Curing Kinetic of an Epoxy-amine System by Calorimetric Method and FT-IR Spectroscopy

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The study presents experimental data regarding the curing reactions of some epoxy systems consisting of diglycidyl ethers of bisphenol A and different amine hardeners at room temperature and at microwaves. The curing reaction of the system composed of an epoxy resin (ROPOXID P 401) and 4,4'-diamino-diphenylmethane (HT 972) was studied by differential scanning calorimetry (DSC) and FT-IR spectroscopy. The degree of conversion obtained using FT-IR method is very close to that obtained using calorimetric method.

Keywords: epoxy, amine, microwaves, kinetic

Epoxy resins are very important due to their multiple applications as adhesives, coatings, encapsulates, casting materials, and binders and as matrix material for high performance composites [1-9]. Epoxies offer high strength, low shrinkage, excellent adhesion to various substrates, effective electrical insulation, chemical and solvent resistance.

An important aspect of thermosetting resin such as an epoxy is the cure kinetics associated with the material in order to optimize the processing conditions to generate specific physical and mechanical properties [10-16].

Epoxy resins react with a large number of hardeners such as aliphatic and aromatic amines, anhydrides, substituted ureas, thiols, dicyandiamide, but the most commonly used chemical classes of curatives are amines [17,18].

The aim of this work was to study the results obtained for the curing process of an epoxy resin based on diglycidyl ether of bisphenol-A (ROPOXID P 401) with 4,4'-diaminodiphenylmethane (HT 972) under microwaves. The curing kinetic of the so-called "hot system" was investigated using differential scanning calorimetry and FT-IR spectroscopy.

Experimental part

Epoxy resins used for the experiments: ROPOXID 500 (dynamic viscosity 14580 mPa.s (25^{0}C); 0.523 - equiv. Epoxy/100g; M=382) and ROPOXID P 401 (dynamic viscosity 1725 mPa.s (25^{0}C); 0.41 - equiv. Epoxy/100g; M=488) were supplied by Policolor and used as received.

Hardeners used for the curing reactions : triethylenetetramine (TETA) (M=146; m.p.=12°C; b.p.=266-267°C; amine index=1410-1460 mg KOH/g), aliphatic amine adduct with propenoxide (T) (amine equivalent – 1.85 %; dynamic viscosity 392.8 mPa.s (25^{0}C) and 4,4'-diaminodiphenylmethane (HT 972) (M=198; m.p.= 89-91°C ; b.p.=221°C) were provided by Fluka 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 on 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 standard for temperature calibration. The heating rate was 10^{0}C/min., all the samples were about 5-10 mg in weight of binary mixtures epoxy resin/ hardener prepared before performing each experiment. The flowing gas was 99.99999% pure nitrogen from Linde. Samples were introduced in aluminum pans hermetically closed and then introduced in the calorimeter at room temperature.

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

Results and discussions

The cure reaction of epoxy resins is a complex process that involves the formation of a rigid three-dimensional network. For studying the curing conditions at microwaves four different epoxy systems were selected as "cold systems" for comparison with the investigated "hot system" as it can be seen in table 1.

As it is well known curing at microwaves accelerates up the crosslinking process. After 30-40 min from the introducing in the oven, probes were completely crosslinked. Differences between classic processes and curing at microwaves are observed analyzing DSC results. Reaction heat determined after curing at microwaves showed a total reticulation comparatively with the same probe at room temperature in the same period of time when a very small grade of reticulation is recorded.

