

# INTERACTIONS BETWEEN CARBON BLACK–EPOXY RESIN COMPOSITES AND CONTINUOUS MICROWAVES—I. ELECTRICAL POWER DEPENDENCE OF THE RATE OF CROSSLINKING OF THE EPOXY MATRIX

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**Abstract**—Crosslinking under continuous microwaves (2.45 GHz) of carbon black–epoxy resin composites with 5% by wt of filler are described through the variations with time of the average temperature of the samples and of the associated loss of electrical power of the electromagnetic radiation, which are correlated with the structural changes of the composite materials. The results are interpreted in terms of dipolar relaxation of the matrix and of conduction at the level of separated conductive aggregates of carbon black particles. The active contribution of the fillers to heating of the mixtures is demonstrated by a study of the electrical power dependence of the kinetics of crosslinking of the matrix.

## INTRODUCTION

Previous work [1] has shown that microwaves (2.45 GHz) are able to activate the crosslinking of DGEBA epoxy resins in the presence of diaminodiphenylmethane (DDM) as curing agent. All the usual transitions of steps of the polycondensation have been isolated, viz. fluidification and gelification of the chemical medium, exothermal conversion of epoxides and cooling beyond the exothermal maximum. The dependence of heating efficiency on the signal of the microwave power, i.e. on the mode of emission of the electrical power at given average power of the incident radiation, has also been studied [2–4]. This mode can be continuous or discontinuous (hit and miss) with a period  $\mathcal{T}$  and a pulse length  $\tau$ . The relaxation of the dipolar entities is induced by the oscillations of the electrical field at 2.45 GHz, whereas the relaxation of short chain segments at much lower frequencies in the 10 Hz–1 kHz range is favoured by the periodic emission of the radiation. The crosslinking under microwaves of epoxy resins filled with aluminium particles has also been studied [5]: the loss of electrical power  $Pu$  is divided into two parts: one,  $Pu_D$ , due to the dipolar relaxation inside the matrix (and eventually to the relaxation of short chain segments) and the other,  $Pu_C$ , to the conduction phenomenon at the level of filler granules. In addition,  $Pu_D$  and  $Pu_C$  can be dependent variables because of the multiple reflexions of the waves when the concentration of aluminium is sufficient.

In this series, the behaviour under microwaves (2.45 GHz) of carbon black (CB)–epoxy resin mixtures which should be considered as model materials for carbon fibre–epoxy composites will be analysed. The present paper reports the results for a composition with 5% by wt of filler.

## EXPERIMENTAL

The microwave treatment of the samples of CB–epoxy resin mixtures is carried out through the microwave apparatus previously described [2, 6] inside a wave guide in which continuous waves (2.45 GHz) propagate according to  $TE_{01}$  mode and in a progressive way. The electromagnetic radiation crosses the samples of matter to be treated which are stored inside Pyrex reactors, where its initial electrical power is partially degraded; the corresponding loss of energy is  $Pu$ . At the same time the temperature of the samples increases sufficiently to activate the crosslinking of the matrix. The variations with time  $t$  of the temperature  $T = T(t)$  and of the loss  $Pu = Pu(t)$  are automatically recorded; the derivatives  $(T)' = dT/dt$  and  $(Pu)' = dPu/dt$  are calculated.

The epoxy resin, kindly provided by Dow Chemicals as DER 331, is of diglycidylether of bisphenol A (or DGEBA) type. DDM (Fluka—Ref.: 32950; purity grade > 98%) is used as curing agent. The thermosetting DGEBA–DDM prepolymer is prepared (1) by pouring fluid DGEBA resin preheated at 60° on fused DDM at 120° inside a Pyrex beaker. The solution which is obtained is clear and slightly yellow. It is then added to carbon black (CB) granules (Cabot—trade mark: Vulcan P) with a size of about 100  $\mu\text{m}$ , consisting of aggregated powder particles of 20 nm dia. The mixtures are then mechanically stirred, degassed at 60° under primary vacuum, and divided into aliquots of 20 g inside Pyrex pillboxes to be stored at  $-18^\circ$ . In this work, the concentration by wt of the filler is 5%.

