

VARIATIONS OF THE DIELECTRIC PROPERTIES OF EPOXY RESINS DURING MICROWAVE CURING

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Abstract—The curing of a particular epoxy resin (diglycidylether of bisphenol-A) by three amino hardeners (4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulphone and 4,4'-diaminodiphenylether) is followed by dielectric measurements performed under microwave heating. The formation on heating of a molecular association, is suggested by the analysis of the dielectric variations on the basis of an additive contribution of all the known constituents in the mixture. The reversibility of this molecular association is demonstrated. Two possible interpretations are proposed and discussed. Dielectric constant variations during curing provide evidence that microwave heating is a very efficient way of energy transfer and for monitoring chemical processes, such as the cross-linking of epoxy resins.

INTRODUCTION

Homogeneous energy transfer required to initiate or to perform the curing of polymers is generally not achieved by normal heating because of the existence of important thermal gradients inside the materials being treated. Dielectric heating, for which the origins of the thermal gradients are essentially different, has led to investigations on microwave curing of polymers. Moreover, during irradiation, energy is directly supplied inside the materials, allowing more efficient and faster heating. On the other hand, it is important to determine how specific the polymerization under microwave field could be, and also the role played by the relaxation of macromolecular polar groups. The main classes of thermosetting polymers involved in microwave curing are polyesters and epoxy resins.

The microwave curing of epoxy resins was first attempted by Williams [1]. More recently, the evaluation of dielectric loss during curing was approached by Wilson and Salerno [2] and interpretations of its variations proposed [3, 4]. The latter studies were performed at 2.45 GHz, essentially on the cross-linking of the diglycidylether of bis-phenol-A (DGEBA) with 4,4'-diaminodiphenylmethane (DDM) as curing agent. Another study concerned the microwave hardening of DGEBA either by 4,4'-diaminodiphenylsulphone (DDS) or by dicyandiamide (DDA) by means of microwave pulse repetitions of low frequency (10 Hz to 1 kHz) in order to study the effects of the dielectric relaxation of macromolecular structural elements [5].

Apart from microwave curing, epoxies have been the subject of many other studies [6]. Particularly, the chemical mechanism of epoxy cross-linking with polyamines was investigated, with or without a tertiary amine as catalyst [7–10].

The present paper is concerned with the cross-linking of DGEBA with DDM, DDS and 4,4'-diaminodiphenylether (DDE). The main experimental

failure is the direct recording and the subsequent analysis of the variations of both the dielectric constants (the real permittivity ϵ' and the dissipation factor ϵ'') and temperature under microwave heating, during epoxy curing. From the data of the temperature dependence of ϵ'' , the initial step in the polymerization will be indicated and its interpretation discussed.

EXPERIMENTAL PROCEDURES

The technique used for both dielectric heating and measurement has been described in some detail with examples of applications [11]. In this method, the accurate measurement of the complex permittivity and the microwave curing of resins are performed in the same resonant cavity. The microwave power level to supply the cavity is the same for measurement and curing. Each experiment consists of sequences of measurements (0.05–0.10 sec) and heating/curing (1–4 sec) steps performed in turn according to the flow chart scheme shown in Fig. 1, e.g. 240 measurements for a standard 16 min experiment. During the measurements, the monitoring of a Voltage Controlled Xtal Oscillator (VCXO) allows a plot of the cavity resonance curve vs microwave frequency to be made when the cavity is loaded with a small volume of resin to be cured (or already cured). The dielectric constants ϵ' and ϵ'' are deduced from the cavity resonance frequency and the resonance transmission by means of the measurement of the perturbation due to a precise volume of a standard material, the dielectric constants of which are well documented at the experimental temperature. The following equations (1) and (2) give dielectric constants ϵ' and ϵ'' respectively as functions of the resonance frequency F_M and transmission τ_M :

$$\epsilon' = 1 + K_c \cdot \frac{V}{v} \cdot \frac{F_c - F_M}{F_c} \quad (1)$$

$$\epsilon'' = K'_c \cdot \frac{V}{2v} \cdot \left(\frac{1}{\sqrt{\tau_M}} - \frac{1}{\sqrt{\tau_c}} \right) \quad (2)$$

where v and V are the material and cavity volume respectively, with $v \ll V$; F_c and τ_c are the resonance frequency and the transmission of the empty cavity respectively; K_c and K'_c are constants depending on the cavity.

