

CROSSLINKING UNDER MICROWAVES (2.45 GHz) OF ALUMINIUM POWDER-EPOXY RESIN COMPOSITES—II. ALUMINIUM CONCENTRATION DEPENDENCE

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Abstract—The metal concentration dependence of the microwave (2.45 GHz) process of crosslinking of aluminium powder-epoxy resin composites is studied at given electrical power. When the filler content increases to 45% by wt (26% by vol), heating of initial prepolymeric mixtures is accelerated and the dielectric absorption of the final structures increased. Beyond this threshold, the reverse effect is observed. This change is attributed to the undergoing by the composites of a transition referred to as energetic transition for which the dielectric loss is maximum, related to the formation of aggregates of metallic particles.

INTRODUCTION

The first paper of this series [1] gave an account of the study of aluminium powder-epoxy resin composites with the same initial volume (17.25 ml) at two filler concentrations (20 and 50% by wt or 9.7 and 30% by vol); it was shown that heating of both heterophase systems in the prepolymeric state is accelerated as the metallic content is increased. Moreover, the plateau values T_p and Pu_p of the temperature T and of the loss of power Pu which consists of two parts (one due to the dielectric loss Pu_D inside the matrix, the other Pu_C resulting from the conduction phenomenon associated to metallic particles—in this work $Pu = Pu_D + Pu_C$ is referred as dielectric loss since the various composite materials are not conductive—are raised with the powder amount at any initial electrical power (P_0) carried by the electromagnetic radiation within a suitable range which does not lead to the burning of the polymeric matter. Nevertheless, the shape of the curves $T = T(t)$ and $Pu = Pu(t)$, where t is time, is changed when one passes from 20 to 50% by wt, especially the exothermal step at 50% is not resolved, because of the major contribution of the metallic particles to the heating of the samples. In addition, at 50%, the maximum of the temperature T_{max} does not exceed that obtained at 20%, contrary to expectation. A possible explanation of such a divergence was suggested; a decrease of heating would be related to the formation of aggregates or denser regions of filler granules, when the powder concentration is high. The present article deals with this hypothesis.

EXPERIMENTAL

The complete procedure of preparation of the composite formulations has been described [2] from epoxy resin of DGEBA type (Lopox 200 from CDF Chimie) with diamino-diphenylmethane (Fluka—Ref. 32950) and aluminium powder (Prolabo—Ref. 20998.296) with particle size after

sifting $<40 \mu\text{m}$. The mixing of various chemicals and metallic filler is carefully carried out and samples are cut off with fixed volume (17.25 ml) corresponding to 20 g of epoxy resin with a density of 1.16, to prevent any volume effect. In fact, the same weight of composite, i.e. 20 g, could have been chosen, but because of density difference between the epoxy material and the metallic powder, drastic volume variations would have been observed, greatly disturbing the propagation, at 2.45 GHz, of the progressive microwaves inside the waveguide (TE_{01} mode). A series of samples with a large range of aluminium concentrations from 0 to 70% by wt (50% by vol) has been prepared (Table 1). The crosslinking under electromagnetic treatment is followed through the variations with time of T and Pu and of their derivatives ($T' = dT/dt$ and $(Pu)' = dPu/dt$; the morphology of final products is examined by optical microscopy.

RESULTS AND DISCUSSION

All experiments of crosslinking of composites are carried out at a given electrical power $P_0 = 30 \text{ W}$. T curves can be divided into two series according to the their shape and the height of final plateau T_p , one from 0 to 40% by wt (22.2% by vol) of aluminium filler (Fig. 1), the other from 45 to 70% by wt (26 to 50% by vol) (Fig. 2), the interval 40–45% by wt belonging to a transition region. For lower concentrations, the exothermal peaks are shifted towards

Table 1. Composition of the various composite samples

Aluminium (wt%)	Aluminium (vol%)	Mass of Al (g)	Mass of resin (g)
0	0	0.00	20.00
10	4.5	2.12	19.09
20	9.7	4.51	18.06
30	15.5	7.24	16.88
35	18.8	8.75	16.25
40	22.2	10.36	15.54
45	26.0	12.10	14.80
50	30.0	14.00	14.00
55	34.4	16.01	13.12
60	39.2	18.23	12.16
65	44.4	20.65	11.12
70	50.0	23.29	10.00

