Eur. Polym. J. Vol. 24, No. 1, pp. 53–59, 1988
Printed in Great Britain. All rights reserved

0014-3057/88 \$3.00 + 0.00

MICROWAVE CURING OF EPOXY RESINS WITH DIAMINODIPHENYLMETHANE—III. PULSE FREQUENCY DEPENDENCE IN PULSED IRRADIATION

NADIR BELDJOUDI and ALBERT GOURDENNE
Laboratoire de Physico-Chimie des Hauts Polymères, Ecole Nationale Supérieure de Chimie de Toulouse, 118 route de Narbonne, 31077 Toulouse Cedex, France

(*Received* 18 *February* 1987)

Abstract—Pulse frequency dependence of the efficiency of the activation of crosslinking reactions of DGEBA epoxy–diaminodiphenylmethane mixtures by pulsed microwaves working at an electromagnetic frequency of 2.45 GHz, a ratio pulse length/pulse period of 1/5 and an average electrical power of 40 W, is studied, through the variations of the initial rates of heating of the samples and the gel times. Three optimized frequencies of pulse (1 kHz, 200 and 23.8 Hz) are found, and their attribution in terms of relaxations of short chain segments is discussed.

INTRODUCTION

In the preceding paper [1], microwave (2.45 GHz) irradiation mode (continuous and pulsed) dependence of the kinetics of crosslinking of DGEBA epoxy–diaminodiphenylmethane systems has been noticed. For pulsed waves, the increase of efficiency of the electromagnetic process of activation of step-growth polymerization, which is measured through the variations of the initial rates of heating of the samples and those of gel times, has been attributed to additional relaxation, besides dipolar relaxation due to the carrier wave (2.45 GHz), maintained by the pulses of energy with a frequency N and which has been connected to motions of short segments of prepolymeric chains. Other chemical species of low mobility could be concerned, such as aggregated curing agent residues. However, this assumed phenomenon of double relaxation should be confirmed by a more complete analysis; this study, which is now reported is an attempt to give a partial answer to that requirement.

EXPERIMENTAL

A prototype of microwave irradiation system [1] is used, resorting to a generator (0–1 kW) of continuous waves with a frequency of 2.45 GHz coupled with a pulse generator which breaks the electric power into pulses of length τ. and period $\mathcal{T}$ or frequency $N = 1/\mathcal{T}$. The peak power P_c is calculated from the average power P_0:

$$P_c = P_0/(\tau/\mathcal{T}) = (\mathcal{T}/\tau)P_0$$

The accessible ranges of period or frequency are from 0.05 to 50 milliseconds (msec) or from 20 kHz to 20 Hz.

The structural change of the samples of prepolymeric matter is followed, as reported elsewhere [2], through the variations with time (t) of the average temperature of the samples $T = T(t)$, the dielectric loss $P_u = P_u(t)$ and the derivatives $(T)' = dT/dt$ and $(P_u)' = dP_u/dt$.

The samples (20 g) before microwave treatment are degassed under vacuum and stored at $-8°$.

RESULTS AND DISCUSSION

Figure 1 presents the series of four curves T, P_u, $(T)'$ and $(P_u)'$ for a sample submitted to a pulse microwave mode with $\mathcal{T} = 5$ msec or $N = 200$ Hz, $\tau/\mathcal{T} = 1/5$ or $\tau = 1$ msec, $P_0 = 40$ W and $P_c = 200$ W. Their relative positions correspond to the situation encountered in the case of continuous process [1]. Their careful analysis well matches in time the various transitions. The location in time of the fluidification transition is determined with half a minute (min): the first maximum of $(T)'$ gives 11.3 min, whereas that of $(P_u)'$ indicates 11.8 min. The gel point takes place at 23.5 min (maximum of P_u), a value very close to that of the second inflexion point in T curve—first minimum of $(T)'$—i.e. 27.5 min, as expected [1]. Moreover, although the exothermal step is very fast, it is defined with good resolution: the point of maximum heating (35.5 min; 208°) is marked by the second peak of $(T)'$ which is sharply drawn. The respective final plateau values of temperature and dielectric loss, $T_p = (46°C)$ and $P_{u_p} = 4.1$ W, show that the final network is in a thermodynamic equilibrium state, resulting from a balance between microwave heating and energy loss by convection transfer from the sample to the external medium.

