

## CROSSLINKING UNDER MICROWAVES (2.45 GHz) OF ALUMINIUM POWDER-EPOXY RESIN COMPOSITES—I. ELECTRICAL POWER DEPENDENCE

YVES BAZIARD and ALBERT GOURDENNE\*

Laboratoire de Physico-Chimie des Hauts Polymères, École Nationale Supérieure de Chimie de Toulouse,  
118, route de Narbonne, 31077 Toulouse Cedex, France

(Received 20 October 1987)

**Abstract**—The activation by microwave (2.45 GHz) heating of aluminium powder–epoxy resin composites is studied for two filler concentrations (20 and 50% by wt or 9.7 and 30% by vol). The classical transitions, such as fluidification and gelification which are encountered for epoxy resin and which are revealed through the curves showing the variations with time (at given electrical power) of the temperature of the samples and of the associated dielectric loss, are clearly marked at the lower metallic content; they are somewhat hidden for the higher content because of the contribution of the filler particles to the loss of energy due to conduction. However, a study of the electrical power dependence shows that in the final crosslinked state of both composites, the variations of the temperature and of the dielectric loss are governed by laws of the same type.

### INTRODUCTION

Previous work has shown that microwaves at 2.45 GHz are efficient for activating the crosslinking of epoxy resins through the conversion as heat of the dielectric loss, provided that the average electrical power of the electromagnetic beam is sufficient [1]. More recently, the dependence of thermal and dielectric properties of these thermosetting prepolymers during their polycondensation step on the mode of emission of the waves has been described [2–4]. When the emission is continuous, the energy transfer from the beam to the polymerizable matter is due to the induced dipolar relaxation. If the emission is periodic where  $\mathcal{T}$  is the period,  $N$  the frequency and  $\tau$  the pulse length, an additional relaxation has to be taken into account, i.e. relaxation of short chain segments linked to  $\mathcal{T}$  or  $N$ , the balance between the magnitude of the respective relaxations being mainly ruled by the value of  $\tau$ . In the present work, the mode of emission used is pulsed, where waves are delivered by a commercial generator and has been published elsewhere [2]:  $\mathcal{T} = 20$  msec,  $N = 50$  Hz and  $\tau = 3$  msec. In comparison with the continuous mode, this last one appears less efficient as far as heating of prepolymeric material. However, the average electrical power of the electromagnetic beam can be much more regulated.

When divided metal–epoxy resin composites are treated with microwaves, the contribution of the filler powder to the process of dissipation of microwave electrical power has to be considered: when the metallic granules are separated, some energy is lost as heat at the level of a thin overlayer of metal due to electronic conduction; the waves are also reflected by the particles and their path through the organic matrix is lengthened so that the dielectric loss inside

the epoxy resin is increased and becomes the same as for the loss by conduction because each granule can be hit several times by the same initial beam. Of course, the contribution of the powder granules should depend on their number and size and also on their chemical nature, since these parameters govern the dielectric behaviour of the composite materials which they form with the epoxy resins, as has been shown in other publications when the filler is aluminium [5] or copper [6].

In the present article, the activation under microwaves of the crosslinking of aluminium powder–epoxy resin composites containing 20% by wt (or 9.7% by vol) on 50% by wt (or 30% by vol) of metallic additive is studied. In both cases, no continuous physical network of particles is observed but significant aggregates exist at the higher aluminium content.

### EXPERIMENTAL

The prepolymeric resins are prepared by mixing in stoichiometric ratios an epoxy resin of DGEBA type (Lopox 200 of CDF Chimie) with a polymerization index  $n \approx 0.1$  with diaminodiphenylmethane, DDM (Fluka—Ref. 32950) with a purity grade of 98% as curing agent, according to a procedure described elsewhere [1]: the convenient amount of epoxy resin previously heated at 60° is poured on fused DDM at 120° and the resulting mixture is mechanically stirred. A final fluid single phase, transparent and lightly yellow, is obtained. It is then degassed under primary vacuum at 75° and added to aluminium powder (Prolabo—Ref. 20998-296) with a purity grade of 99% and a particle size, after sifting, below 40  $\mu\text{m}$  (mean dia  $\approx 20$   $\mu\text{m}$ ); this mixture is also stirred, homogenized through ultrasonics and again degassed at 60°. Samples are then cut off, poured inside cylindrical Pyrex pillboxes with good transparency to microwaves, submitted to further degassing at 60° and stored at  $-30^\circ$  until electromagnetic treatment. The initial volume of samples at ambient is kept constant at 17.25 ml so as to prevent any volume effect towards the waves; the

\*To whom correspondence should be addressed.

volume corresponding to 20 g of prepolymer with a density of 1.16. From this base, suitable aluminium content expressed in percentages by wt and vol are chosen with respect to the metal density (2.7). The description of the chemicals would not be achieved if data on conductivity of aluminium were not provided. In fact, d.c. conductivity measurements of powder samples compressed under 250 kg/cm<sup>2</sup> give values  $< 10^{-1} \Omega^{-1} \cdot \text{cm}^{-1}$  at 25°C instead of  $3.77 \cdot 10^5 \Omega^{-1} \cdot \text{cm}^{-1}$  as expected for pure metal. This divergence results from the coating of the granules with a layer of alumina which drastically decrease the electrical properties, as previously shown [5].