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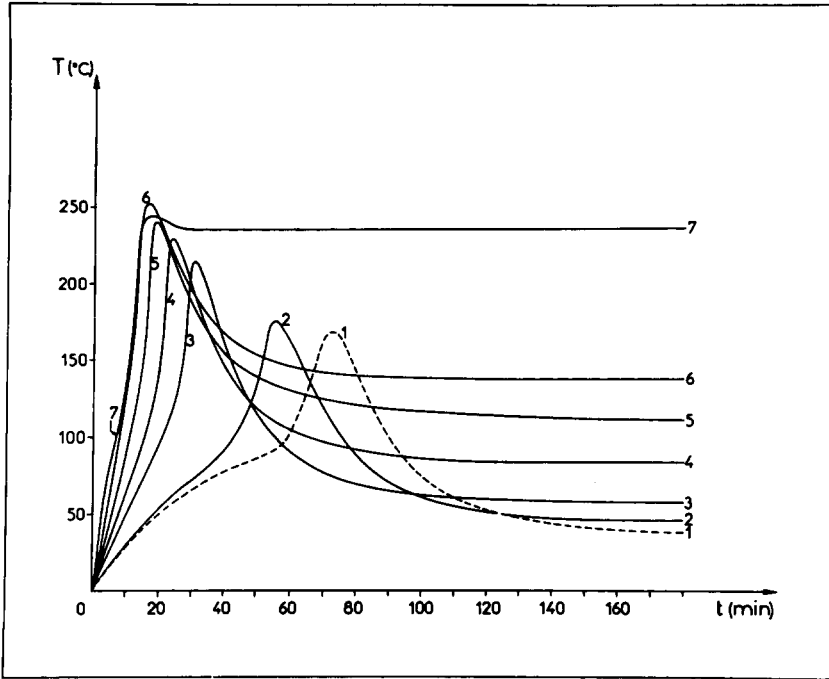


Fig. 1. Aluminium concentration (wt%) dependence, at $P_o = 30$ W, of $T = T(t)$: (1) 0%; (2) 10%; (3) 20%; (4) 30%; (5) 35%; (6) 40%; (7) 45%.

short times when the metallic content increases, whereas the intensity of their maxima grows (Table 2). This change is very similar to that encountered in the study of the electrical power dependence of T curves for the composite with 20% by wt of filler [1]. (T'

curves (Fig. 3) corroborate the evolution of the temperature, especially at the level of their maxima (which correspond to the inflexion point of the T segment of the exothermal step) but the fluidification is not marked, except for the resin (first maximum)

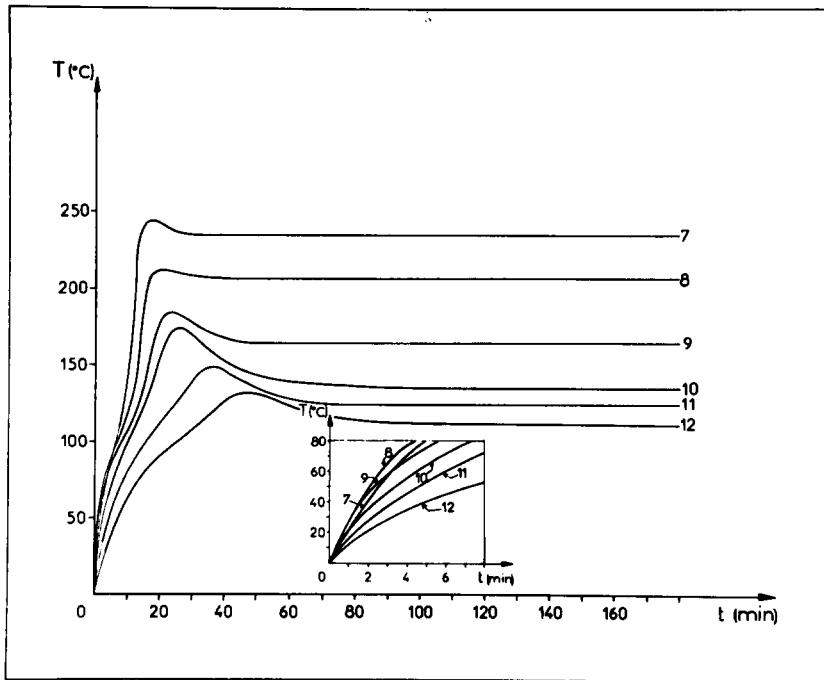


Fig. 2. Aluminium concentration (wt%) dependence, at $P_o = 30$ W, of $T = T(t)$: (7) 45%; (8) 50%; (9) 55%; (10) 60%; (11) 65%; (12) 70%.