During curing, the microwave frequency is adjusted to the last measured value of the resonance frequency by means of

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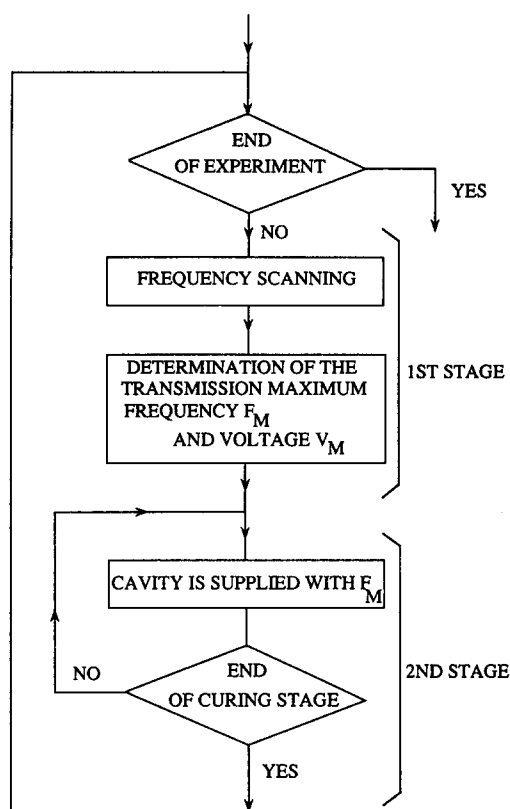


Fig. 1. Flow chart for each experiment consists in succession of measuring stages (1st stage, 0.05 sec) and curing stages (2nd stage, 1–4 sec). Curing is performed by supplying the resonant cavity with the frequency of the maximum transmission determined during frequency scanning.

the VCXO. Thus, the resin heating or curing is optimized. Moreover, the respective times of measurement and curing stages are determined to avoid any specific effect of pulsed microwaves, as already observed for the curing of polyurethanes [12] and epoxy resins [13]: the duration of the measurement stage must be short enough, compared to the curing period, to provide sufficient energy transfer and sample heating; a low frequency must be used in order to avoid any pulse effect [13].

A scheme of the experimental set-up has been given [11]. Oscillator monitoring, resonance curve and ϵ' and ϵ'' and T plotting in real time are performed by a microcomputer interfaced by two 12-bit converters, digital-to-analog (DAC) and analog-to-digital (ADC). The basic frequency of the voltage controlled oscillator is *ca* 50.680 MHz. After frequency multiplication and amplification, average frequency and power are brought to 2430 MHz and 6 W respectively, with elementary steps in frequency of *ca* 10 kHz. The resonant cavity is a TE_{013} monomode rectangular cavity of total volume *ca* 1000 cm³, and the perturbation volumes are *ca* 0.25–0.5 cm³. The analysed sample is always placed at the geometric centre of the cavity. Transmission is measured through a crystal detector. The cavity quality factor is *ca* 1800 when unperturbed by a sample.

During each experiment, the resin sample temperature was measured by means of a fluorimetric thermometer (Luxtron Fluoroptic 1000A) with a rare-earth based phosphor as sensor, set at the end of an optical fibre. Temperature T and both ϵ' and ϵ'' are recorded by the microcomputer at each measurement step.

For all the experiments, the standard used was 1-decanol, the dielectric constants of which at 25° ($\epsilon' = 2.67$ and

$\epsilon'' = 0.4135$) are close to those of epoxy resins. Moreover, as cavity perturbations depend on the sample shape, similar volumes of epoxies and of standard were used. The samples were put into PTFE cylindrical sample-holders (10 mm dia, 10 mm height and half-filled) supported by a quartz tube (2 mm dia) in which the thermometer optical fibre was inserted.

