

MICROWAVE CURING OF EPOXY RESINS WITH DIAMINODIPHENYLMETHANE—IV. AVERAGE ELECTRICAL POWER AND PULSE LENGTH DEPENDENCE IN PULSED IRRADIATION

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Abstract—Pulse length dependence of the efficiency of the activation of curing reactions of epoxy-diaminodiphenylmethane resins by pulsed microwaves (2.45 GHz) is studied at three pulse periods (1, 5 and 42 msec) or frequencies (1000, 200 and 23.8 Hz) previously revealed for a pulse length (τ)/pulse period (\mathcal{F}) ratio of 1/5, which lead to the fastest heating of the resins. The variations of τ at given period and higher values of τ/\mathcal{F} show that there is a τ value for which the heating process is also optimized. On the other hand, at smaller ratios, the reactions are less activated than in the case of continuous mode. These results are discussed in terms of energy exchanges between waves and samples by resorting to the double relaxation process which associates dipolar and segmental relaxations.

INTRODUCTION

Previous papers [1-3] have shown that microwaves working at 2.45 GHz can perform the crosslinking of epoxy resins. The use of pulsed modes of energy emission provides an acceleration of the heating process, which depends on the pulse frequency values [3]. This variation is assumed to be due to a double relaxation phenomenon consisting of the dipolar relaxation at 2.45 GHz maintained by the carrier wave and of the low frequency segmental relaxation brought by the pulsed emission mode and associated with motions of short chain segments. For prepolymeric DGEBA epoxy-diaminodiphenylmethane resins, three pulse periods (1, 5 and 42 msec) or frequencies (1000, 200 and 23.8 Hz) for a given pulse length (τ)/pulse period (\mathcal{F}) ratio of 1/5 and an average electrical power $P_o = 40$ W were used. Thus all measurements were done at constant peak power $P_c = (\mathcal{F}/\tau) P_o$ and τ/\mathcal{F} have not been changed. But the time of periodical application of the electromagnetic beam has been drastically modified, passing from $\tau = 8.4$ msec for $\mathcal{F} = 42$ msec to 0.2 msec when $\mathcal{F} = 1$ msec. Obviously such variations of τ should affect the energy transfer between the waves and the prepolymeric samples and consequently the efficiency of microwave activation of crosslinking. The present paper describes the effect due to that change.

EXPERIMENTAL

The irradiation experiments were carried out through a wave guide line previously described [2, 4], using a generator of microwaves working at 2.45 GHz, coupled with a pulse generator which can break the continuous emission of electrical power into pulses. This emission is now periodical with a period \mathcal{F} (or a frequency $N = 1/\mathcal{F}$) and a pulse length τ . The peak power P_c is deduced from the average electrical power P_o :

$$P_c = P_o / (\tau / \mathcal{F}) = (\mathcal{F} / \tau) \cdot P_o$$

P_c depends on τ/\mathcal{F} and P_o , parameters which are separated variables.

The samples (20 g) consist of the same prepolymeric mixture of DGEBA epoxy resin with $n = 0.19$ and diaminodiphenylmethane as used previously [3].

The variations with time during the microwave treatment of the temperature of the samples $T = T(t)$, of the associated dielectric loss $P_u = P_u(t)$, and of the derivatives ($T' = dT/dt$ and $(P_u)' = dP_u/dt$) are continuously recorded with a microcomputer, to be later analyzed.

RESULTS AND DISCUSSION

The average electrical power P_o dependences at given pulsed mode ($\mathcal{F} = 5$ msec; $\tau/\mathcal{F} = 1/5$) of $T = T(t)$, ($T' = dT/dt$, $P_u = P_u(t)$ and $(P_u)' = dP_u/dt$) are shown in Figs 1, 2, 3 and 4, through a series of P_o values: 20-30-40-50 and 57 W, or P_c values: 100-150-200-250 and 285 W. A simple correlation between P_o or P_c and the main experimental parameters such as the maximum of P_u and its abscissa (which is incidentally the gel time) and the coordinates of the exothermal maximum, is observed (Table 1). When P_o increases, the maxima of T and P_u curves are shifted towards low times. This change means that the end of the crosslinking process (abscissa of T_{max}) is reached more and more rapidly, and that the sol-gel transition (abscissa of $P_{u,max}$) occurs earlier and earlier. The same tendency is also observed for the fluidification transition, much better in $(P_u)'$ curves (1st maximum) than in $(T)'$ curves (1st maximum). Similar results were presented previously [1] when the power signal was periodically emitted but not squared.

