Microwave-assisted Crosslinking of some Epoxy Resins with 4-aminoazobenzene

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The curing reactions at microwaves for two different systems consisting of diglycidyl ether of bisphenol A (DGEBA) and 4-aminoazobenzene (AAB) and diglycidyl ether of ethylene glycol (DGEEG) and AAB were studied through differential scanning calorimetry (DSC) and FTIR spectroscopy.

Keywords : epoxy, azo, microwaves, FTIR, calorimetry

The use of epoxy resins for advanced materials with better properties has grown considerably in the last years. Epoxy resins are one of the most important classes of thermosetting polymers because of their versatility, good chemical adhesion, low shrinkage and excellent adhesion to most types of surfaces. They are used in many applications such as paints and coatings, casting and impregnation resins, matrices for composite materials, sealing agents.

Polymers with photoresponsive residues have been extensively investigated because of their application in optical switching [1], optical data storage [2,3] and optoelectronics [4]. For such applications the main structural type of compounds used for grafting on the polymer backbone was azo dyes. Because of the demanding to increase chromophore loading covalent attachment to the polymer as pendant group, co-monomer or cross-linking agent for reactive residues from the polymers have been investigated extensively [5-7]. It is also of interest the fact that the polymers with mesogenic aromatic structures in both the main chain and the side chain are capable of forming liquid crystalline phases and as a result in cured products somewhat better organization at the molecular level may be achieved [8-10].

In this context we reported the results obtained for the curing process under microwaves for two types of epoxy resins using as hardener AAB the simplest amino azo chromogen.

Experimental part

The epoxy resins used for the experiments were DGEBA (0.53 - equiv. epoxy/100g; M=377.36) supplied by Policolor and DGEEG (0.583 - equiv. epoxy/100g; M=343.05) made by us in the laboratory.

The hardener used for the curing reactions was 4-aminoazobenzene (AAB) (M=197.24; m.p.=127^{0}C; b.p.=366^{0}C; assay = min.99%) provided by Merck and used as received.

Curing reactions were conducted into a microwave oven EG 1031NP-DK-1 Hyundai (Power – 1000 W; Frequency – 2.45 GHz; Volume - 31 L, multimode cavity), the power of the microwaves being adjusted only by modifications of the irradiation time. The epoxy resin – amine mixtures were prepared at room temperature by adding the curing agent while continuously stirring and heating at a temperature value less than the curing temperature until a homogeneous solution was obtained.

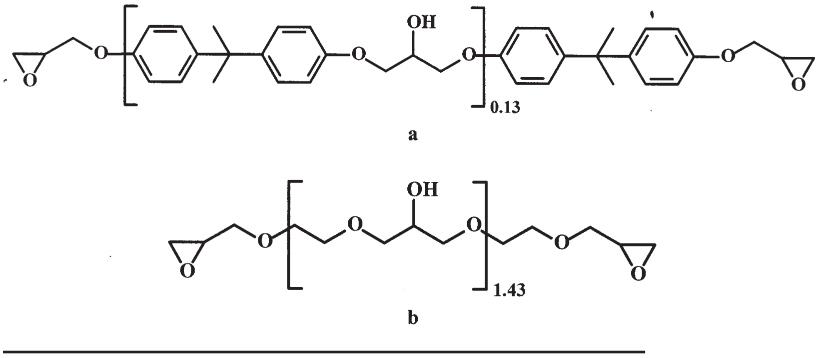
The curing grade obtained by irradiation of the reaction mixtures at microwaves was determined by calorimetric measurements using a Du Pont 2000 thermal analysis system. The calorimeter was calibrated using indium as standard. The heating rate was 10^{0}C/min., all the samples were about 5-10 mg in weight binary mixtures epoxy resin/hardener prepared before performing each experiment. The flowing gas was 99.99999% pure nitrogen from Linde. Samples were introduced in aluminium pans hermetically closed and then introduced in the calorimeter at room temperature.