Now we are going to refer to the most "optimized" frequencies i.e. the frequencies which, for a given average power P_0 value, lead to the highest initial rates of heating of the samples, and the lowest gel times. Other data such as the coordinates of the maximum of T and the value of the maximum of P_u are not taken into account, for they are uncertain because of energy loss by convection from the samples towards the surrounding air which shifts the T curves on one hand, and of the lack of precision in the measurements of P_u due to their low intensity on the other hand, as previously reported [1].

Figure 2 and 3 present both series of T and P_u curves recorded at $P_0 = 40$ W when $\mathcal{T}$ varies between

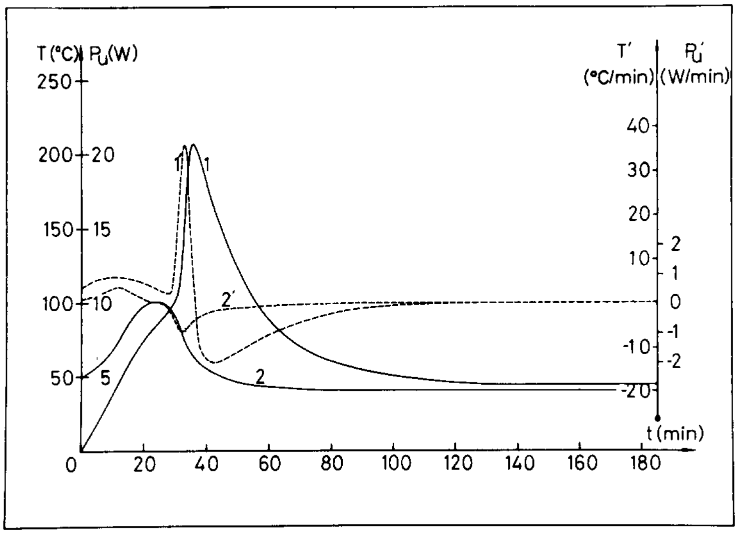


Fig. 1. Crosslinking reaction of the epoxy resin at $P_0 = 40$ W, with $\mathcal{T} = 5$ msec and $\tau/ = 1/5$. (1): $T = T(t)$. (1′): $(T)' = dT/dT$. (2): $P_u = P_u(t)$. (2′): $(P_u)' = dP_u/dt$.

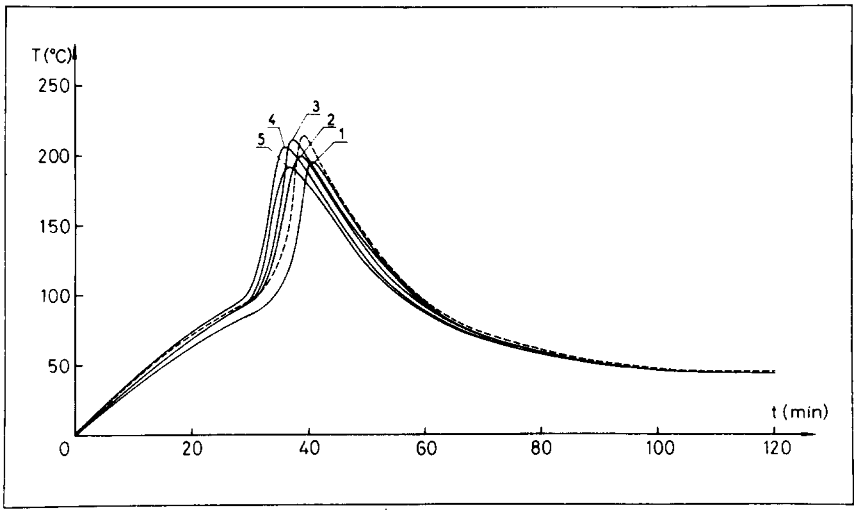


Fig. 2. Pulse period dependence of the temperature $T = T(t)$ at $P_0 = 40$ W. (1) 22 msec; (2) 32 msec; (3) 37 msec; (4) 42 msec; (5) 50 msec. Dotted line: continuous mode.

