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Curing under Continuous Microwaves (2 450 MHz) of Thermosetting Epoxy Prepolymers: Final Statement

*Patrick Alazard, Michel Palumbo, Albert Gourdenne**

Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques
Laboratoire Catalyse, Chimie Fine et Polymères, 118, route de Narbonne,
31077 Toulouse Cedex 4, France
Fax : (+33) 5 62 88 56 00; E-mail: Albert.Gourdenne@ensiacet.fr

Summary: After some recalls on the dielectric behavior of the organic materials, a parametrical study of the activation by continuous microwaves (2 450 MHz) of the curing reaction of an epoxy resin of DGEBA type in presence of diamino-biphenyl-methane used as crosslinking agent, is carefully described. The recording during the irradiation of the variations of the average temperature of the chemical medium and of the associated dielectric loss on the one hand, and the determination of the glassy transition temperature of the final networks on the other hand, allows optimization procedures of the electromagnetic treatment of the initial prepolymeric mixtures.

Keywords: activation, crosslinking, epoxy resin, kinetics, microwaves

Introduction

Microwave activation of polymerization reactions at 2 450 MHz first came into use in the early seventies. Experiments were carried out inside domestic ovens or multimode cavities. No significant results were obtained in such a way, because one resorted too much to broad empiricism. This situation was due to insufficient background of the implied researchers either in chemistry or in electromagnetism. The state of this research improved around later, when quantitative banks of microwave irradiation were built, allowing the possibility of recording the variations versus time of the average temperature of the organic materials under irradiation and of the associated dielectric loss due to activated dipolar relaxation.[1,2] The analysis of the data thus gained gave scientists access to the kinetics of the reactions and to a knowledge of the structural changes which occur inside the chemical medium during the polymerization. However, the geometrical dimensions of the wave guide elements compatible with the working frequency and used as applicators, disqualify this type of equipment for industrial transfer operations. Nevertheless, such experiments are necessary so as to identify the mechanisms of polymerization under microwave irradiation for future wide-scale

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applications. More recently, the microwave frequency was replaced by a radiofrequency of 27.12 MHz which seems to be more efficient towards the curing of thermosetting prepolymers [3,4]. Both frequencies lead to similar conclusions as for the nature of the interactions between the oscillating electrical field and the organic materials to be polymerized and which work when curing reactions of epoxy resins (step polymerization) or of unsaturated polyester - styrene mixtures (chain polymerization) develop. Moreover, when microwaves are applied, two types of wave emission can be used, continuous or pulsed. When pulsed waves are applied, the kinetics of polymerization can be accelerated or delayed in comparison with those obtained in the case of the continuous modes of emission [4,5]. On the other hand, microwaves [6] or radiofrequencies [7] have been applied with success to activate the crosslinking reaction of composite materials with thermosetting polymeric matrix, which constitute model systems for the study of interaction between waves and bi-phased matter. But now, additional parameters should be taken into consideration, as the chemical nature of the fillers, transparent to the waves (silica), or electrically conductive (metals and carbon-black), and their shape and volume concentration.

The present paper opens with some comments on the dielectric loss in organic matter under electromagnetic irradiation; then, the microwave curing reaction, according to a step polymerization mechanism, of a DGEBA epoxy resin or diglycidylether of bisphenol A, in presence of 4,4'-diaminodiphenylmethane used as crosslinking agent, is carefully described. In the conclusion, the possible extension of the electromagnetic activation to various polymerization reactions, carried out in homogeneous (liquid state) or two-phase media.