In order to evaluate the optimum resin / hardener ratio necessary for isothermal study, a dynamic study was carried out. The end of the curing reaction was indicated by the absence of any thermal effects. Comparative determinations were done for the same epoxy systems at room temperature and after crosslinking at microwaves. Comparing these two sets of evaluations it clearly results the advantage of curing at microwave which is the total

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Table 1
CURING PARAMETERS AT MICROWAVES FOR EPOXY - AMINE SYSTEMS

Curing steps at microwaves	Cold systems				Hot system
	ROPOXID 500 +TETA (1)	ROPOXID 500 + T (2)	ROPOXID P 401 + TETA (3)	ROPOXID P 401 + T (4)	ROPOXID P 401 + HT 972 (5)
	Time (min.) / Power (%)				
1	10 / 10	10 / 10	20 / 10	10 / 10	5 / 50
2	10 / 10	10 / 10	10 / 10	10 / 10	5 / 50
3	5 / 30	10 / 10	10 / 10	10 / 10	5 / 50
4	5 / 10	10 / 10	5 / 30	10 / 10	5 / 50
5	---	---	---	---	5 / 50
6 (after curing treatment)	5 / 50	5 / 30 5 / 30	5 / 50	5 / 50	5 / 50 5 / 50

Table 2
REACTION HEAT FOR EPOXY – AMINE SYSTEMS (1-4)

epoxy – amine system	Reaction heat (J/g)		
	initial	after 120 min. at room temperature	after curing at microwaves 50 min
1	434.4	175	7.075
2	402.2	233.2	0
3	385.2	235.8	1.481
4	355.8	244.4	0

reaction time of minutes compared with the time of hours required for the classical curing process. It is to be mentioned that for reactive systems cured at microwaves the reaction rate is very high and that is the reason for what a reaction kinetic cannot be done. For this kind of systems, the reaction rate at normal temperature is low and allows the obtaining of kinetic data regarding curing reaction at microwaves. Results were similar to those obtained from calorimetric measurements.

Differential scanning calorimetry was one of the methods used for studying kinetic of the epoxy curing reactions. The measured reaction heat is linked to the number of functional groups involved in the curing process.

Curing reaction for epoxy resins is a complex process with many reactions that take place simultaneously and are interconnected. Curing with amines is not a simple stepwise reaction, reaction rate depending both on the amine basicity and the constitution of the components in the resin-curing agent mixture.

For the measurements was used a calorimeter DSC DuPont 2100, with a software that calculate data using Borchardt - Daniels method. For isothermal cure reaction, the kinetic model can be expressed as:

$$d\alpha / dt = k(T) \cdot [1-\alpha]^n \qquad (1)$$

where:

α =conversion degree;

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

n=reaction order

If ΔH_T is the partial reaction enthalpy at T temperature and ΔH_0 is total reaction enthalpy, equation becomes:

$$\frac{dH}{dt} \cdot \frac{1}{\Delta H_0} = k(T) \cdot \left[1 - \frac{\Delta H_T}{\Delta H_0}\right]^n \qquad (2)$$

where dH/dt is the reaction heat.

The temperature dependent function or rate constant is:

$$k(T) = Ze^{-E/RT} \qquad (3)$$

where:

E = activation energy (J / mol);

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

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

Thus, equation (2) becomes:

$$\frac{dH}{dt} \cdot \frac{1}{\Delta H_0 \left[1 - \frac{\Delta H_T}{\Delta H_0}\right]^n} = Ze^{-E/RT} \qquad (4)$$

in addition, after logarithmation equation became:

$$\ln\left[\frac{dH}{dt} \cdot \frac{1}{\Delta H_0}\right] = \ln(Z) - \frac{E}{RT} + n \cdot \ln\left[1 - \frac{\Delta H_T}{\Delta H_0}\right] \qquad (5)$$

This equation can be solved by linear regression method with general formula:

$$z = a + b \cdot x + c \cdot y \qquad (6)$$

By multiple regression approximations, the following parameters were calculated: activation energy, reaction order, pre-exponential factor, conversion degree, specific constant as a function of temperature, half-life time function of temperature.

