On-line Monitoring of Epoxy Resin Cure using Infrared Spectroscopy

F.Fouchal, J.A.G.Knight, P.Dickens, N.Garrington

Rapid Manufacturing Group, Faculty of Technology and Computing Science
De Montfort University, Leicester, LE1 9BH, UK

Abstract

The method described can be used to observe the cure in epoxy resins, it is a sensor to serve as an on line monitoring system of physical change of the resins during the curing time and the future behaviour of the part built. It is also proposed that the method can be applied in Stereolithography (SL). In this paper the method permits a rapid determination of the state of chemical reaction happening in an epoxy resin diglycidyl ether of bisphenol A (DGEBA) with a curing agent triethylenetetramine stoichiometric mixture. It uses a mid infrared Fourier transform (FT-IR) technique to analyse the mixture via an embedded fibre optic and an FT-IR spectrometer operating in the region of 4000-700 cm^{-1}. An accurate concentration versus time of epoxy amine and the hydroxyl groups gave a good estimate of the extent of reaction. The chemical group peaks at 1132cm^{-1} and 3300-3400cm^{-1} where used to follow the disappearance of the epoxy, and the amine respectively, while the peak at 2970cm^{-1} was used as reference peak. A review of a number of techniques used in the study of the curing process of epoxy resins and a number of methods used in an on-line monitoring of thermoset resin cure process is referred to

Keywords: Streolithography, epoxy/amine cure, FT-IR spectroscopy, extent of reaction, fiber optic sensor.

1-Introduction

Epoxy resins have been widely used for adhesives, protective coatings and matrices of many materials used in advanced technologies, they are also used to build rapid prototyping parts via the streolithography process. The other major use is for fiber-reinforced composites made from high strength and high modulus fibers, embedded in a matrix. The curing process of polymers such as epoxy resins entails the conversion of liquid monomers, or prepolymers, which can contain reactive epoxy groups, into three-dimensional polymer networks. The mechanism and kinetics of the curing process determine the polymer network morphology, which in turn determines the physical and mechanical properties of the cured product. For these reasons, a fundamental understanding of the curing process is the first target to optimize the processing of fiber reinforced epoxy composites.

2-1-Litteraure survey

Various techniques have been used to investigate the curing of epoxy resins, and these are briefly reviewed.

Mijovic[1] used calorimetry measurements to investigate the orientation of the dipoles in microwave and thermal fields and compared them to see if this could lead to different network morphology. Two parameters were used to characterise the advancement of the reaction, which were the degree of cure α and the glass transition temperature T_g. These were calculated from the measurements of the heat evolved in the cure. It was found that these parameters increased

faster with temperature and time in the thermal field rather than in the microwave, and that a broader T_g range suggested a broader molecular weight distribution and hence morphological heterogeneity. When Mijovic[2] used High Performance Liquid Chromatography, it was found that three types of hydrogen bond complexes were participating in the reaction of epoxy resin with an amine. This was described by three reaction schemes, epoxy amine complex with amino group, epoxy hydroxyl complex with amino group and epoxy hydroxyl complex with amine hydroxyl complex, which occured only after the hydroxyl complex increased to saturation. The author set out an approach for the calculation of the rate of the reaction, in which some of the associated rate constants were unreliable. However, the reactivity ratio of the consumption of primary amine hydrogen atoms, on the reactivity of the secondary amine hydrogen atom on the same amino group, was used to characterise the polymer cross-linking morphology.

Gonis[3] used differential scanning calorimetry (DSC), to evaluate the activation energies for epoxies of varying chain lengths. It was deduced that as the reaction proceeded, highly branched macromolecules began to form and a step increase in viscosity was indicative of the onset of gelation. In the dynamic mode, only the over-all reaction process could be analysed. In the isothermal measurement, the fractional conversion, α, was determined by dividing the heat evolved during cure by total exothermal energy. The overall kinetics of cure was stated and used to calculate the activation energy and produce the rate equation.

Neilsen[4] used the analytical capabilities of Gel Permeation Chromatography for studying the curing process. He calculated the average molecular weight of various polymer chain lengths, the activation energy and estimated the rate of reaction as a function of temperature and conversion. The author reported that the equation used was not consistent when calculating the activation energy.

Dynamic Dielectric Analysis was used by Maistros[5]; measurements of capacitance and inductance over the curing period of epoxy resin with an amine were carried out. A correlation to the relative permeativity controlled by the ionic character of the different stages of curing was made. Immediately after mixing a high interaction between the reactant induced a high degree of ion in the mixture.