Dielectric loss in molecular or polymeric organic materials

The dielectric loss, expressed as an electrical power or P_u, in organic molecular or polymeric matter submitted to electromagnetic waves of electrical power or P_0, is given by the general formula : $P_u = P_u(t) \propto 2\pi.f.\varepsilon''.v.E^2$, in which t, f, ε'', v and E are the time, the frequency of oscillation of the electrical field, the loss factor , with $\varepsilon^* = \varepsilon' - j.\varepsilon''$, the volume of the sample and E the modulus of the applied electrical field. At 2 450 MHz, P_u is due to dipolar relaxation, activated by the electromagnetic beam: the dipolar species tend to be in line with the oscillating field. So, the dielectric loss is of mechanical energy type. But the motion of relaxing entities is more or less hindered by their physical interactions with the surrounding chemical medium (viscosity effect). Consequently, this phenomenon of internal friction leads to a partial conversion of P_u into heat or Q. When the temperature is sufficiently high, the activation of polymerization reactions can operate. Thus, the conversion of electricity into heat includes two steps: from electrical energy (P_0), one reaches mechanical energy (P_u), with $P_u = \alpha.P_0$ and $\alpha < 1$, and heat (Q), with $Q = \beta.P_u$ and $\beta < 1$, or $Q = \alpha.\beta.\ P_0$, with $\alpha.\beta << 1$.

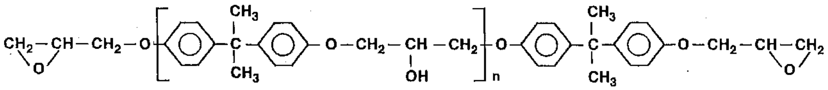
$$\underset{(P_0)}{\text{Electrical energy}} \Rightarrow \underset{(P_u)}{\text{Mechanical energy}} \Rightarrow \underset{(Q)}{\text{Heat}}$$

The residual dielectric loss, $(1 - \alpha).P_u$, or irrecoverable energy, is used to activate the Brownian motion inside the samples and other possible non-exothermic physical phenomena. Both average values of α and β, estimated from liquid epoxy resins, are close to 25%. Consequently, the energetic yield, or $\alpha.\beta$, is low (~ 6%).

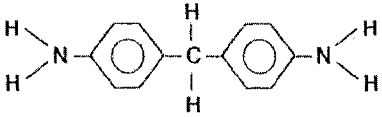
Experimental

Microwave irradiation experiments at 2 450 MHz [1,2] are carried inside a wave guide element used as applicator. The waves are progressive - no stationary system is formed - and propagate according to the TE_{01} mode. Moreover, the electrical field is polarized and parallel to the small side of the section of the guide. The prepolymeric matter (20 ml) to be irradiated is poured into cylindrical pyrex pill boxes - transparent to the electromagnetic beam - used as reactors. The irradiation is carried out inside an element of wave guide. Watt-meters distributed along the wave guide line give access, for an applied electrical power P_0, to the values of the transmitted power or P_t, of the reflected power by the reactor or P_r, and of the power due to conduction loss in the metallic walls of the apparatus or P_a. The conduction loss at given P_0 is obtained from blanks. The powers P_t and P_r are absorbed through load charges, in order to avoid the establishment of systems of stationary waves which would create hot spots of energy. Moreover, each reactor constitutes an open thermodynamic system which exchanges energy with the external medium (air at 20 °C circulating inside the wave) through thermal convection. The dielectric loss, or P_u , due to dipolar relaxation, is given by the expression $P_u = P_0 - (P_t + P_r + P_a)$. The average temperature or T, is recorded through a non-interactive probe, immersed in silicon oil contained inside a pyrex tube plunged in the chemical medium. The variations versus time or t of T and P_u, at given P_0, are visualized on the screen of a computer and stored before mathematical treatment. Four types of curve are obtained : $T = T(t)$, $P_u = P_u(t)$, $(T)' = dT/dt$ and $(P_u)' = dP_u/dt$.

The organic system which is used as a model system for the study of the interactions between microwaves and reactive organic matter, consists of an epoxy prepolymer which associates an epoxy resin of DGEBA type (condensation index: 0.06) and 4,4'-diaminodiphenylmethane, or DDM, as curing agent, in stoechiometric ratio epoxide/amino-proton = 1).



diglycidylether of bisphenol A



4,4'-diaminodiphenylmethane

The dielectric relaxation spectra of the initial prepolymeric mixture in fluid state shows that the absorption of the epoxides at room temperature appears as a broad peak centered around 3 GHz [8]. As for the absorption of the other polar groups (hydroxyls, primary and secondary amines), it is located at lower frequencies. So, the epoxides relax at the working microwave frequency or 2 450 MHz, and the electromagnetic activation of the polymerization reaction is possible.