Diglycidyl ether of bisphenol-A (DGEBA) was purified by two successive chromatographic elutions on alumina in benzene solution, and checked for dimer or oligomer absence by chemical analysis and i.r. spectroscopy. The three curing agents, DDM, DDS and DDE (synthesis grade), were supplied by Schuchardt. Mixtures with DGEBA were prepared in various proportions in order to obtain convenient values of the relative molecular ratio R defined by:

$$R = \frac{n_H}{n_{DGEBA}} \quad (3)$$

$$\left(\frac{n_H}{n_{DGEBA}} \right)_{\text{Stoichiom}}$$

where n_H and n_{DGEBA} are number of moles of hardener and DGEBA respectively, the stoichiometry corresponding to $R = 1$. The mixtures were prepared by dissolution in DGEBA at 80° for DDM, and at 125° for DDS. For DDE, suspensions were obtained at 115°. Samples were stored at –18°.

RESULTS

The recordings of ϵ' , ϵ'' and T during DGEBA cross-linking were performed as a function of time for six selected values of the relative molecular ratio R from 0.4 to 1.4 (step 0.2), each of them on five different samples with weights ranging from 400 to 600 mg (step 50 mg). This process guaranteed both the reproducibility of the experiments and the validity over the whole range of perturbations of the linear perturbation laws [equations (1) and (2)].

The pure compounds (before mixing) were previously analyzed in order to determine the dependences of the dielectric constants on temperature [14]. DGEBA was heated to 190° (using additional i.r. heating beyond 140°), and ϵ' , ϵ'' and T variations were recorded as functions of time. DGEBA exhibits an ϵ'' maximum around 50° [14]. Additional i.r. heating was also necessary to initiate the heating of pure amino hardeners since their dissipation factor in the solid state ($\epsilon'' = 0.02$ at 25°) is very weak. Figure 2 represents the dielectric constant variations of the hardeners with temperature. A sharp ϵ'' increase is observed beyond 150° for DDS and at *ca* 100° for DDM, while no such variation is observed for DDE.

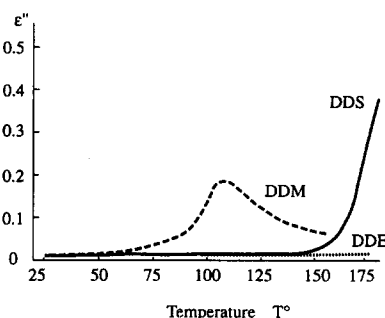


Fig. 2. Dissipation factor ϵ'' vs temperature for DDS, for DDM and for DDE.

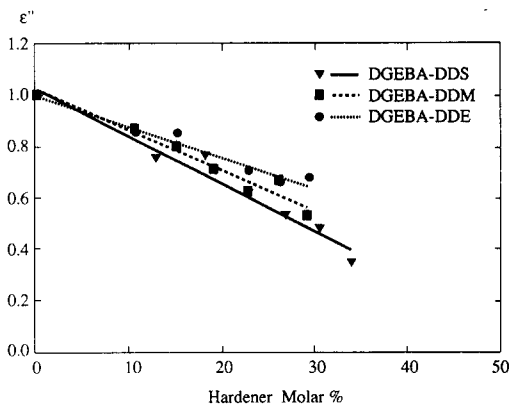


Fig. 3. Dielectric behaviour, as a function of the molecular ratio R , of epoxy-hardener mixtures, measured at room temperature, for the three hardeners.

The dielectric behaviour of epoxy-hardener mixtures, measured at room temperature, is presented as a function of R for the three mixtures (Fig. 3).

For a pre-cured resin no such maximum or increase is recorded. Figure 4 shows an example of curves obtained for three different ratios. Between 25° and 120° approx., the curves were obtained under natural cooling at the end of the polymerization cycle, after the maximum of temperature. For cured resins therefore, monotonous and weak variations of ϵ' and ϵ'' with temperature are always recorded whatever amino hardener is used.

Figures 5 and 6 show examples of typical polymerization behaviours of DGEBA with DDM and DDE respectively (similar curves were previously reported for a DGEBA-DDS system [11]). The initial temperature is 25°. Each of the ϵ' , ϵ'' and T vs time curves exhibits a maximum during the heating kinetics. The first one observed is the maximum of ϵ'' , then the maximum of ϵ' and the last is that of T . The maximum of ϵ'' was previously noticed with similar compounds from loss tangent [2] and absorbed power [3] measurements.