The activation energy was determined to be 58.4 kJ/ mole and the order of reaction exhibits the best-fit value of 0.62. This information provides the parameters necessary

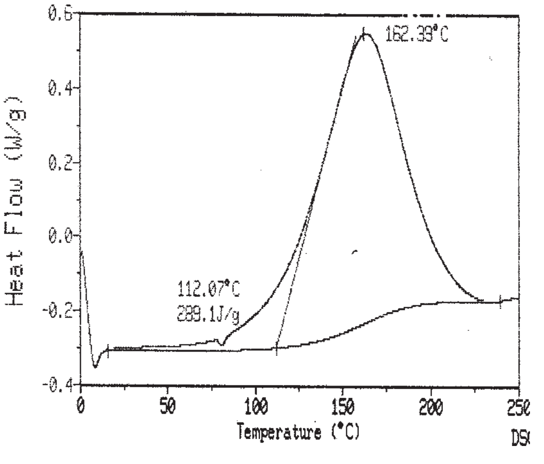

Fig. 1. Reaction heat for epoxy – amine system 5

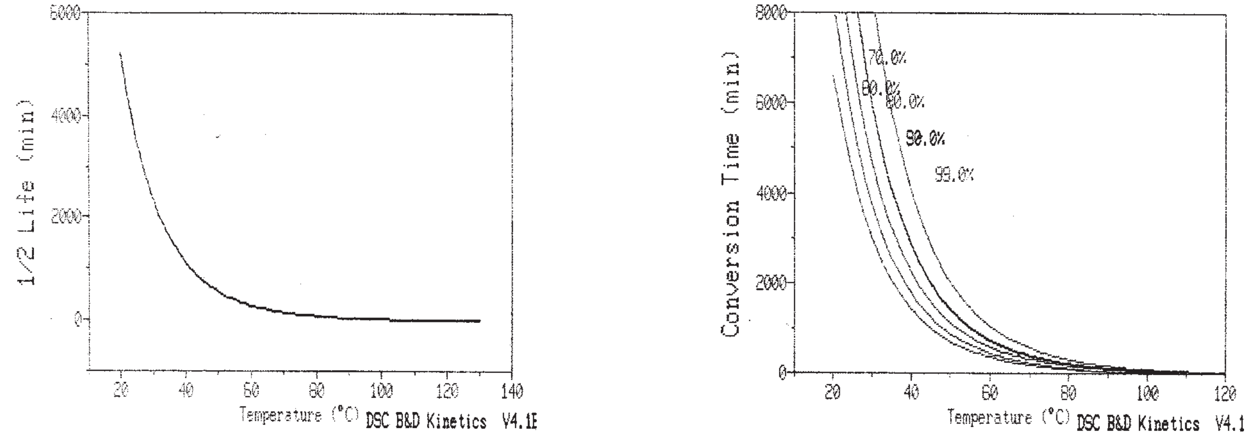

Fig 2. Product lifetime and time for attaining conversion as function of temperature