FT-IR spectra were recorded on a JASCO FT-IR 6300 spectrometer using ATR Specac Golden Gate (sapphire/diamond) accessory.

Results and discussion

Curing epoxy resins under microwaves speed up the reticulation processes and became a widely used method because of its multiple advantages. Because we intended to obtain compounds with low molecular mass which contain epoxy residues after partial curing with amino azo dyes we investigated systems having a molar ratio hardener : epoxy resin = 1 : 2.

Differences between classic processes that consist of thermal curing and curing under microwaves are observed



Scheme 1. Epoxy resins used for experiments a) DGEBA; b) DGEEG

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analyzing DSC results comparatively with FT-IR spectroscopy.

As it is well known curing epoxy resins with amines is not a simple stepwise reaction, the reaction rate depending both on the amine basicity and constitution of the components in the resin-curing agent mixture. For the measurements multiple non-linear regression software using Borchardt - Daniels method allows to estimate the optimum values for reaction order, activation energy and pre-exponential factor as it was previously presented [11].

For estimation was it supposed no changes of the mechanism taking place within the examined temperature range and the kinetic model can be expressed as:

$$d\alpha / dt = k(T)\cdot[1-\alpha]^n = Ze^{-E/RT}\cdot[1-\alpha]^n$$

where:

α=conversion degree;

$k(T)$=specific constant at T temperature (1/ s);

n=reaction order

E = activation energy (J / mol);

Z = pre-exponential factor or Arrhenius frequency factor (1 / min);

R = universal gas constant (8.314 J / mol.K).

Usually for molar ratios that assure the total reticulation, the kinetic evaluation is complicated because with increasing reaction degree a partial vitrification of the reaction mixture occurs and after that the reaction is no longer controlled by the kinetics of the chemical reaction but only through diffusion processes. But for the reaction conditions imposed from the beginning that will assure a maximum conversion of 0.5 for the epoxy groups it is expected that the viscosity of reaction masses will be sufficiently low to allow the total kinetic control of the reaction and negligible diffusion processes.

The reaction heat determined from DSC measurements for both systems studied was evaluated using the first exothermal peak from the series of three peaks recorded in the temperature range 175^0-400^{0}C. For the first system (DGEBA-AAB) analyzed where the aromatic epoxy resin was involved, the reaction heat ΔH= 144.6 J/g was higher than that recorded for the system which contain the aliphatic epoxy resin (DGEEG) having a reaction heat ΔH= 109.7 J/g.

In order to obtain the activation energy for the curing processes the temperature values obtained for a conversion degree was investigated. From the slope of the straight line obtained and showed in figure 4, activation energies and pre-exponential factors of the cure processes can be calculated in the whole range of conversion.

The activation energy was determined to be 207.5 kJ/mole and the order of reaction was found to have a best-fit value of 2.71 for DGEBA-AAB system, while for DGEEG-AAB system the activation energy was 122.6 kJ/mole and reaction order 2.62. This information provides the parameters necessary for the description of the cure kinetics of the epoxy sample. Thus, product lifetimes and degrees of conversion at different temperatures can be predicted.