The plateau values of the temperature (T_p) and of the dielectric loss ($P_{u,p}$) increase linearly with P_o (or P_c), as shown in Fig. 5, where the thermal gradient $\Delta T_p = (T_p - T_o)$ between the samples and the external medium at room temperature (T_o) is preferred to T to eliminate the fluctuations of T_o . These linear laws

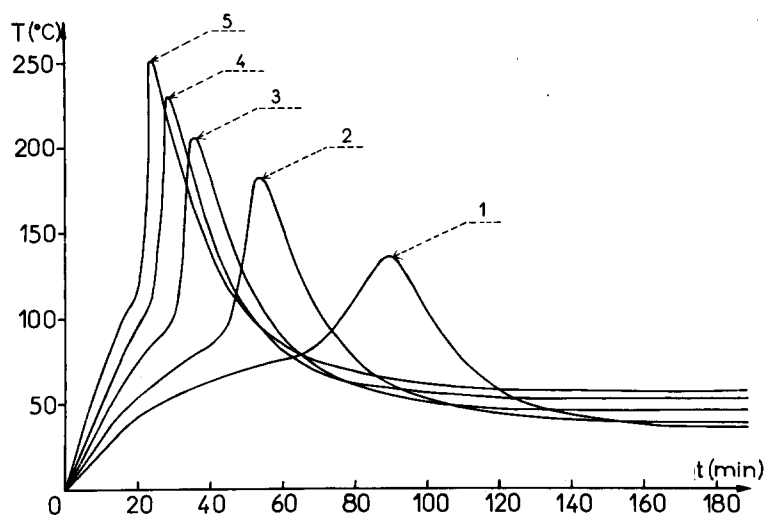


Fig. 1. Average electrical power P_o dependence in pulsed mode ($\mathcal{F} = 5$ msec; $\tau = 1/5$) of $T = T(t)$.
(1) 20 W; (2) 30 W; (3) 40 W; (4) 50 W; (5) 57 W.

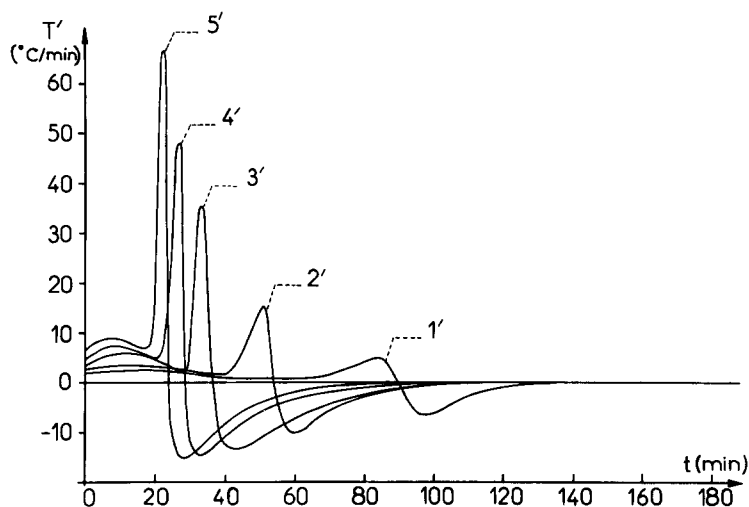


Fig. 2. Average electrical power P_o dependence in pulsed mode ($\mathcal{F} = 5$ msec; $\tau = 1/5$) of $(T') = dT/dt$.
(1) 20 W; (2) 30 W; (3) 40 W; (4) 50 W; (5) 57 W.