The various steps of the thermally activated curing process (inside an oven) of the prepolymeric mixture - previously pre-cooled at - 18 °C during several hours - which leads to final crosslinked polymeric networks, are now well known. In the initial physical state, strong Van der Waals bonds have been developed between the various components of the thermosetting system which appears more or less turbid. The structure of the chemical medium is now that of a crystalline - like one. When the temperature is increased, the physical interactions are partially broken, the medium becomes fluid, transparent and, of course, less polar. Then, when the temperature is sufficient, the exothermic polymerization reaction starts working. The viscosity effect, associated with the progress of the reaction, hinders more and more the Brownian motion and lowers the kinetics of curing. Before long, the medium is completely gelled and consequently the relaxation of the polymeric chains is drastically restricted. The structural change which occurs in the epoxy system, when it passes from the fluid state to the gel, does not involve the formation of micro-gels, contrary to the case of the gelation process of the unsaturated polyesters - styrene resins [9]. The last step of the curing process which generates an exothermic peak, corresponds to the formation of a highly crosslinked network from the gelled state. All preceding variations will be encountered in the case of the microwave polymerization of the epoxy resins.

Results and discussion

Figures 1 and 2 display the curves T = T(t), $P_u = P_u(t)$, (T)' = dT/dt and $(P_u)' = dP_u/dt$, when a sample of epoxy prepolymer (20 ml), pre-cooled at -18°C, is irradiated under continuous microwaves, at P_0 = 40 watts. The data start being recorded from 0°C. The shape of the T curve underlines the usual steps of an exothermic curing reaction. T starts growing from 0°C.

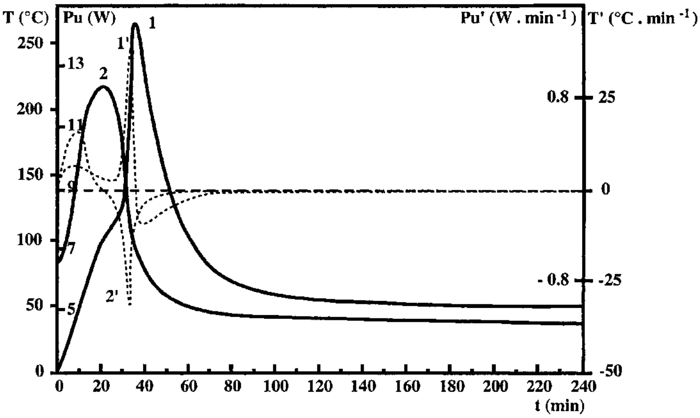


Figure 1. Curing under microwaves at P_0 = 40 W. (1): T = T(t); (2): $P_u = P_u(t)$; (1'): (T)' = dT/dt; (2'): $(P_u)' = dP_u/dt$

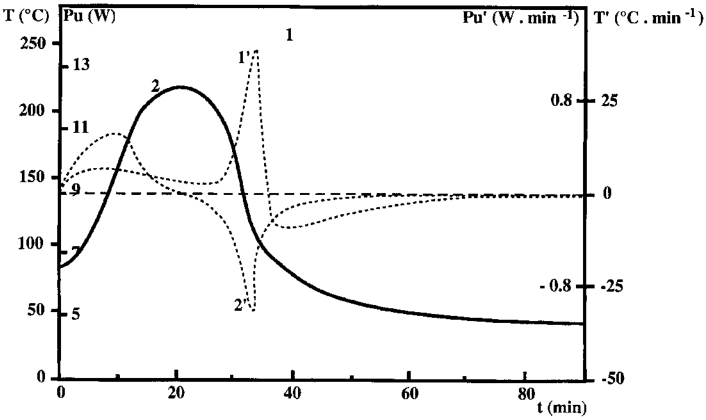


Figure 2. Curing under microwaves at P_0 = 40 W. (90 minutes). (1): T = T(t); (2): $P_u = P_u(t)$; (1'): (T)' = dT/dt; (2'): $(P_u)' = dP_u/dt$

The fusion of the crystalline-like structure is quickly undergone; it is located in time at the first inflexion point, or at the first maximum of (T)', that is at 7.0 minutes. Then, the gelation process begins through the reaction of condensation. It is admitted that the complete gelled structure is located at the foot of the exothermic peak, when the corresponding experimental value of the extent of the reaction is assumed to be grossly around 70 %. The second inflexion point of the T curve, positioned in time at 24 minutes through the second maximum of (T)', is attributed to the sol-gel transition which separates the liquid state (easy dipolar relaxation) and the gelled state (restricted relaxation because of the high viscosity of the chemical medium).