To characterize the change of ϵ' and ϵ'' with temperature directly, we eliminated the time parameter between the kinetic curves $\epsilon' = f(t)$, $\epsilon'' = f(t)$

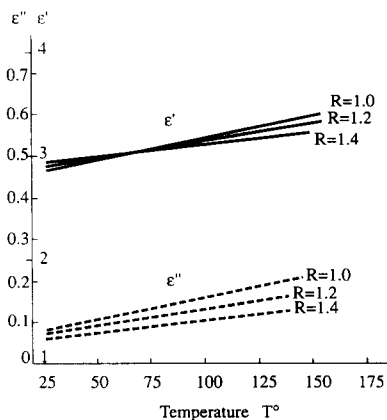


Fig. 4. ϵ' and ϵ'' vs temperature for a cured resin. The curves correspond to three molecular ratios of the curing agent DDS ($R = 1, 1.2$ and 1.4).

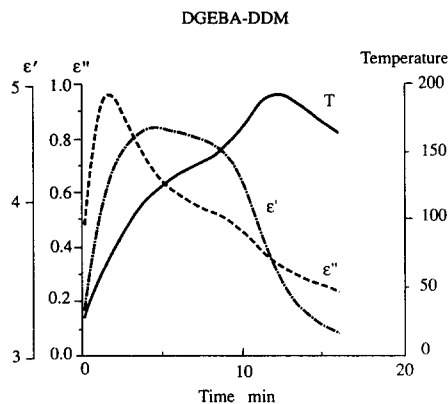


Fig. 5. An example of the curing kinetics of a DGEBA-DDM system ($R = 1$), shown by means of the permittivity ϵ' , dissipation factor ϵ'' and temperature variations with time. Each parameter has a maximum value. The first maximum is always the maximum of ϵ'' ; the second is the maximum of ϵ' ; the last is the maximum of temperature.

and $T = f(t)$. Figures 7–9 show the variations of ϵ'' with temperature for DGEBA-DDS, DGEBA-DDM and DGEBA-DDE systems, as functions of R .

DISCUSSION

In order to analyse the development of the chemical reaction, it is necessary to interpret both the heating kinetics [5, 13] and the ϵ' and ϵ'' variations with temperature from all the known contributions of the constituents which participate in or are produced by the reaction and of the crosslinked polymer formed.

From comparison between the temperature dependences of ϵ'' in pure DGEBA [14], and in DGEBA-DDM and DGEBA-DDE systems (Figs 8 and 9), it turns out that the dissipation factors of the last two systems behave additively in the range 25–100°. This statement is reinforced by the observation of similar curves for DGEBA-based industrial systems and also for the pure DGEBA-DDA system for which the maximum of ϵ'' ca 50° is noticeable (Fig. 10). In this respect, we first supposed the dielectric constant to be additive: ϵ'' is a linear function of the dissipation factor of each constituent respectively, weighted by its volume fraction. At any

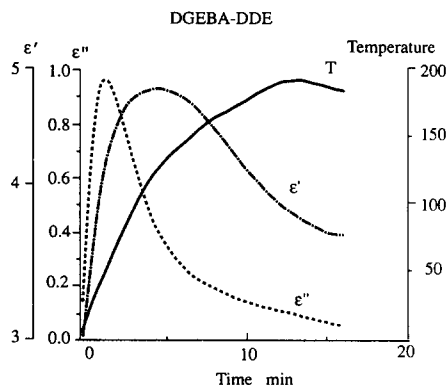


Fig. 6. As Fig. 5 for a DGEBA-DDE system ($R = 1$).

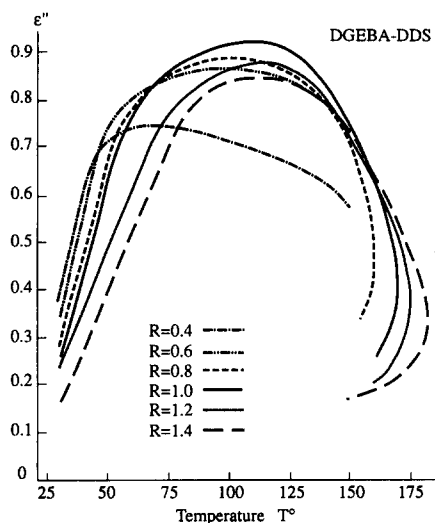


Fig. 7. Dissipation factor variations represented by ϵ'' vs temperature variations for DGEBA-DDS systems corresponding to six values of R . The value of T for the maximum increases with R and the value of the maximum of ϵ'' is maximum for $R = 1$.

