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MICROWAVE CURING OF EPOXY RESINS WITH DIAMINODIPHENYLMETHANE—II. CROSSLINKING UNDER CONTINUOUS OR PULSED WAVES

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Abstract—Samples of DGEBA epoxy resins with diaminodiphenylmethane as curing agent are submitted for crosslinking to microwaves applied with continuous or pulsed regimes. The variations with time of temperature and of the associated dielectric loss show that the discontinuous process is more efficient then the continuous for activation of the step-growth polymerization. No difference is observed between the elastic moduli of the final products obtained in the two cases, indicating that their chemical structures are very similar.

INTRODUCTION

In the first paper of the series [1], the behaviour under microwaves at 2.45 GHz of DGEBA epoxy resins with diaminodiphenylmethane (DDM) as curing agent was analyzed through the variations with time of the temperature of the samples and of the corresponding dielectric loss due to dipolar relaxation at a given average electrical power (P_0) associated with the electromagnetic beam. The shape of the power signal inside the wave guide was not taken into account, but anyway the average power P_0 value could be certified. In fact, the signal was discontinuous and consequently the emission of waves was pulsed, with a frequency of 50 Hz. As a matter of fact, the true emission can be described thus: a carrier wave was generated by a magnetron with a frequency of 2.45 GHz, working in a hit-or-miss mode. Thus, the production of electrical energy was discontinuous: the waves were delivered every twentieth millisecond i.e. that the period $\mathcal{T}$ is 20 milliseconds (msec), during a time τ of approximately 3 msec.

Various commercial pieces of microwave apparatus can deliver pulsed modes of waves with relatively good definition, and have been used to cure films of thermosetting polyurethane resins [2]: the frequency of the carrier wave was also 2.45 GHz, whereas the pulse period varied from 2 to 200 msec, and the length of pulse τ from 0.15 to 120 msec. It was found through a mechanical test (Persoz hardness) that there was a dependence of the hardness of the crosslinked films on the peak pulse power and the pulse period.

In the present paper, the dependence of the rate of crosslinking of DGEBA–DDM systems on the type of microwave emission, i.e. continuous or pulsed, through our formalism which has been developed elsewhere for thermosetting resins [1, 3], with recording of the temperature of the samples, the dielectric loss (P_u), the time t, and the derivatives $(T)' = dT/dt$ and $(P_u)' = dP_u/dt$. The elastic moduli E of the final networks is also determined.

EXPERIMENTAL

A microwave generator delivers microwaves of frequency 2.45 GHz in a continuous regime. Its coupling with a pulse generator breaks the microwave power into pulses of energy of length τ, periodically emitted with a period $\mathcal{T}$. Then the waves are forced to propagate inside a wave guide according to TE_{01} mode, where the samples of polymerizable matter are placed. Beyond the pulse generator, the wave line is identical to that which has been described by some of us [4]; it allows the measurements of the temperature of the prepolymeric mixtures and the dielectric loss during the irradiation.

Figure 1 presents the power signals due to various microwave modes. The solid line P_0 corresponds to the continuous emission (here $P_0 = 50$ W). The break of this line with the pulse generator leads to a square signal of length τ_1 and height P_c or peak power, generated with a period $\mathcal{T}_1$. P_c is given by:

$$P_c = P_0/(\tau_1/\mathcal{T}_1) = \left(\frac{\mathcal{T}_1}{\tau_1}\right) P_0$$

where P_0 is the average power. In the case of the figure: $\mathcal{T}_1 = 5$ msec; $\tau_1 = 2.5$ msec; $P_0 = 50$ W and $P_c = 100$ W. So,