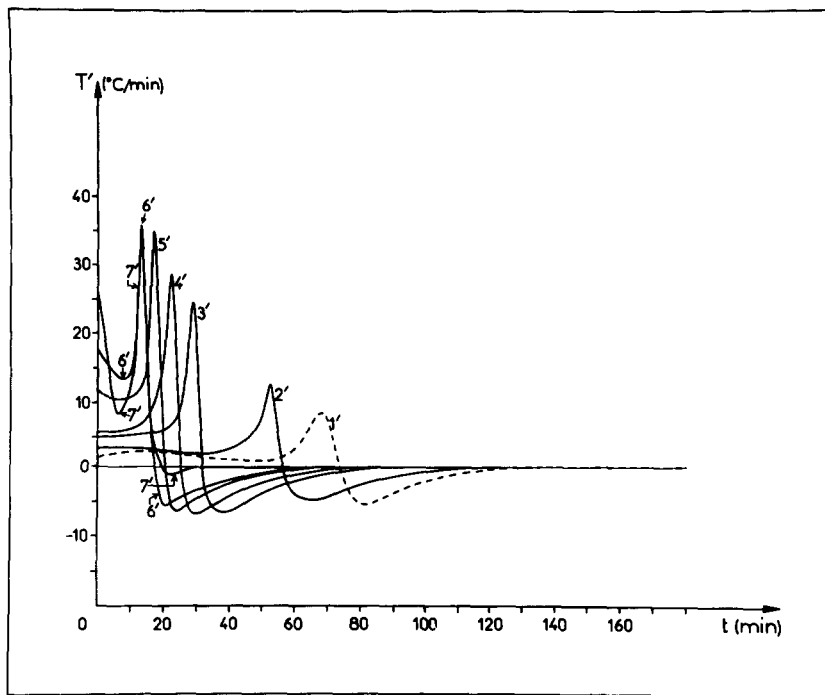


Fig. 3. Aluminium concentration (wt%) dependence, at $P_o = 30$ W, of $(T)' = dT/dt$: (1') 0%; (2') 10%; (3') 20%; (4') 30%; (5') 35%; (6') 40%; (7') 45%.

where it is widely spread. The T_p values, are continuously raised until 40% by wt (Table 2). The same tendency of variation of T curves is also observed in the corresponding Pu curves (Fig. 4): the peaks, which are linked to the gelification, are shifted towards low times when the metal concentration increases and the intensity of their maxima is raised; in addition, the duration of the sol-gel transition is reduced since the peaks become narrower. Moreover, the transition of fluidification is faster and faster, as is shown in $(Pu)'$ curves (Fig. 5) through the position in time of the positive peak.

The second series of T curves, from 45 to 70% by wt of metallic filler (Fig. 2) exhibits a quite different shape from that of the first series, especially at the level of thermal plateaux which partially overshadow the exothermal polymerization peaks on the one hand and which see their intensity decrease when the metallic content increases on the other hand. The divergence between both series also extends to the

changes of their shape, i.e. of the kinetics of heating of the samples and consequently of the location in time of structural changes. In fact, the exothermal peaks are shifted towards long times with increasing concentrations and the intensity of their maxima is reduced. There is no more similarity between this concentration dependence at a given electrical power and the electrical power dependence at a given concentration which has been previously described [1], when it exists for the preceding series. The filler rather acts then as a diluent which delays the kinetics of polymerization. The transition of fluidification is not always detected in $(T)'$ curves (Fig. 6). Corresponding Pu curves (Fig. 4) also indicate a change of thermal and dielectric behaviour from the 45% by wt region: the peak linked to the gelification still appears at 45 and 50% but it is replaced by an undulating segment which becomes straight at 70% (curve 12). Moreover, T_p and Pu_p values are differently self-correlated to aluminium concentrations. In fact, un-

Table 2. Aluminium concentration dependence, at $P_o = 30$ W, of main experimental parameters of the crosslinking reactions of the various composites

Aluminium (wt%)	Aluminium (vol%)	Pu_{max} (W)	Abscisse of Pu_{max} (min)	T_{max} (°C)	Abscisse of T_{max} (min)	Pu_p (W)	T_p (°C)
0	0	7.0	50	168	74	4.5	38
10	4.5	7.5	49	175	55	5.0	46
20	9.7	10.5	24	214	30	6.5	58
30	15.5	11.0	18	229	26	7.0	83
35	18.8	14.0	13	240	21	8.0	111
40	22.2	17.5	11	251	17	9.5	137
45	26.0	18.5	12	243	20	15.0	228
50	30.0	19.5	15	212	22	18.5	206
55	34.4	—	—	184	25	19.0	164
60	39.2	—	—	174	27	19.0	135
65	44.4	—	—	150	36	20.0	125
70	50.0	—	—	133	53	17.5	112