Kozeiski[6] used chemiliminescence (CL) measurements to investigate the curing of epoxy resin with an amine. Some peaks from the plot of intensities of the emitted light against time were assigned to the hydroperoxide reaction and oxidation of the resin. The conclusion was made that a reasonable correlation existed between gelation and CL. However this technique is very sensitive to the increase in the viscosity during the network formation, while gelation is not the only phenomena that occurs in the network construction.

2-2-Conclusion of the literature review

From this investigation it has been concluded that none of these techniques are suitable to describe the development of the chemical reaction between epoxy resin and curing agents. The most consistent technique in monitoring the curing of epoxy amine system was the Fast Fourier Transform InfraRed (FT-IR) spectroscopy, and the results from the DSC technique could be very useful to adjust the FT-IR results.

3-How does Infrared spectroscopy work?

It is intended to concentrate on vibrational spectroscopy, and to use an FT-IR spectrometer to study the Mid-infrared region of electromagnetic spectra. Here the technique will examine the fundamental vibrations of organic and complex inorganic, which covers the region 2.5 to 25µm. The interaction between the electrical component of electromagnetic radiation and the dipolar motion in the molecules is the basis of vibrational spectroscopy. The dipole of the molecule must change during the vibration. CH, NH and OH groups are the most explicit bonds in the mid-infrared region. Heteropolar A-B molecules absorb in the infrared region, but homopolar A-A molecules do not.

FT-IR spectroscopy is a powerful and versatile technique for monitoring transient chemical change during the cure process, and structural change during the deformation process. It offers a unique possibility to obtain detailed information about molecular orientation and relaxation behaviour. The goal is to identify the characteristic Mid-infrared band assignments, monitor their change during the curing process, and use them to evaluate the reaction rate, and deduce the kinetics of reaction and mechanical properties of the products.

4-Experiment preformed

4-1-The embedding of the sensor in the resin for an on-line monitoring of the cure reaction

An optical interface was made from a set of gold-coated mirrors, a pair of chalcogenide optical fiber cables aligned by means of a micro holder. This was set on the same bench as the spectrometer. It was built to achieve the appropriate alignment of the two fiber optic ends, a micro meter was added as mean of adjusting the gap between the fibers end faces. The embedded fiber optic sensor operating in the mid-infrared band of the electromagnetic spectra, is shown in Figure 1.

-a-

-b-

Figure 1 Two optical fibers axially aligned

(a- not embedded yet), (b- under running experiment, while embedded in the epoxy/amine system)

The setup for the embedding method was linked to a Jasco 410 spectrometer fitted with a powerful fast Infrared HgCdTe detector; coupling two Chalcogenide fiber optic cables via an optical interface carried this out. The described MCT detector was cooled in liquid nitrogen, which provided a high signal to noise ratio. Figure.1 shows also that a mixed resin poured on the fiber optic sensor at the gap between the ends faces, which is already adjusted, by an incorporated micrometer before collecting any data.

Note: (The equivalent set-up in the stereolithography machine is described in Figure 9).

4-2-Sample preparation from DGEBA/TETA reaction and Data collection

A set of frequencies was chosen (1132 cm^{-1}, 3300-3400 cm^{-1} and 2970 cm^{-1}) to follow the development of the reaction. Analysis of the data enabled the information on the rate of reaction at any time during the cure to be obtained.