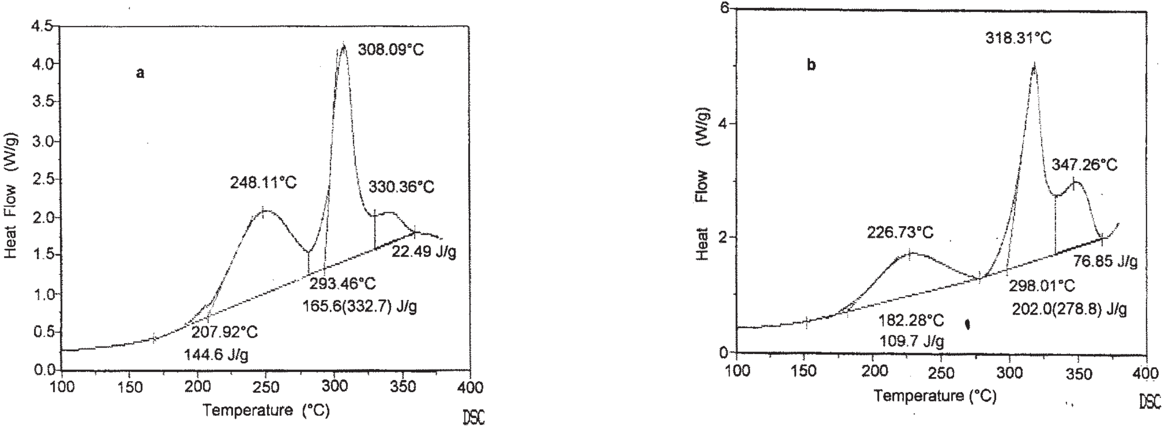

Fig. 1. The DSC curves for the systems : a) DGEBA-AAB; b) DGEEG-AAB

Table 1

CURING PARAMETERS FOR EPOXY - AMINE SYSTEMS

Reaction parameters	**DGEBA + AAB**	**DGEEG + AAB**
Reaction order – n	2.71	2.62
Activation energy – E (KJ/mole)	207.5	122.6
Pre-exponential factor – log Z (min^{-1})	21.01	12.68

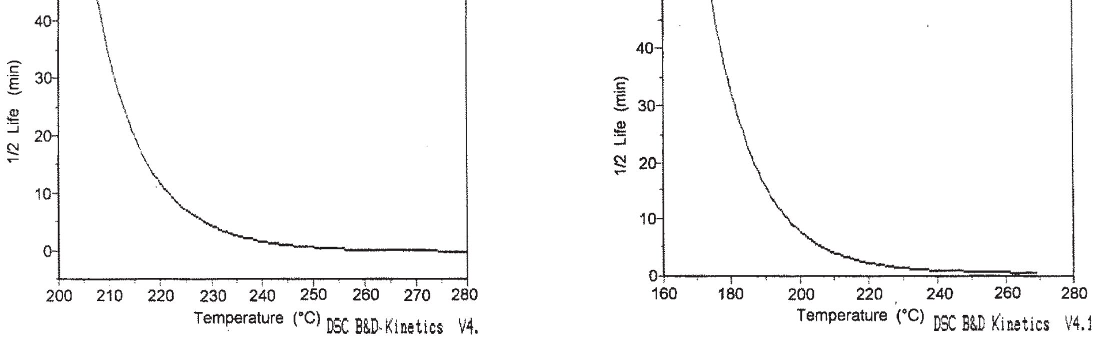

Fig. 2. Product lifetime for a) DGEBA-AAB; b) DGEEG-AAB

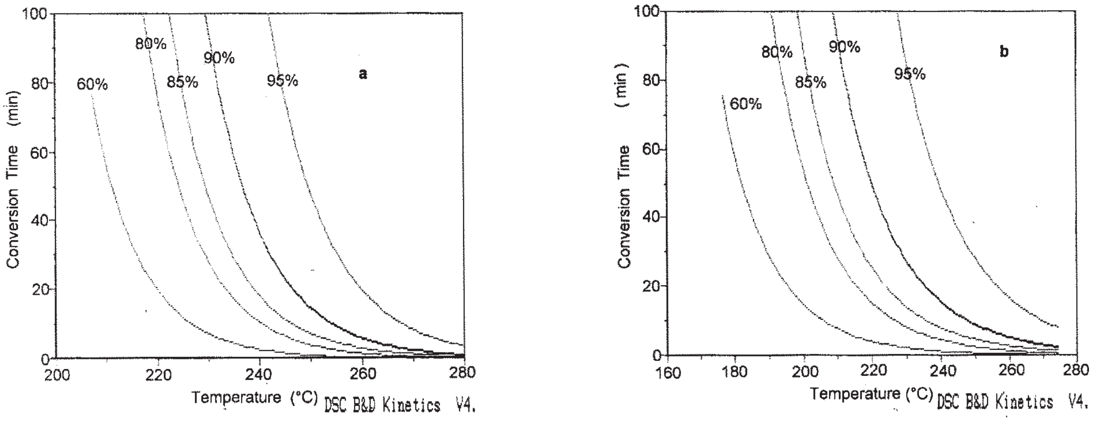

Fig. 3. Time for attaining conversion as function of temperature for a) DGEBA-AAB; b) DGEEG-AAB