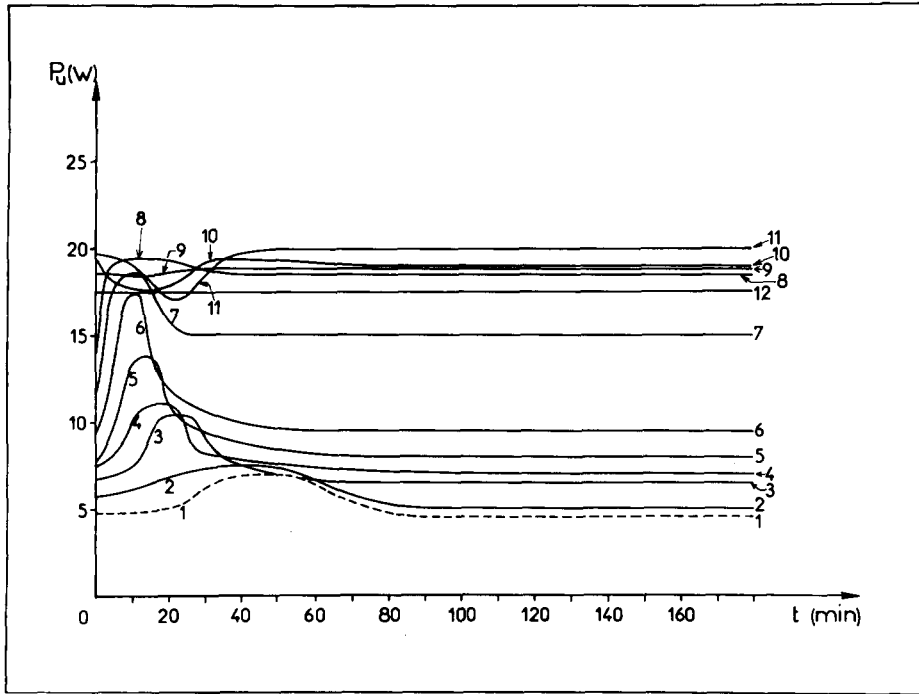


Fig. 4. Aluminium concentration (wt%) dependence, at $P_o = 30$ W, of $P_u = P_u(t)$: (1) 0%; (2) 10%; (3) 20%; (4) 30%; (5) 35%; (6) 40%; (7) 45%; (8) 50%; (9) 55%; (10) 60%; (11) 65%; (12) 70%.

like T_p which decreases from 45%, P_{u_p} continues more or less its growth up to 65% by wt, when it would have to drop down as T_p if the thermal and dielectric behaviour of the composites below 45% by

wt were related in the same way as in the preceding series. In $(P_u)'$ curves (Fig. 5), the first positive peak, which is usually linked to the fluidification, can hardly be attributed to such a transition because of