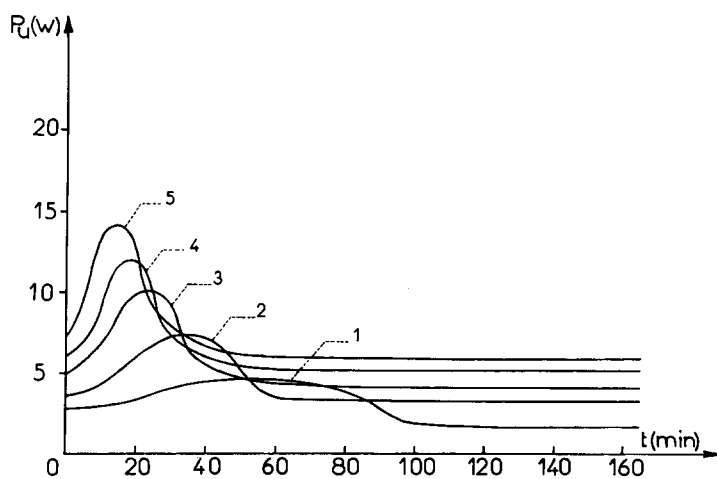


Fig. 3. Average electrical power P_o dependence in pulsed mode ($\mathcal{F} = 5$ msec; $\tau = 1/5$) of $P_u = P_u(t)$.
(1) 20 W; (2) 30 W; (3) 40 W; (4) 50 W; (5) 57 W.

Table 1. Average electrical power P_o dependence in pulsed mode ($\mathcal{F} = 5$ msec; $\tau/\mathcal{F} = 1/5$ of experimental parameters. (1) 20 W; (2) 30 W; (3) 40 W; (4) 50 W; (5) 57 W

No. curve	P_o (W)	$P_{u_{max}}$ (W)	Gel time (min)	T_{max} ($^{\circ}$ C)	Abscissa of T_{max} (min)	T_p ($^{\circ}$ C)	P_{u_p} (W)
1	20	4.7	56.0	138	89.0	33	2.0
2	30	7.4	34.0	183	53.0	39	3.1
3	40	10.1	23.5	208	35.7	46	4.1
4	50	12.0	18.4	230	28.5	53	5.2
5	57	14.0	14.0	252	23.5	57	5.9

of variation show that all final crosslinked structures are quasi-identical, however high P_o values may be. Moreover, there is also direct proportionality between P_{u_p} and ΔT_p (or T_p); the thermal part of the

dielectric loss P_{u_p} , responsible for heating of the samples (ΔT_p), is proportional to P_{u_p} , at least within the temperature range of our experiments, where the networks are in the glassy state.

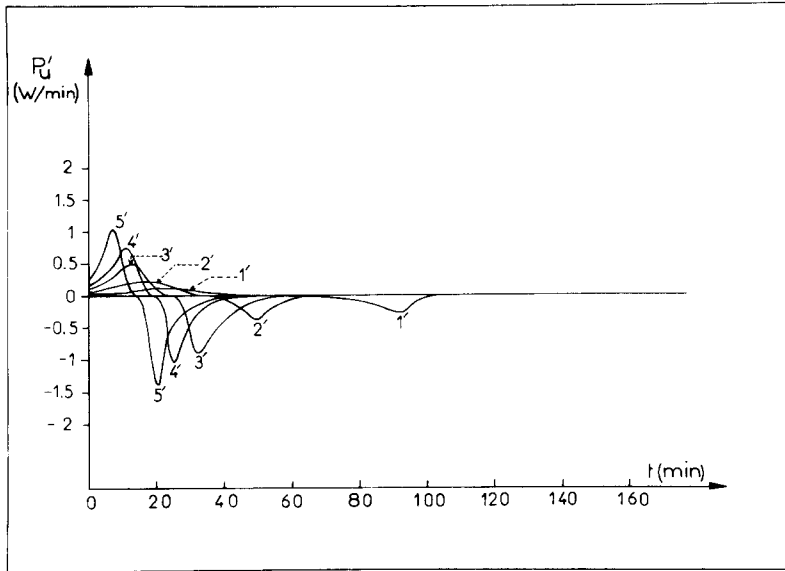


Fig. 4. Average electrical power P_o dependence in pulsed mode ($\mathcal{F} = 5$ msec; $\tau = 1/5$) of $(P_u)' = dP_u/dt$. (1) 20 W; (2) 30 W; (3) 40 W; (4) 50 W; (5) 57 W.

