

This item was submitted to [Loughborough's Research Repository](#) by the author.  
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

## **Monitoring the polymerization of a diglycidyl ether bisphenol-A/2,2'-dimethyl-4,4'-methylenebis (cyclohexylamine) matrix with a Fourier transform infrared optical fibre sensor**

PLEASE CITE THE PUBLISHED VERSION

PUBLISHER

Professional Engineering Publishing / © IMECHE

VERSION

VoR (Version of Record)

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Fouchal, Farid, J.A.G. Knight, and Phill M. Dickens. 2019. "Monitoring the Polymerization of a Diglycidyl Ether Bisphenol-a/2,2'-dimethyl-4,4'-methylenebis (cyclohexylamine) Matrix with a Fourier Transform Infrared Optical Fibre Sensor". figshare. <https://hdl.handle.net/2134/4724>.

This item was submitted to Loughborough's Institutional Repository (<https://dspace.lboro.ac.uk/>) by the author and is made available under the following Creative Commons Licence conditions.



For the full text of this licence, please go to:  
<http://creativecommons.org/licenses/by-nc-nd/2.5/>

# Monitoring the polymerization of a diglycidyl ether bisphenol-A/2,2'-dimethyl-4,4'-methylenebis(cyclohexylamine) matrix with a Fourier transform infrared optical fibre sensor

F Fouchal<sup>1\*</sup>, J A G Knight<sup>2</sup> and P M Dickens<sup>1</sup>

<sup>1</sup>Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough, UK

<sup>2</sup>Faculty of Science, De Montfort University, Leicester, UK

**Abstract:** An optical fibre sensor (OFS) for the online monitoring of the polymerization reaction is described in this paper. The sensor, based on Fourier transform infrared (FT-IR) and differential scanning calorimetry (DSC) analysis, was used to study the reaction between diglycidyl ether bisphenol-A (DGEBA) and 2,2'-dimethyl-4,4'-methylenebis(cyclohexylamine) (DMMB-CHA). Changes in concentrations of reactants and products were monitored over the curing period at different temperatures by the FT-IR technique, and from DSC runs the variation in the enthalpy of reaction over time for different curing temperatures was determined. Plots of fractional conversions versus time from the two methods were produced and compared. An attempt to deduce glass transition temperatures from the fractional conversion curves produced by FT-IR is also described. This involved the use of the fitting polynomial calculated from the DSC results. As a result, a sensor designed for embedding into a system curing at elevated temperature was constructed and tested.

**Keywords:** epoxy resins, cure behaviour, processing composites, embedded optical fibre sensors

## 1 INTRODUCTION

Epoxy resins are often used as matrices in advanced composites, although during their processing stages many difficulties have been experienced by industrial users in achieving similar and optimum properties from repeated operations. *In situ* monitoring of the curing resin is one solution to lessen this limitation. The work presented in this paper deals with one of the major factors involved in processing composites, that is, temperature. The effect of this parameter on the reaction of epoxy resin with amine was investigated using a Fourier transform infrared (FT-IR) optical fibre sensor (OFS) and differential scanning calorimetry (DSC). Data produced by these two methods were plotted as fractional conversions against time and then compared for different temperatures.

The FT-IR investigation was carried out to monitor the chemical changes occurring during the curing process of the epoxy/amine reaction following two routes—one

involved transmitting an infrared beam through a prepared sample, and the second employed an OFS that was embedded into the sample. The intensities of infrared electromagnetic waves ( $4000\text{--}400\text{ cm}^{-1}$ ) travelling through a sample changed at some frequencies owing to resonance with the vibrations of the chemical bonds in the molecular structure of the mixture. These changes were collected as a series of infrared spectra representing the different stages of the reaction over time. The second method used in this research was a thermal study of the same epoxy resin/amine reaction using DSC method to investigate the effect of varying cure temperatures on the enthalpy of reaction to produce a relation between glass transition temperature and fractional conversion. Discussion of the results and comparative study between findings of the FT-IR and the DSC methods were also carried out.

## 2 LITERATURE REVIEW

### 2.1 FT-IR based optical fibre sensors

Many online monitoring experiments have been reported on the curing of epoxy resins. Most of them have been based

*The MS was received on 14 October 2003 and was accepted after revision for publication on 4 May 2004.*

\*Corresponding author: Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK.

on near-infrared and Raman spectroscopy [1], and some are reviewed in this section. Powell [2] prepared a transmission sensor using two optical fibres to follow the changes in characteristic near-infrared absorption bands of the resin during the cure reaction over the range 4450–4760  $\text{cm}^{-1}$ . Quantitative information on concentrations of active functional groups in the resin system was obtained using spectral interrogation techniques. Qualitative information on the extent of cure was also obtained by tracking the refractive index of the resin, which increases as a function of the crosslink density.

George *et al.* [3] have used an FT-IR spectrometer together with silicone resin clad optical fibre to monitor the cure of an epoxy-amine resin from 4000 to 10 000  $\text{cm}^{-1}$ . The ends of the fibre optic were placed at a desired separation in a microcapillary tube, which was then immersed into the resin. They were able to follow quantitatively the change in absorption of the epoxy, amine and hydroxyl groups. The primary amine absorption at 5067  $\text{cm}^{-1}$  was the most sensitive for monitoring the early stages of the cure. However, strong absorptions due to the silica fibre and silicone cladding prevented analysis in some regions.

Cossins [4] has applied evanescent optical fibre spectroscopy to monitor the cure of low refractive index epoxy resin using silica optical fibre. Spectra within 4000 and 5000  $\text{cm}^{-1}$  were obtained, with absorption changes being observed at 4925  $\text{cm}^{-1}$ , which are due to the depletion of the primary amine stretching/bending combination, and at 4725  $\text{cm}^{-1}$ , which are due to an increase in the C–N overtone. The author also reported that overtones of C–O bands occurred in the mid-infrared region and only weaker second and third overtones were seen in the near-infrared region which is defined as the wavelength range between 4000 and 14 000  $\text{cm}^{-1}$ .

Nishio *et al.* [5] have demonstrated the effectiveness of using the near-infrared evanescent wave from glass to monitor the cure of epoxy resins, but using the more controlled optics of the pyrometer reentry experiment (Pyrex) IRS (Institute für Raunfahrt Systeme) element. The use of near-infrared IRS has an advantage over the mid-IR technique where the sampling depth is extremely small ( $\ll 1 \mu\text{m}$ ), and so surface chemistry may be examined with great specificity against this.

Compton *et al.* [6] described initial attempts to extend the use of a commercial near-infrared probe into the mid-IR. Silicone cladding was stripped off a 120  $\mu\text{m}$  diameter arsenic germanium selenide fibre, and was immersed into the specimen of interest. The specimen was then sampled by the evanescent wave at the fibre optic/specimen interface.

Dury *et al.* [7] embedded arsenic germanium selenide chalcogenide fibres and heavy metal fluoride glass fibres in uncured graphite/epoxy and graphite/polyimide composites to monitor the cure process. The produced spectra were of sufficient quality to monitor the inside formation (1785 and 1710  $\text{cm}^{-1}$ ) during the cure cycle. However, the heavy metal fluoride glass showed changes in the amine stretch region at 3400  $\text{cm}^{-1}$ . Dury *et al.* [8] in another publication, described the use of a sapphire sensing fibre embedded in the composite so as to allow monitoring in an autoclave environment at 250 °C for 8 h.

Mijovic and Andjelic [9] have concluded that the mid-IR frequencies could only be transmitted through the chalcogenide and metal halide fibres, even over limited frequency intervals. They reported that, in the majority of cases encountered in their laboratory, over 80 per cent of the signal was absorbed by the optical fibre, making it impossible to differentiate between spectra taken at different stages of the cure of an epoxy resin.