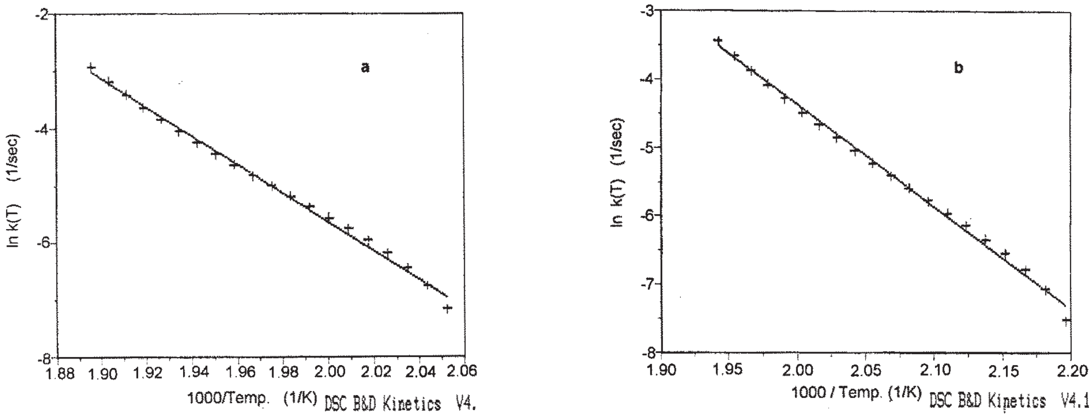

Fig. 4. Plots of log reaction rate versus inverse temperature for a) DGEBA-AAB; b) DGEEG-AAB

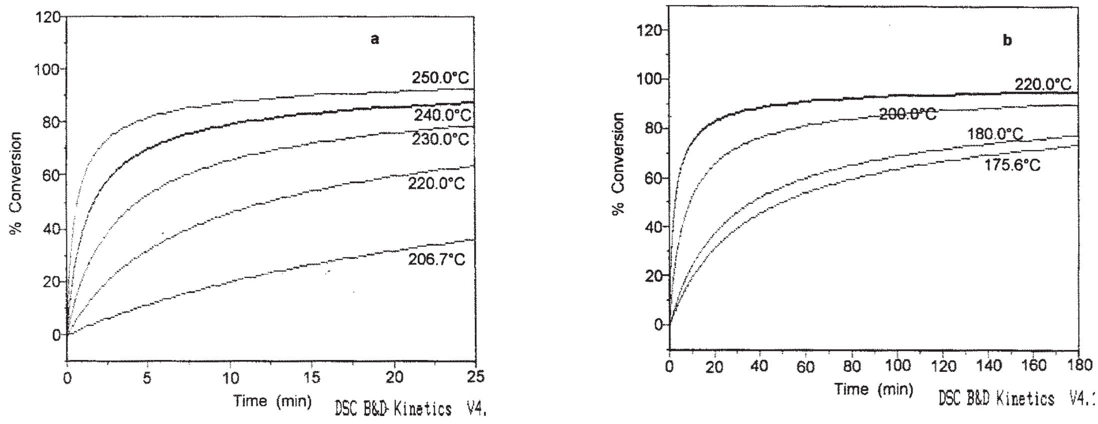

Fig. 5. The dependence of conversion versus time at different temperatures for a) DGEBA-AAB; b) DGEEG-AAB

Conversion-time curves under isothermal curing conditions were obtained by normalizing the integral heat flow curves with respect to the total enthalpy of reaction of fully reacted samples. For the investigated systems using calorimetric measurements in the case of DGEBA-AAB a higher value of conversion was obtained after 25 min at 250^{0}C and also for DGEEG-AAB system after 60 min at 220^{0}C. Otherwise at lower temperatures for the first case after 25 min at 240^{0}C only a 0.8 conversion was obtained and for the second one the same value for conversion was obtained at 200^{0}C after 70 min.