temperature, the total sample dissipation factor ϵ'' depends on the dissipation factor ϵ''_i and the volume fractions Φ_i of each constituent according to:

$$\epsilon'' = \Phi_E \cdot \epsilon''_E + \Phi_A \cdot \epsilon''_A + \Phi_P \cdot \epsilon''_P. \quad (4)$$

E, A and P indexes refer to the epoxy resin, the curing agent and the growing polymer respectively.

A similar additive relation may be developed for ϵ' . The orders of magnitude of the contributions of resin and hardener respectively are however too close to allow the simplifications used below for ϵ'' .

In fact, each of the terms of equation (4) depends on temperature, and the equation should be verified at any T . However, from the observations of the differences in the dependence on temperature of DGEBA-DDS systems on the one hand (Fig. 7) and of DGEBA-DDM or DGEBA-DDE systems on the other hand (Figs 8 and 9), the relative importances of the three terms in equation (4) can be discussed, so

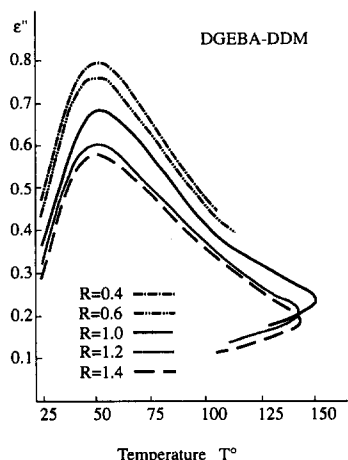


Fig. 8. As Fig. 7 for DGEBA-DDM systems.

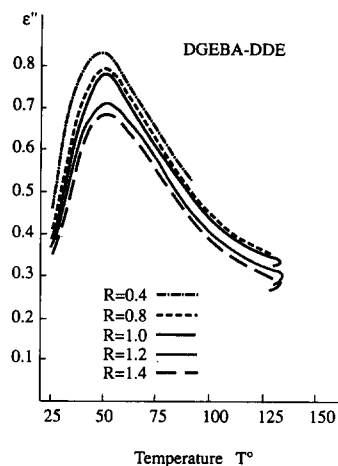


Fig. 9. As Fig. 7 for DGEBA-DDE systems.

that this equation can be simplified. When the microwave supply is stopped just before the onset of the second temperature jump corresponding to the exothermic effect of the chemical reaction (i.e. a short time before the maximum temperature), the ϵ'' vs temperature curves are followed back to the initial state. It has been previously observed for DGEBA-DDS systems, by means of FTIR measurements [13], that at 130° under microwave conditions only 4-7% of epoxy functions are converted into polymer, within a treatment duration equivalent to the present experimental conditions; this value of 4-7% can be considered as negligible, being within the measurement error range. Thus, there is no polymer formed when the values of dielectric constants reach their maxima as on Figs 5 and 6: i.e. the molar fraction Φ_P is negligible up to this point, and consequently the third term in equation (4) is also negligible.

From Fig. 2 it can be concluded that, in the same domain of temperature (up to 75° for DDM-based systems, up to 130° for DDS-based systems and at

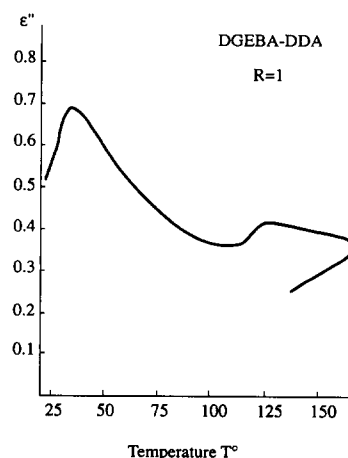


Fig. 10. Temperature dependence of the dissipation factor ϵ'' for a DGEBA-DDA system ($R = 1$). The separation between the contribution of DGEBA (up to 100°) and the chemical reaction (above 100°) is noticeable.