## RESULTS AND DISCUSSION

Figure 1 shows the morphology of the composite with 5% by wt of CB, thermally crosslinked inside an oven, observed through optical microscopy ( $G = 60$ ). The aggregates are separated and no percolation network with physical contact between granules is formed.

Figure 2 presents the variations with time of  $T = T(t)$ ,  $Pu = Pu(t)$ ,  $(T)' = dT/dt$  and  $(Pu)' = dPu/dt$  for a sample of composite submitted to continuous microwaves with initial power  $P_0 = 20\text{ W}$ .

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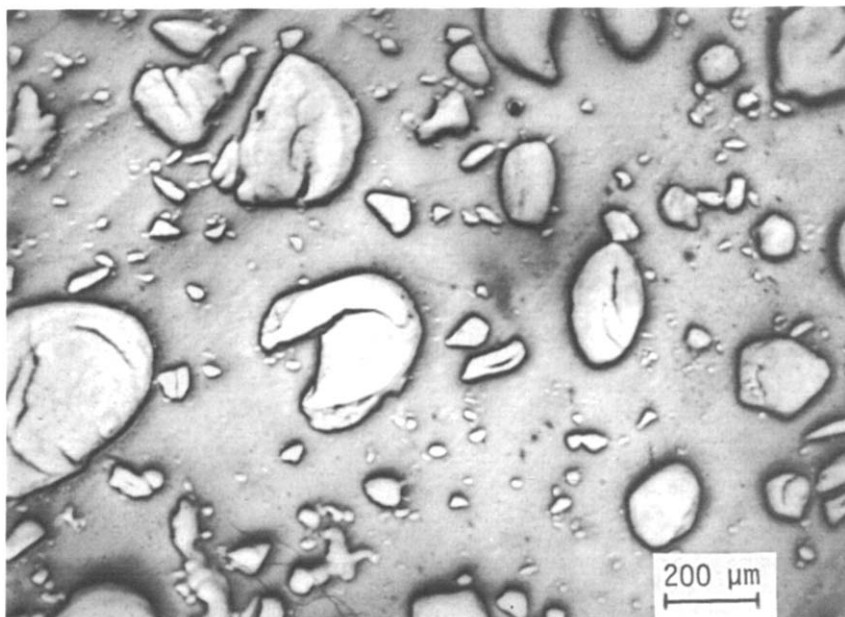


Fig. 1. Morphology of the epoxy resin-CB (5% by wt) composite ( $G = 60$ ).

This low value of power is chosen so as to observe significant changes in  $Pu$  unless the sample of matter burns. The shape of all curves is characteristic of a step growth reaction of a thermosetting DGEBA resin with its curing agent [1, 2]. Analysis of the variations of  $T = T(t)$  reveals the three usual steps of such a process and the associated transitions: (1) preheating period from  $0^\circ$  including the fluidification (first inflexion point) at 12.3 min and the sol-gel transition at 22.0 min (second inflexion point); (2) fast exothermal reaction of conversion of epoxides from the sol-gel transition until the exothermal maximum (31.6 min;  $239^\circ$ ); (3) cooling period beyond this maximum, during which chemical energy resulting

from the crosslinking conversion of epoxides is dissipated through convection from the sample to the surrounding medium, until the plateau value  $T_p = 122^\circ$ . The third inflexion point (30.1 min;  $220^\circ$ ) which is located in time by the position of the second peak in  $(T)'$  curve, corresponds to the highest rate of heating of the sample. The variations of  $Pu = Pu(t)$  also give a gel time of 22 min (abscisse of the maximum of  $Pu$  or  $Pu_{max}$ ), as in the case of  $T$  variations. In the final crosslinked state,  $Pu$  takes a plateau value  $Pu_p = 6.3$  W with an energetic yield  $Pu_p/Po = 31.5\%$  instead of 42.0% at the gel point and 20.5% at  $t = 0$ . The variations of this ratio obviously depend on the temperature and of the various structural states of the