The final crosslinking step which follows the complete gelation, is started by a fast exothermal conversion of epoxide functions within a short time (increase of 15 or 20 % of the extent of the condensation), and generates a great deal of energy within a few minutes: the temperature rapidly increases. Such a variation is only possible, because the thermal effect keeps the temperature of the medium at a level higher than the glassy transition of the epoxy network in formation, according to the Time - Temperature - Transformation (TTT) cure diagram [10], and consequently allows the condensation reaction. Now, let us consider the ascendant part of the peak of temperature which reaches its ceiling at 264.4 °C : it presents an inflexion point (33.3 min, 210.1 °C), which corresponds to the maximum of the heating rate or dT/dt, that is to say that the kinetics of conversion of the epoxides are the fastest at that time, since the rate of production of chemical heat varies as the rate of the reaction. Moreover, the fact that the temperature goes through a thermal maximum, means that the chemical heat which is still produced beyond the maximum, provided that the temperature is higher than the glassy transition temperature, can no more counterbalance the loss of energy through thermal convection from the sample towards the external medium (air at $T_0 = 20$ °C, circulating inside the wave guide applicator). So, beyond the maximum, the temperature does not cease going down, the viscosity increases and the polymerization finally stops. At the end, T takes a plateau value or $T_p = 49.7$ °C, much lower than the glassy transition temperature - determined through DSC, at a heating rate value of 10°C/min - of the formed network or $T_g = 175.0$ °C. This result constitutes a proof that the crosslinked epoxy resin still absorbs microwaves in the glassy state.

As for the P_u curve , it shows that, at the beginning of the electromagnetic treatment, the dielectric loss varies in the same way as the temperature. The electrical loss increases quickly because of the high polarity of the chemicals due to strong physical bonding in the crystalline-like medium. Then, an inflexion point is observed, beyond which the time dependence of P_u

changes : the fusion has become significant and the polarity of the prepolymeric matter drops, whereas the microwave activated dipolar relaxation inside the liquid rises. One assumes that the fusion transition is located at 8.5 minutes (abscissa of the inflexion point), whereas that determined from the T curve is 7.0 minutes. This time gradient, due to uncertainty in the measurements, is not significant : the interesting result is that both times are of the same magnitude. But, even when it is expected that, beyond the transition, the temperature reaches a plateau value, the dielectric loss goes down, whereas T still increases. Such a divergence finds its origin in the progress of the curing reaction which starts as soon as the preceding transition is undergone. Indeed, two phenomena with antagonistic effects enter into competition : i) the increase of temperature which helps the dipolar relaxation - P_u is expected to rise -, and ii) the increase of viscosity of the chemical medium in relation with the extent of the conversion of the epoxies, which progressively decreases the dielectric loss. Indeed, the increasing viscosity not only restricts the dipolar relaxation of the polar species working at the microwave frequency, but also induces a shift of the dielectric absorption towards low frequencies which initiates a progressive decoupling between microwaves and the organic prepolymer on curing. The conversion of epoxies which absorb in the 2 450 MHz region, has also to be taken into consideration. The presence of a maximum is a compromise between all preceding phenomena. By comparing the relative position in time of the T and P_u curves, the maximum of P_u can be attributed to the sol-gel transition, located now at 20.5 min, instead of the preceding value extrapolated from the T curve, that is 24.0 min. But, since the locating in time of a maximum is easier and more accurate than that of an inflexion point, the abscissa of the maximum of P_u is chosen for that of the sol-gel transition. Moreover, one can add that the variations of the dielectric loss are quasi immediate, whereas their thermal effect is consecutive and delayed in time. Consequently, the time gradient between both values is not surprising. The fact that P_u decreases, whereas T does not cease growing, means that the curing reaction does not need now any electromagnetic activation: the reaction is auto-activated through chemical heat on production. Therefore, microwave heating could be used in order to initiate the polymerization process until its auto-activation, and then removed. At the end, the dielectric loss tends towards a plateau value or $P_{up} = 4.5$ W.