Their vibrations at frequencies characterized the reactants and products involved in the reaction. The values corresponded to vibrations of the functional groups observed in the curing of DGEBA (diglycidyl ether of 2,2'-bis(4- hydroxypheny) propane) with Triethylenetetramine (The reaction scheme, for this process is shown in Figure 2).
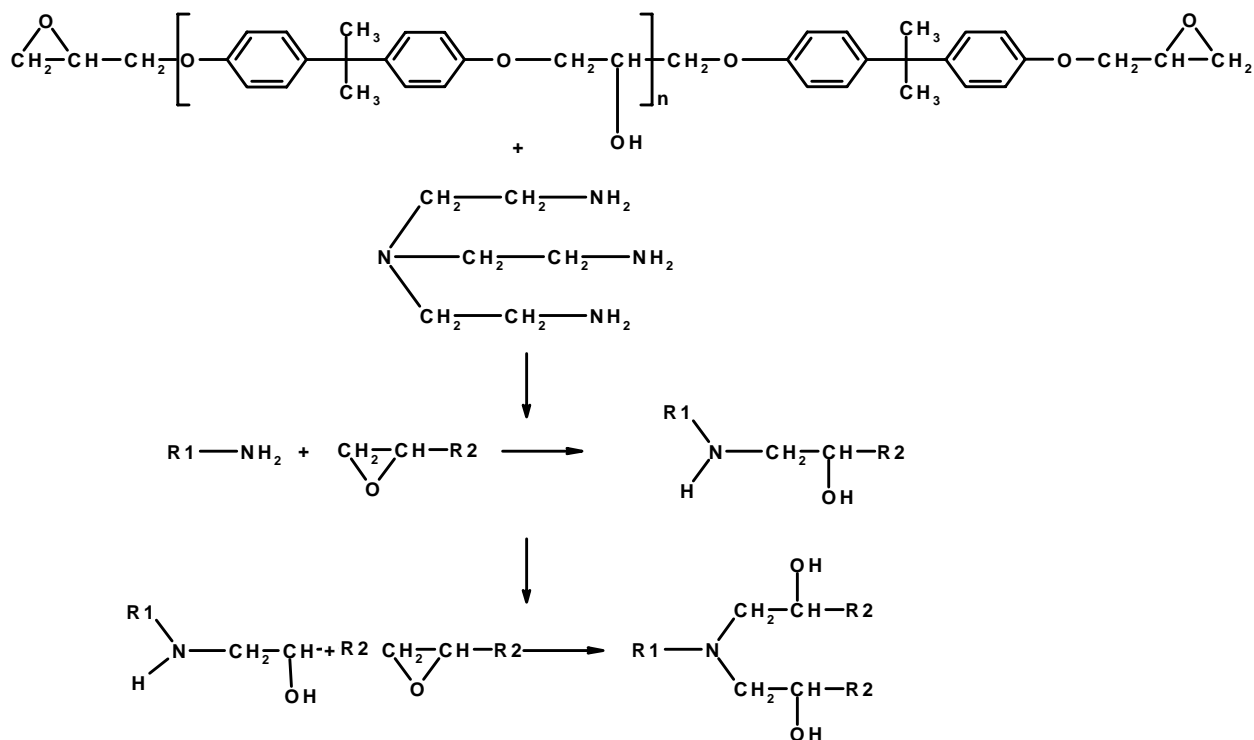

Figure 2. The reaction scheme of the epoxy resin with a tiethylenetetramine

4-3-Results

Peaks were selected from the spectrum (Shown in Figure 3) to determine the state of cure as a function of time. This was achieved by determination of the rates of consumption of the oxirane ring group (Corresponding peak P2 is shown in Figure 4), the primary amine

(Corresponding peak P3 is shown in Figure 5) and appearance of hydroxyl (Corresponding peak P4 is shown in Figure 5), along with the disappearance of secondary amines. The increase of the tertiary amine was determined using mathematical manipulations.

From Figure 4 it can also be seen that the epoxy peak and ether were vibrating at the same frequency and were detected a $1132cm^{-1}$. This is supported by confirming the existence of this peak in spectrum of pure DGEBA epoxy resin. However the change recorded at this peak is due only to the disappearance of the epoxy group vibrations as can be seen in the reaction scheme, while the ether group, which was not reacting does not participate to that change
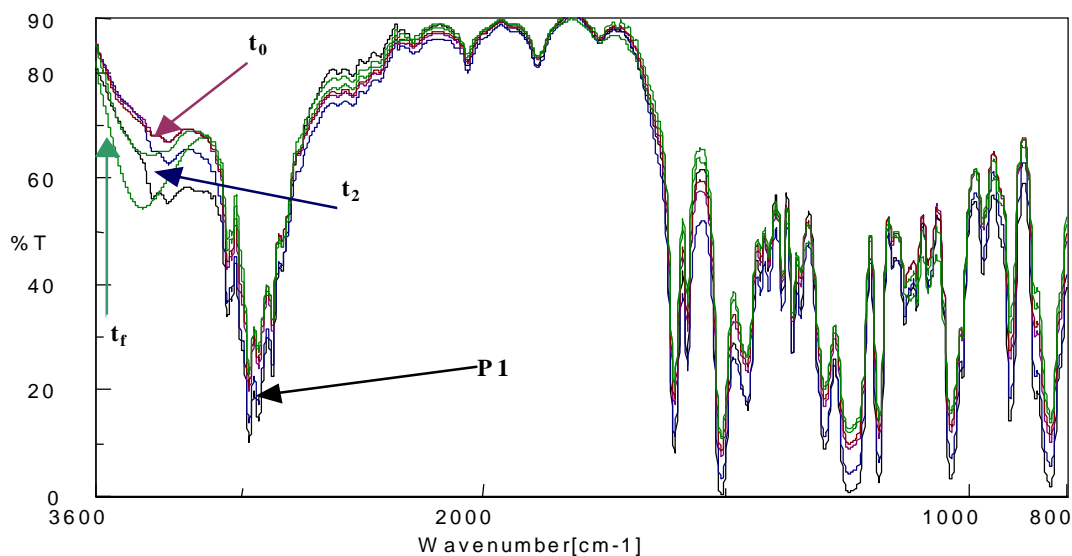