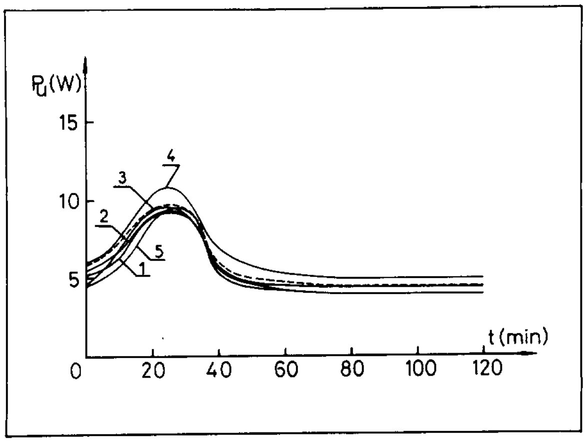


Fig. 3. Pulse period dependence of the dielectric loss $P_u = P_u(t)$ at $P_0 = 40$ W. (1) 22 msec; (2) 32 msec; (3) 37 msec; (4) 42 msec; (5) 50 msec. Dotted line: continuous mode.

Table 1. Pulse period dependence of the experimental parameters ($\mathscr{T}$: 22–32–37–42 and 50 msec)

Curve No.	Period (msec)	Frequency (Hz)	$P_{u_{max}}$ (W)	Gel time (min)	T_{max} (°C)	Abcissa of T_{max}(min)	T_p (°C)	P_{u_p} (W)
1	22	45.5	9.3	26.8	195	38.1	43.0	4.0
2	32	31.3	9.3	25.5	194	37.0	43.0	4.0
3	37	27.0	9.5	25.0	212	35.8	43.0	4.5
4	42	23.8	10.7	24.4	208	35.5	45.5	4.8
5	50	20.0	9.5	27.2	200	38.4	44.0	4.0
Continuous mode	—	—	9.7	26.0	214	38.1	44.5	4.5

Table 2. Pulse period dependence of the experimental parameters ($\mathscr{T}$: 2–5–7 and 12 msec)

Curve No.	Period (msec)	Frequency (Hz)	$P_{u_{max}}$ (W)	Gel time (min)	T_{max} (°C)	Abcissa of T_{max}(min)	T_p (°C)	P_{u_p} (W)
1	2	500	9.3	27.0	195	38.5	43.0	3.8
2	5	200	10.1	23.5	208	35.7	46.0	4.1
3	7	143	10.0	25.4	211	37.0	46.0	4.0
4	12	83	9.4	25.8	126	38.4	43.5	3.8
Continuous mode	—	—	9.7	26.0	214	38.1	44.5	4.5

Table 3. Pulse period dependence of the experimental parameters ($\mathscr{T}$: 0.5–1 and 2 msec)

Curve No.	Period (msec)	Frequency (Hz)	$P_{u_{max}}$ (W)	Gel time (min)	T_{max} (°C)	Abcissa of T_{max}(min)	T_p (°C)	P_{u_p} (W)
1	0.5	2000	9.8	26.4	210	38.8	44.0	3.8
2	1.0	1000	10.4	24.4	216	36.2	47.0	4.7
3	2.0	500	9.3	27.0	195	38.6	43.0	3.8
Continuous mode	—	—	9.7	26.0	214	38.1	44.5	4.5