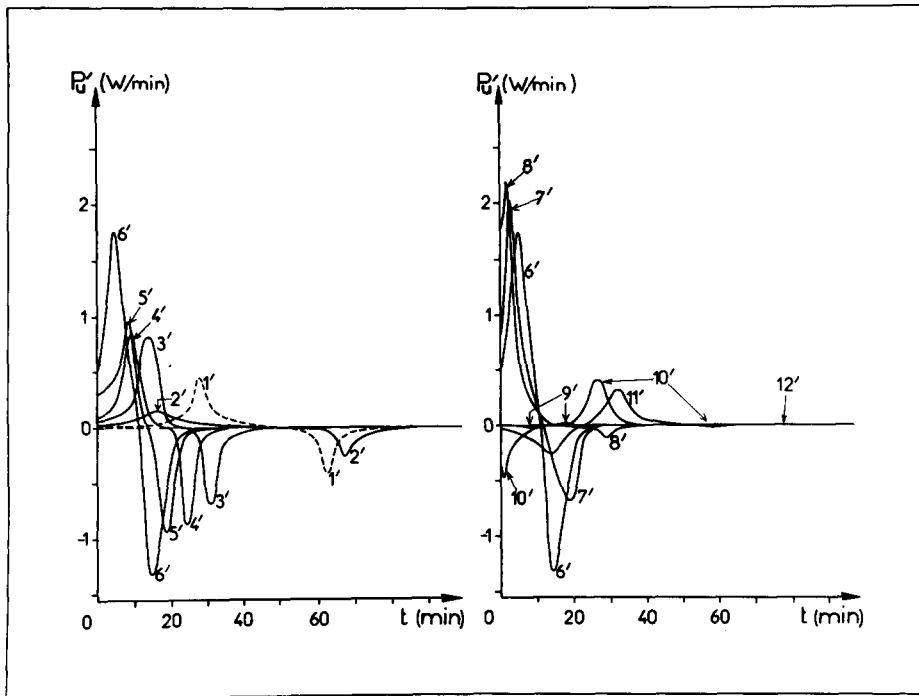


Fig. 5. Aluminium concentration (wt%) dependence, at $P_o = 30$ W, of $(P_u)' = dP_u/dt$: (1') 0%; (2') 10%; (3') 20%; (4') 30%; (5') 35%; (6') 40%; (7') 45%; (8') 50%; (9') 55%; (10') 60%; (11') 65%; (12') 70%.

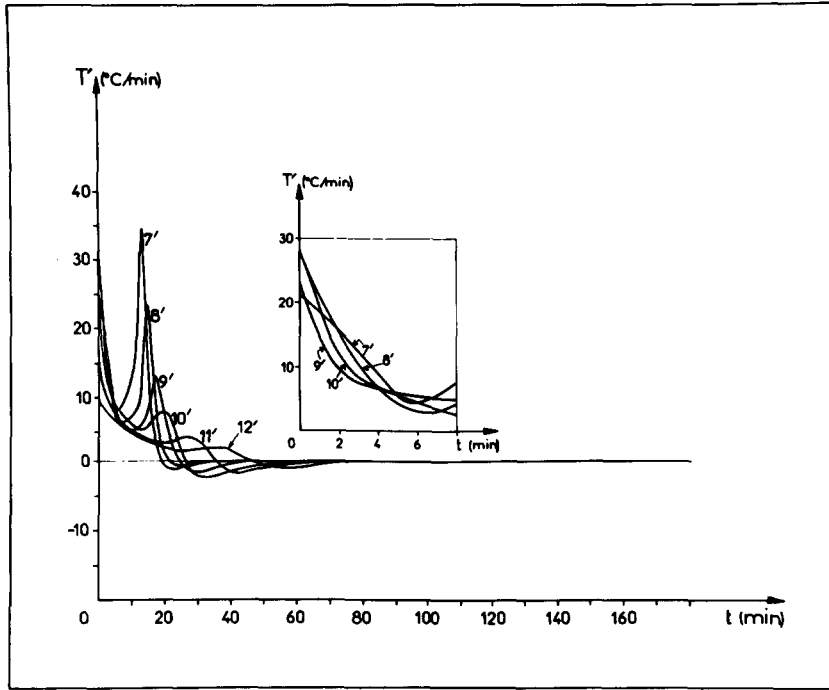


Fig. 6. Aluminium concentration (wt%) dependence, at $P = 30 \text{ W}$, of $(T') = dT/dt$: (7') 45%; (8') 50%; (9') 55%; (10') 60%; (11') 65%; (12') 70%.

the contributions of particles and also because of the shape of the corresponding segments in Pu curves which will be discussed later in this paper.

Figure 7 shows the variations with the metallic content of T_p and Pu_p in curves 1 and 2. These

parameters express the thermal and dielectric properties of samples of heterophased matter in the solid state at constant volume (17.25 ml), except for shrinkage due to network formation from the prepolymeric resin. First, T_p regularly increases until