In the reviewed literature, the deployment of OFS based on FT-IR analysis to monitor the cure of epoxy resin was limited to the near-infrared region of the electromagnetic waves [2–5]. Apart from some attempts to perform an online monitoring of the cure reaction of epoxy resins [6–8] in the mid-IR region, there was a lack of work using optical probes and mid-FT-IR for studying the fundamental vibration of the organic molecules existing in the curing mixture, mainly owing to the non-availability of optical fibres capable of guiding vibration from this electromagnetic range. It has also been found that the many studies reported in the near-infrared region were based on overtones, while studies in the mid-infrared region rely on fundamental vibrations. Therefore, a method that uses an embedded FT-IR OFS in the mid-infrared region of the electromagnetic waves was proposed for monitoring the changes occurring to reactants and products of an epoxy/amine reaction by focusing on the variations in the intensity of light transmitted at 1131  $\text{cm}^{-1}$ , which was due to the oxirane ring. This vibration existed in the spectrum of the epoxy before it was mixed with amine, and no traces of it on the spectrum of the amine were detected. It also showed a progressive change in the intensity of the transmitted light as the cure progressed, together with a slight shift from 1135 towards 1131  $\text{cm}^{-1}$ .

## 2.2 Using FT-IR and DSC together

In all papers reviewed, FT-IR and DSC were used together as complementary methods to achieve results that could not be achieved by a single technique separately. Thermal analysis is usually used for studying the macromolecular behaviour of material, whereas the spectral analysis deals with molecular changes occurring during reaction. In some cases such as in aerospace, a simple monitoring system, which is not voluminous and light, is in great demand. Therefore, if a system capable of monitoring the macro- and micromolecular properties of a material simultaneously could be proposed, a step towards satisfying aerospace industry requirements would be achieved.

Some of the many research studies that have been reported using FT-IR and DSC together have been reviewed. Némec *et al.* [10] have used DSC and FT-IR for a study of low-temperature phase transition as two complementary methods. Delpech *et al.* [11] have studied a bisphenol-A based polycarbonate for characterization purposes using FT-IR and DSC techniques. Pouliot *et al.* [12] have used ATR-FT-IR to evaluate the degree of order of

the intercellular lipid alkyl chain, since the  $\text{CH}_2$  vibrational stretching frequency  $\nu(\text{CH}_2)$  is sensitive to average conformational order, and it increases as the disorder increases. Moreover, the DSC results were in accordance with the temperature dependence of  $\nu(\text{CH}_2)$ . Wieczorek *et al.* [13] have used DSC together with the FT-IR method to reach a conclusion that could not be achieved by either of these techniques separately. Akovali and Atalay [14] have used FT-IR to obtain the relative values of crystallinities of high-density polyethylene, and they used DSC and X-ray analysis to obtain the absolute values. Tanikawa and Miyajima [15] have used DSC and FT-IR to study the polymorphism of hydrated ceramides containing  $\alpha$ -hydroxy fatty acid and how cholesterol-3-sulphate affects it. The use of these two techniques was useful because the study was carried out in the range 30–100 °C and much of the data from the two techniques were in good agreement.

In this paper, an attempt to produce some DSC information from an FT-IR spectroscopic study is also proposed. Monitoring the cure of an epoxy resin by looking at quantitative changes in concentrations of reactants and products is one of the routes to achieve this goal. However, for a thermal analysis, knowledge of the changes in the enthalpy of reaction and glass transition temperatures on account of different curing schedules is an important result. From the proposed work, prediction of the changes in the enthalpy of reaction and the glass transition temperatures of curing epoxy resin from an FT-IR study is possible.

### 2.3 Band assignment

The most common reference band given by other researchers [16] using FT-IR to investigate the epoxy/amine reactions was the C–H stretching frequency associated with the aromatic hydrogen in the monomer chain backbones at 1510  $\text{cm}^{-1}$ . It exhibited a very strong absorption and was not involved in the crosslinking reactions. Ether bands [17] are usually found between 1000 and 1200  $\text{cm}^{-1}$ , while secondary amine and hydroxide bands [18] occur at 3300–3500  $\text{cm}^{-1}$ . As these two later absorptions are so close to one another, the net effect is that they merge into one broad absorption peak. The epoxide band [19] at 915  $\text{cm}^{-1}$  was a very strong absorption, but the hydroxyl vibration at the same frequency makes it unusable.

Gao and Ci [20] have used FT-IR to study the spectroscopic features of human breast benign and malignant tissues and defined a narrow and symmetric band in the C–O stretching region at 1163  $\text{cm}^{-1}$ . Dodoff [21] has carried out a conformational and vibrational analysis of N-3-pyridinylmethane sulphonamide and revealed a medium vibration at 1135  $\text{cm}^{-1}$  corresponding to  $\nu(\text{ring})$ ,  $\delta(\text{CH})$  and a strong vibration at 1127  $\text{cm}^{-1}$  corresponding to  $\rho(\text{CH}_3)$ . Djaoud *et al.* [19] have also looked at the vibrational properties of sol–gel prepared nanocrystalline titanium dioxide ( $\text{TiO}_2$ ) thin films, and revealed that the strong bands centred at 1248 and 1116  $\text{cm}^{-1}$  originated in the C–O–C bonds of

**Table 1** Assignments of the main bands of the epoxy/amine reaction from textbooks and published papers

Peak ( $\text{cm}^{-1}$ )	Assignment
3472	Harmonic C=O + $\text{NH}_2$
3464	Harmonic C=O
3446–3415	$\text{NH}_2$ antisymmetric
3389–3330	$\text{NH}$
3338	$\text{NH}_2$ symmetric
3210	Harmonic $\text{NH}_2$
3038	Benzene ring
2987–2853	$\text{CH}_2$
1603	Benzene ring
1514	Benzene ring
1395 and 1377	C–N–C
1289 and 1275	C–N
1178, 1020	Benzene ring
1149	C–N–C
950	Benzene ring
3400	Broad and associated OH stretch
3600	Sharp and unassociated OH stretch

