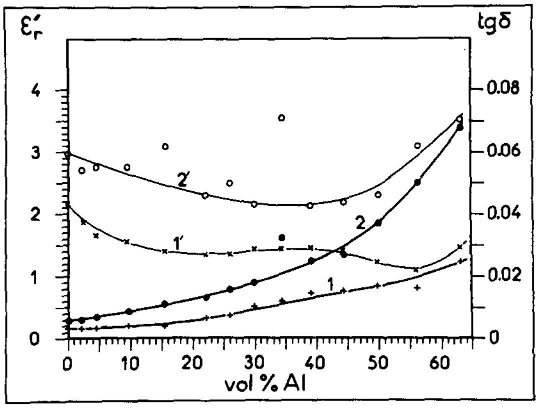


Fig. 4. Aluminium volume concentration dependence of ϵ''_r and $t_g\delta$ at a given frequency: $f = 200$ kHz—(1) ϵ''_r, (1') $t_g\delta$; $f = 1$ kHz—(2) ϵ''_r, (2') $t_g\delta$.

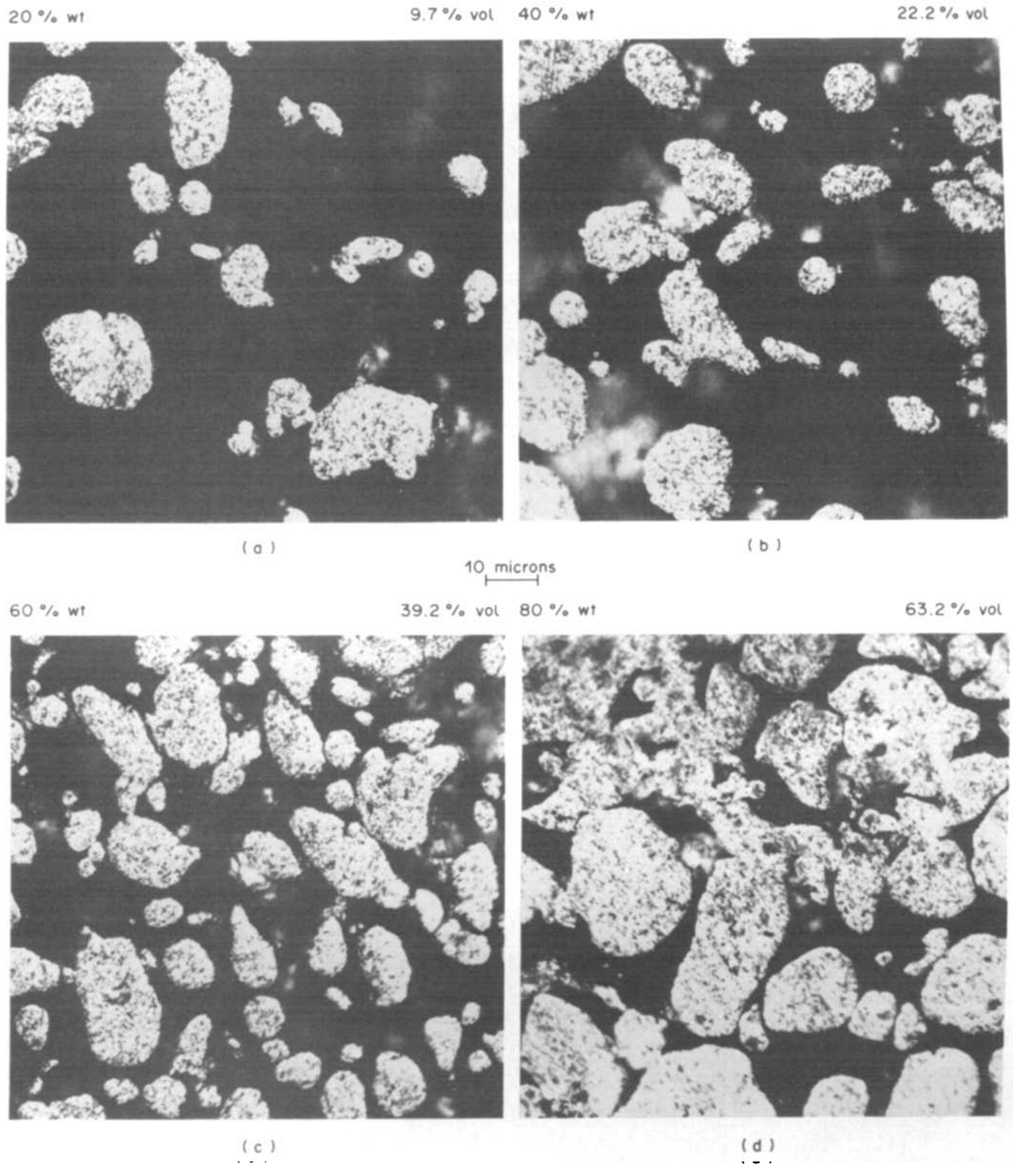


Fig. 5. Morphology of aluminium powder–epoxy resin composites at various filler concentrations (% by wt or by vol, respectively): (a) 20 or 9.7; (b) 40 or 22.2; (c) 60 or 39.2; (d) 80 or 63.2.

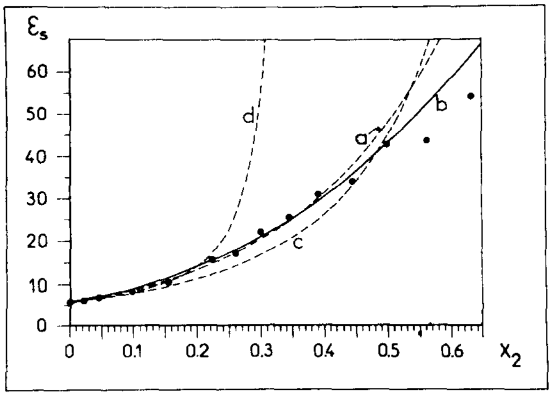


Fig. 6. Aluminium volume fraction x_2 dependence of ϵ_s: (●) experimental data; (a) Lichtenecker's law with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} = 404$; (b) proposed formula in this work; (c) Bruggeman's formula with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} \to \infty$; (d) Böttcher's formula with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} \to \infty$.

Table 2. Aluminium volume fraction x_2 dependence of ϵ_{s2}

x_2	ϵ_s (●)	ϵ_s (b)	ϵ_s (c)	ϵ_s (d)
0	5.56	5.56	5.56	5.56
0.022	6.09	6.20	5.94	5.95
0.045	6.81	6.93	6.38	6.43
0.097	8.33	8.83	7.55	7.84
0.155	10.05	11.43	9.21	10.39
0.222	15.24	15.15	11.81	16.65
0.260	16.81	17.66	13.72	25.27
0.300	22.04	20.64	16.21	55.60
0.344	25.25	24.38	19.69	—
0.392	30.52	29.06	24.74	—
0.444	33.67	34.91	32.35	—
0.500	42.29	42.22	44.48	—
0.563	43.37	51.86	66.62	-
0.632	53.82	64.37	111.56	—

(●) Experimental data; (b) proposed formula in this work; (c) Bruggeman's formula with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} \to \infty$; and (d) Böttcher's formula with $\epsilon_{s1} = 5.56$ and $\epsilon_{s2} \to \infty$.

nium powder–epoxy resin composites are not metal-like conductors when the filler particles are in physical contact, i.e. the expected electrical percolation, for metallic granules, does not operate. The reason for the non-conducting character of these composites is the coating of metallic particles with a layer of alumina resulting from partial oxidation.

The treatment of the data shows, within the frequency range, that the two observed relaxation processes are of Cole–Cole type with interacting species. The extrapolated values of the static permittivity ϵ_s from Argand diagrams $\epsilon_r' = \epsilon_r' (\epsilon_r'')$ at zero frequency are related with the aluminium volume fraction x_2 through the power law $\epsilon_s = \epsilon_{s1} (1 + x_2)^5$, where ϵ_{s1} is the static permittivity of the crosslinked resin, provided x_2 does not exceed 0.50.

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