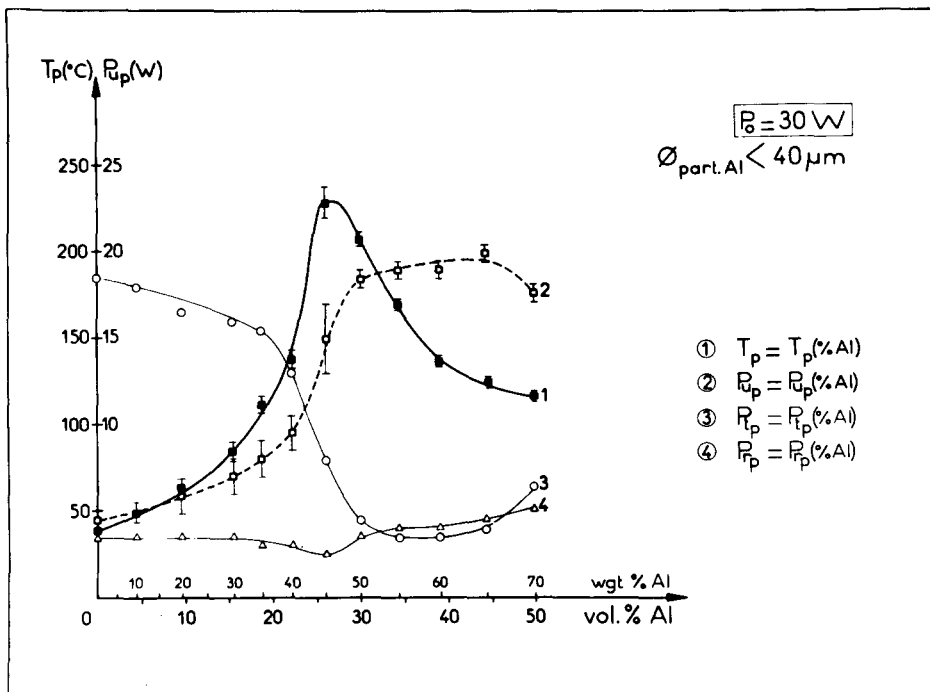


Fig. 7. Aluminium concentration (wt% and vol%) dependence, at $P_o = 30 \text{ W}$, of the plateau values of the temperature (T_p) and of the various measured powers (Pu_p , Pt_p and Pr_p): (1) T_p ; (2) Pu_p ; (3) Pt_p ; (4) Pr_p .