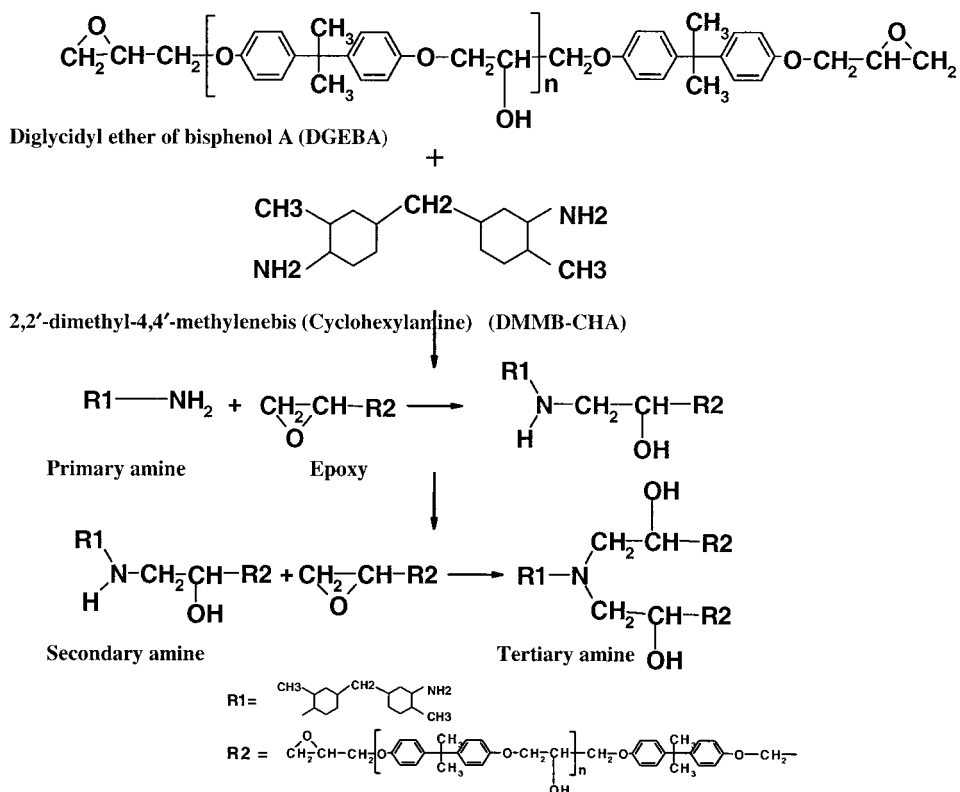
polyethylene glycol. Martin *et al.* [22], in their study for comparison of real-time monitoring of copolymer formation and composition, have reported FT-IR interval reference bands in the monomer composites that included  $-\text{CO}-\text{O}-$  at 1163  $\text{cm}^{-1}$ . Némec *et al.* [10] have defined the  $\rho\text{CH}_3$  vibration from 1133 to 1136  $\text{cm}^{-1}$  by FT-IR and at 1132  $\text{cm}^{-1}$  by FT-Raman. Inauen *et al.* [23] described the vibration frequencies of phenol-oxirane at 1112  $\text{cm}^{-1}$ , the  $(1 + 3\tau)$  at 1167  $\text{cm}^{-1}$  and the  $(1 + \delta)$  at 1176  $\text{cm}^{-1}$  from fluorescence emission spectra.

Table 1 summarizes the major frequencies reported in many studies [24–30] for the epoxy resin/amine reaction within the mid-infrared region of the electromagnetic spectrum.

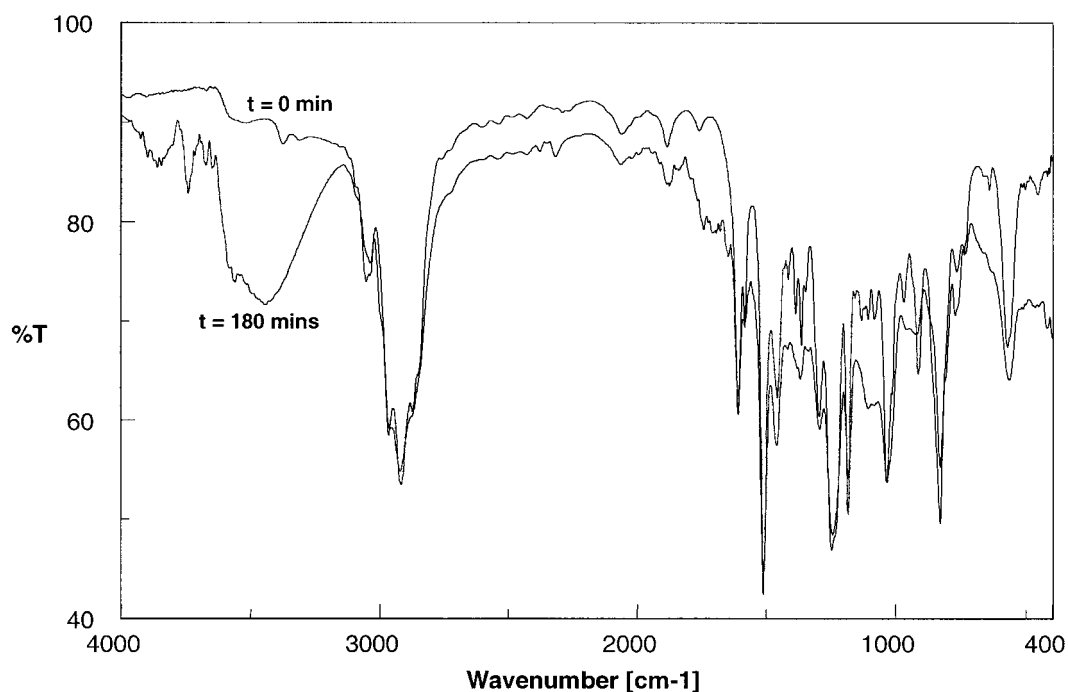
## 3 EXPERIMENTAL METHODS

### 3.1 Sample preparation

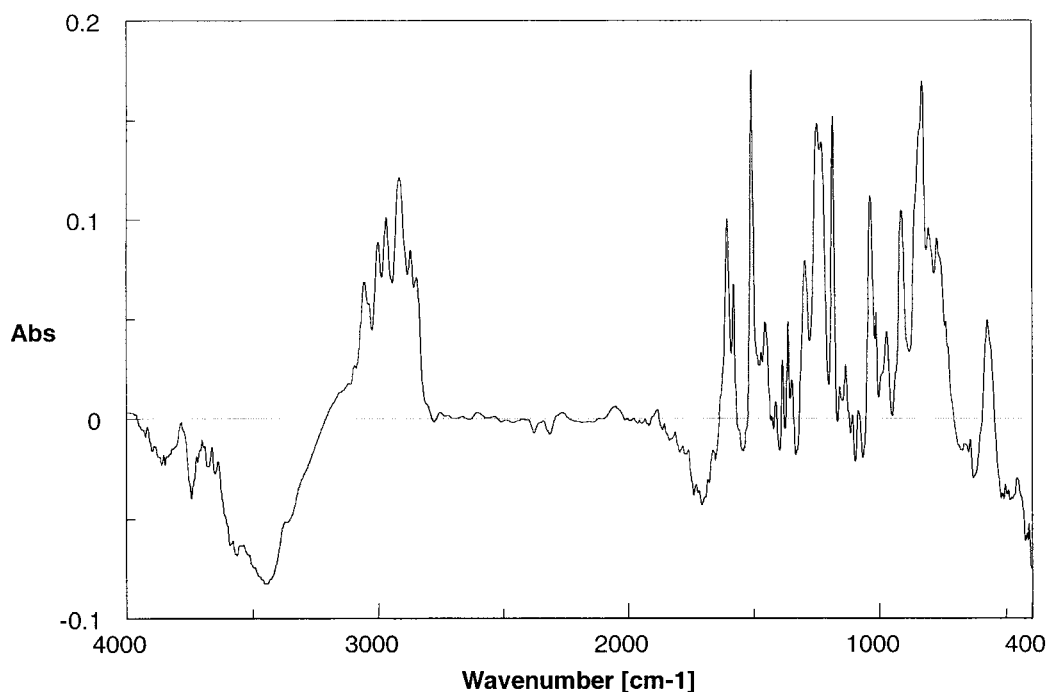
The chemical system involved in this study was diglycidyl ether of bisphenol-A DGEBA (Araldite 256,) cured with a 2,2'-dimethyl-4,4'-methylenebis(cyclohexylamine) (DMMB-CHA) (hardener 2976), provided by Ciba Specialty Chemicals Incorporated. Their chemical structures are included in the reaction scheme shown in Fig. 1. The epoxy monomer was a viscous liquid with an epoxide equivalent weight of 186.56 g, and the amine hardener was a liquid with an amine equivalent weight taken as 59.5 g. The amine was added to the resin and mixed manually (in a stoichiometric ratio of 10 g DGEBA with 3.2 g amine). The mixing was repeated for each curing temperature for 3 min in a vacuum chamber, and the procedure was carried out in the same manner for every sample. For the kinetic study, chemical conversion during mixing was neglected. For the DSC study, the average time of mixing and placing the disc into the heating cell and then inserting it in the spectrometer was 5 min.