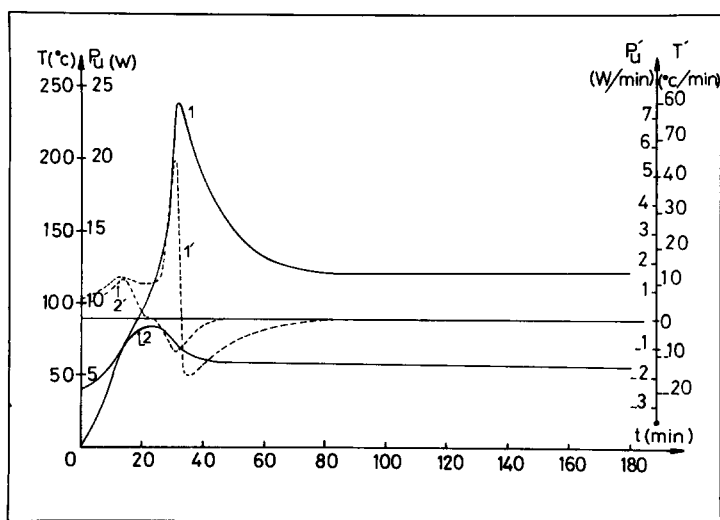


Fig. 2. Crosslinking reaction of the epoxy resin-CB (5% by wt) composite at  $Po = 20$  W: (1)  $T = T(t)$ ; (1')  $(T)' = dT/dt$ ; (2)  $Pu = Pu(t)$ ; (2')  $(Pu)' = dPu/dt$ .

Table 1. Crosslinking of a CB (5% by wt)-epoxy resin composite at  $P_o = 20$  W: main experimental parameters

Fluidification		Gelification		3rd Inflection point in $T = T(t)$		Maximum of temperature		Plateau values	
$t$ (min)	$T$ ( $^{\circ}$ C)	$t$ (min)	$Pu_{max}$ (W)	$t$ (min)	$T$ ( $^{\circ}$ C)	$t$ (min)	$T$ ( $^{\circ}$ C)	$T_p$ ( $^{\circ}$ C)	$Pu_p$ (W)
12.3	59	22	8.4	30.1	220	31.6	239	122	6.3

samples. Table 1 collects the values of the main experimental parameters of the "kinetics" of the step growth.

The electrical loss  $Pu$  can be divided into two parts,  $Pu = Pu_D + Pu_C$ , as previously mentioned [5],  $Pu_D$  due to dipolar relaxation of chemical species inside the organic matter, and  $Pu_C$  to electrical conduction at the level of CB aggregates, in which electrical percolation and eventually electronic hopping take place with a large temperature dependence. Consequently, these aggregates strongly absorb the electrical energy of the radiations the more as they are not very dense. The combination of the dipolar relaxation and of the conduction cause heating of the samples. When the temperature is sufficient, the crosslinking can take place. Nevertheless, one has to mention the possibility of reflexion of the radiations on the CB domains since these are conductive, i.e. that the path of the waves inside the organic matter would be increased, and that consequently  $Pu_D$  would be raised.  $Pu_C$  would be also higher since the CB aggregates could be hit several times by the same initial beam. So,  $Pu_C$  and  $Pu_D$  would have to be considered as dependent variables through the multiple reflections.