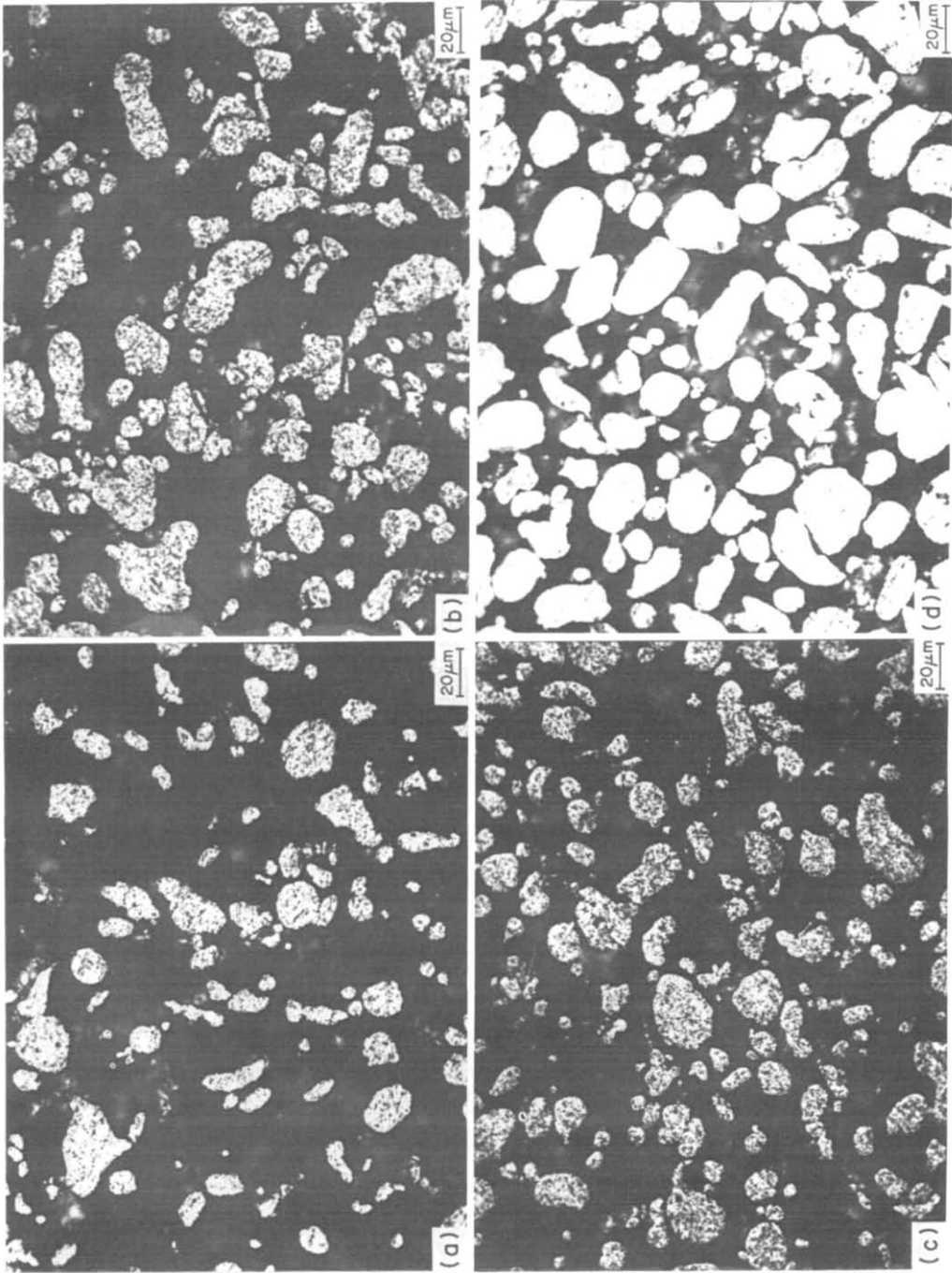


Fig. 8. Morphology ($\times 400$) of crosslinked aluminum powder-epoxy resin composites at variable filler concentrations (wt% or vol%, respectively): (a) 30 or 18.8%; (b) 40 or 22.2%; (c) 50 or 30%; (d) 70 or 50%.

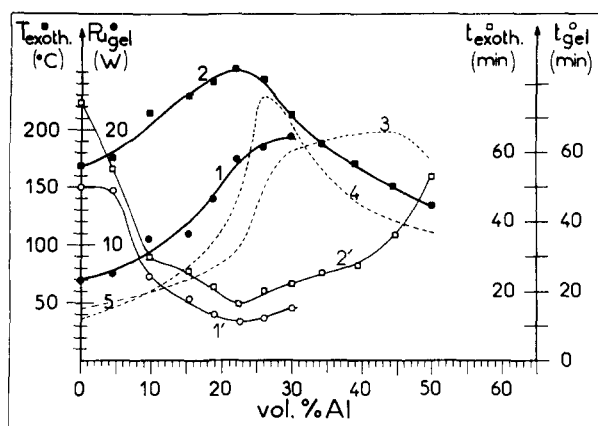


Fig. 9. Aluminium volume concentration dependence at $P_0 = 30$ W of various experimental parameters: (1) $P_{u_{gel}}$; (1') t_{gel} ; (2) $T_{exoth.}$; (2') $t_{exoth.}$; (3) P_{u_p} ; (4) T_p .

40% by wt, i.e. within the concentration range corresponding to the first series of T and P_u curves earlier analysed and quickly jumps to a maximum (228°) for the value of 45% by wt; beyond this critical concentration, T_p starts decreasing. Besides, the variations of P_{u_p} are attendant on those of T_p up to 45%, with the same increase, but at higher aluminium contents the dielectric absorption appears almost steady or grows very slightly up to 65% by wt; then it starts declining. Thus, beyond 45%, there is no correlation between T_p and P_{u_p} ; especially the decrease of T_p is not expected. In addition, the sense of variation of the transmitted power P_{t_p} , which first decreases and then becomes constant, and the quasi-invariance of the reflected power P_{r_p} are in good agreement with the P_{u_p} values and indicate that the materials preserve their dielectric character since, if they became conductive, P_{r_p} would have been raised and P_{t_p} would have disappeared. Thus, the existence of a maximum in the T_p curve and of a significant jump in the P_{u_p} values show that an energetic transition is undergone by the composites around 45% by wt of aluminium powder and at $P_0 = 30$ W. Before giving an interpretation of this phenomenon, an examination of the morphology of the composites is necessary. Figure 8 collects some observations by optical microscopy ($\times 400$): at 30% by wt, the metallic particles are isolated and uniformly distributed; between 40–50%, the granules start forming aggregates, much larger at 50%, in which they can be in contact with the others, but no continuous physical network of a percolation type is observed; the morphology at 70% shows that the formation of such a structure cannot be excluded. There is no electrical conduction phenomenon, as reported in a previous work [2], because the aluminium granules are coated with insulating alumina.