Figure 3. Change in spectrum of the mixture over time as shown, t_0 for initial time and t_f final time
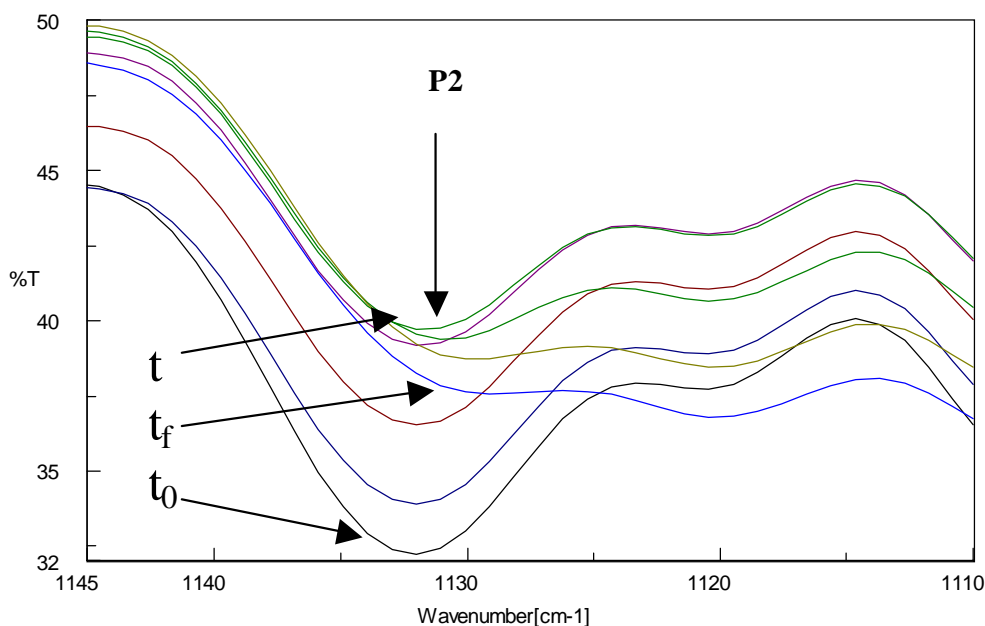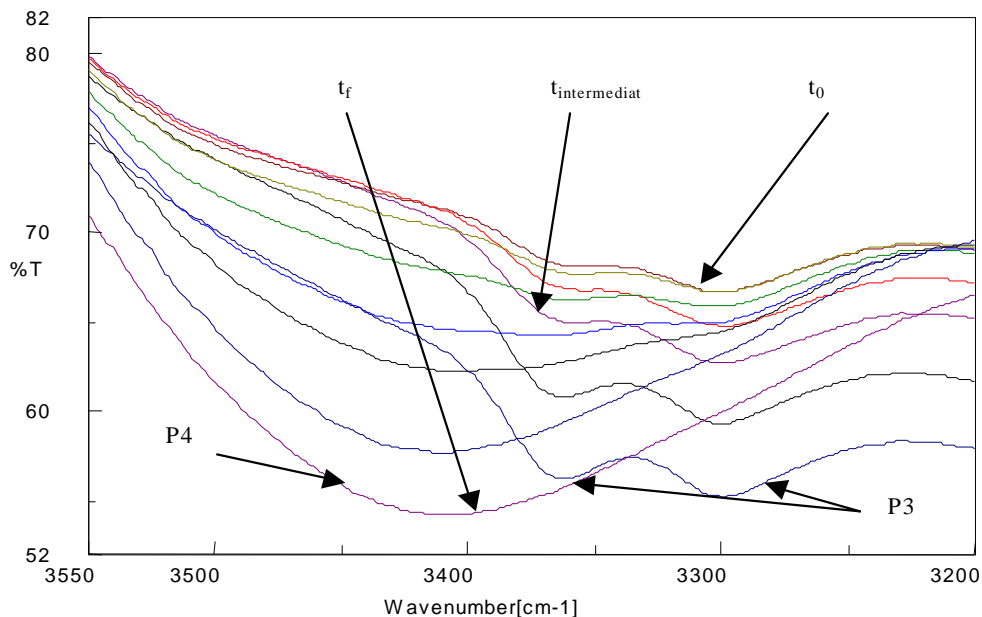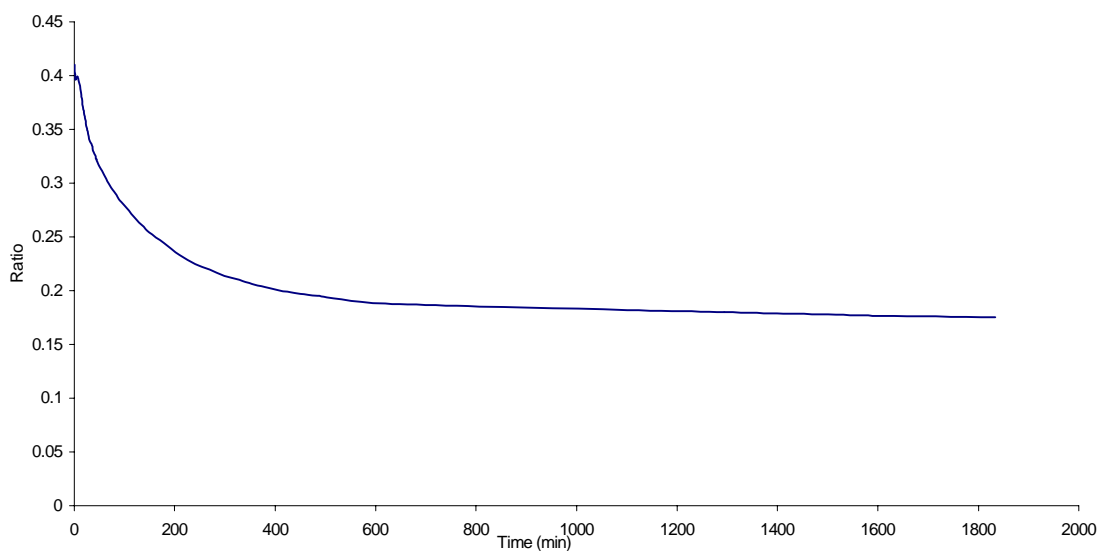