**Fig. 1** Schematic diagram of an epoxy (DGEBA) and amine (DMMB-CHA) reaction



**Fig. 2** Overlapping spectra of epoxy resin with amine taken at time zero and after 180 min, when cure is completed



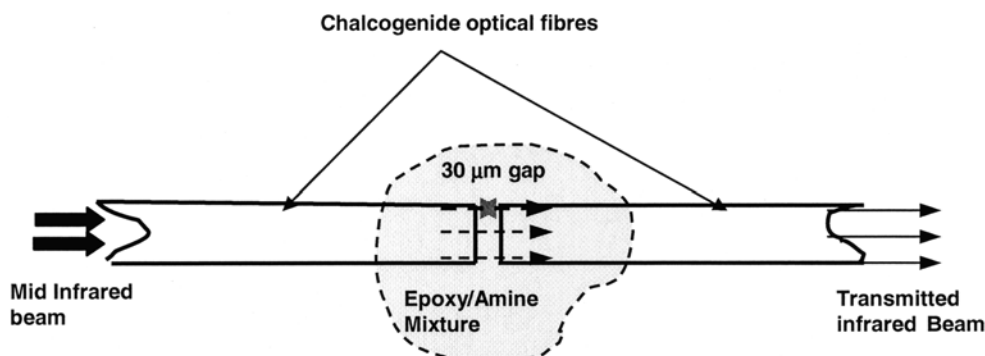
**Fig. 3** Difference spectrum between spectra taken at zero cure time and full cure time of the epoxy/amine system

### 3.2 Cure monitoring using direct FT-IR transmission

After using the FT-IR technique by directly transmitting the infrared beam through the prepared sample, a difference spectrum was produced as shown in Fig. 3 by subtracting the two absorbance spectra shown in Fig. 2 of samples cured at 100 °C for 180 min and for 0 min. From investigating this difference spectrum it has been revealed that the peak at  $1603\text{ cm}^{-1}$  on the difference spectrum shown in Fig. 3 did not change during the entire curing reaction.

To cure the sample inside the spectrometer, a cell fitted with a controllable heating element was constructed and a high level of thermal insulation was incorporated into it

avoid dissipating heat to the optical instrumentation of the spectrometer. Fluctuations in the overall temperature at the centre of the heating cell were less than 1 K over the entire curing period (calibration was carried out by embedding a calibrated thermocouple into a potassium bromide (KBr) disc, which was then introduced into the heating cell). The recorded background spectrum consisted of absorbances due to the surrounding media through which the infrared beam travelled (impurities in the air, the optics and the KBr disc). To give a pure infrared spectra of the studied materials, the background spectrum was subtracted from every spectrum collected over the curing period. For both direct and indirect transmission studies, the whole set-up was heated to the curing temperature before introduction



**Fig. 4** Two optical fibres axially aligned and embedded into an epoxy/amine system (the mid-infrared beam is transmitted through the curing sample)

of the resin/amine mixture into it to eliminate any possible heat loss.

### 3.3 Cure monitoring by embedding the OFS into the resin

An OFS suitable for operating in the mid-infrared range of the electromagnetic spectrum was constructed, and an optical interface (gold-coated mirrors) was used to couple the chalcogenide optical fibres to a Jasco 410 spectrometer that was fitted with a photoconductive mercury cadmium telluride (MCT and HgCdTe) detector, which was cooled in liquid nitrogen to provide a high signal-to-noise ratio. A holder was designed for axial alignment of the pair of chalcogenide optical fibre cables at their facing ends on which a micrometer was fitted to facilitate the adjustment of the gap within 20–30  $\mu\text{m}$ . To allow the flow of the resin into the gap, the set-up was immersed into a curing sample as shown in Fig. 4.

### 3.4 Investigating the isothermal cure

A Perkin–Elmer (DSC-4) instrument was used to measure the glass transition temperature,  $T_g$ , and the residual exotherm,  $\Delta H_r$ , of epoxy resin samples cured for various time periods. DSC runs for samples cured at 80, 100, 120, 140 and 150  $^{\circ}\text{C}$  were performed, and then graphs of the enthalpy of reaction,  $\Delta H_r$ , versus the glass transition temperature,  $T_g$ , were produced. The residual exotherm was used to calculate the extent of the reaction as a function of time.

## 4 RESULTS

### 4.1 FT-IR OFS study

The FT-IR OFS was utilized to obtain the infrared spectra of the epoxy/amine samples cured at four different temperatures over the complete curing time. Figure 5 shows overlapping views of four spectra taken after 0, 120, 300 and 11 400 s of curing time for samples cured at 100  $^{\circ}\text{C}$ . Similar overlapping views are produced for temperatures of 120, 140 and 150  $^{\circ}\text{C}$ . A clear change in the physical state of the epoxy/amine mixture can be seen between 3200 and 3400  $\text{cm}^{-1}$ .

The procedure adapted to process the FT-IR spectra involved monitoring the absorption bands associated with the most active chemical groups in the molecular structure of the mixture, which was the epoxy ring which opened by a coupling reaction with the amine [31]. For determination of the rate of reaction or degree of chemical conversion, Jasco software was used to measure the changes in absorbance over time at specific IR frequencies. The absorption due to the C–H stretching frequency at 1603  $\text{cm}^{-1}$  did not change over the curing time and was used as a reference peak. An investigation of spectra obtained for the complete range of IR frequencies led to the observation of two peaks that were assigned to changes taking place in the studied mixture.

#### 4.1.1 Peak detection and assignment

Changes in peak areas were monitored at regular time intervals by repeating the same measurement procedure for every spectrum until curing was complete. Based on the findings of Dodoff [21] and Némec *et al.* [10], the disappear-

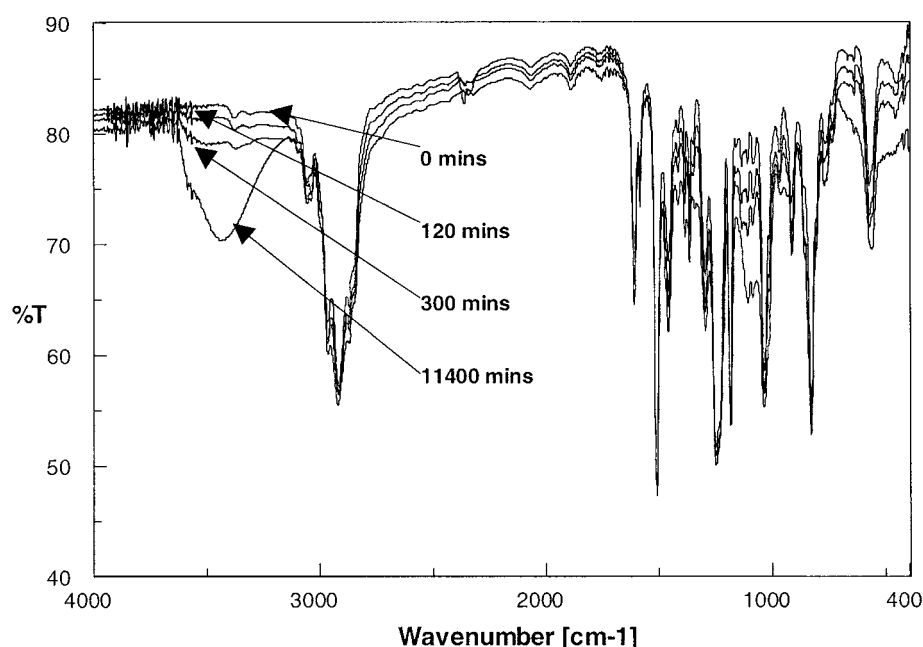


Fig. 5 Overlapping spectra of samples cured at 100  $^{\circ}\text{C}$  for 0, 120, 300 and 11 400 s



ance of the peak at  $1131\text{ cm}^{-1}$  (initially existing only in the pure epoxy) is due to the C–O bond of the oxirane ring, which opens when the reaction of epoxy resin with amine occurs. Changes in concentration of the epoxy resin were monitored from the variation in the peak area under this infrared vibration, and these changes were also used to determine the fractional conversion.