The microwave apparatus has been fully described [7] and only the principle of its working will be presented here: microwaves (2.45 GHz) are delivered by a commercialized generator in pulsed regime with a period  $\mathcal{T} = 20$  msec or a frequency  $N = 50$  Hz, a pulse length  $\tau = 3$  msec and an average electrical power  $P_0$  and forced to progressively propagate inside a waveguide according to TE<sub>01</sub> mode, where they hit the polymerizable matter. The variations with time of the temperature of the samples  $T = T(t)$  and of the electrical loss  $Pu = Pu(t)$  are recorded during the electromagnetic treatment and their derivatives  $(T)' (= dT/dt)$  and  $(Pu)' (= dPu/dt)$  calculated. Analysis of the corresponding curves gives information on the structural changes inside the samples [1].

## RESULTS AND DISCUSSION

Figure 1 presents the variations with time of  $T = T(t)$ ,  $Pu = Pu(t)$ ,  $(T)' = dT/dt$  and  $(Pu)' = dPu/dt$  for a sample of DGEBA-DDM prepolymer (20 g) used as a blank, at an average electrical power  $P_0 = 30$  W. The curves are similar in shape to these previously published [1], but with lower resolution in  $(T)'$  because  $P_0$  is weak. However, the choice of such a value is governed because the thermal level of aluminium powder-epoxy resin composites, which heat much more than the blank, must not exceed certain limits, beyond which they would burn. The classical steps of the crosslinking process are seen on  $T$  curve. The first period called preheating starts from

0°C to the sol-gel transition for which  $Pu$  is maximum (50 min; 7.0 W) and includes the fluidification on the prepolymer which is positioned in time as the first maximum of  $(Pu)'$  at 28 min; the first maximum of  $(T)'$  would have to have appeared at the same time as expected [1], but the variations of  $(T)'$  in this region are obviously not significant, as those of  $T$ , and cannot provide useful information. Nevertheless, the temperature of the fluidification transition extrapolated for the  $T$  curve from the abscisse of the peak of  $(Pu)'$  is 61°, a value very near to others determined from both first peaks of  $(T)'$  and  $(Pu)'$  with higher  $P_0$  [1]. Gelification spreads widely as shown by the  $Pu$  peak; it also corresponds to the second inflexion point in the  $T$  curve [minimum of  $(T)'$ ] in agreement with the observation also made when the step-approach reaction is thermally activated inside an oven (classical heating). Beyond the gel point, the fast exothermic main conversion of epoxides takes place:  $T$  quickly increases, whereas  $Pu$  drops down because of viscosity effects resulting from the crosslinking process in progress. The heating rate of the sample which varies as  $(dT/dt)$ , is maximum at the inflexion point of the exothermal segment, or at the third inflexion point of the  $T$  curve. After the maximum of  $T$ , no more chemical heat is produced and the sample begins to cool because of loss of energy due to thermal convection; this loss of energy as heat is given by the formula:  $b \cdot m \cdot c_p \cdot (T - T_0)$ , where  $m$ ,  $c_p$ ,  $T$ ,  $T_0$  and  $b$  are respectively the weight, specific heat, temperature of the sample, average temperature of the surrounding medium ( $20^\circ \pm 1^\circ$ ) and the convection factor mainly depending on the shape and dimensions of the sample. In the final state where the matrix is crosslinked and glassy,  $T$  and  $Pu$  have plateau values  $T_p$  and  $Pu_p$  resulting from a balance between the dielectric loss, or more exactly its thermal part, and the loss of energy by convection.

Figure 2 shows the four curves for a sample (17.25 ml) of an aluminium powder-epoxy resin com-