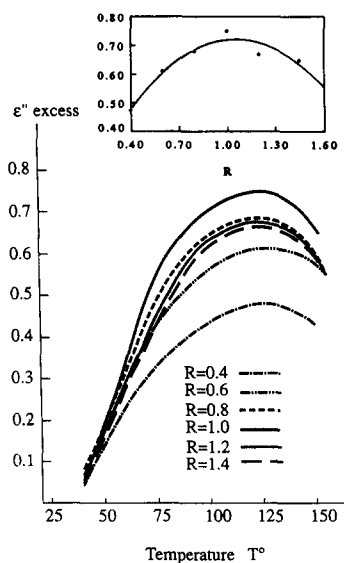


Fig. 11. $\epsilon''_{\text{excess}}$ vs. temperature for DGEBA-DDS systems taking into account the contribution of DGEBA. The value of $\epsilon''_{\text{excess}}$ is underestimated because the contributions of the curing agent and of the cross-linked resin are neglected. Insert: the maximum value on each curve as a function of R .

least up to 175° for DDE-based systems) the dissipation factor ϵ'' of the hardeners also is negligible. Considering that the volume factor Φ_A is also small it follows that the second term $\Phi_A \cdot \epsilon''_A$ in equation (4) is also negligible.

The reduced form of equation (4) $\epsilon'' \propto \Phi_E \epsilon''_E$ is verified for DGEBA-DDE systems, and approximately verified for DGEBA-DDM systems. On the other hand, it is not verified for DGEBA-DDS systems, for which a new function $\epsilon''_{\text{excess}}(T)$ has to be introduced:

$$\epsilon''_{\text{excess}}(T) = \epsilon''(T) - \epsilon''_E(T) \cdot \Phi_E(T) \quad (5)$$

which features the deviation (a new notation has been chosen to emphasize the temperature dependence of the parameters).

The temperature dependence of the new function is plotted on Fig. 11 for several DGEBA-DDS systems, with respect to the molecular ratio R , defined by equation (3), as a second parameter. Figure 12 shows the temperature dependence of the same function for

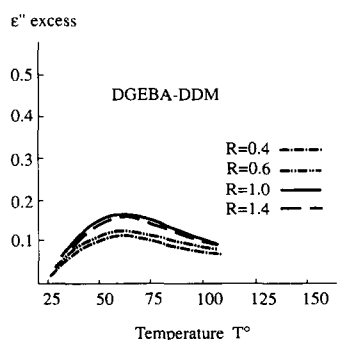


Fig. 12. As Fig. 11 for DGEBA-DDM systems.

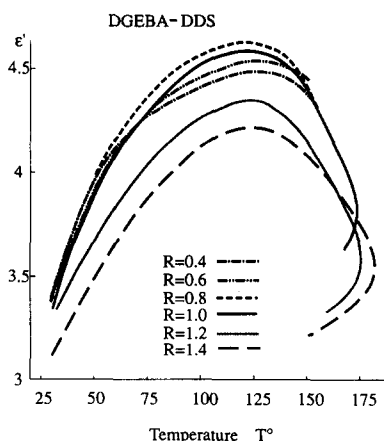


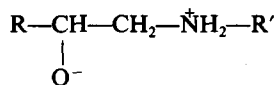
Fig. 13. Temperature dependence of the permittivity ϵ' of DGEBA-DDS systems, with several values of the molecular ratio R as a second parameter.

DGEBA-DDM systems: in this case the amplitude of the excess function appears to be noticeably smaller than for the DGEBA-DDS systems. For DGEBA-DDE systems, there is no difference between the variations of $\epsilon''(T)$ and the ϵ'' contribution of DGEBA, so that the importance of the $\epsilon''_{\text{excess}}$ function is negligible.