Fourier transform infrared spectroscopy was used to follow the kinetic of curing of epoxy resins under microwaves because it is possible to detect the variation of functional group if spectra were analyzed at consecutive periods of time. This is due to the fact that, if the degree of conversion increases the intensity / area of the absorption bands of terminal groups decreases. For quantitative analysis a reference band is used. The FT-IR measurements were performed at room temperature immediately after curing and no polymerization was assumed to occur during the measurements, given the very slow reaction rates at room temperature.

FT-IR spectra show structural characteristics of the reaction partners and both systems analysed besides bands used for the conversion evaluation of the epoxy groups and some important and visible changes, that confirm the advancing of the reaction. Thus the peaks at 3370 cm^{-1} and 3469 cm^{-1} characteristic for amino group from the hardner (AAB) disappeared during the process and at the end of the reaction a new large band at 3388 cm^{-1} correponding to hydroxy groups formed during the curing. As characteristic bands which make difference between systems investigated are to be mentioned more intense ν_{CH2} bands for the system DGEEG-AAB at 2868 cm^{-1} and 2910 cm^{-1}.

For the first system studied we use the absorption band at 915 cm^{-1} of the terminal epoxy groups which decreases during the curing reaction while for the second system the absorption band for the epoxy group is situated at 908 cm^{-1}. The reference peak area used as an internal standard for the normalization of epoxy peak area was situated at 829 cm^{-1} for both systems investigated.

The conversion of the curing process was estimated with the formula:

$$\eta = \left[1 - \frac{\left(A_{epoxy}/A_{ref}\right)_t}{\left(A_{epoxy}/A_{ref}\right)_0}\right]\cdot 100$$

in which :

η - conversion %;

$(A_{epoxy} / A_{ref})_t$ - the ratio between the absorption area peak of the terminal epoxy group and the reference peak area at the time t;

$(A_{epoxy} / A_{ref})_0$ - the ratio between the absorption area peak of the terminal epoxy group and the reference peak area at the initial moment.

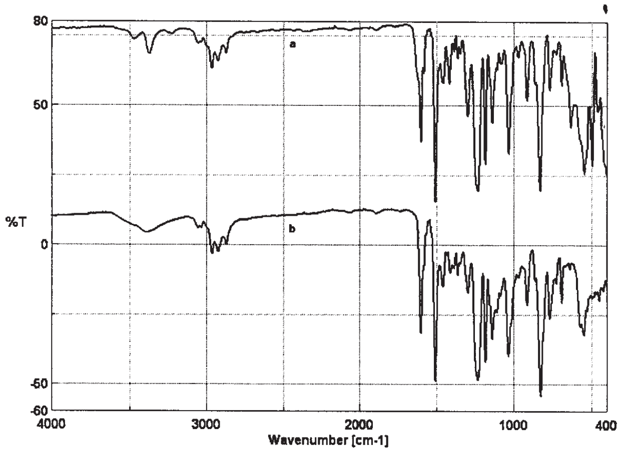

Fig. 6. FT-IR spectrum for DGEBA-AAB a) before and b) after the irradiation at microwaves

The degree of conversion during the development of the reactions under microwaves for both systems analyzed can be calculated. The FT-IR method showed is a more precise indicator of extent of cure than DSC, as it directly measures the chemistry taking place, rather than the heat evolved.

The initial slope of the curves is steeper for higher temperatures. Next to that, the slope gets very small after a certain amount of time, which can be assigned to a diffusion-controlled reaction mainly for the first system investigated because of the higher viscosity attained during reaction. The degree of conversion shows auto acceleration in the initial stages indicated by a slight positive curvature, more pronounced for the system DGEEG-AAB.