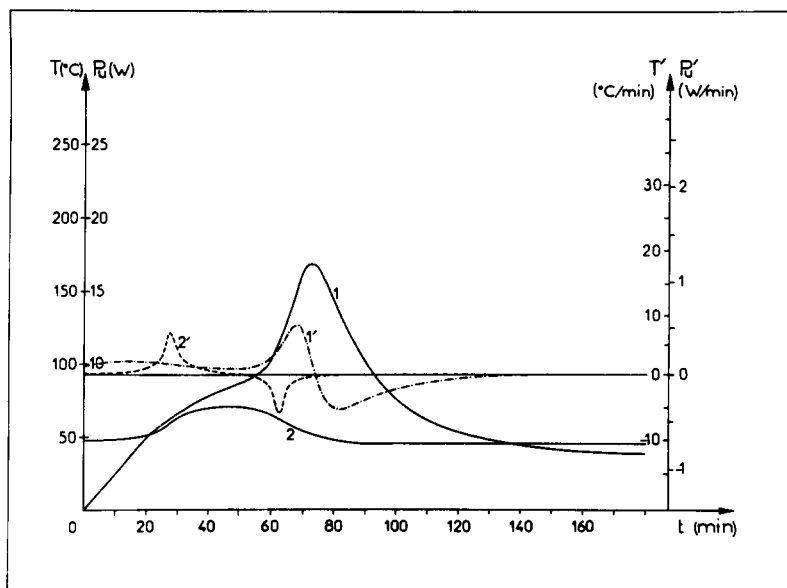


Fig. 1. Crosslinking under microwaves at  $P_0 = 30$  W of the epoxy resin: (1)  $T = T(t)$ ; (1')  $(T)' = dT/dt$ ; (2)  $Pu = Pu(t)$ ; (2')  $(Pu)' = dPu/dt$ .

Table 1. Crosslinking of aluminium powder-epoxy resin composites at  $P_o = 30$  W: values of main experimental parameters

Aluminium (wt %)	Aluminium (vol %)	$Pu_{max}$ (W)	Abscisse of $Pu_{max}$ (min)	$T_{max}$ ( $^{\circ}$ C)	Abscisse of $T_{max}$ (min)	$Pu_p$ (W)	$T_p$ ( $^{\circ}$ C)
0	0	7.0	50	168	74	4.5	38
20	9.7	11.0	24	214	30	6.5	58
50	30.0	19.5	15	212	22	18.5	206

posite with 20% by wt of filler, or 4.52 g of metal and 18.07 g of organic matter, where all the particles are separated (Fig. 3) so that hopping of electrons is unexpected, submitted to microwave treatment at  $P_o = 30$  W. The curves are similar in shape to those of the blank, but their peaks are shifted to shorter times, whereas they become narrower and their intensities increase. Table 1 shows the variations of the main experimental parameters, where the maxima of  $T$  and  $Pu$  are referred to as  $T_{max}$  and  $Pu_{max}$ ; it indicates that the crosslinking is accelerated because of the thermal contribution of aluminium granules to the activation of the step-growth polymerization, which is well shown in  $T_p$  value ( $58^{\circ}$  instead of  $38^{\circ}$ ). On the other hand, the  $Pu$  curve around its maximum remains oblate and the first peak of  $(T)'$  linked to fluidification is not seen, although the transition still exists [first maximum of  $(Pu)'$ ].

From these results, it seems that larger amounts of powder should more and more increase the rate of heating and crosslinking of the composites. Figure 4 collects the curves when a concentration of 50% by wt of filler, i.e. 14.0 g of metal and 14.0 g of prepolymer for a total volume of 17.25 ml, is used. They are now completely different: the peaks of  $T$  and  $Pu$  curves (Curves 5 and 6) are not separated from  $T_p$  and  $Pu_p$ , which are, besides, much higher than above (Table 1), respectively  $206^{\circ}$  and 18.5 W. Such a situation makes difficult the correlations between the various inflexion points and maxima and the

fluidification and sol-gel transitions because of overlapping of  $T$  and  $Pu$  peaks and  $T_p$  and  $Pu_p$  segments. Nevertheless, the values in time of  $T_{max}$  and  $Pu_{max}$  are smaller, as expected from the tendency still encountered. In addition  $Pu_{max}$  is also raised as it could have been expected from the preceding experiment for the composite with 20% in wt of aluminium, but  $T_{max}$  is at the very least stationary ( $212^{\circ}$  instead of  $214^{\circ}$ ), i.e. the variations of  $T_{max}$  and  $Pu_{max}$  start being opposite. This difference could be related to the beginning of the formation of large aggregates between metallic particles (Fig. 3). As a matter of fact, one may suppose that the granules inside the aggregates or dense domains of particles are not hit by the waves and then do not participate in the electrical loss and consequent heating of the sample, unless  $Pu$  drops down at the same time if it is not especially quantitatively proportional to the metallic content, as it is likely. The part played by the aggregates in the thermal and dielectric behaviour of the composites will be extensively analysed in a subsequent article [8]. In addition, the observed discrepancy in  $T_{max}$  cannot be attributed to a significant change of thermal conductivity, since it has been shown [9, 10] that this physical parameter continuously increases with the aluminium concentration.