An extended study of the P_0 dependence of polymerization kinetics has been carried out, when it varies from 10 to 50 W. The series of the corresponding T and P_u curves are respectively gathered in Figures 3 and 4, and the co-ordinates of the various maxima and the plateau values, T_p and P_{up}, collected in Table 1. All temperature curves present the same type of shape previously encountered for $P_0 = 40$ W, but some variations should be underlined as for their exothermic peak: when P_0 drops, it is shifted towards the high values of time - such a dependence means that that the kinetics of polymerization are more and more delayed -, and it broadens out. A similar tendency of P_0 dependence is observed in the case of P_u curves. At the highest values of time, the discrimination of the final segments of all T or P_u curves becomes impossible.

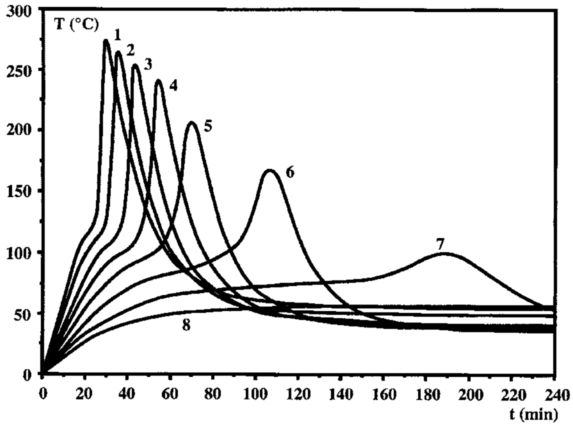


Figure 3. Curing under microwaves at variable P_0. Curves T = T(t). (1): 50W; (2): 40 W; (3): 35 W; (4): 30 W; (5): 25 W; (6): 20 W; (7): 15 W; (8): 10 W

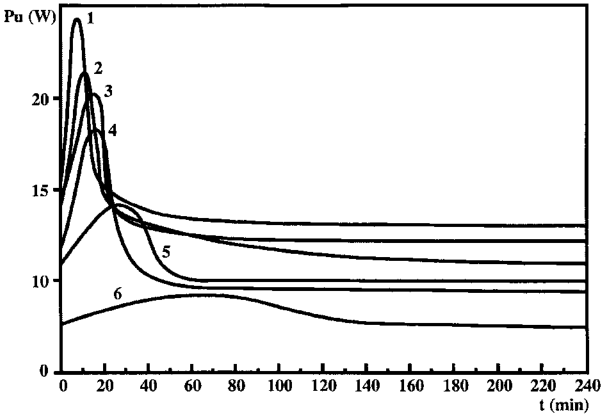


Figure 4. Curing under microwaves at variable P_0. Curves $P_u = P_u(t)$. (1) : 50 W; (2): 40 W; (3): 35 W; (4): 30 W; (5): 25 W; (6): 20 W; (7): 15 W; (8): 10 W

Table 1. P_0 dependence of the various kinetic parameters and of the glassy transition temperatures of the epoxy networks.

Curve N°	1	2	3	4	5	6	7	8
P_o (W)	50	40	35	30	25	20	15	10
P_u max								
Abscissa (min)	17.0	20.5	25.0	32.5	41.0	53.5	90.7	177.3
Ordinate (W)	15.0	12.3	9.8	8.9	7.6	5.7	3.9	2.7
T max								
Abscissa (min)	29.5	35.5	43.0	54.0	70.0	106.0	185.3	222.7
Ordinate (°C)	273.3	264.0	253.1	239.7	206.1	167.5	103.0	56.8
P_{up} (W)	6.6	4.5	4.0	3.0	2.9	2.4	1.9	2.1
T_p (°C)	55.2	49.7	42.4	41.1	38.2	36.4	53.1	56.2
T_g (°C)	175.9	175.0	174.6	172.6	172.0	/	/	/
$T_{g\infty}$ (°C)	183.5	183.8	183.8	185.0	187.8	/	/	/