The broad peak at  $3300\text{--}3400\text{ cm}^{-1}$  in all spectra collected clearly distinguishes the conversion at different curing times, which is probably due to a combination peak from OH and  $\text{NH}_x$  absorption that can change in the opposite direction. However, the peak of major interest in the present study corresponds to the epoxy ring vibration at  $1131\text{ cm}^{-1}$ . Figure 6 is an expanded view obtained from a sample cured at  $150^\circ\text{C}$ .

#### 4.1.2 Transition moment for absorption

To produce quantitative information from FT-IR data, it is necessary to relate changes occurring to a selected peak on the spectrum to the chemical bonds involved in the studied system. To have absorption at any particular frequency, firstly the transmitted radiation must possess the proper energy that corresponds to the energy difference between the molecular states of the corresponding bonds. Secondly, the transition moment of the molecule must be non-zero.

The dipole moment for a molecule is defined as,

$$\mu = \sum e_i r_i \quad (1)$$

where  $e$  is the electric charge,  $r$  is the distance separating the interacting charges in the molecules and the expected value

of the dipole operator is

$$\mu = \langle \psi_n | \mu | \psi_m \rangle \quad (2)$$

where  $\psi_n$  and  $\psi_m$  are the stationary state wave functions associated with energy levels  $n$  and  $m$  of the molecule. The square of the transition moment is that actually observed in infrared absorption spectroscopy.

The integrated intensity of an absorption band is termed the dipole strength  $D$  of a transition, which can be determined experimentally as the area under an infrared band, plotted in units of molar extinction coefficient versus wave number as

$$D = \int \left( \frac{\epsilon}{\tilde{\nu}} \right) d\tilde{\nu} = |\langle \psi_n | \mu | \psi_m \rangle|^2 \quad (3)$$

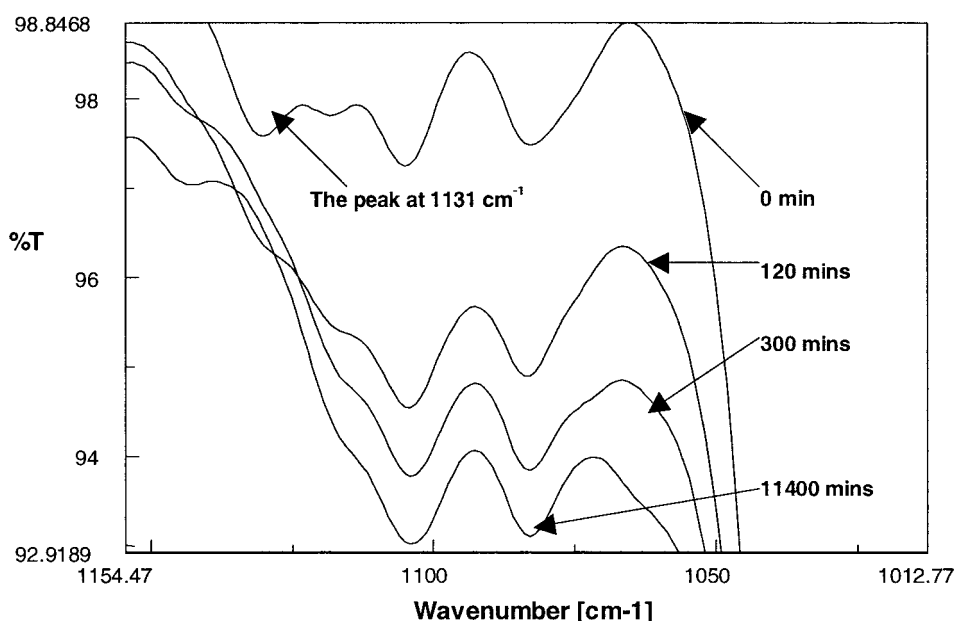
It has been concluded from the above demonstration that the area under an infrared band is proportional to the number of atoms involved in the reaction.

#### 4.1.3 Determination of the fractional conversion from an FT-IR study

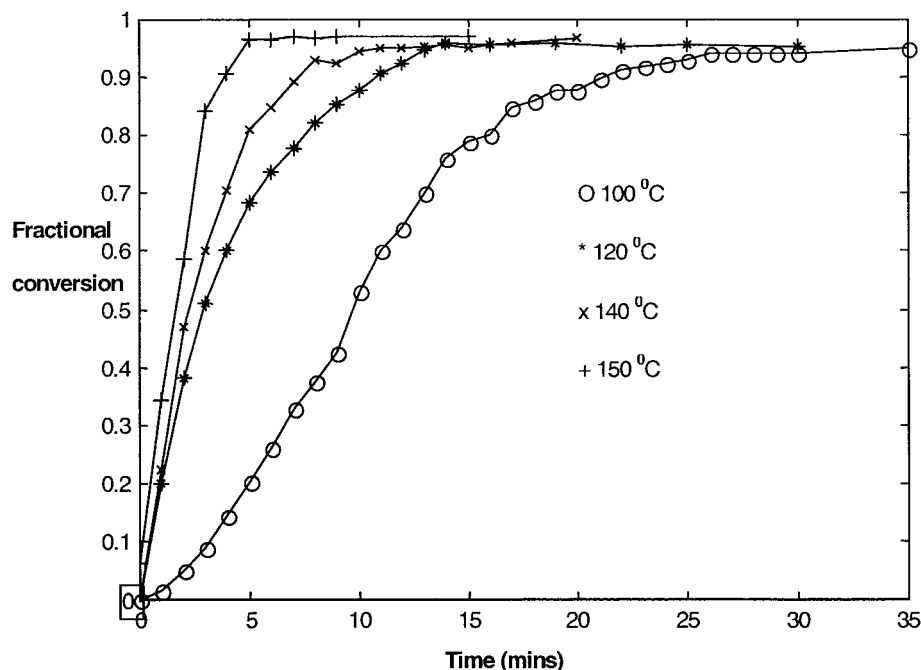
The Beer–Lambert law relates absorbance,  $A$ , to absorptivity  $a$ , sample thickness,  $d$ , and concentration,  $c$ , in the following manner

$$A = a \cdot d \cdot c \quad (4)$$

Because absorbance is related to concentration, the extent of reaction for epoxide groups can be determined from an absorption or transmission spectrum. The time dependence of frac-



**Fig. 6** Expanded view of the overlapped spectra taken at different stages of cure for an epoxy/amine sample cured at  $150^\circ\text{C}$  (the peak of interest here is at  $1131\text{ cm}^{-1}$ )