Figures 5 and 6 show the two pairs of curves  $T$ ,  $(T)'$  and  $Pu$ ,  $(Pu)'$  for the composite with 20% by wt of aluminium, when  $P_o$  takes successive values of 25, 30, 40 and 50 W. When  $P_o$  increases, the shape of

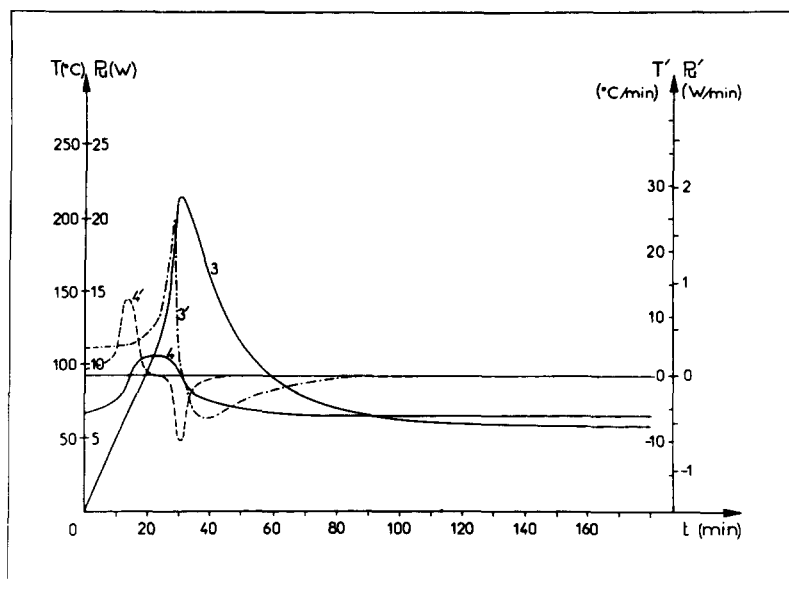


Fig. 2. Crosslinking under microwaves at  $P_o = 30$  W of the composite with 20% by wt of aluminium: (3)  $T = T(t)$ ; (3')  $(T)' = dT/dt$ ; (4)  $Pu = Pu(t)$ ; (4')  $(Pu)' = dPu/dt$ .