Conversion grows rapidly in the first minutes of curing reaching 0.45 for the first system and almost 0.5 for the second system. After that we can consider that reaction stops because the conversion remains constant and independent of time. The experimental results recorded for the system DGEBA-AAB suggested that viscosity at the end of the reaction grows more rapidly than that for the second system and reaction will be controlled by a diffusion mechanism after the conversion reaches 0.5.

For the system DGEEG-AAB the curing process proceeds at a high rate even from the initial moment of the reaction and at a 30% from the nominal power of the oven the maximum conversion of 0.5 was attained after 45 min. This is due to the higher mobility of aliphatic epoxy resin molecules (DGEEG) comparatively with the aromatic epoxy resin (DGEBA).

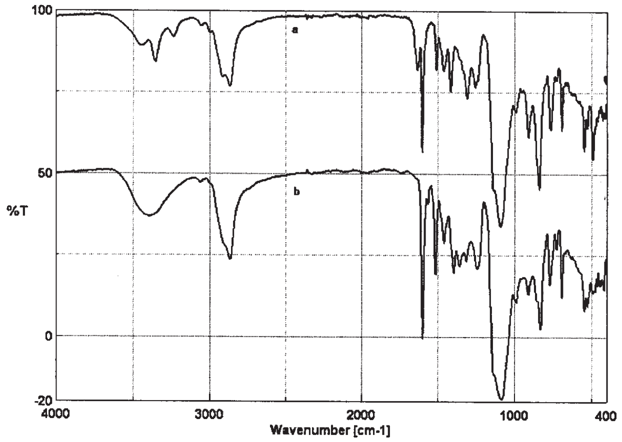

Fig. 7. FT-IR spectrum for DGEEG-AAB a) before and b) after the irradiation under microwaves

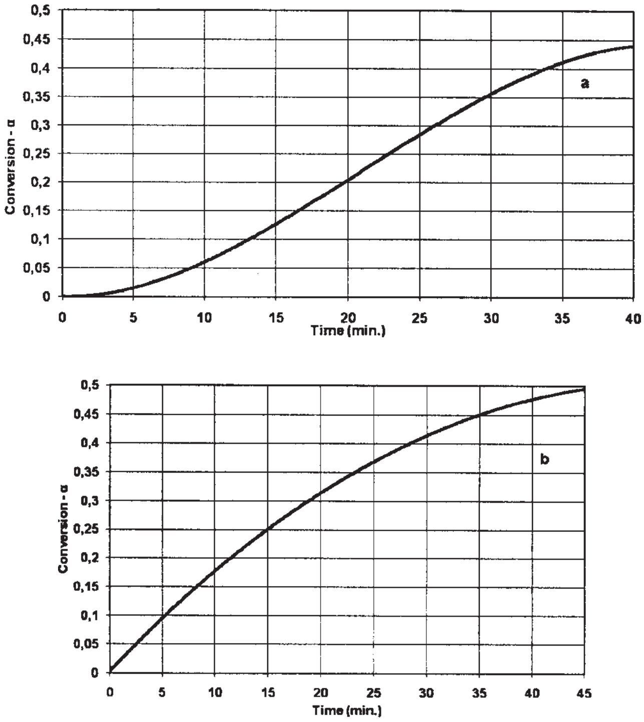

Fig. 8. Conversion under microwaves determined for a) DGEBA-AAB; b) DGEEG-AAB

In the same conditions, at microwaves, for the system DGEBA-AAB, the conversion versus time curve exhibits an S shape. The curing process begins after ten minutes probably due to the slow motion of the epoxy molecules (DGEBA) in order to attain a suitable position to attack the amine hardener which is also a bulky molecule. The activation energy evaluated from DSC measurements is supporting of this hypothesis. Thus, for the system DGEBA-AAB an activation energy E=207.5 KJ/mole was recorded, while for the system DGEEG-AAB this value is appreciably lower E=122.6 KJ/mole.