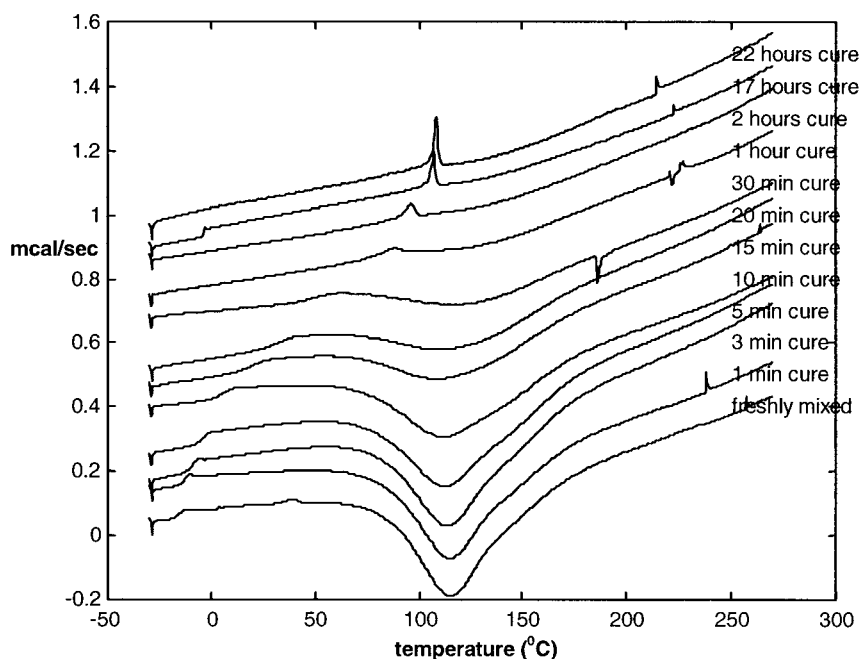
**Fig. 7** Plot of fractional conversion versus time given by FT-IR for the DGEBA/DMMB-CHA reaction at four different curing temperatures: 100, 120, 140 and 150 °C

tional conversion has been found by investigating scans at different cure temperatures, and a formula for the calculation of the fractional conversion  $\alpha$  can be written as follows

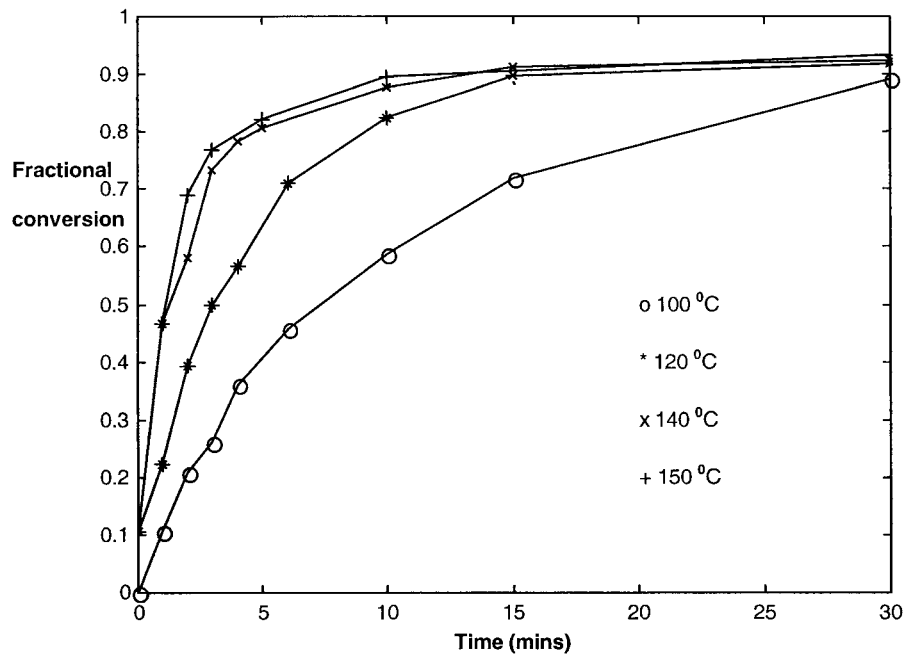
$$\alpha_e(t) = 1 - \frac{(A)_{t=t}}{(A)_{t=0}} \quad (5)$$

Experimental spectra rarely give zero baseline absorbance, but the reference band allows this baseline error to be corrected. The practical formula for fractional conversion is therefore

$$\alpha_e(t) = 1 - \frac{(A_{1131}/A_{1603})_{t=t}}{(A_{1131}/A_{1603})_{t=0}} \quad (6)$$



**Fig. 8** DSC scans of a DGEBA/DMMB-CHA mixture cured at 80 °C for different periods of time

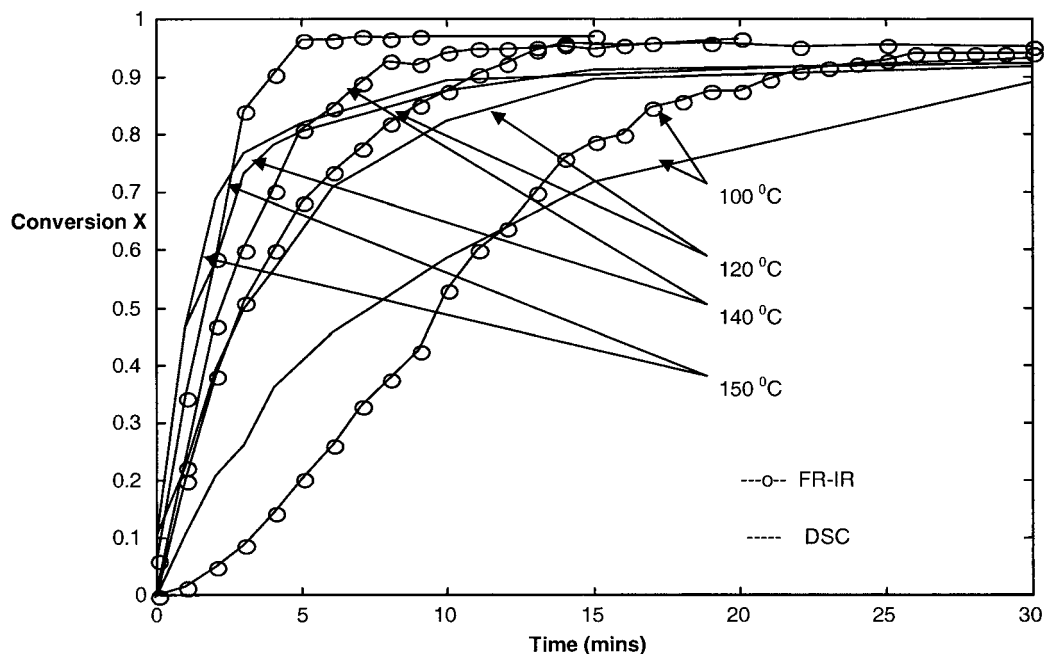


**Fig. 9** Plot of fractional conversion versus time given by DSC for the DGEBA/DMMB-CHA reaction at four different curing temperatures: 100, 120, 140 and 150 °C