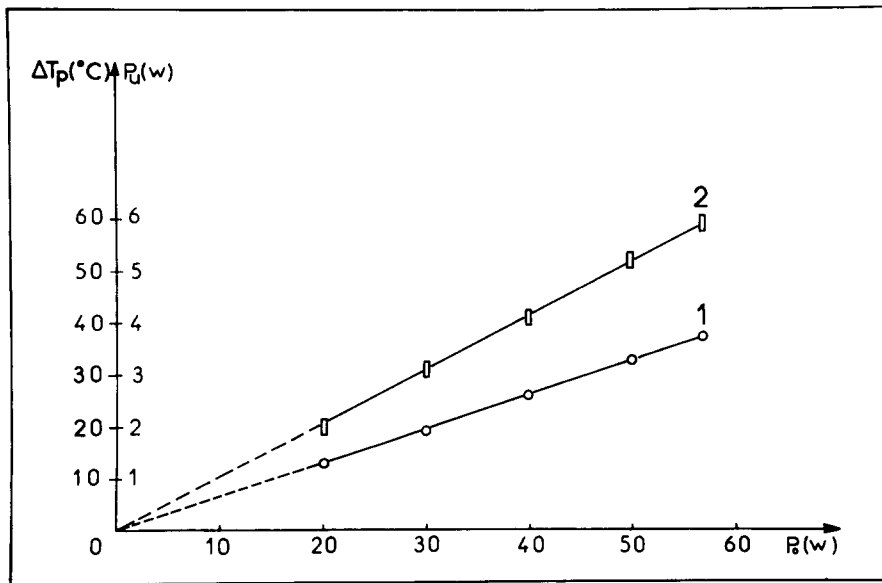


Fig. 5. Average electrical power P_o dependence of ΔT_p and P_{u_p} in pulsed mode ($\mathcal{F} = 5$ msec; $\tau = 1/5$) (1) $\Delta T_p = \Delta T_p(P_o)$; (2) $P_{u_p} = P_{u_p}(P_o)$.

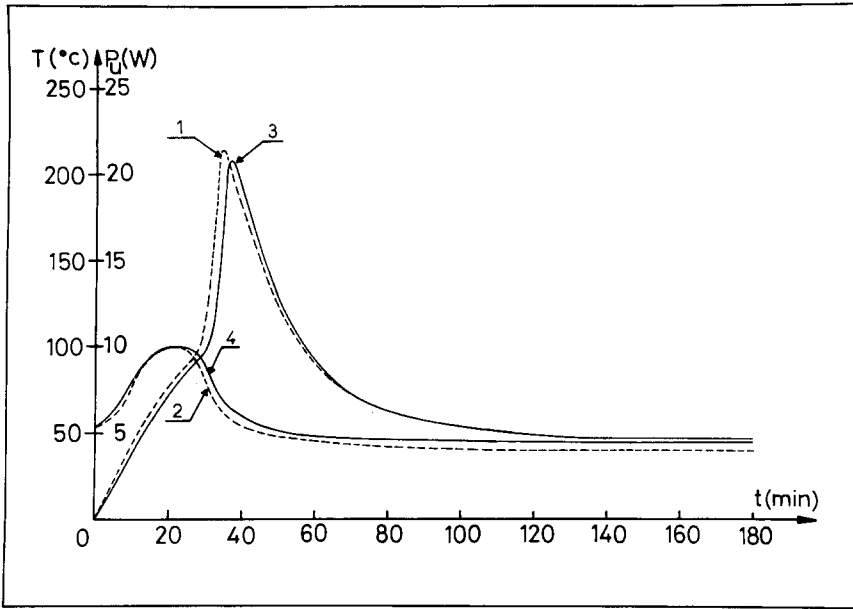


Fig. 6. Comparison between the activation processes under continuous and pulsed ($\mathcal{T} = 1$ msec and $\tau/\mathcal{T} = 1/10$) modes. Continuous mode: (1) $T = T(t)$; (2) $P_u = P_u(t)$. Pulsed mode: (3) $T = T(t)$; (4) $P_u = P_u(t)$.