The T dependence of P_u at given P_0 constitutes another approach of the kinetics of the step polymerization (Figure 5). All curves present a maximum which corresponds to the sol-gel transition. In addition, the final segments are discriminated for all P_0 values, except 10 W, because of lack of experimental precision. Curves of same type have previously encountered

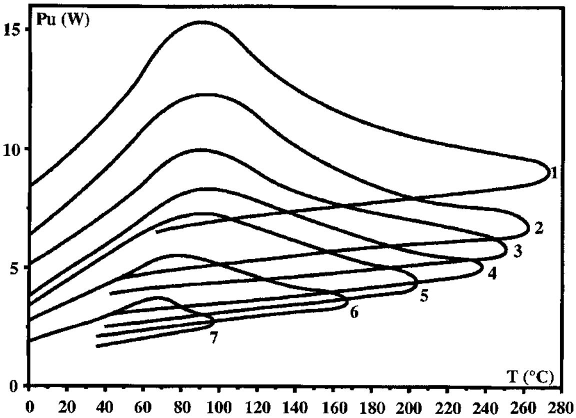


Figure 5. Curing under microwaves at variable P_0. Curves $P_u = P_u(T)$. (1): 50 W; (2): 40 W; (3): 35 W; (4): 30 W; (5): 25 W; (6): 20 W; (7): 15 W

when the temperature dependence of the loss factor or ε'' was recorded elsewhere, in the case of DGEBA/diaminodiphenylsulphone mixtures crosslinked under microwave irradiation [11]. But no information on the progress of the curing reaction and on the structural changes which occur during the polymerization, was provided and no attribution of the singular points of the various curves done. Nevertheless, such similarity between the T dependence of ε'' and P_u incites to think that the measure of the dielectric loss (P_u)gives an idea of the variations of the loss factor (ε'') during the polymerization reaction under microwaves ($P_u \propto K.\varepsilon''$).

The determination of the glassy transition temperature, or T_g, of the final crosslinked DGEBA/DDM networks, carried out through Differential Scanning Calorimetry or DSC, provides information upon the extent of the crosslinking reaction of the epoxy resin which varies as T_g. Figure 6 shows the P_0 dependence of T_g, determined at a heating rate value of 10 °C/min, when the power varies from 25 to 50 watts. All values are close to 174 °C. Lower levels of the applied power (20, 15 and 10 W) lead to fluid materials under-crosslinked: their thermal characterization can not be performed in good conditions. For P_0 = 10W, a polymerization reaction can not be excluded, but its kinetics are too slow to be appreciated with accuracy. The P_0 dependence of the glassy transition temperature which is assumed to vary as the progress of the curing, indicates that it slightly increases from 172.0 to 175.5 °C, when P_0 grows from 25 to 50 W, that is to say that the different values of the extent of conversion of the epoxies at given electrical power, are grossly of the same magnitude. Experiments carried out at higher P_0 values induce thermal degradation of the samples at core.

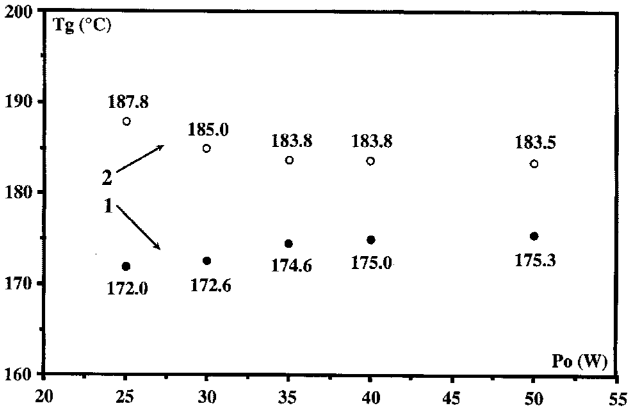


Figure 6. Po dependence of the glassy transition temperatures. (1): T_g; (2): $T_{g\infty}$