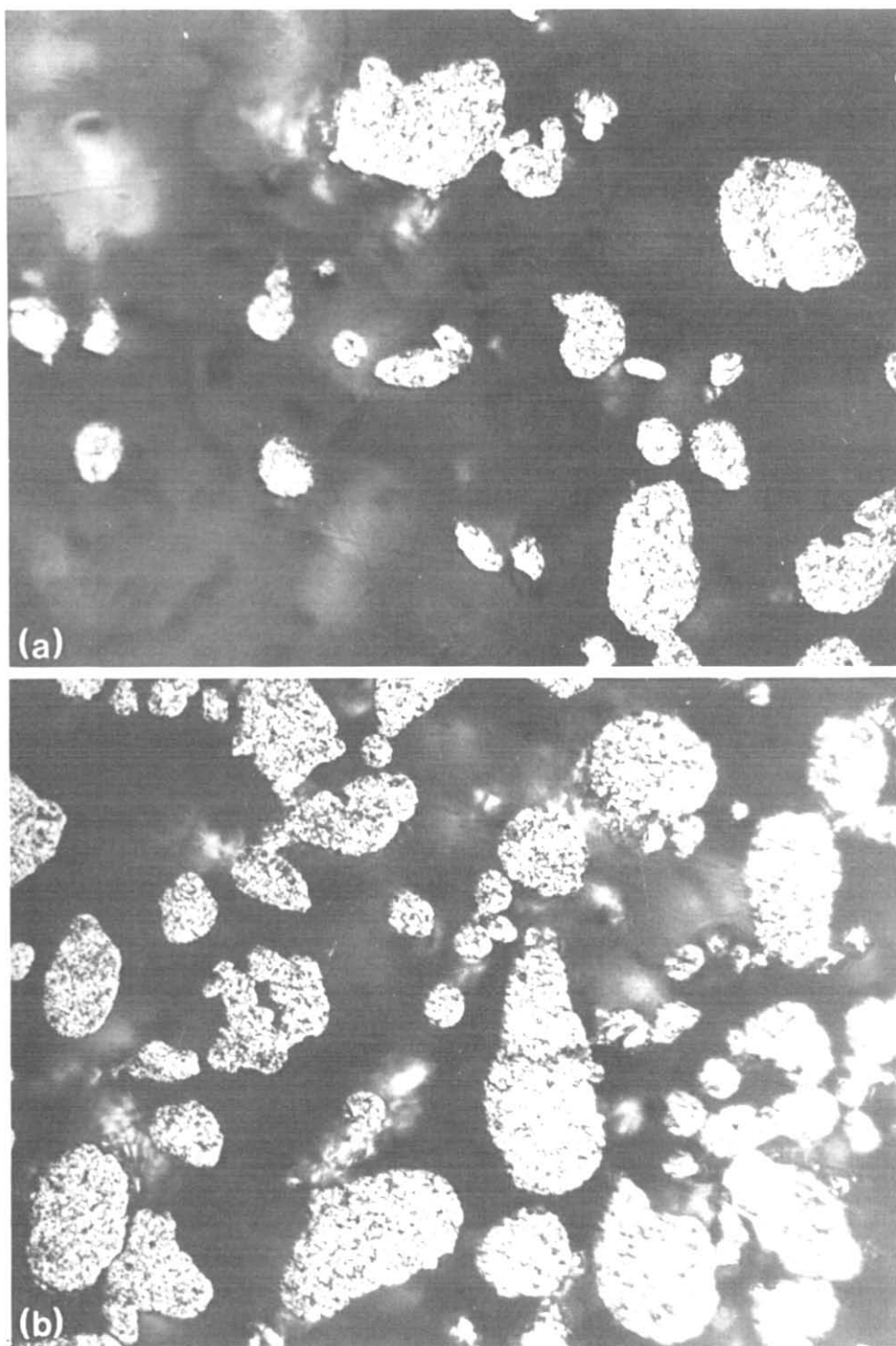


Fig. 3. Morphology of composites with 20 and 50% by wt (or 9.7 and 30% by vol) of filler (optical microscopy:  $\times 800$ ).

all  $T$  and  $Pu$  curves is preserved, but the peaks become narrower and narrower and more and more intense and shifted towards shorter times (Table 2), whereas the fluidification and gelification transitions are still marked.  $T_p$  and  $Pu_p$  are also increased and vary linearly with  $Po$ , within experimental error, as shown in Fig. 7 where the thermal gradient  $\Delta T_p = T_p - T_o$  between the sample and the sur-

rounding medium ( $T_o$ ) is preferred for further thermodynamic treatment of energy data, especially when the convection loss  $\Delta E = b \cdot m \cdot c_p \cdot \Delta T_p$  is considered. From these assumed linear laws of variation, some interesting conclusions can be drawn:

(1) All samples which have been crosslinked at different  $Po$  values, are structurally homogeneous,

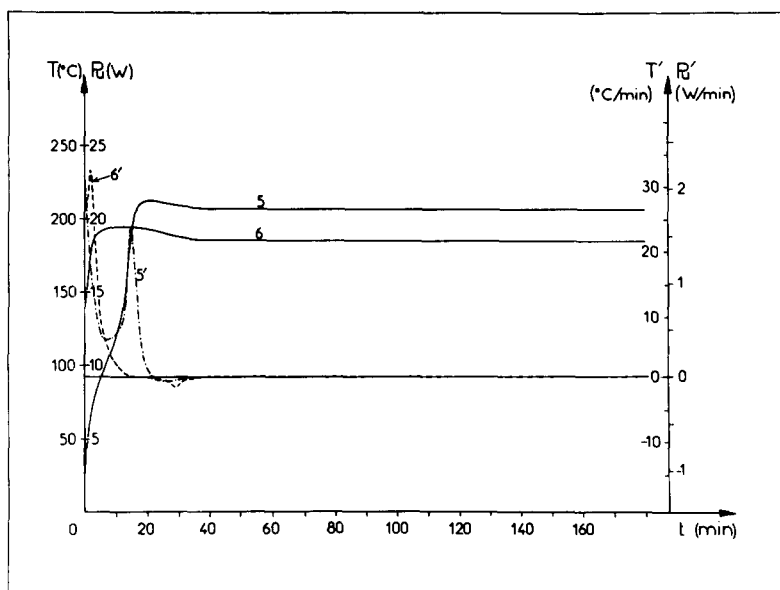


Fig. 4. Crosslinking under microwaves at  $P_o = 30$  W of the composite with 50% by wt of aluminium: (5)  $T = T(t)$ ; (5')  $(T)' = dT/dt$ ; (6)  $P_u = P_u(t)$ ; (6')  $(P_u)' = dP_u/dt$ .

since their thermal and dielectric behaviours are governed by the same linear functions of  $P_o$ .

(2) No physical changes (such as the glass transition expected around  $160^\circ$ ) for the matrix are observed, which would affect the specific heat of the composite and consequently the  $T_p$  and  $P_{up}$  curves with slope breaks.

(3)  $\Delta T$  or  $T$  and  $P_{up}$  are also directly proportional, although  $P_{up}$  consists of two parts resulting from different mechanisms of energy loss, one,  $P_{uD}$ , due to dipolar relaxation inside the organic material, the other,  $P_{uC}$ , resulting from conduction at the level of

metallic charges on the surface of residual aluminium; further comment on the relative contributions of  $P_{uD}$  and  $P_{uC}$  cannot be made since they are dependent variables through the multiple reflections of the waves.

(4) An apparent loss factor at 2.45 GHz can be defined as  $P_{up}/P_o$  and is constant at 0.22, whatever the temperature (for crosslinking epoxy resin at  $P_o = 30$  W,  $P_{up}/P_o = 0.15$ ).