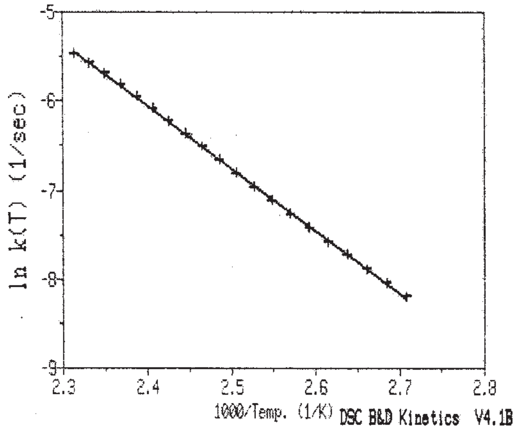

Fig. 3 Log reaction rate versus inverse temperature kinetics plot

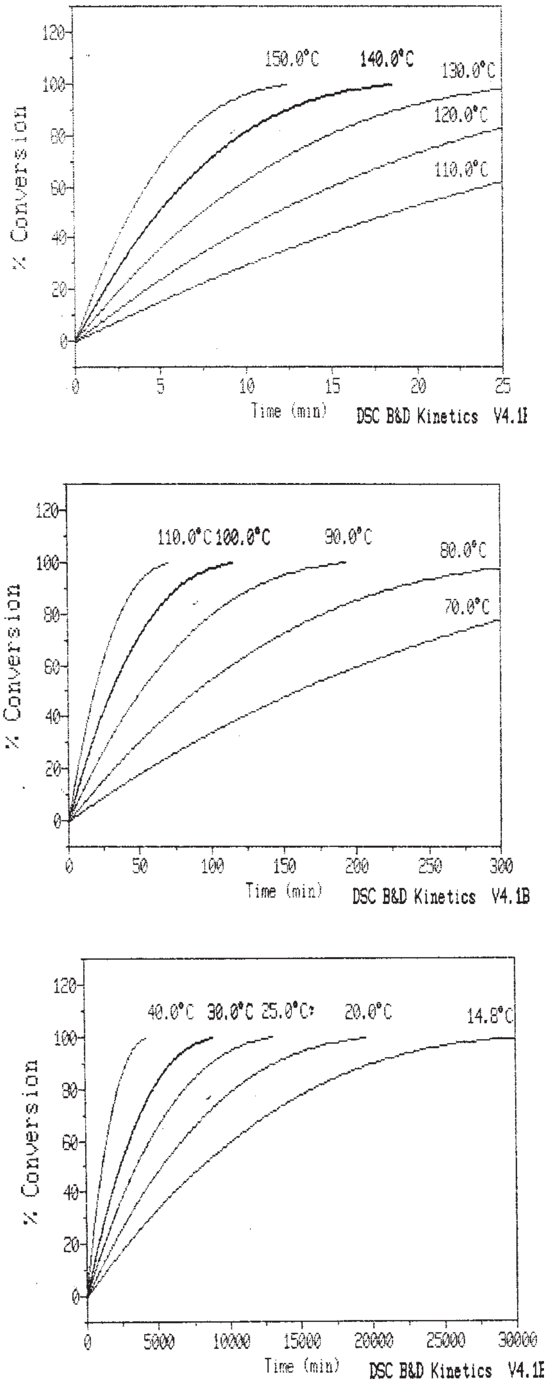

Fig. 4 Conversion versus time at different temperatures

for the description of the cure kinetics of the epoxy sample. Thus, product lifetimes and degrees of conversion at different temperatures can be predicted.

The isothermal conversion curves show that it takes increasingly longer times for the epoxy resin to full curing as the temperature is decreased. At temperatures below 100^0C the resin achieves complete cure after 75 min.

The isothermal kinetic analysis shows that it grows rapidly in the first minutes of curing reaching a maximum and then the reaction is stopped because the limitation of diffusion due to the molecular weight the increase and increase in the density of crosslinking from the chemical structure all these leading to a restriction of chains mobility.

Isothermal DSC experiments at different temperatures were performed to analyze the cure kinetics of the epoxy resin system 5. The series of isothermal DSC data measured experimentally within a temperature range of 15-150^0C with a 10^0C increment are shown in Figure 4. 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, the time for complete curing at normal temperature (25^0C) was very long, approximately 170 h.

The FT-IR measurements were performed at room temperature immediately after the oven cure and no polymerization was assumed to occur during the measurements, given the very slow reaction rates at room temperature.

For the infrared analysis the reference band at 915 cm^{-1} due to the epoxy group is used. The reference peak area used as an internal standard for the normalization of epoxy peak area was aromatic at 829 cm^{-1}.

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

$$\eta = \left[1 - \frac{\left(A_{915}/A_{829}\right)_t}{\left(A_{915}/A_{829}\right)_0}\right] \cdot 100$$

in which : η - conversion %, $\left(A_{915}/A_{829}\right)_t$ - the ratio between the absorption area peaks at 915 cm^{-1} and 829 cm^{-1} at the time t, $\left(A_{915}/A_{829}\right)_0$ the ratio between the absorption area peaks at 915 cm^{-1} and 829 cm^{-1} at the initial moment.