For the DGEBA-DDS systems, whatever the value of the molecular ratio R in Fig. 11, the excess function $\epsilon''_{\text{excess}}(T)$ shows a maximum at 125°. The deviation from simple additivity of the absorption factor may be interpreted as follows: either it shows the occurrence of a new specific interaction between DGEBA and hardener molecules created as the temperature increases, or it is the expression of a dielectric relaxation related to a polar entity inside the material (this point will be discussed in a later paper, concerned with the interpretation of broadband spectroscopy results). On the other hand, the decreasing parts of curves over 125° cannot be interpreted as a relaxation, because ϵ' also decreases at the same time, as shown in Fig. 13. It follows that the most probable explanation is the formation of a polar entity inside the material, resulting from the mixture of DGEBA and DDS. Moreover, on Fig. 11, the maximum for $\epsilon''_{\text{excess}}(T)$ is shown for the stoichiometric value of the molecular ratio ($R = 1$: see insert on Fig. 11). These facts suggest the existence of a molecular interaction between the epoxy resin DGEBA and the hardener DDS, as an intermediate step between the mixing of the two reactants and the cross-linking reaction itself. The formation of these particular species is reversible, for changing temperature back from 125° to room temperature restores the system to the initial state and viscosity. Increase of temperature over 125° also causes the disappearance of these species, which are then consumed by the cross-linking reaction, involving decrease of ϵ'' .

Because of the reversibility, we must note that the assumption of a highly polar intermediate association is obviously contrary to other explanations involving either the hydroxyl groups resulting from epoxy ring opening as previously supposed by Wilson and Salerno [2], or the "gel point" hypothesis as supposed

by Le Van [4]. Moreover, in the present via, the formation of a complex such as



is not considered as reversible (see for instance Ref. [7]) so that another explanation must be found for the intermediate entity.

On the other hand, reversibility is well established in epoxy chemistry for cross-linking under acidic conditions or with Lewis acids. An intermediate constituent (an oxonium ion) is described, the formation of which is clearly reversible [15]. Besides the reversibility character, the formation of this complex is fast and, consequently, the apparent kinetics of reaction depend on the slow step of the transformation of the complex. Therefore, the overall reaction appears as monomolecular.

The situation is opposite to the reaction of epoxies with Lewis bases such as tertiary amines as well as other amines. As far as kinetics are concerned, the cross-linking reaction then appears as bimolecular without a reversible early step. The well known use of a tertiary amine as a catalyst leads to a complex in which the unshared electron pair of the nitrogen atom is responsible for the bond with the less substituted carbon in the epoxy ring. In the present experiments, no catalyst is used and the preparations are free of hydroxyl groups, and they are anhydrous. So, the first explanation to be proposed is the formation of a polar intermediate complex as an early step in the reagent approach, by an SN_2 mechanism according to Ingold. The nitrogen atoms in a DDS amino group behaves like a Lewis base and its unshared electron pair brings the link with the less substituted carbon in an epoxy ring. Such a complex leads to an electron delocalization around the epoxy oxygen atom and thus the complex shows a strong polarity. To satisfy the observation of reversibility, we must restrict this explanation to a physically bonded state. Van der Waals' forces can be suggested to form a weak and reversible linkage, rigid enough to increase dipole moments.

Another explanation can be proposed following Smith's hypothesis of the formation of hydrogen bonds between the oxygen atom of the epoxy ring, as an hydrogen acceptor, and another atom as an hydrogen donor [7]. Moreover, Smith's complexes are reversible. To satisfy the stoichiometry of complexation, the only hydrogen donor atoms which may be proposed are the nitrogen atoms of amines. In a very different chemical situation, the abilities of amines are well established for protein and nucleic acid structures [16]. The hydrogen-bonded molecules can carry dipoles of increased sizes. Dipole moments and polarity increase also. On the other hand, hydrogen bonds are labile enough to justify the observed reversibility.

CONCLUSION

The existence of an intermediate polar entity resulting from weak DGEBA-amine molecular inter-

actions has been indicated. It justifies the use of microwaves for the curing of epoxies by aromatic amines such as 4,4'-diaminodiphenylsulphone because the energy transfer efficiency is increased. Nevertheless, we must consider the variations of this experimental polarity during the curing treatment to monitor conveniently the microwave supply to material. Indeed, too violent energy transfer during the early stage of the cross-linking reaction can accelerate the process by an excessive and useless increase of temperature. So, besides the general efficiency of microwave heating and curing, it is possible to improve performance by careful monitoring of microwave power supply. Furthermore, the use of pulsed microwaves will lead to similar results with a weaker average power supply associated with higher electric field peak values.

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