Figures 8 and 9 present respectively, the pairs of curves  $T, (T)'$  and  $P_u, (P_u)'$  of the composite (17.25 ml) at 50% in wt of filler for various  $P_o$ : 10,

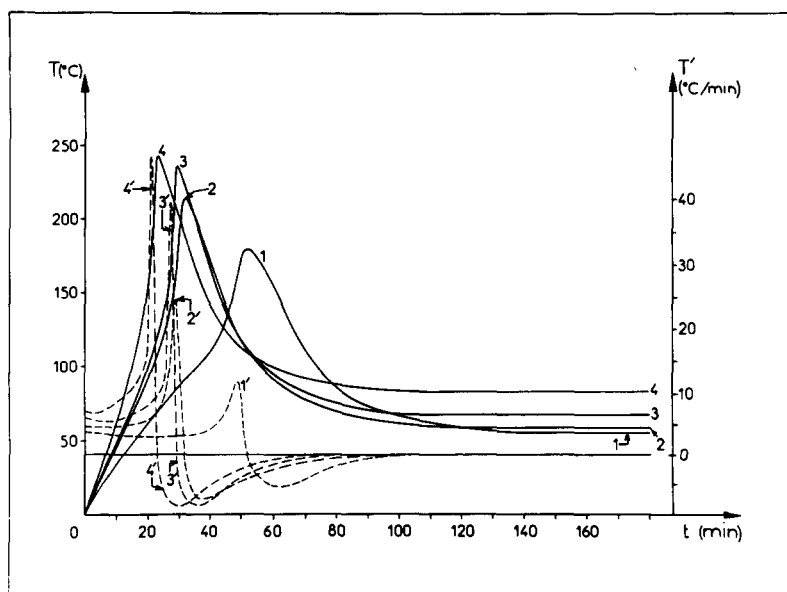


Fig. 5. Crosslinking under microwaves of the composite with 20% by wt of aluminium: electrical power dependence of  $T = T(t)$  and  $(T)' = dT/dt$ .  $T = T(t)$ : (1)  $P_o = 25$  W; (2)  $P_o = 30$  W; (3)  $P_o = 40$  W; (4)  $P_o = 50$  W.  $(T)' = dT/dt$ : (1')  $P_o = 25$  W; (2')  $P_o = 30$  W; (3')  $P_o = 40$  W; (4')  $P_o = 50$  W.

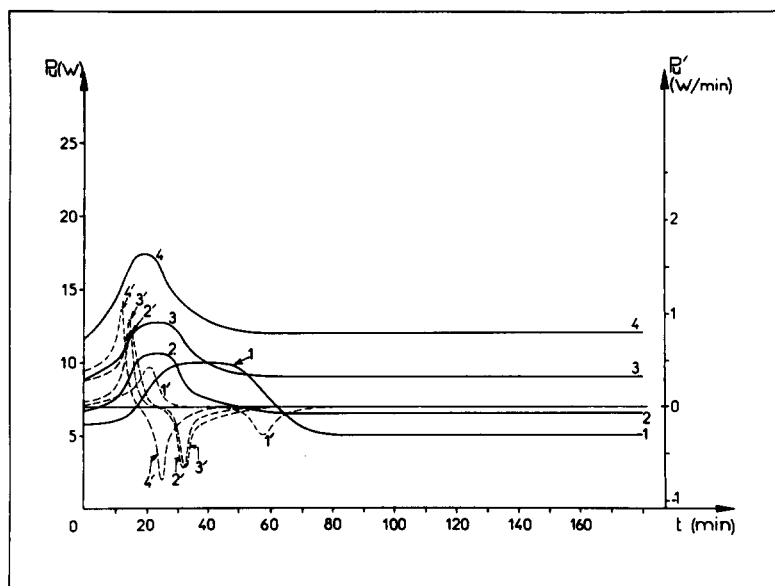


Fig. 6. Crosslinking under microwaves of the composite with 20% by wt of aluminium: electrical power dependence of  $Pu = Pu(t)$  ( $Pu' = dPu/dt$ ).  $Pu = Pu(t)$ : (1)  $Po = 25$  W; (2)  $Po = 30$  W; (3)  $Po = 40$  W; (4)  $Po = 50$  W. ( $Pu' = dPu/dt$ ): (1')  $Po = 25$  W; (2')  $Po = 30$  W; (3')  $Po = 40$  W; (4')  $Po = 50$  W.