From all these observations, the transition can be explained by resorting to the formation of aggregates of filler particles. First, below 45%, the variations of T_p and P_{u_p} are concomitant. The mechanism of electrical loss inside the composite materials involves at the same time the dielectric loss P_{u_D} by dipolar relaxation of the chemical entities in the polymeric matrix and the loss of Joule effect due to conduction P_{u_C} through thin layers of aluminium granules sub-

mitted to microwave radiations. The contributions due to the reflexions of waves on the metallic particles are also included in P_{u_D} and P_{u_C} : everything occurs as if the path of the microwaves inside the resin was enlarged and the number of particles raised; so T_p and P_{u_p} increase with the filler amount. This last parameter is not the only one which has to be considered. Indeed, the temperature dependence of both mechanisms of loss should be also considered. The maximum of heating is observed at 45% by wt. Beyond this concentration, the temperature drops, whereas P_{u_p} tends to a plateau value. Such a change of variation takes place when the formation of aggregates becomes significant. A first explanation of the existence of the transition was suggested in the preceding paper [1]: the particles inside the aggregates would not see the waves and consequently the associated thermal effect would be reduced. This assumption is convenient to interpret the thermal behaviour of the samples, but remains insufficient to justify the stability of P_{u_p} which stays at a high level. An electrical phenomenon between or inside the aggregates cannot be considered, since the composites keep their dielectric behaviour at any aluminium concentration [2]. A possible interference with the thermal conductivity must be also rejected, for it varies almost linearly with no discontinuity within the concentration domain [3, 4]. From all these considerations, the only explanation of the quasi-stability of P_{u_p} beyond the critical value of 45% by wt, is that a change in the mechanisms of electrical loss due to the metallic particles occurs, with different thermal effects, leading to less efficient heating of the composites. Such a proposal is not unreasonable, since it is known that the conversion of electrical energy to heat inside the matter is never complete.

All previous comments are related to the dielectric and thermal properties of crosslinked aluminium powder-epoxy resin composites. They can also be extended to the prepolymeric systems, where the sol-gel transition is used as structural reference for the dielectric absorption $P_{u_{max}}$ referred now as $P_{u_{gel}}$. Figure 9 presents the variations of $P_{u_{gel}}$ (curve 1) with the filler volume concentration, at least up to 30% by vol (50% by wt); no P_u peak appears beyond this

content during the polymerization. Nevertheless, the energetic transition observed in the solid state around 26% by vol (45% wt) still exists but at lower metal content (around 22% by vol). Such a result is not surprising because of the higher dipolar activity of the fluid polymeric matrix, which increases not only the dielectric loss of the organic material but also, through the temperature of the samples, the conduction loss due to metallic particles. The associated gel time or t_{gel} (Fig. 9, curve 1') given by the abscisse of Pu_{gel} shows that the sol-gel transition is undergone earlier and earlier up to 22% by vol, in the region where Pu_{gel} is maximum. The opposite variations of the maximum of the temperature reached during the polymerization, i.e. T_{max} referred now as T_{exoth} (Fig. 9, curve 2) and of the associated time t_{exoth} (Fig. 9, curve 2'), also indicate that the most efficient heating is obtained around the energetic transition. Moreover, it is interesting to note that the peak of the T_{exoth} curve is located at a lower concentration than that of the T_p curve (Fig. 9, curve 4), because the thermal level of the samples is higher at the end of the crosslinking than for the final networks in thermodynamic equilibrium.

CONCLUSION

This study underlines the filler concentration dependence of the dielectric and thermal properties of aluminium powder-epoxy resin composites, cross-linked or not, when submitted to microwave treatment at 2.45 GHz. The most interesting result is the

existence of an energetic transition linked to the formation of aggregates of the metallic granules, and undergone at a concentration of 45% by wt (26% by vol) for the final materials and 40% by wt (22.2% by vol) in the gelled state with, in the case of the present work, an average aluminium particle size of 20 μm and an initial electrical power of 30 W. Beyond all these critical values, the temperature starts decreasing whereas the dielectric absorption is more or less stabilized. This result, which is still not explained, could be due to a change, with the filler content, of the mechanisms of dissipation of the microwave energy at the level of the aggregates, in relation with the physical properties of the materials. Further publications will deal with copper powder-epoxy resin and carbon black-epoxy resin composites, in order to extend the generalized model for the description of the interactions between microwaves and conductive powder-thermosetting resin systems.

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REFERENCES

1. Y. Baziard and A. Gourdenne. *Eur. Polym. J.* **24**, 873 (1988).
2. Y. Baziard, S. Breton, S. Toutain and A. Gourdenne. *Eur. Polym. J.* **24**, 521 (1988).
3. V. A. Nieberlein and B. Steverding. *J. Mater. Sci.* **12**, 1658 (1977).
4. W. J. Tomlinson and D. Stapley. *J. Mater. Sci.* **12**, 1689 (1977).