The P_0 dependence of the plateau values T_p and P_{up} (Figures 7 and 8) shows that it is of linear type from 25 W. Now, if one considers that the structure of all corresponding samples crosslinked in such conditions is quasi-identical, since their glassy transition temperature is comparable ($T_g \propto 174$ °C), the reported behavior is that of a given epoxy network. Such a linearity means that the same relaxation processes work, because no transition is detected. The expressions of T_p and P_{up} are respectively: $T_p = 19.73 + 0.71\ P_0$ and $P_{up} = -\ 2.30 + 0.18\ P_0$.

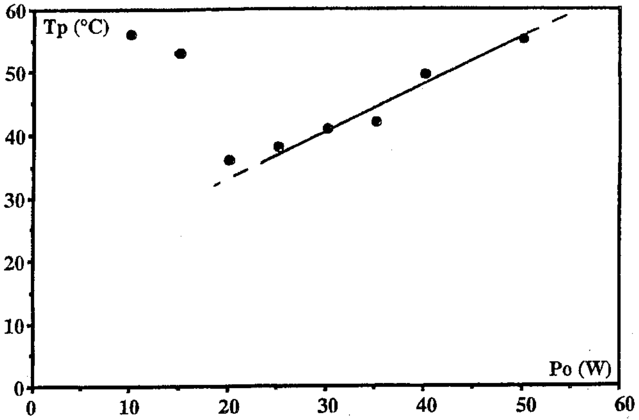


Figure 7. Curing under microwaves at variable P_0. Curves $T_p = T_p(P_0)$. (1): 50 W ; (2): 40 W; (3): 35 W; (4): 30 W; (5): 25 W; (6): 20 W; (7): 15 W; (8): 10 W

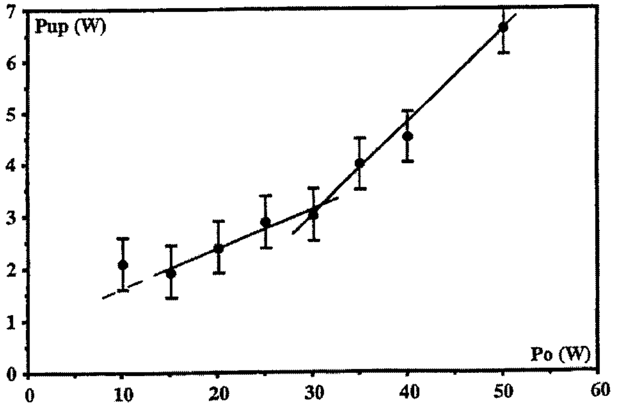


Figure 8. Curing under microwaves at variable P_0. Curves $P_{up} = P_{up}(P_0)$. (1): 50 W ; (2): 40 W; (3): 35 W; (4): 30 W; (5): 25 W ; (6): 20 W; (7): 15 W ; (8): 10 W

The constant term of the expression of T is 19.73, that is to say the temperature of the air circulating inside the wave guide used as applicator or 20 °C. Of course, the P_{up} dependence of T_p is also linear. The coefficient of P_0 in the expression of T_p can be deduced owing to the fact that the sample is in thermodynamic equilibrium. Indeed, the loss of energy of the polymeric sample by thermal convection towards the external medium (air) is given by the expression $- h.s.(T_p - T_0)$, in which h, s and T_o are respectively the convection coefficient, the external area of the sample and the temperature of the air or $T_0 = 20$ °C, whereas the thermal energy brought by microwaves is Q, with $Q = \beta.P_u = \alpha.\beta.P_0$. The thermodynamic equilibrium is reached when $Q - h.s.(T_p - T_0) = 0$. At the end, one obtains: $T_p = T_0 + (\alpha.\beta/h.s).\ P_0$, with $\alpha.\beta/h.s = 0.71$.

Now, when P_0 is lower than 25 W, T_p keeps values much higher than those extrapolated from the straight line, even if the applied power is smaller. On the other hand, the same tendency is observed for P_{up}, but with less spectacular deviations, since the values of the dielectric loss are small. All these anomalies are due to the fact that the crosslinked epoxy resins are under-polymerized and consequently more polar or less transparent to microwaves, that is to say abler to be heated through dielectric loss.