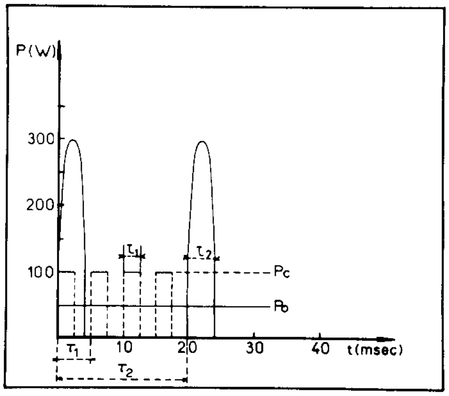


Fig. 1. Modes of microwave irradiation. Mode I: pulsed; $\mathcal{T} = 5$ msec; $\tau = 2.5$ msec; $P_0 = 50$ W and $P_c = 100$ W; Mode II: continuous; $P_0 = 50$ W; Mode III: pulsed; $\mathcal{T} = 20$ msec; $\tau = 3$ msec and $P_0 = 50$ W.

both modes, continuous and pulsed, deliver the same average electrical power. The signal generated by most of industrial microwave generators is more complicated: its shape which is not square and its pulse length τ_2 depends on P_0, but, on the other hand, its period keeps a constant value of 20 msec. In our example: $P_0 = 50$ W and $\tau = 3$ msec.

The epoxy resin is of DGEBA type (DER-331 of Dow Chemicals) and diaminodiphenylmethane (Ref: 32950 of Fluka). The weight of all samples is 20 g.

RESULTS AND DISCUSSION

Figure 2 presents the variations with time (t) of the temperature $T = T(t)$ of a sample of prepolymeric matter submitted to a continuous microwave (2.45 GHz) beam at $P_0 = 50$ W, of the associated dielectric loss $P_u = P_u(t)$, and of the calculated derivatives $(T)' = dT/dt$ and $(P_u)' = dP_u/dt$. All curves have the same shape as that of the curves recorded when an industrial generator is used with a period of 20 msec [1]. First, the polymerizable medium undergoes the fluidification transition located in time at the first inflexion point of T curve or at the maxima of $(T)'$ and $(P_u)'$, after 12 min. Then, the gel point is obtained when P_u is maximum (20 min; 12.5 W). Beyond this transition, P_u starts decreasing because of the crosslinking process which hinders the dipolar relaxation and therefore the dielectric loss, whereas the rise of T is observed due to the major epoxy conversion. At the exothermal maximum, the step-growth mechanism is stopped. At least, the temperature falls from this point, since no more chemical heat is generated which counterbalanced in the previous step the loss of energy of the sample of heat transfer due to convection towards the external medium. The final plateau values of T (50°) and P_u (5.0 W) indicate that the crosslinked network is in a thermal equilibrium under the microwave beam.

Pulsed microwaves with the same average electrical power ($P_0 = 50$ W) are used for activation of the polymerization process. Their efficiency will be measured with reference to that of the continuous waves, mainly through the initial rate of heating of the samples and the gel time; other experimental parameters such the coordinates of the point of fluidification and of the maximum of T, and the value of the maximum of P_u, are not determined with sufficient precision to be taken into account. Such a situation is due to our wish to follow simultaneously the variations with time of the thermal behaviour of the samples and their dielectric response, which requires low values of P_0 to prevent the prepolymeric matter from being burnt.

The emission mode dependence of T and P_u curves is shown in Figs 3 and 4. The numbering of the curves corresponds to the various modes of irradiation: previously presented in Fig. 1:

I—pulsed mode with $\mathcal{T} = 5$ msec, $\tau = 2.5$ msec, $P_0 = 50$ W and $P_c = 100$ W
II—continuous mode with $P_0 = 50$ W
III—pulsed mode (provided by an industrial generator) with $\mathcal{T} = 20$ msec, $\tau = 3$ msec and $P_0 = 50$ W

The positions of the T curves (Fig. 3) indicate that the well defined pulsed mode (Curve 1) is the most efficient mode, since the initial rate of heating is the highest. Then one finds the curve corresponding to the continuous mode (Curve 2). The less activated process (Curve 3) corresponds to Mode III, although it is pulsed. This order is maintained if the coordinates of the respective maxima of T are compared (28 min–216°; 31 min–205°; 36 min–203°). Nevertheless, their values should be carefully considered,