The degree of conversion at different isothermal temperatures can be thus calculated. The FT-IR method shown it 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 and then, the slope gets very small after a certain amount of time, which can be assigned to a diffusion-controlled reaction. At all temperatures, the degree of conversion shows auto acceleration in the initial stages indicated by a slight positive curvature.

The conversion grows rapidly in the first minutes of curing reaching maximum conversion and from this value, we can consider that the reaction stops because it remains constant and independent of time. This behaviour is due to the molecular weight increase, the chains beginning to branch out and thus mobility is very slow.

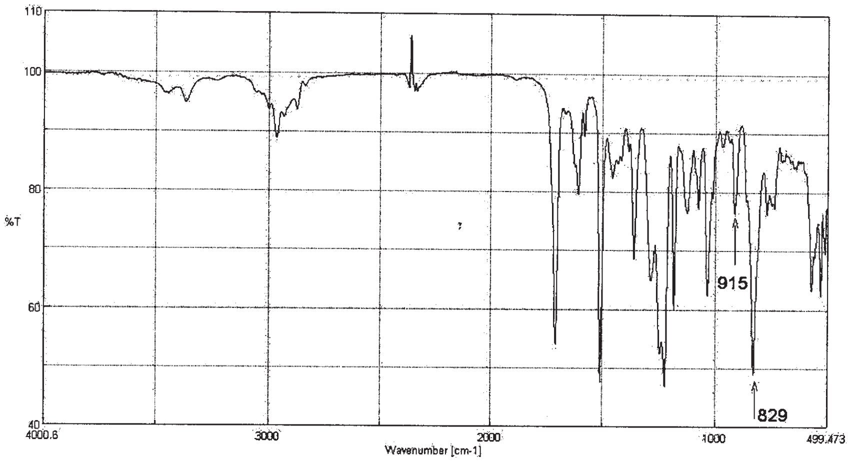

Fig. 5 FT-IR spectrum of the uncured resin system

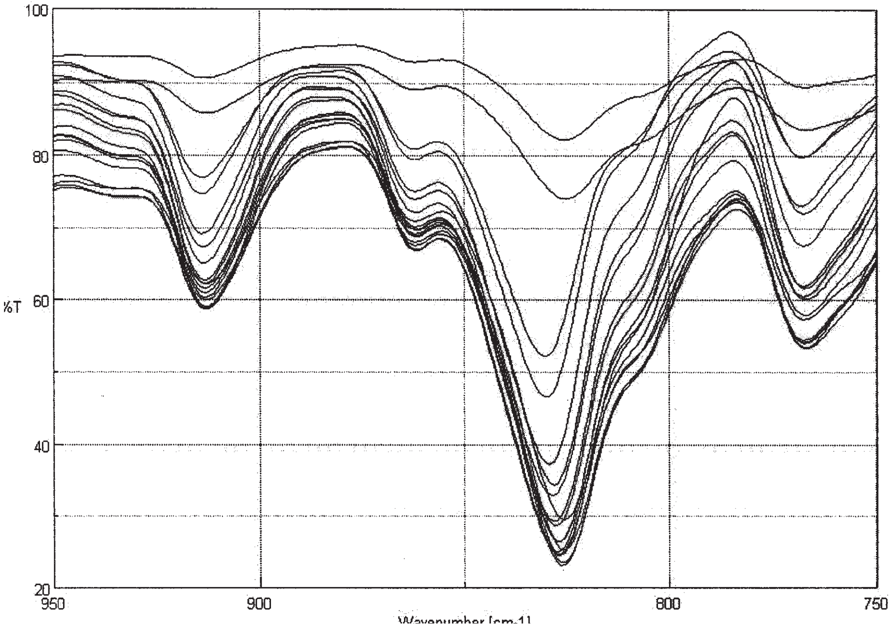

Fig. 6 FT-IR reference bands of the resin system for different cure times at microwaves