Figure 4. Change in the peak at $1132cm^{-1}$ with   time for oxirane ring of epoxy

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Figure 5. The disappearance of the double peak atat 3300-3365 cm^{-1} and the appearance of the peak at 3400 cm^{-1} over 24hours time

Figure 6 shows the ratio of the area measured under the peak P2 at 1135 cm^{-1} to the area under the selected refrence P1 peak, as can be seen from Figure 4 at 2970 cm^{-1}. This ratio is proved[7] to be directly proportional to the extent of reaction, hence to the concentration of the group causing the vibration. Figure 7 shows the ratio of the area under the peak P3 at 3300-3400 cm^{-1}, characteristic of the used amine as curing agent, to the area under the reference peak P1. This is also directly proportional to the change in the concentration of the amine over the curing period.

Figure 6. Ratio of area under epoxy group peak to area under reference peak
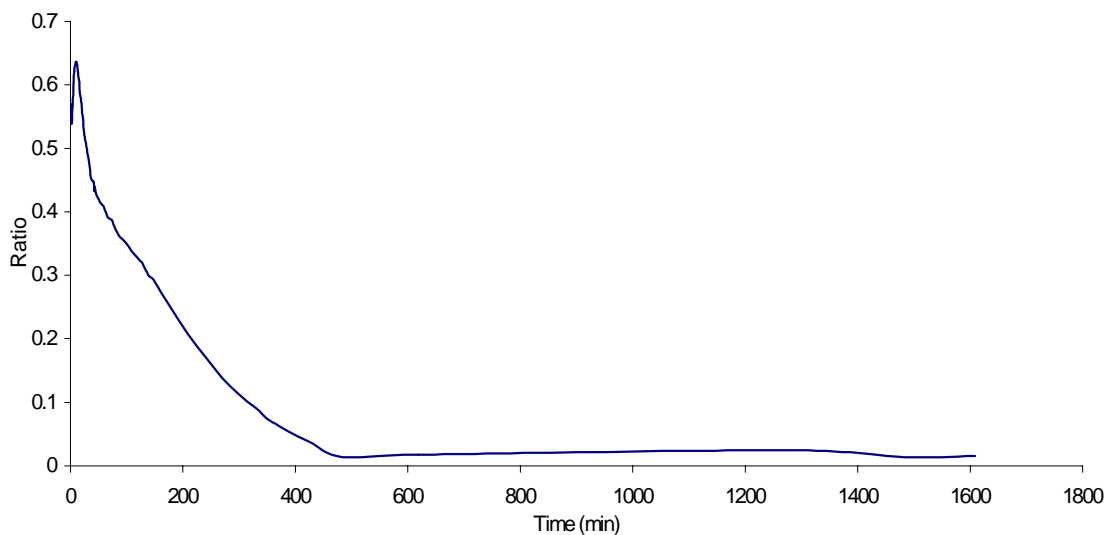
Figure 7.Ratio of area under amine group peak to area under reference peak

5-Data Analysis

5-1-Kinetic Mechanism

The reaction under study was a stoichiometric mixture of Epoxy resin /Amine system prepared at room temperature; DGEBA (Araldite MY 750), which had an average molecular weight < 700, and TETA (Hardener HY 951) were used. These were obtained from Ciba Specialty Chemicals Inc.

The stoichiometric amounts used in this experiment were 46 grams of TETA to 186.56 grams of DGEBA.

This reaction follows the kinetic equations described in (1) and (2).

$$E + P \xrightarrow{K_1} S \tag{1}$$

$$E + S \xrightarrow{K2} T \tag{2}$$

k_1 and k_2 define the bi-reaction $R_{1,i}$ $R_{2,i}$ involved in this mixture, which are the reaction of the Epoxy *(E)*with the Primary amine *(P)* and the reaction of the Epoxy with the Secondary amine *(S)*, to end up with a Tertiary amine *(T)*.

Under appropriate kinetic conditions, the following reactions occur in the epoxy-amine mixture, primary amines and epoxy, secondary amine and epoxy. On this basis, the general equations for the rate of epoxy-amine reactions in terms of; the rate of disappearance of epoxy groups, primary amine groups, secondary amine groups and the appearance of tertiary amine as product of the reaction. The system of equations in (3) describes these rates or reactions.

$$\begin{bmatrix} \dfrac{d[E]}{dt} = -k_1[E][P] - k_2[E][S] - -a \\[2mm] \dfrac{d[P]}{dt} = -k_1[E][P] - - - - - - - b \\[2mm] \dfrac{d[S]}{dt} = k_1[E][P] - k_2[E][S] - -c \\[2mm] \dfrac{d[T]}{dt} = k_2[E][S] - - - - - - - d \end{bmatrix} \qquad (3)$$

To solve this set of differential equations, the first step to carry out is translation of the above equations to expressions, which relate the amounts of material of epoxy, primary amine, secondary amine and tertiary amine at any time over the curing period. Further manipulation gives,

$$n_t = n_s + (n_p - n_s)^1 \frac{k_1}{k_1 - k_2}\left[1 - \left(\frac{n_p}{n_p - n_s}\right)^{1 - \frac{k_2}{k_1}}\right] \qquad (4)$$

Substituting the above equation n_t in the equation b from the system (3) gives the differential equation which represents the studied Epoxy-amine system,

$$\frac{dn_s}{dt} = \frac{k_1}{v}\left(n_e - 2n_s + (n_p - n_s)\frac{k_1}{k_1 - k_2}\left[1 - \left(\frac{n_p}{n_p - n_s}\right)^{1 - \frac{k_2}{k_1}}\right]\right)(n_p - n_s) \qquad (5)$$

For a numerical solution of the ordinary differential equation (5), a fourth and fifth Runge-Kutta formula was used. These formulas do not use iterative methods to solve the non-linear equation; they are self-starting, not requiring more than immediate past values of n_s. However several function evaluations per integration step were needed.

In this work the ode45 function was used in the Matlab program to solve the above equation. For correlation between the experimental concentration of the reactant and products involved in the studied system and the simulated data estimated by the above model, an extra development is needed. This is based on the a kinetics of reaction mechanism, for which non-linear least squares method was used, it is build on Newton's Gauss method. An application for the studied system is briefly described in the following section.