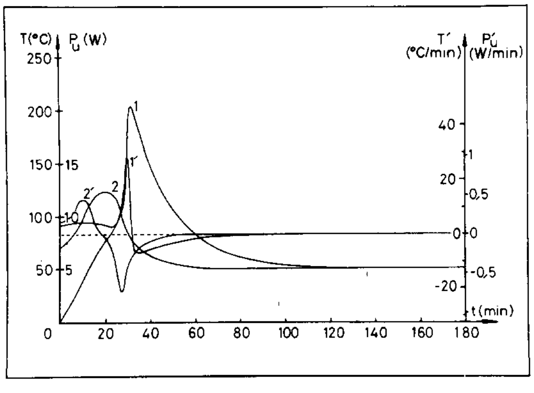


Fig. 2. Crosslinking reaction of DGEBA–DDM resin under continuous mode (Mode III) at $P_0 = 50$ W. (1): $T = T(t)$. (2): $P_u = P_u(t)$. (1′): $(T)' = dT/dt$. (2′): $(P_u)' = dP_u/dt$.

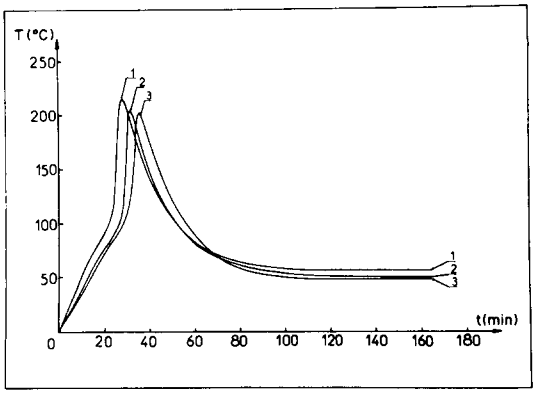


Fig. 3. Mode dependence of the temperature $T = T(t)$ at $P_0 = 50$ W. (1) Mode I; (2) Mode II; (3) Mode III.

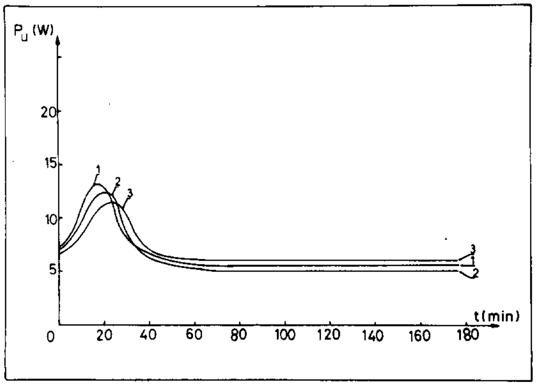
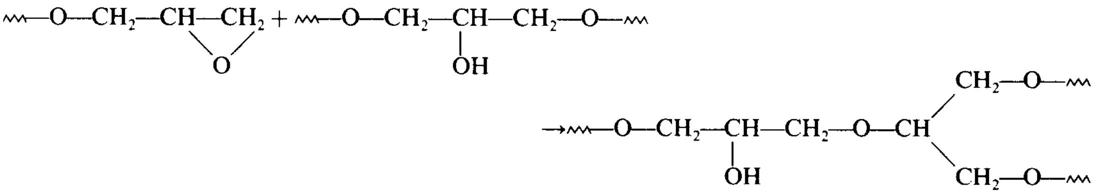


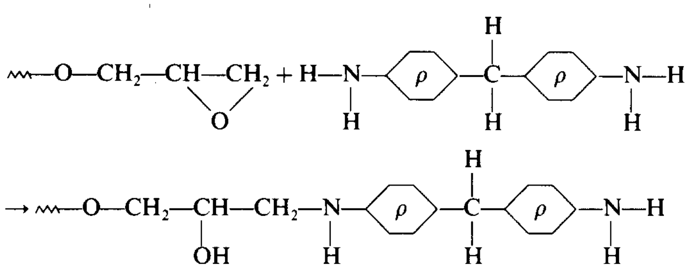
Fig. 4. Mode dependence of the dielectric loss $P_u = P_u(t)$ at $P_0 = 50$ W. (1) Mode I; (2) Mode II; (3) Mode III.