After their initial thermal characterization which provides T_g values, all samples crosslinked through microwaves at P_0 higher than 25 W, are thermally post-cured inside the oven of the DSC equipment through a series of successive analyses, in order to increase the extent of the curing reaction. A final glassy transition temperature, or $T_{g\infty}$, higher than T_g, is obtained (Figure 6). The P_0 dependence of $T_{g\infty}$ shows that it reaches its maximum value or 187.8 °C, for $P_0 = 25$ W, whereas that of the corresponding Tg is 172.0 C°, value which indicates that the used power leads to the lowest extent of the polycondensation reaction under microwaves, at least in the P_0 range studied. But, it is admitted that the structural homogeneity of the final post-cured samples varies as that of the networks just issued from polymerization reactions, and consequently, as that of the corresponding gels. If such a law is extended to microwave cured epoxy materials, one can obviously assume that the best structural homogeneity should be expected for $P_0 = 25$ W, since the rate of formation of the gel network is then the lowest, and that consequently its physical structure would have to be more homogeneous than that of the other gels obtained at upper values of P_0. Actually this is what is observed, because the corresponding $T_{g\infty}$ value is the highest of the series.

Conclusion

All results which have been described, and which are reproducible through a few hundred polymerization experiments, show that continuous microwaves are efficient to activate the curing reactions of epoxy resins of DGEBA type, when tetra-functional amino-compounds are used as crosslinking agents. The optimization of the electromagnetic treatment leads to final epoxy products with glassy transition temperatures comparable within two degrees to those of the products crosslinked through classical thermal activation carried out inside an oven. Moreover, the values of elasticity modulus of the epoxy networks, determined through uniaxial compression, are very close to 3 GPa, whatever the mode of activation of the polymerization reactions may be. So, one can assume that there is no specific effect of microwave energy on the three-dimensional epoxy structures; it is the mode of heating of the prepolymeric matter which is specific, since heat is created inside the organic medium, whereas it is brought through an external thermal source in the case of a classical thermal activation carried out inside an oven. On the other hand, direct comparisons between both kinetics of polymerization activated by classical or microwave heating can not obviously proposed, because, at given temperature, the corresponding physical states of the organic prepolymers are completely different. Indeed, when the curing is carried inside an oven, the motion of the dipolar species is random, whereas that working in the case of microwave heating is forced to be in line with the oscillating electrical field.

Now, when fillers are added to prepolymers in order to form composite materials, two cases should be considered. When the additives are inorganic and transparent to microwaves, such as glass fibers and silica powders, the electromagnetic beam is scattered when it goes through the fillers because of a gradient of optical index between the mineral and organic components. If they are electrically conductive, as metallic powders or carbon fibers, the waves are reflected by the fillers and an electrical loss or P_c, due to electronic conduction, has to be added to the dielectric loss. Moreover, in this last case, the propagation of the waves quickly becomes complicated, when the volume fraction of the additives increases, since various phenomena develop, such as multi-reflection of the beam, aggregation of the fillers and electric percolation.

Of course, the microwave activation works in all step polymerization reactions which can be thermally activated, and has been also applied to the initiation of chain polymerization reactions, as curing of unsaturated polyester - styrene mixtures. However, there are some limitation of the use of this electromagnetic process in polymer synthesis:

i) the experiments should be carried out in bulk, without any solvent - if this condition is not respected, the solvent absorbs microwaves and poor effects due to microwaves on the kinetics of polymerization are expected;

ii) micellar structures, usually encountered in radical polymerization (emulsion and suspension), can not be stabilized, when the electromagnetic beam is applied, they explode;

iii) in the case of heterogeneous polymerization using stereospecific catalysts in order to produce stereoregular polymeric chains, a change of the mechanisms of catalysis induced by electrical conduction at the level of the catalytic substrates is expected and would have to lead to a variation of configuration of the synthesized polymers, or even the non-formation of the monomer - catalytic site complex.

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