20 and 50 msec or N between 50 and 20 Hz and that the ratio $\tau/\mathscr{T}$ keeps the constant value of 1/5. The T series is much better resolved than the P_u series which nevertheless confirms the regular progress of the step-growth reactions. The dotted T curve corresponds to the continuous mode and is used as reference; the other thermal curves have been drawn for respective periods 22–32–37–42 and 50 msec (Curves 1–5). When $\mathscr{T}$ increases from 22 msec to 42 msec, the exothermal peaks are shifted towards low times (Table 1), whereas the initial rate of heating (from the origin until the gel point) increases. All these changes demonstrate that the electromagnetic process of activation becomes more and more efficient, unless the electrical power is increased. If $\mathscr{T}$ has larger values, a reverse effect is observed: Curve 5 corresponds to a period of 40 msec. No intermediate period between 42 and 50 msec is tested, since the associated variation of frequency is small ($N = 20$ Hz if $\mathscr{T} = 50$ msec and $N = 23.8$ Hz if $\mathscr{T} = 42$ msec) and any drastic change in the T curves series is not expected within this interval. On the contrary, when the period is 22 msec (or $N = 45.5$ Hz), the reaction of crosslinking is less activated than that obtained under continuous mode, although pulsed microwaves are applied. Two other optimized fre-

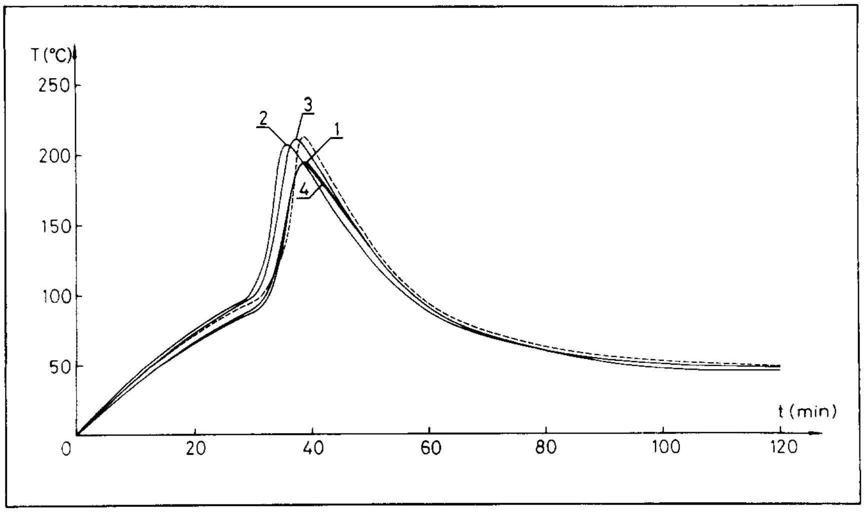


Fig. 4. Pulse period dependence of the temperature $T = (t)$ at $P_0 = 40$ W. (1) 2 msec; (2) 5 msec; (3) 7 msec; (4) 12 msec. Dotted line: continuous mode.

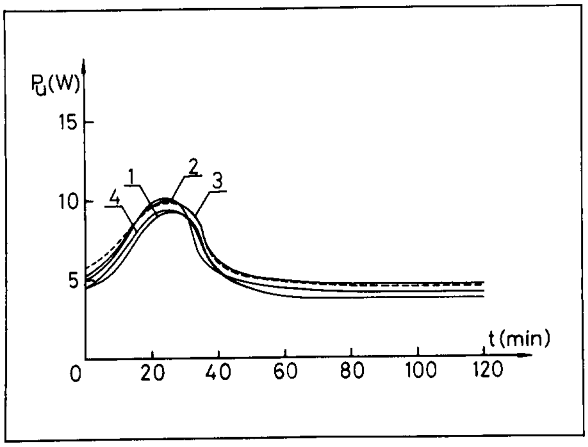


Fig. 5. Pulse period dependence of the dielectric loss $P_u = P_u(t)$ at $P_0 = 40$ W. (1) 2 msec; (2) 5 msec; (3) 7 msec; (4) 12 msec. Dotted line: continuous mode.