Figure 6 shows the variations with time of T and P_u for continuous irradiation (curves 1 and 2) and pulsed emission (curves 3 and 4) with $\mathcal{T} = 1$ msec and $\tau/\mathcal{T} = 1/10$ at the same average power P_o of 40 W. The continuous process leads to slight acceleration, although it is not pulsed and that the respective dielectric losses are hardly different (Table 2). On the basis of our hypothesis which implies a segmental relaxation at the same time as the dipolar relaxation at 2.45 GHz, an explanation of such a variation can be proposed on the basis of the diffusion of heat

brought by the segmental relaxation through the polymerizable medium being delayed because of shortness of the pulse.

When the ratio τ/\mathcal{T} exceeds $1/10$ and for the same average power $P_o = 40$ W and period $\mathcal{T} = 1$ msec, the electromagnetic treatment leads to faster heating of the resins (Figs 7 and 8) up to the value of $1/4$, which gives a gel-time of 19.0 min instead of 23.8 min for continuous mode (Table 3). Beyond that critical value, T and P_u curves are shifted towards the continuous wave curves. This reverse tendency when

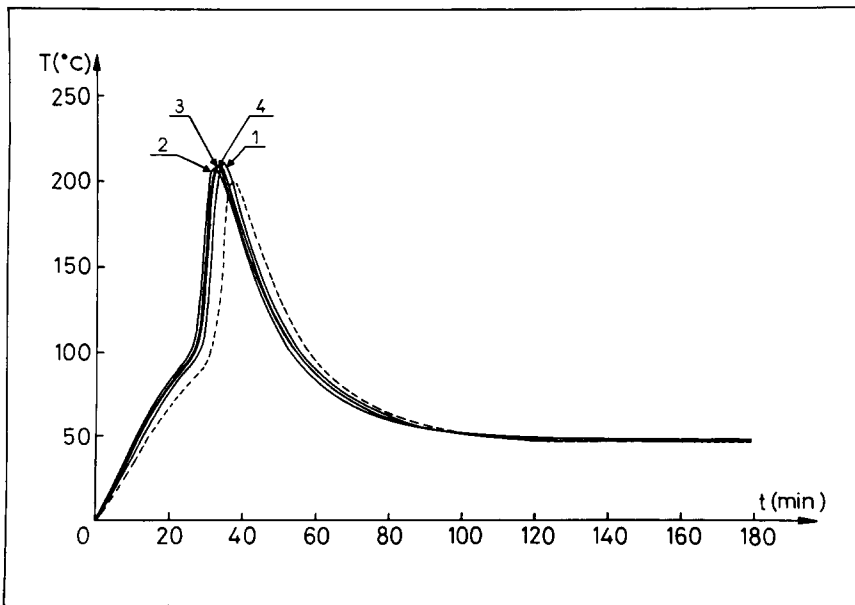


Fig. 7. Pulse length (τ) dependence at $\mathcal{T} = 1$ msec and $P_o = 40$ W of $T = T(t)$ (1) $\tau/\mathcal{T} = 1/5$; (2) $\tau/\mathcal{T} = 1/4$; (3) $\tau/\mathcal{T} = 1/3$; (4) $\tau/\mathcal{T} = 1/2$; dotted line: continuous mode.

Table 2. Comparison between the activation processes under continuous and pulse ($\mathcal{F} = 1$ msec and $\tau/\mathcal{F} = 1/10$) modes

No. curve	τ/\mathcal{F}	P_c (W)	P_{max} (W)	Gel time (min)	T_{max} (°C)	Abcissa of T_{max} (min)	T_p (°C)	P_{up} (W)
1, 2	—	40	10	21.2	218	35.3	47	4.0
3, 4	1/10	400	10	22.5	215	36.3	47	4.5

τ/\mathcal{F} increases, which changes the pulsed mode into the continuous, where the relaxation is purely dipolar, is proof of a double relaxation which combines the high frequency dipolar relaxation at 2.45 GHz and the low frequency (20–1000 Hz range) segmental relaxation which corresponds to the motion of short chain segments.

A critical value of τ/\mathcal{F} beyond which the rate of heating starts decreasing, is also found for two other periods (5 and 42 msec) or frequencies (200 and 23.8 Hz), that it is to say respectively 1/2 and 1/3. Table 4 collects the experimental conditions of the irradiation modes which lead to best heating of the resins with the same average electrical power $P_o = 40$ W.