Figures 3–6 show the series of curves recorded for various  $P_o$  values (5, 10, 15, 20 and 25 W) and values of the main experimental parameters are presented in Table 2. Examination of the curves show that the value  $P_o = 5$  W is insufficient to activate the crosslinking of the composite material. On the other hand, the others are efficient. However, the value  $P_o = 25$  W would be the limit because of the thermal level ( $T_{max} = 259^{\circ}$ ) which could induce a risk of degradation of the material. When  $P_o$  passes from 10

to 25 W, the exothermal peak is shifted towards low times, whereas its intensity increases (Fig. 3); the same tendency is observed with  $Pu$  curves (Fig. 5), the fact is that the sol-gel transition happens faster and faster, and with  $(T)'$  and  $(Pu)'$  curves which reveal the transition of fluidification which occurs earlier (Figs 4 and 6). Moreover, the plateau values  $T_p$ , or better  $\Delta T_p = T_p - T_o$  where  $T_o$  is the average temperature of the surrounding medium ( $T_o \sim 20^{\circ}$ )—the thermal gradient is taken into consideration in the expression of the loss of energy  $\Delta E$  as heat by the samples towards the external medium:  $\Delta E = b \cdot m \cdot C_p \Delta T_p$  where  $b$ ,  $m$  and  $C_p$  are respectively the shape factor, the weight and the specific heat of the composite materials—and  $Pu_p$  are also increased; their variations with  $P_o$  are linear as shown in curves 1 and 2 of Fig. 7, except for  $P_o = 5$  W, a value too low to start the crosslinking, like  $Pu_0$  (absorption at initial time and  $0^{\circ}$ ) and  $Pu_{max}$  (curves 3 and 4). Curve 5 presents the variations with  $P_o$  of  $Pu_p$  for a composite consisting of a silicone matrix transparent to microwaves and the same amount of 5% by wt of CB filler. An interpretation of the positions of the various curves in relation with the electrical loss  $Pu$  can be made, if one assumes that the spatial distribution of the CB aggregates is independent of the nature and the structural state of the matrix, except for the shrinkage of the samples due to the crosslinking and their expansion in relation with temperature. The linearity of  $Pu_p$  with  $P_o$  for the CB-silicone composite indicates that the relative absorption  $Pu_p/P_o$  remains constant in spite of the variations of temperature. When one passes to the crosslinked CB-epoxy composite, the linearity between  $P_o$  and  $Pu_p$  is always observed, i.e. that the dielectric loss  $Pu_D$

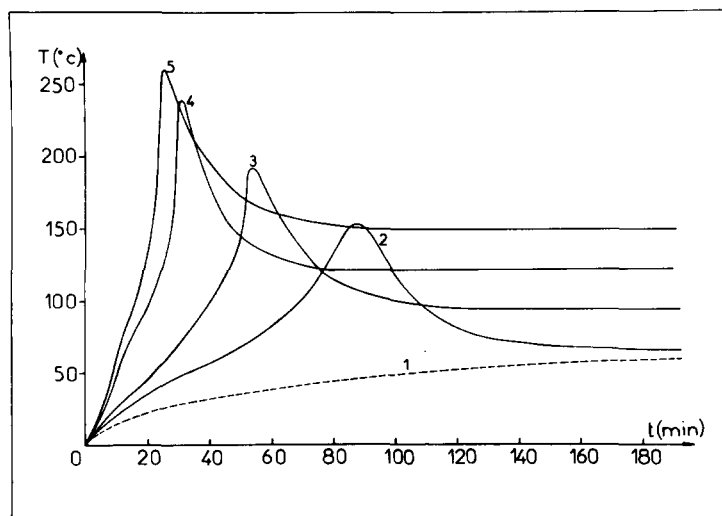


Fig. 3. Electrical power  $P_o$  dependence of  $T = T(t)$ : (1) 5 W; (2) 10 W; (3) 15 W; (4) 20 W; (5) 25 W.