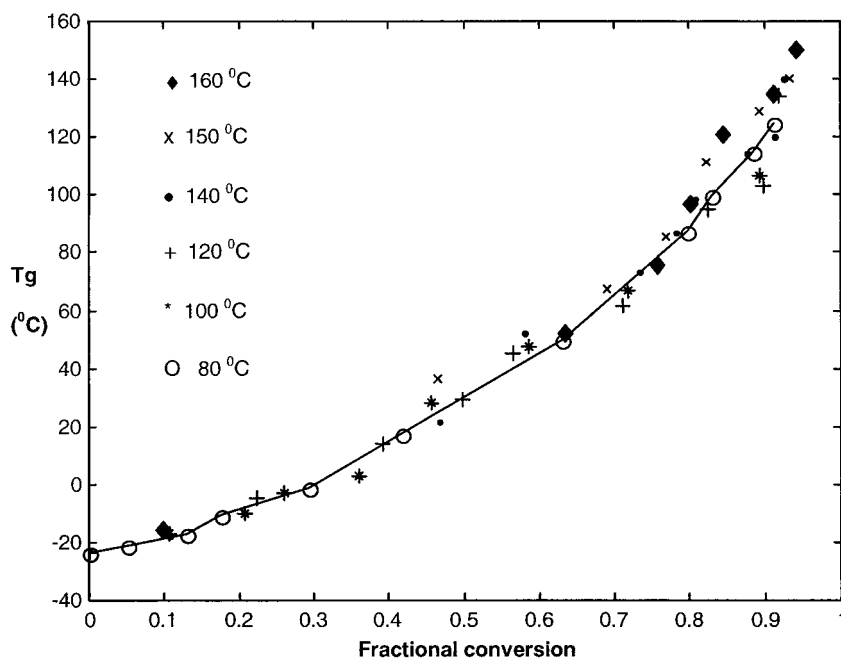
where  $A_{1131}$  and  $A_{1603}$  represent the peak areas for epoxide (oxirane ring) and reference aromatic groups (benzene ring) respectively. Curves of fractional conversion of epoxy resins cured by DMMB-CHA hardener at four different temperatures, 100, 120, 140 and 150 °C, were produced using equation (6) and are shown in Fig. 7.

#### 4.2 DSC study

Figure 8 shows a differential scanning calorimetry run of a sample cured at 80 °C for different lengths of time, and the same DSC runs for samples cured at 100, 120, 140 and 150 °C were also performed. Both glass transition tempera-



**Fig. 10** Graph showing a comparison of the results from the DSC and FT-IR methods used to investigate the cure of the epoxy/amine system at four different curing temperatures



**Fig. 11** Glass transition temperatures versus the fractional conversion produced by DSC for samples cured at 80, 100, 120, 140, 150 and 160 °C

ture,  $T_g$ , and enthalpy of reaction,  $\Delta H_r$ , changed with time—the  $T_g$  increased while  $\Delta H_r$  decreased until the reaction was completed. The residual exotherm was used to calculate the extent of the reaction according to equation (7). It can be seen in Fig. 8 that, although in the later stages of cure,  $T_g$  continues to show an increase and the residual exotherm is not measurable from the DSC scans. The residual enthalpy of reaction becomes very small and difficult to determine accurately at high conversion rates.

The total enthalpy of reaction ( $\Delta H_T = -102.6$  cal/g epoxide) was determined in a similar way by scanning an initial (uncured) sample. The fractional conversion  $x$  was quantitatively calculated as

$$x = 1 - \frac{\Delta H_r}{\Delta H_T} \quad (7)$$

The kinetic rate of the reaction changed with curing temperature. These data are used for the prediction of the chemical conversion achieved after any cure schedule.

The changes in the glass transition temperature and the residual enthalpy of reaction were monitored and the results were used to obtain the fractional conversion for the epoxy resin/amine system as a function of time. To plot the curve of the glass transition temperature against fractional conversion, the same procedure as that adopted by Wang [17] was used. A universal graph was also developed to enable fractional conversion to be obtained as a function of time and curing temperature. For the four chosen curing temperatures, 100, 120, 140 and 150 °C, glass transition temperatures determined by DSC method were converted to the fractional conversion measured using residual enthalpies

of reaction as shown in Fig. 9, in the same manner as that reported by Wang [17].

### 4.3 Comparing the fractional conversions from FT-IR and DSC

These values of fractional conversion produced by DSC were compared graphically with values of fractional conversion at the same curing temperatures found by FT-IR OFS. The results are shown in Fig. 10.

The glass transition temperatures might be deduced from the fractional conversion curves produced by an FT-IR spectroscopy study using the fitting polynomial equation (8) already calculated by the DSC technique in a previous publication [32], which describes the curves illustrated in Fig. 11. The graph of  $T_g$  versus fractional conversion at 80 °C is perfectly representative of the complete range of curing temperatures, as can be seen from the figure

$$y = 141.09x^2 + 29.753x - 22.472 \quad \text{with } R = 0.9987 \quad (8)$$

## 5 DISCUSSION

An optical fibre sensor was designed, constructed and embedded into a epoxy resin/amine matrix for composites to monitor the cure on a real-time basis. Spectra collected by FT-IR OFS were processed by monitoring the bands associated with the most active chemical groups in the molecular structure of the mixture. Based on the findings of Dodoff [21] and Némec *et al.* [10], the disappearance of the peak at  $1131 \text{ cm}^{-1}$  initially existing only in the epoxy

is due to the C–O bond of the oxirane ring, which opens when the reaction of epoxy resin with amine occurs. The  $\rho\text{CH}_3$  existing in the epoxy monomer also vibrates between 1132 and 1136  $\text{cm}^{-1}$ , but these vibrations are not supposed to disappear in the present reaction, which led to the conclusion that, at this frequency, the oxirane ring is clearly disappearing and shifting from 1131 to 1135  $\text{cm}^{-1}$ . The vibration of the C–O bond was also unaffected by other vibrations. It shifted gradually to the left towards lower wavelengths as the cure progressed. The reference peak used in this work was at 1603  $\text{cm}^{-1}$ , which is due to the C–H stretching frequency characteristic of the benzene ring. It did not change during the reaction since it was not involved in it.

It has also been concluded from a theoretical demonstration that the area under an infrared band of an FT-IR spectrum is proportional to the number of atoms involved in the reaction. By using the 1131  $\text{cm}^{-1}$  peak, which corresponds to the epoxy ring vibration, changes in the amount of uncured epoxy resin over the curing period were plotted against time. These were converted to the fractional conversion versus time. It has been found that the maximum fractional conversion produced by the FT-IR OFS method ranges from 93 to 96 per cent for the four curing temperatures. These values of fractional conversion were compared graphically with the values of fractional conversion at the same curing temperatures that were found by DSC study for the same mixture.

From the curves shown in Fig. 10, the maximum fractional conversion achieved ranged from 93 to 96 per cent for the four curing temperatures. These results suggested that there was no side reaction involving epoxide at high temperature. However, a smaller amount reacted at lower temperature, making it impossible to reach 96 per cent conversion at a cure temperature of 100 °C.

FT-IR spectroscopy and DSC studies show that the reaction stops when the glass transition temperature,  $T_g$ , of the molecular network reaches a value close to the curing temperature. A further increase in temperature above the actual  $T_g$  results in a new increase in mobility of the reactive groups in the system, and the reaction continues until the mobility at higher temperature becomes low enough to stop it.

Results from the two methods are close to each other, particularly below 75 per cent conversion and at temperatures above 100 °C, for which after 20 min cure all the results align at 93 per cent conversion, shifting gradually to 96 per cent late in the cure. The graphical presentation is limited to the first half-hour of the reaction, where the reaction was almost completed.

## 6 CONCLUSION

The FTIR spectroscopy method has once again proven to be capable of measuring the change in concentrations of the reactants and products involved in the curing epoxy/amine

reaction. A chalcogenide optical fibre type was selected to build the OFS sensor designed, constructed and tested successfully for transmitting mid-infrared electromagnetic waves. It was embedded into an epoxy/amine mixture for real-time monitoring of the curing process as a measure of the progress in the reaction over the polymerization stage. Careful analysis of the collected FT-IR spectra led to a new peak for monitoring the opening of the epoxy ring at 1131  $\text{cm}^{-1}$ .