because they change within a series of identical experiments, when the respective position of the initial heating segments is reproducible. Such fluctuations are due to the magnitude of the loss of energy by convection when T increases. Indeed the instantaneous loss of energy which is proportional to the thermal gradient $\Delta T = (T - T_0)$ between the sample (T) and the external medium (T) induces a shift of T and t coordinates of the maxima of T all the more significant as the production of chemical heat is confined in time, and which disqualifies them from being reliable experimental parameters. Such an objection cannot be made concerning the initial step of heating, since it has been previously shown that no epoxy functions are converted during this period [1]. The highest efficiency of Mode I is also encountered in P_u curves (Fig. 4), especially at the level of their maxima (17 min–13.2 W; 20 min–12.5 W; 23 min–11.5 W).

The differences between the three modes of irradiation towards the heating and kinetics of crosslinking of the resins cannot be interpreted by resorting to the microwave dependence of the reactivity of the chemical species (epoxides and amines) of the constituents of the prepolymer through the vibrations of their atoms since the microwave photon is too small ($h\nu = 1.0\ 10^{-5}$ eV) to initiate such motions of atoms. In the same way, no significant change in the chemical reactivity is expected from the thermal effect of the beam, more especially as the temperature profiles are similar for the three modes. One could also think that new inter-chain linkages would appear when microwaves are applied, for instance ether bridges resulting from the condensation from epoxides with hydroxyl groups carried by DGEBA entities:



instead of those expected from the reaction of epoxides with diamines:



This hypothesis of ether linkages has been rejected because their formation would have probably decreased the elastic moduli related to networks obtained according to the various modes, which have been determined through uniaxial compression from cylinders, whereas their average values are very similar, respectively 2.7, 2.6 and 2.6 GPa for Modes I, II and III.

Another possible explanation of the difference of behaviour of samples submitted to the different modes resorts to relaxation of chain segments. Indeed the pulsed waves could induce, besides the dipolar relaxation maintained owing to the carrier wave working at 2.45 GHz, the relaxation of flexible segments in correlation with the law of emission of energy with a period $\mathcal{T}$ or a frequency $N = 1/\mathcal{T}$: for our experiments $N = 200$ Hz for Mode I, and $N = 50$ Hz for Mode III. On the basis of this hypothesis, Mode I leads to an optimized activation due to the combination of the relaxation of the dipoles at 2.45 GHz with the relaxation of segments of epoxy chains at 200 Hz. Thus, for the same average electrical power ($P_0 = 50$ W), the energetic yield would be improved, the conversion of electrical power as heat being performed through motions of dipoles and segments. On the contrary, Mode III with a frequency $N = 50$ Hz hardly maintains the local motions, when the continuous regime is used as reference and no synergistic effect between both types of relaxation is observed.

The three irradiation modes lose their selectivity when the resins are crosslinked; especially in the final stage the plateau values of T and P_u are almost confused since the networks are in the glassy state, and all chains segments are immobilized.

CONCLUSIONS

All results show the dependence of the behaviour of fluid DGEBA–DDM resins on the mode of microwave irradiation, continuous or pulsed. When pulsed regimes are used, one can expect a combination of two relaxations for dipoles and flexible chain segments. However, many complementary studies have to be performed for a better understanding of the interactions between the microwaves and the thermosetting resins. For instance, for a given formulation, many optimized pulse frequencies are probably possible in relation with the relaxation of various flexible chain segments and also with that due other types of chemical constituents, such as aggregated or not curing agent molecules. On the other hand, the determination of the elastic modulus of samples crosslinked under continuous or pulsed microwaves modes gives proof that the final structures are nearly identical since the elastic moduli have the same value independently of the choice of the mode, and that consequently they do not indicate any specific microwave effect which could exist.

REFERENCES

1. Q. Le Van and A. Gourdenne. *Eur. Polym. J.* **23,** 777 (1987).
2. H. Julien and H. Valot. *Polymer* **26,** 506 (1985).
3. A. Gourdenne and Q. Le Van. *Int. Symp. On Macromolecules IUPAC* **A(1),** 128 (1981).
4. M. Teffal and A. Gourdenne. *Eur. Polym. J.* **19(6),** 543 (1983).