Comparison between various frequencies N , lengths of pulse τ and the gel times on the one hand, and the initial rates of heating on the other hand, shows that the highest heating rate is obtained at $N = 1000$ Hz and $\tau = 0.25$ msec. When τ increases with decreasing periods (2.5 msec for 200 Hz and 14 msec for 23.8 Hz), heating becomes less efficient independently of the frequency.

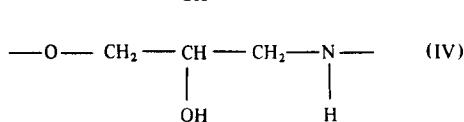
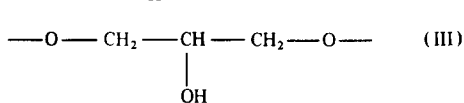
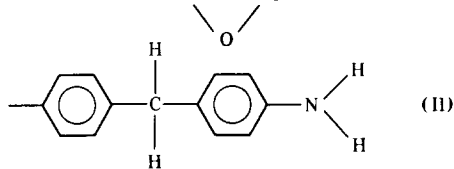
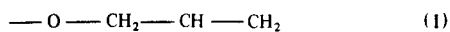
On the basis of our previous hypothesis [3] that the segmental relaxation is maintained owing to various pulsed microwave emission modes, an interpretation of the double relaxation phenomenon leading to dipolar relaxation and to segmental relaxation can be proposed.

(a) Dipolar relaxation

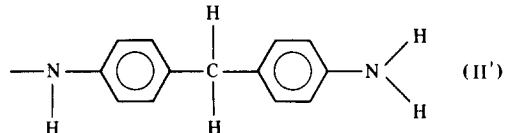
It is induced by the carrier wave (2.45 GHz) and corresponds to high frequency motions of dipolar chemical entities, these being mainly in our case epoxide functions which are known to relax in the 3 GHz region [1, 5] with a period of $3.3 \cdot 10^{-7}$ msec much below the lowest pulse value (0.25 msec); therefore it works as soon as the microwaves are applied and contributes to heating of the resins in bulk.

(b) Segmental relaxation

It concerns various segments, indexed in the preceding paper. They are:



I and II can be considered as “pendant chains”, once linked to DGEBA chains or DGEBA-diaminodiphenylmethane; III and IV belong to the chains. Another type of segment II' derived from II has to be considered:



All these segments carry dipolar groups which are sensitive to the carrier wave (2.45 GHz) in spite of the Van der Waals bonding in which they are involved, and/or of their own weight, and which, nevertheless, relax. Consequently the segments are stretched and twisted under the orientation effect with the electrical field of the dipolar oscillators but

 Table 3. Pulse length (τ) dependence at $\mathcal{F} = 1$ msec and $P_o = 40$ W of the experimental parameters

No. curve	τ/\mathcal{F}	P_c (W)	P_{max} (W)	Gel time (min)	T_{max} (°C)	Abcissa of T_{max} (min)	T_p (°C)	P_{up} (W)
1	1/5	200	10.6	22.4	215	34.0	47	4.7
2	1/4	160	10.6	19.0	208	32.0	47	4.8
3	1/3	120	10.5	21.6	210	33.7	47	4.5
4	1/2	60	10.3	22.4	210	34.0	47	4.3
Continuous mode	—	40	9.8	23.8	199	37.7	47	4.3

 Table 4. Pulse period dependence of the critical τ/\mathcal{F} values at given average power $P_o = 40$ W

\mathcal{F} (ms)	N (Hz)	Critical τ/\mathcal{F}	τ (ms)	P_o (W)	P_c (W)	Gel time (min)
1	1000	1/4	0.25	40	160	19.0
5	200	1/2	2.50	40	80	20.2
42	23.8	1/3	14.00	40	120	20.3