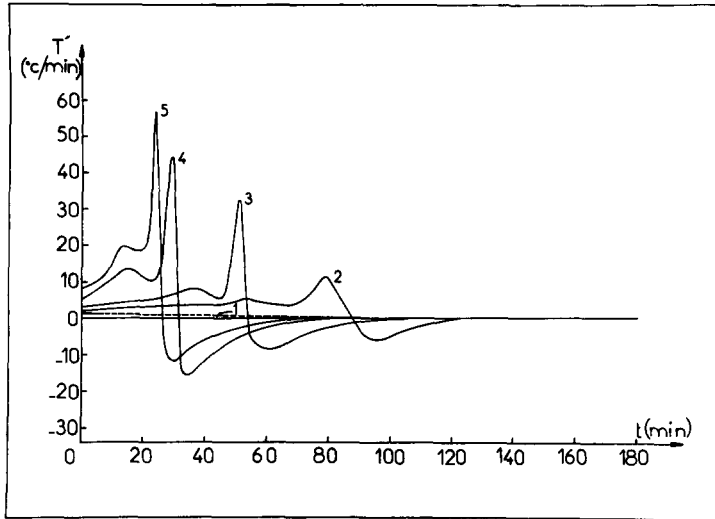


Fig. 4. Electrical power  $P_0$  dependence of  $(T)' = dT/dt$ : (1) 5 W; (2) 10 W; (3) 15 W; (4) 20 W; (5) 25 W.

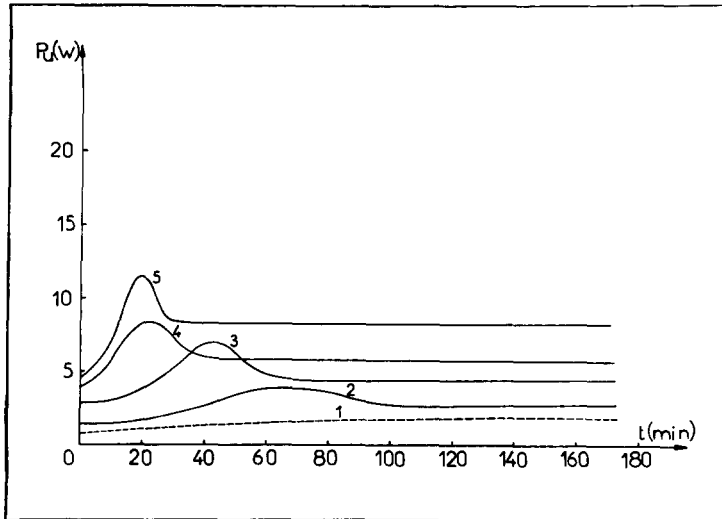


Fig. 5. Electrical power  $P_0$  dependence of  $P_u = P_u(t)$ : (1) 5 W; (2) 10 W; (3) 15 W; (4) 20 W; (5) 25 W.

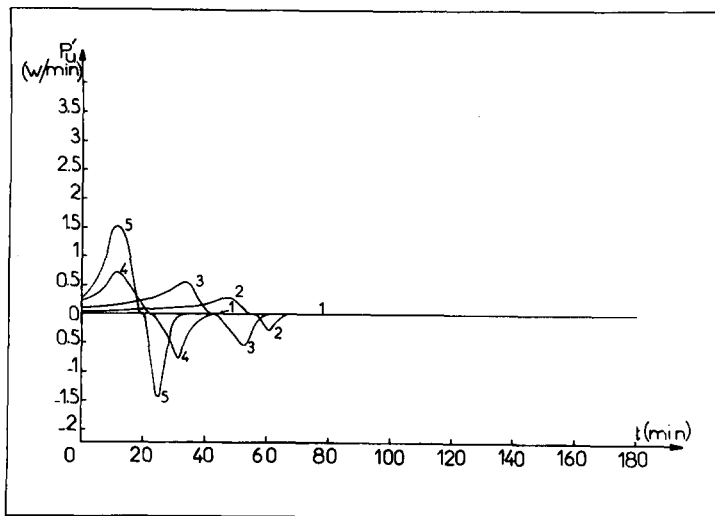


Fig. 6. Electrical power  $P_0$  dependence of  $(P_u)' = dP_u/dt$ : (1) 5 W; (2) 10 W; (3) 15 W; (4) 20 W; (5) 25 W.