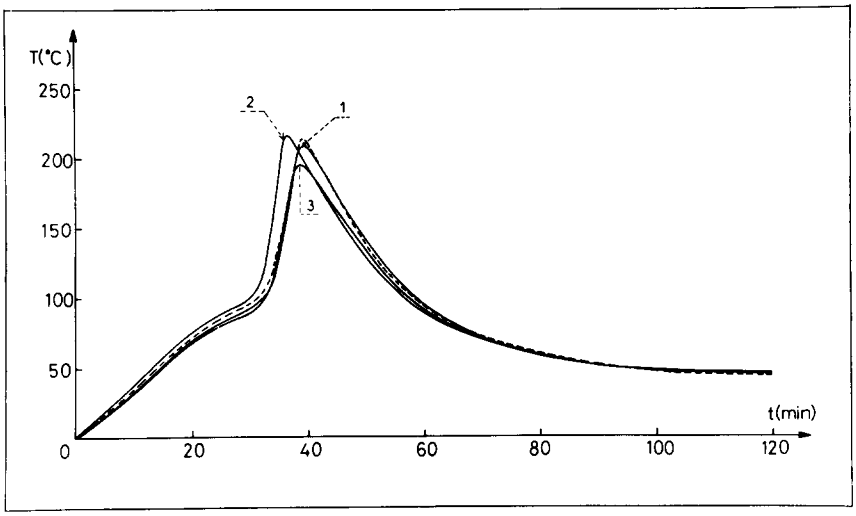


Fig. 6. Pulse period dependence of the temperature $T = T(t)$ at $P_0 = 40$ W. (1) 0.5 msec; (2) 1 msec; (3) 2 msec. Dotted line: continuous mode.

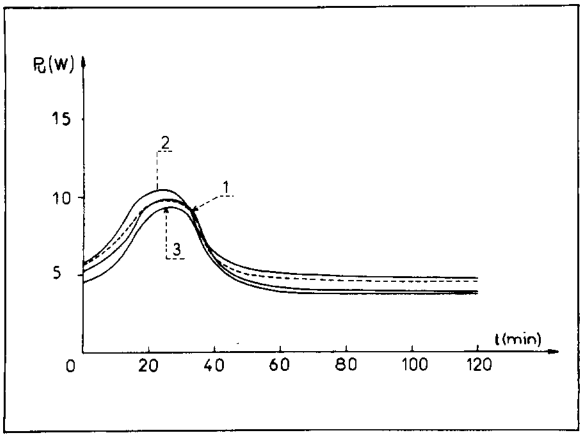


Fig. 7. Pulse period dependence of the dielectric loss $P_u = P_u(t)$ at $P_0 = 40$ W. (1) 0.5 msec; (2) 1 msec; (3) 2 msec. Dotted line: continuous mode.

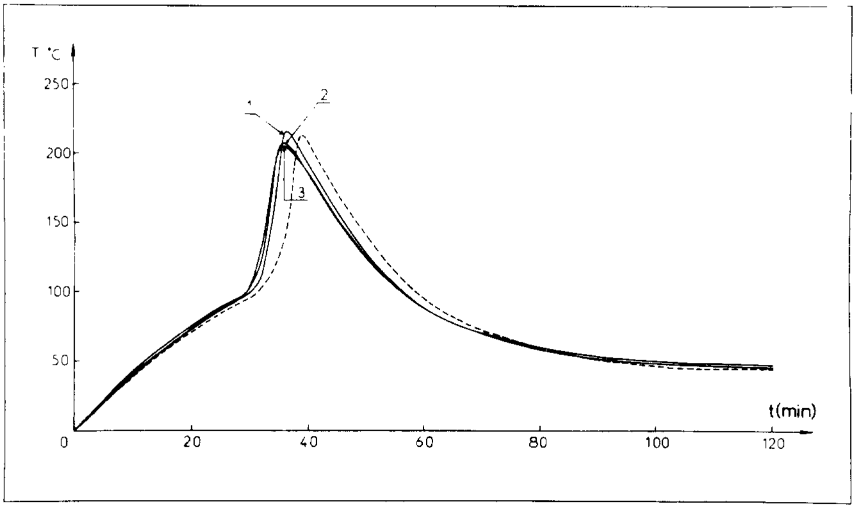


Fig. 8. Pulse period dependence of the temperature $T = T(t)$ at $P_0 = 40$ W. (1) 1 msec; (2) 5 msec; (3) 42 msec. Dotted line: continuous mode.