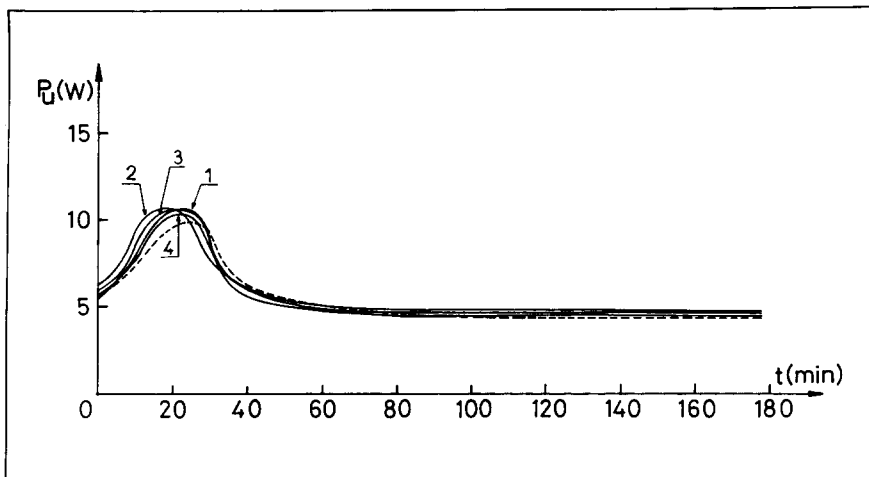


Fig. 8. Pulse length (τ) dependence at $\mathcal{T} = 1$ msec and $P_o = 40$ W of $P_u = P_u(t)$ (1) $\tau/\mathcal{T} = 1/5$; (2) $\tau/\mathcal{T} = 1/4$; (3) $\tau/\mathcal{T} = 1/3$; (4) $\tau/\mathcal{T} = 1/2$; dotted line: continuous mode.

because of their length or size, they cannot follow the motions of the dipolar groups. However, they should be actuated by a low frequency motion more or less activated by the electrical peak power P_c periodically applied. The frequency of such a motion depends on the chemical structure of the segments—for given $\tau/\mathcal{T} = 1/5$ and $P_o = 40$ W, three frequencies have been detected (1000, 200 and 23.8 Hz) which could correspond to the series of segments I, II, II', III and IV and/or their possible combinations, although some could not participate—and its amplitude and consequently the instantaneous resulting thermal effect, at given average electrical power, are linked to the pulse length τ . For a low value of τ as in the case of Fig. 7 (curves 3 and 4) where $\tau = 0.1$ msec, the rate of heating is slightly lower than that due to the continuous mode, but the variations with time of the dielectric loss are of the same magnitude for both modes. The only explanation of this result is that the segmental entities which are concerned at that frequency (1000 Hz) absorb the fast transferred energy, but also that resulting heat is not immediately diffused through the polymerizable matter. Moreover, this local heating causes a transient acceleration of the motion of the segments, i.e. an increase of its frequency. When τ goes to higher values, energy transfer to the samples becomes more homogeneous and heating is accelerated by the double relaxation: the segmental relaxation is responsible for the acceleration of the heating process, since the rate of heating is decreased with increasing values of τ/\mathcal{T} beyond the critical value i.e. when the dipolar relaxation is increased. The critical τ/\mathcal{T} value corresponds to a compromise between the dipolar (continuous mode) and segmental (pulsed mode) relaxations which both consume electrical energy that they partially convert to heat inside the samples.

As far as the fact that the pulsed mode at 1000 Hz accepts the lowest critical τ value (0.25 msec), it means that the thermal response to the segmental relaxation is the shorter as the mobility—or flexibility—of the concerned segments is high. This is entirely compatible with the mechanism of energy transfer through the conversion to heat of the associ-

ated dielectric loss which induces a positive variation of the entropy of the chain segments, this being fastest when the initial state corresponds to a still high Brownian motion of them.

CONCLUSION

This study has shown that the activation under pulsed microwaves of the crosslinking reactions of epoxy resins greatly depends, at given average electrical power P_o and pulse period \mathcal{T} or frequency N , on the pulse length τ by monitoring the respective contributions of both dipolar and segmental relaxations. An optimization of heating is obtained for a critical value of τ which makes a compromise between these two relaxation processes. If τ is small, electrical energy is transferred as heat to samples in local zones spreading in the vicinity of the concerned segments at a given frequency, with increase of entropy. The interactions between the resins and the pulsed waves are also governed by the intensity of the average electrical power P_o which, if it increases the temperature T and dielectric loss P_u decreases the experimental resolution between the various modes of microwave energy emission.

The next papers of the present series will refer to the extension of the results obtained for liquid resins to crosslinked final products where pendant chain segments really do not exist.

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