20, 30 and 35 W. Whereas the shape of  $Pu$  curves is preserved when  $Po$  is raised, that of  $T$  curves changes radically from what is observed for the former composites (Fig. 5). In first  $T$  curves at  $Po = 10$  and 20 W,

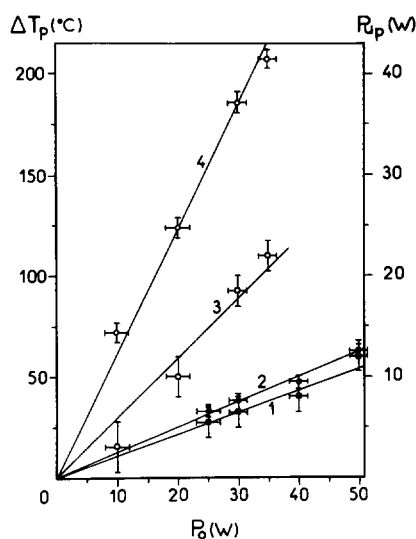


Fig. 7. Electrical power dependence of plateau values  $T_0$  and  $Pu_p$  for both composites: 20% by wt of filler—(1)  $Pu_p = Pu_p(Po)$ ; (2)  $\Delta T_p = \Delta T_p(Po)$ . 50% by wt of filler—(3)  $Pu_p = Pu_p(Po)$ ; (4)  $\Delta T_p = \Delta T_p(Po)$ .

the gelification is still observed, but its identification becomes uncertain when  $Po = 30$  and 35 W. The same comments are applicable to  $Pu$  including the transition of fluidification. On the other hand, the general variation of the main experimental parameters, still encountered for the composite at 20% by wt of aluminium when  $Po$  is increased, is also found: all  $T$  and  $Pu$  peaks are shifted towards short times and their intensities become higher (Table 3);  $T_p$  and  $Pu_p$  increase and also more or less linearly depend on  $Po$  (Fig. 7) with an apparent dielectric loss  $Pu_p/Po$  of 0.70 instead of 0.22 for the preceding composite. So both composites in solid state behave in the same way towards the electrical power but with different dielectric loss.

## CONCLUSION

The reported study shows that the crosslinking of aluminium powder-epoxy resin composites can be activated by microwave heating at 2.45 GHz. The dielectric loss  $Pu$  inside the samples for given initial electrical power  $Po$  is divided in two parts: one,  $Pu_D$ , due to dipolar relaxation of the resin and the other,  $Pu_C$ , to surface conduction of aluminium particles. The contribution of the alumina layer which coats the granules is low because of its thickness and the used frequency. The kinetics of the electromagnetic process of crosslinking appear very sensitive to the metal

Table 2. Electrical power dependence of the main experimental parameters of the reactions of crosslinking of the composite at 20% by wt of aluminium

$Po$ (W)	$Pu_{max}$ (W)	Abscisse of $Pu_{max}$ (min)	$T_{max}$ (°C)	Abscisse of $T_{max}$ (min)	$Pu_p$ (W)	$T_p$ (°C)
25	10.0	43	178	52	5.5	55
30	11.0	24	214	30	6.5	58
40	13.0	24	236	29	8.0	67
50	17.5	18	243	23	12.0	83

Table 3. Electrical power dependence of the main experimental parameters of the reactions of crosslinking of the composite at 50% by wt of aluminium

$P_o$ (W)	$Pu_{max}$ (W)	Abscisse of $Pu_{max}$ (min)	$T_{max}$ (°C)	Abscisse of $T_{max}$ (min)	$Pu_p$ (W)	$T_p$ (°C)
10	4.5	41	133	64	8.0	95
20	12.5	19	189	27	10.0	144
30	19.5	15	212	22	18.5	206
35	23.0	10	230	20	22.0	230

content, i.e. to the number of filler particles, which increases both parts of the electrical loss through multiple reflexions of the waves on the metallic particles. The contribution of the powder when its

concentration is 50% by wt is so great that the classical transitions observed during the step-growth polymerization, such as fluidification and gelification which affect the matrix, are almost obscured, al-