Moreover the electron donating ability of NH group is further enhanced in the intermediates obtained after the first addition of AAB to aliphatic epoxy residue from DGEEG comparatively with intermediates obtained after the first addition of AAB to aromatic epoxy residue from DGEBA. This is another reason for growing up the reaction rate for

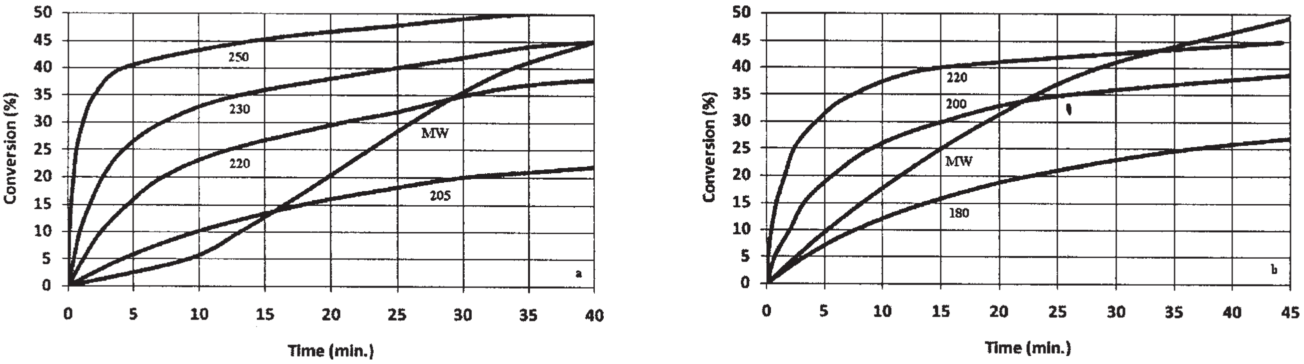

Fig. 9. Comparative conversions profiles for thermal curing under microwaves for a) DGEBA-AAB; b) DGEEG-AAB

DGEEG –AAB system comparatively with DGEBA-AAB system.

However due to the too bulky aromatic rings the DGEBA mobility is lower than for DGEEG, which may explain the lower rate for the curing process of DGEBA at the beginning of reaction and a lower conversion obtained in the same conditions than for DGEEG. The maximum conversion obtained after 40 min was 0.45 for the first system while for the second after 45 min. the conversion obtained is almost theoretical (0.5).

If we analyze the results obtained from calorimetric measurements and FT-IR measurements after curing under microwaves it can be assumed that the curing process under microwaves goes on much faster than for a conventional thermal process.

A major difference between process conducted under microwaves and by conventional thermal curing was that probably because of the formation of hydroxyl groups during the curing process, under microwaves they will absorb more energy that will lead to the maintaining the reaction rate of the reaction during the process almost to the end of it while in the case of conventional thermal reactions for the corresponding curve, conversion grows more slowly at values higher than 0.3.

From the comparison of conversion profiles for the systems studied and having in mind the kinetic equations that govern the processes being the same for thermally activated curing and hardening under microwaves, it can be concluded that under microwaves conversion versus time curves suggest a large temperature variation during the curing reactions. Thus for DGEBA-AAB system temperature profile can vary from 180°C at the beginning of the reaction to 230°C at the end of it while for DGEEG-AAB system the profile is more steeper at the beginning of the process.

Conclusions

The curing process occurs with a higher reaction rate under microwaves than for thermal classical process for both systems studied, due to the formation of hydroxyl groups during the curing that will absorb more energy leading to an accelerating reaction.

Differences observed in the behaviour of the epoxy resin systems studied may be explained on the basis of the epoxy resins structures, respectively electron donating ability of the secondary amine intermediates formed during the process.

The curing process of DGEEG with AAB under microwaves is a valuable alternative choice to the thermal classical processes having a great advantage in relationship with low curing times and high degree of conversion comparatively with classical processes thermally activated.

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