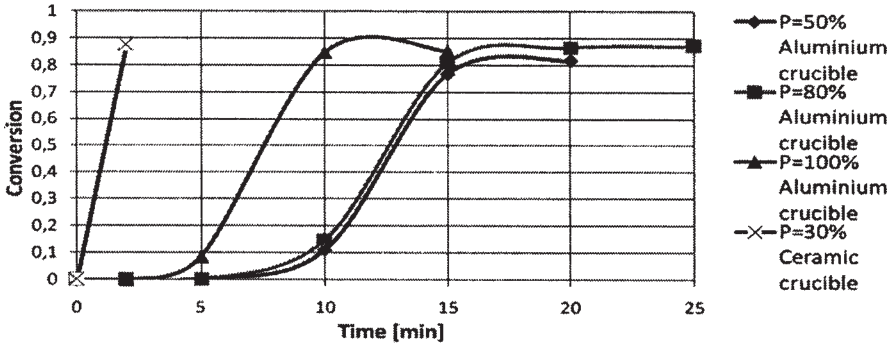

Fig. 7 Conversion at microwaves determined by FT-IR at different power values

The changes that correspond to full conversion of the epoxy groups are observed at temperatures higher than 130^{0}C for this resin formulation. The study found some differences in the evolution of the curing reaction due to variations in heating patterns and depending on the type of crucible used (ceramic or aluminium). It was found that aluminium crucible gives better results due to the heating uniformity attained, the S form of the conversion curve being a strong proof on this direction. If it was used, a ceramic crucible the time of the curing reaction is very short but the reaction is very hard to conduct, so the final product is affected by decomposition because of the temperature attained during the synthesis at microwaves.

At all temperatures, it was found the agreement between experimental and DSC model results mainly for low temperatures, because at high conversion the reaction is controlled by a diffusion mechanism. For this reason as can be seen, the values obtained for FT-IR method are very close to the DSC data at low temperatures and low degree of conversion. Although the DSC conversion determined directly from the total released enthalpy does not take into account, the possible differences of enthalpy for the reaction of primary and secondary amines the superpositions of FT-IR, and DSC conversion-time curves were verified.

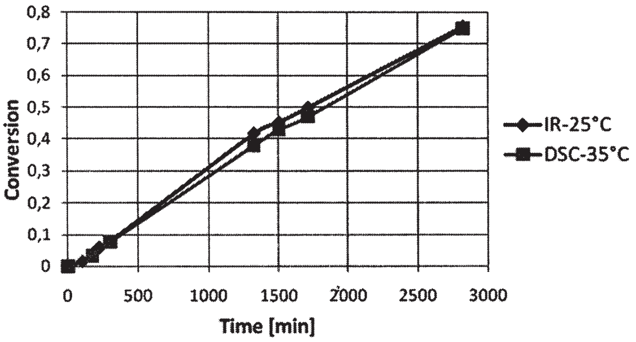

Fig. 8 Conversion determined by FT-IR and DSC at normal temperatures

Conclusions

The kinetics analysis provides valuable information on the cure characteristics of the thermosetting resin. This kinetics model provides a tool for quantifying formulation parameters, predicting process rates and estimating product lifetimes.

As predicted theoretically the epoxy resin concentrations decreased slowly during curing. The changes that correspond to full conversion of the epoxy groups occur at temperatures higher than 130^{0}C for this resin formulation. The same trend in the evolution of the curing process at microwaves corresponds to the setting of the microwave oven at 50% of the nominal power (1000W) using an aluminium crucible.

The results indicate that when the sample was cured at low temperatures (below 100^{0}C) the epoxy did not reach 100% conversion at prolonged curing times because of the diffusion controlled reaction phase and because of the limited hardener solubility.

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