5-2-Solution of a Non-linear equation by Least Squares

For a function $y(x)$, which is a non-linear function of the coefficient, the following procedure is required, it is based on Newton-Gauss least squares method. Assuming that there exists an initial estimate of these coefficients $a_1, a_2, a_3,...,a_m$ of a polynomial $P(x)$ and that by adding infinitesimal increments $\delta_1, \delta_2, \delta_3,.....,\delta_m$ an improved estimate may be obtained. The new value of y_i is given by,

$$y(x_i) + \sum_{j=1}^{m} \left(\frac{\partial y}{\partial a_j} \right) \cdot \delta a_j \qquad (6)$$

Then it is required that the difference between the initial, and the new value is minimum, which then rearranged to give,

$$\left(\frac{\partial S}{\partial \delta a_k} \right) = -2 \sum_{i=1}^{n} \left(y_i - y(x_i) - \sum_{j=1}^{m} \left(\frac{\partial y}{\partial a_j} \right) \delta a_j \right) \left(\frac{\partial y}{\partial a_k} \right) \qquad (7)$$

$$\therefore \sum_{j=1}^{m} \delta a_j \cdot \sum_{i=1}^{n} \left(\frac{\partial y}{\partial a_j} \right) \left(\frac{\partial y}{\partial a_k} \right) = \sum_{i=1}^{n} \left(y_i - y(x_i) \left(\frac{\partial y}{\partial a_k} \right) \right) \qquad (8)$$

The term, $y_i - y(x_i)$, is known as the residual, r_i. The expression above is a set of m simultaneous equations for the m increments $\delta_1, \delta_2, \delta_3, \ldots, \delta_m$.

These equations may be obtained by forming a matrix D that contains as elements $D_{i,j}$, the value of the derivative $\left(\frac{\partial y}{\partial a_j} \right)$, evaluated when $x=x_i$, and a vector r for which the general element $r_i = y_i - y(x_i)$ \qquad (10)

The solution to the equation (8) is given by,

$$\delta a = \left((D)^T (D) \right)^{-1} (D)^T r \qquad (11)$$

Having obtained the increments δa, they are added to the original a values, $a=a+\delta a$, and the procedure is repeated until $\delta a \cong 0$.

Figure 8. shows a plot of the simulated concentration changes over the curing period, of the epoxy, primary, secondary and tertiary amines. The curve in circles shows the experimental data for the concentration of the epoxy as recorded by FTIR spectroscopy.
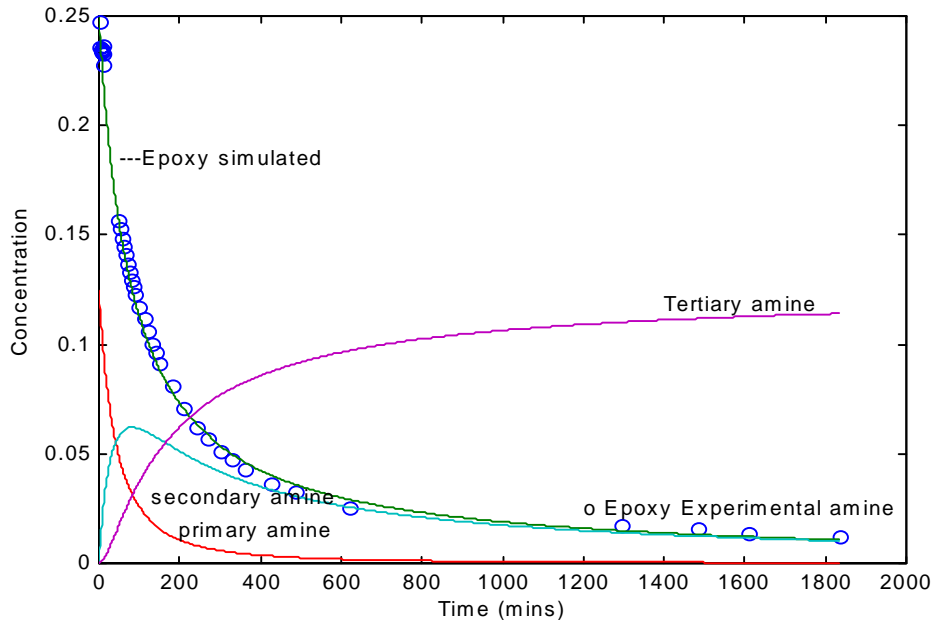