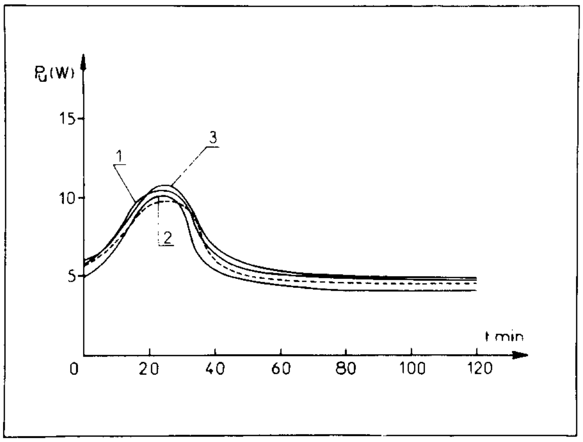


Fig. 9. Pulse period dependence of the dielectric loss $P_u = P_u(t)$ at $P_0 = 40$ W. (1) 1 msec; (2) 5 msec; (3) 42 msec. Dotted line: continuous mode.

quencies are also detected through two series of periods: 2–5–7 and 12 msec (Figs 4 and 5; Table 2) 0.5–1 and 2 msec (Figs 6 and 7; Table 3) where only $\mathcal{T}$ values are considered which lead to more activated processes than that due to the continuous mode. The more efficient periods are 5 msec and 1 msec, which respectively correspond to frequencies of 200 Hz and 1 kHz.

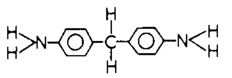
Figures 8 and 9 collect the three curves related to the optimized frequencies: Curves 1 with $N = 1$ kHz, Curves 2 with $N = 200$ Hz and Curves 3 with $N = 23.8$ Hz. They are almost indistinguishable within the initial step of heating which is mainly taken into account in this work. Nevertheless the three pulsed modes are more efficient than the continuous.

The mechanism of improvement of efficiency of crosslinking reactions of epoxy prepolymers due to the use of pulsed microwaves is not obvious. However, the pulse frequency range which has been explored in the present work (20 Hz–20 kHz), suggests dielectric relaxation of chain segments in despite of other possibilities. Indeed recent results [3] on the dielectric characterization of DGEBA epoxy resins and fluid DGEBA epoxy–diaminodiphenylmethane mixtures show that the dipolar epoxide, hydroxyl and amine functions respectively absorb, when the measurements are carried out at room temperature (20°C), around 3 GHz, 600 MHz and 6 MHz. Then, the contribution of larger species, such as chain segments, which certainly relax at lower frequencies because of their size and the interactions that they develop through Van der Waals bonding with the surrounding matter. There is no lack of segments potentially concerned if one considers the distribution of the chemical species (Table 4) which constitute the polymerizable matter: diaminodiphenylmethane (I), pure DGEBA resin (II) oligomeric DGEBA resin (III) with $n = 0.19$ and adducts (I/II) and (I/III).

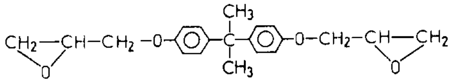
This list of chemical species should be restricted because of great reactivity of the amine protons of the curing agent which have still reacted at 25% with the

Table 4. Chemical structure of the constituents of the prepolymeric resin

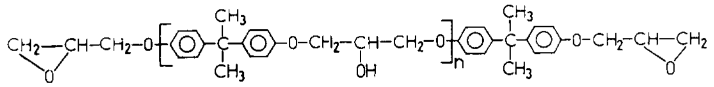
(I)



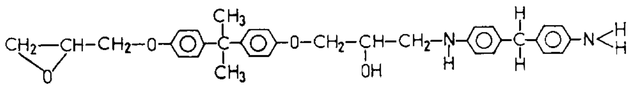
(II)