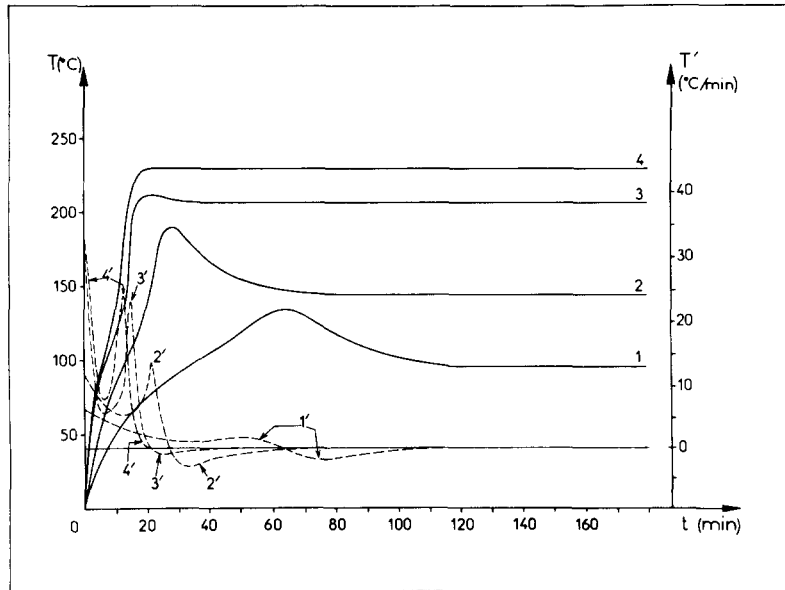


Fig. 8. Crosslinking under microwaves of the composites with 50% by wt of aluminium: electrical power dependence of  $T = T(t)$  and  $(T)' = dT/dt$ .  $T = T(t)$ : (1)  $P_o = 10$  W; (2)  $P_o = 20$  W; (3)  $P_o = 30$  W; (4)  $P_o = 35$  W.  $(T)' = dT/dt$ : (1')  $P_o = 10$  W; (2')  $P_o = 20$  W; (3')  $P_o = 30$  W; (4')  $P_o = 35$  W.

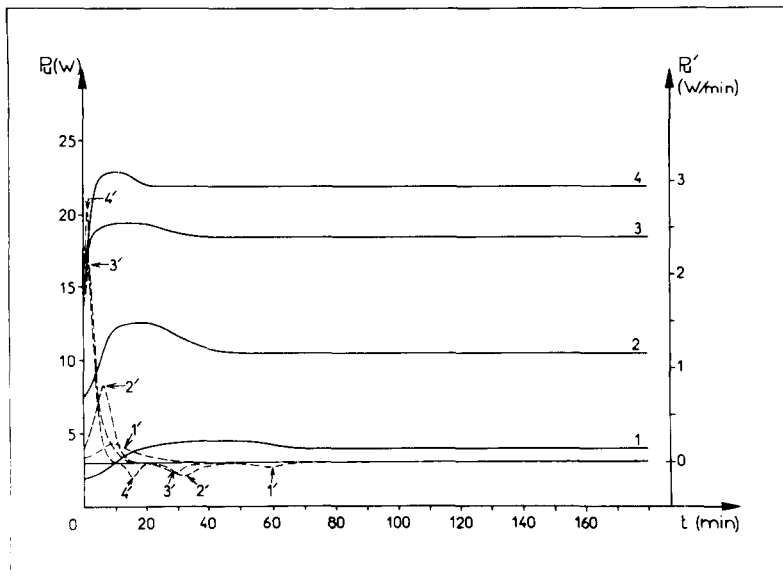


Fig. 9. Crosslinking under microwaves of the composite with 50% by wt of aluminium: electrical power dependence of  $Pu = Pu(t)$  and  $(Pu)' = dPu/dt$ .  $Pu = Pu(t)$ : (1)  $P_o = 10$  W; (2)  $P_o = 20$  W; (3)  $P_o = 30$  W; (4)  $P_o = 35$  W.  $(Pu)' = dPu/dt$ : (1')  $P_o = 10$  W; (2')  $P_o = 20$  W; (3')  $P_o = 30$  W; (4')  $P_o = 35$  W.

though at 20% by wt they are easily observed. In any case, the crosslinking reactions of the epoxy resin are accelerated in comparison with the blank, to a greater extent with increasing aluminium content. However, the experiment at 50% seems to show a change in the contribution of particles linked to the formation of aggregates of granules. This problem has been already considered through study of the aluminium concentration dependence at given  $P_0$  which will be reported in the next paper [8]. On the other hand, the high values of the ratio  $P_u/P_0$  (which can be considered as an apparent loss factor) 0.22 and 0.70 for crosslinked composites with 20 and 50% by wt of metal, indicate that the aluminium powder-epoxy resin materials could be used as dielectric absorbers.

*Acknowledgement*—Financial assistance from Electricité de France (Direction des Études et Recherches) is gratefully acknowledged.

#### REFERENCES

1. Q. Le Van and A. Gourdenne. *Eur. Polym. J.* **23**, 777 (1987).
2. N. Beldjoudi, A. Bouazizi, D. Douibi and A. Gourdenne. *Eur. Polym. J.* **24**, 49 (1988).
3. N. Beldjoudi and A. Gourdenne. *Eur. Polym. J.* **24**, 53 (1988).
4. N. Beldjoudi and A. Gourdenne. *Eur. Polym. J.* **24**, 265 (1988).
5. Y. Baziard, S. Breton, S. Toutain and A. Gourdenne. *Eur. Polym. J.* **24**, 521 (1988).
6. Y. Baziard, S. Breton, S. Toutain and A. Gourdenne. *Eur. Polym. J.* **24**, 633 (1988).
7. M. Teflal and A. Gourdenne. *Eur. Polym. J.* **19**, 543 (1983).
8. Y. Baziard and A. Gourdenne. *Eur. Polym. J.* **24**, 881 (1988).
9. V. A. Nieberlein and B. Steverding. *J. Mater. Sci.* **12**, 1658 (1977).
10. W. J. Tomlinson and D. Stapley. *J. Mater. Sci.* **12**, 1689 (1977).