Table 2. Electrical power dependence of main experimental parameters of the crosslinking reactions of the composite

Curve No.	Electrical power $P_o$ (W)	$T_{max}$ (°C)	$Pu_{max}$ (W)	Gel time (min)	Abscisse of $T_{max}$ (min)	$T_p$ (°C)	$Pu_p$ (W)
1	5*	—	—	—	—	—	—
2	10	152	3.9	66	88.0	66	2.7
3	15	191	7.0	43	54.0	94	4.4
4	20	239	8.4	22	31.6	122	6.3
5	25	259	11.5	20	26.0	150	8.3

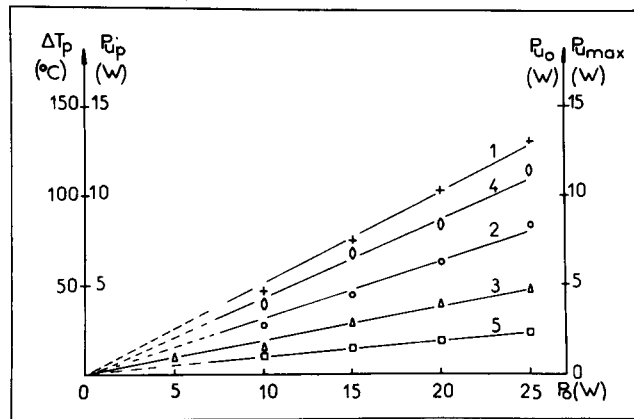


Fig. 7. Electrical power  $P_o$  dependence for an epoxy resin-CB (5%) composite of: (1)  $\Delta T_p$ ; (2)  $Pu_p$ ; (3)  $Pu_0$ ; (4)  $Pu_{max}$  (Ref. 5  $Pu_p$  for a silicone-CB (5%) composite).

which now exists because of the polarity of the matrix, is also a linear function of  $P_o$ . The effect of the polarity of the polymeric matter is more obvious at the level of  $Pu_{max}$  since it is well known that the highest polarity of the matrix is encountered at the sol-gel transition which provides a structural reference for all samples treated at various  $P_o$  values. The absorption  $Pu_0$  at initial time is smaller than in the final crosslinked state because the absorption of the resin is weaker. This linear dependence of  $\Delta T_p$  for the final composites with  $P_o$ ,  $Pu_p$ ,  $Pu_D$  and  $Pu_C$  could be due to the fact that the phenomenon of multiple reflection does not occur because of the small number of CB aggregates. Nevertheless, the coming paper will discuss the filler concentration dependence of  $Pu_p$  and  $\Delta T_p$  at higher concentrations for which these parameters are not linearly correlated.

#### CONCLUSION

The results on the behaviour under continuous microwaves (2.45 GHz) of CB-epoxy resin composite systems which have just been discussed underline the major contribution to heating of the samples of the conductive filler domains which are not in physical contact. The spatial distribution of the CB granules uniform inside the prepolymeric matrix preserves the mechanism with three steps of the crosslinking reaction of the epoxy matrix, in which the filler domains intervene rather as catalysts owing to the

fact that their number is small and that, consequently, multiple reflection is not expected. This situation would be responsible for the linear variations of the temperature of the crosslinked samples against various powers: (1) initial power of the radiation  $P_o$  (2), dielectric loss  $Pu_D$  inside the matrix, (3) loss of electrical power  $Pu_C$  due to electrical conduction at the level of CB aggregates. Nevertheless, the CB concentration dependence of the composites has to be studied in view of correlating the joint thermal effects of both main processes of dissipation of energy, i.e. dielectric relaxation and conduction.

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