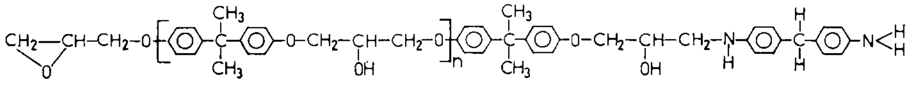
(III)



(I+II)



(I+III)



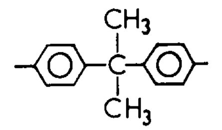
epoxide functions during the preparation of the prepolymeric mixtures to give adducts (II/II) and (I/III). Therefore, no free diaminodiphenylmethane is expected and the composition of the thermosetting medium is resumed to the constituents (II), (III), (I/II) and (I/III), which is stabilized in time within the first step of heating of the samples but at the proximity of the sol–gel transition [2]. The number of chain segments which could intervene in the dielectric loss processes is limited to five, as shown in Table 5.

A short analysis of the capacity of such segments for relaxing under pulsed microwaves helps to understand their respective contributions to the dielectric response of the prepolymer.

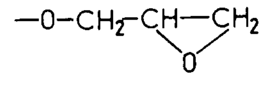
Segments (a):	bisphenol residue; not flexible and unpolar
Segments (b):	"pendant chain" with epoxide terminal function; flexible and polar; submitted to double relaxation (dipolar relaxation due to the carrier wave (2.45 GHz) since the epoxide absorbs at 3 GHz and segmental relaxation brought by the pulsed mode)
Segments (c):	flexible and polar
Segments (d):	flexible and polar; identical to the segments related to the β transitions in the crosslinked networks
Segments (e):	"pendant chain"; heavy and polar

Table 5. Chemical structure of various chain segments

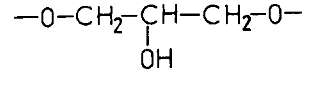
(a)



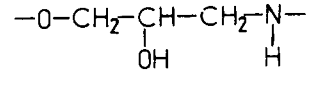
(b)



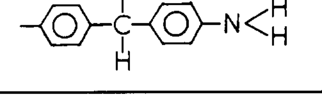
(c)



(d)



(e)



The contribution of segments (a) need not be taken into account, at least at first, but all the others are able to respond to the pulse electrical excitation. Because of dipolar interactions between the active segments, their law of motion is doubtless complicated. However, it is possible to think of a resonating effect which can happen for each type, the frequency then observed playing the part of a resonance frequency (23.8 Hz, 200 Hz and 1 kHz), for which the dielectric loss is maximum.

CONCLUSION

The results show that the use of pulsed microwaves constitutes a sophisticated means to activate the crosslinking reactions. When the pulse frequencies are judiciously chosen, the reactions are faster than those brought about by continuous waves. This effect is assumed to be due to a double relaxation which is a combination of dipolar relaxation linked at the level of the epoxide and hydroxyl groups to the frequency (2.45 GHz) of the electromagnetic waves, and of the segmental relaxation maintained by the discontinuous emission of electrical energy according to a periodical low frequency law. By comparison with the dielectric analysis, the resolution at low frequencies of local motions of the chains is higher and therefore the use of pulsed microwaves could logically open up an interesting polymer spectroscopy, the more as the length τ could vary independently of the pulse frequency and that the response of the segments is correlated to that time of application of microwave energy. The next article will describe the τ dependence of the energy transfer from the electromagnetic beam to our model epoxy resins.

Acknowledgement—A research scholarship was granted to one of us (N.B.) from the Algerian Ministry of Higher Education.

REFERENCES

1. N. Beldjoudi, A. Bouazizi, D. Douibi and A. Gourdenne. *Eur. Polym. J.* **24**, 49 (1988).
2. Q. Le Van and A. Gourdenne. *Eur. Polym. J.* **23**, 777 (1987).
3. F. Legros, D. Le Pen, A. Gourdenne and A. Fourrier-Lamer. To be published.