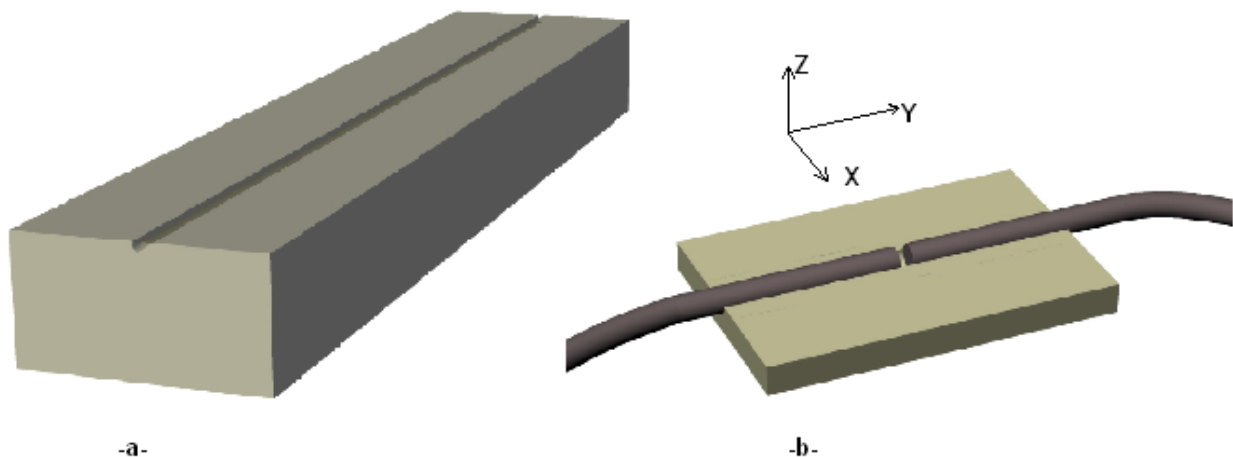**Figure 8. Plotting of concentrations**.

7-Conclusion

For an optimum processing of epoxy resins in making parts, coating or composite materials, an understanding of the phase transfer from monomers to polymers is needed. The achievement of such a goal may result in a capability to reach the required physical properties by setting the adequate processing schedule.

An optical fiber sensor has been developed and successfully embedded in an epoxy /amine system to monitor the progress of the reaction over its curing period, results of which can be translated in physical parameters. A plan is also given for an implementation of this sensor in streolithography resin, during its curing process in the SLA machine under UV laser. The monitoring will be carried out for the post cure and later for the chemical status of the structure forming the end part over the operating period.

Mid-Infrared spectroscopy is a most suitable technique to follow the curing of the epoxy hardener mixture. It was noticed that many frequencies from the obtained spectra were changing in a significant fashion; these were correlated to a number of reacting groups in the mixture, and their progress was monitored over time. It is clear that this technique provided a direct measurement of the change in concentration over time of any element involved in the reaction. The method developed to process data is capable of calculating all the chemical parameters of the investigated reaction. This is based on converting the measured variations in concentrations over the curing period to two constants of reactions k_1, and k_2, representing the reaction involving the epoxy and the primary amine and the reaction of the epoxy and the secondary amine respectively, which is achieved by minimizing the difference between the experimental data and the result from the simulated model. The values for the reaction DGEBA and TETA of the constants of reaction are, $k_1 = 0.96$ mins^{-1} and $k_2 = 0.68$ mins^{-1}.

7-Recomendation

Figure 9 shows the groove made in the part built in the SL machine. The diameter of the groove is designed to carry the optical fiber sensor, height of one layer in the SL is left inbuilt from the diameter of the groove, this permits the implementation of the optical fiber cable see Figure 9 b.

-a-   -b-

Figure 9 Set-up of the optical fiber sensor to be implemented in the SLA machine

Part building is then continued; the next layer is spread until the sensor will be completely immersed, the 30-microns gap as shown in Figure 9 b. will be filled with the resin. When the UV curing laser of 200 microns beam diameter passes over the sensor, at hatch velocity of 525 inches/second, the resin in the gap will cure. A number of spectra can be collected from which the change in the molecular structure of the resin will be measured. The effect of the laser curing the top layers will also be recorded.

The sensor will carry the monitoring process of the reaction progress in the post cure stage of the part under UV light, as well as in the future of the part, where the exterior condition in which the part will operate participate to the degradation of the molecular structure of the material.

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