Adaptation of the FT-IR method to a quantitative evaluation of changes in concentrations was performed via monitoring changes in peak area at this frequency which were converted to fractional conversion. These were later translated into glass transition temperatures using a fitting polynomial produced from the DSC study. Comparison of fractional conversions from the FT-IR and DSC methods was carried out, and the degree of correlation was found to be satisfactory up to 75 per cent of the chemical conversion.

For future research a number of recommendations are being considered, such as using a filter at the end face of a single optical fibre to allow one frequency (1135  $\text{cm}^{-1}$ ) to pass through and reach the detector at the other end. Recording changes in the intensity of the transmitted beam will be used as a measure of the change in the concentration of the epoxy resin in the mixture. Another possibility is using a photoelectric detector sensitive only to the 1135  $\text{cm}^{-1}$  vibration which might be translated into an electrical signal as a method for monitoring the progress of the reaction.

## REFERENCES

- 1 Debakker, C. J., George, G. A., St John, N. A. and Fredericks, P. M. The kinetics of the cure of an advanced epoxy resin by Fourier transform Raman and near-infrared spectroscopy. *Spectrochim. Acta Part A—Molecular Spectrosc.*, 1993, **49**, 739–752.
- 2 Powell, G. R., Crosby, P. A., Waters, D. N., France, C. M., Spooner, R. C. and Fernando, D. In situ cure monitoring using optical fibre sensors—a comparative study. *Smart Mater. Struct.*, 1998, **7**, 557–768.
- 3 George, G. A., Cole-Clarke, P., St John, N. and Friend, G. Real-time monitoring of the cure reaction of TGDDM/DDS epoxy resin using fibre optic FT-IR. *Polymer*, 1991, **42**, 643–657.
- 4 Cossins, S., Connell, M., Cross, B., Winter, R and Kellar, J. In situ near-IR cure monitoring of a model epoxy matrix composite. *Appl. Spectrosc.*, 1996, **50**, 900–905.
- 5 Nishio, E., Ikuta, N., Okabayashi, H. and Hannah, R.W. Effectiveness of using NIR evanescent wave. *Appl. Spectrosc.*, 1990, **44**, 614.
- 6 Compton, D. A. C., Hill, S. L., Wright, N. A., Dury, M. A., Piche, J., Stevenson, W. A. and Virdine, D. W. In situ FT-IR analysis of a composite curing reaction using a mid-infrared transmitting optical fiber. *Appl. Spectrosc.*, 1988, **42**, 972.
- 7 Dury, M. A., Elandjian, L. and Stevenson, W. A. Composite cure monitoring with infrared transmitting optical fibers. *Proc. SPIE*, 1988, **986**, 130.

- 8 Dury, M. A., Elandjian, L., Stevenson, W. A., Driver, R. D., Leskowitz, G. M. and Curtiss, L. E. Fiber optic smart structures and skins II. *Proc. SPIE*, 1989, **1170**, 150.
- 9 Mijovic, J. and Andjelic, S. In situ real-time monitoring of reactive system by remote fibre-optic near-infrared spectroscopy. *Polymer*, 1995, **36**(19), 3783–3786.
- 10 Némec, I., Cisarova, I. and Micka, Z. The crystal structure and vibrational spectra of mono-l-valinium nitrate: DSC, FTIR, and X-ray diffractational study of low-temperature phase transition. *J. Solid State Chem.*, 2001, **158**, 1–13.
- 11 Delpech, M. C., Coutinho, F. M. B. and Habibe, S. M. E. Bisphenol A-based polycarbonate: characterisation of commercial samples. *Polym. Test.*, 2002, **21**, 155–161.
- 12 Pouliot, R., Germain, L., Auger, F. A., Tremblay, N. and Juhasz, J. Physical characterisation of stratum corneum of an in vitro human skin equivalent produced by tissue engineering and its comparison with normal human skin by ATR-FTIR spectroscopy and thermal analysis (DSC). *Biochim. Biophys. Acta*, 1999, **1439**, 341–352.
- 13 Wiecek, W., Such, K., Florjanczyk, Z. and Stevens, J. R. Polyacrylamide based composite polymeric electrolytes. *Electrochim. Acta*, 1995, **13–14**, 1417–2420.
- 14 Akovali, G. and Atalay, A. Comparison of crystallinities of high density polyethylene determined by different techniques. *Polym. Test.*, 1997, **16**, 165–171.
- 15 Tanikawa, S. and Miyajima, K. Calorimetric and infrared spectroscopic study of phase behavior of hydroxyceramides/cholesterol-3-sulfate system. *Chem. and Phys. Lipids*, 1995, **77**, 121–130.
- 16 Jahromi, S. Liquid crystalline epoxide thermosets: a deuterium nuclear magnetic resonance study. *Macromolecules*, 1994, **27**, 2804–2813.
- 17 Wang, X. and Gillham, J. Competitive primary amine/epoxy and secondary amine/epoxy reactions: effect on the isothermal time-to-vitrify. *J. Appl. Polym. Sci.*, 1991, **43**, 2267–2277.
- 18 Gilbert, M. D. and Schneider, N. S. Mechanism of the dicyandiamine/epoxide reaction. *Macromolecules*, 1991, **24**, 360–369.
- 19 Djaoued, Y., Badilescu, S., Ashrit, P. V. and Robicahud, J. Vibrational properties of sol–gel prepared nanocrystalline TiO<sub>2</sub> thin films. *The Internet J. Vibr. Spectrosc.*, 2001, **5**, 6.
- 20 Gao, T. and Ci, Y. Fourier transform infrared spectroscopy features of human breast benign and malignant tissues. *The Internet J. Vibr. Spectrosc.*, 1999, **3**, 5.
- 21 Dodoff, N. I. Conformational and vibrational analysis N-3-pyridinylmethane sulphonamide. *The Internet J. Vibr. Spectrosc.*, 1999, **4**, 3.
- 22 Martin, S. J., McBrierty, V. J. and Douglass, D. C. Comparison of real time monitoring of copolymer formation and composition by NMR, FTIR and numerical simulation. *Macromolecules*, 2001, **34**, 8934–8943.
- 23 Inauen, A., Howel, J. and Leutwyler, S. Intermolecular bonding and vibrations of phenol-oxirane. *J. Chem. Phys.*, 1999, **110**(3), 1463–1474.
- 24 Finzel, M. C. and Delong, J. Effect of stoichiometry and diffusion on an epoxy/amine reaction mechanism. *J. Polym. Sci.*, 1995, **33**, 673–689.
- 25 Scherzer, T. Ft-ir-rheo-optical characterisation of the molecular orientation behaviour of amine cured epoxy resins during cyclic deformation. *Polymer*, 1996, **37**(26), 5807–5816.
- 26 Don, T. M. and Bell, J. P. Fourier transform infrared analysis of polycarbonate/epoxy mixture cured with an aromatic amine. *J. Appl. Polym.*, 1998, **69**, 2395–2407.
- 27 Sandner, B. and Kammer, S. Crosslinking copolymerisation of epoxy methacrylates as studied by Fourier transform Raman spectroscopy. *Polymer*, 1996, **37**(21), 4705–4712.
- 28 Hamerton, I. and Hay, J. N. Probing the cure of C<sup>13</sup> labelled bisphenol A dicyanate ester in carbon fibre reinforced composites using solid state C<sup>13</sup> NMR, SEM and FTIR. *Polym. Bull.*, 1997, **38**, 433–438.
- 29 Johnck, M. and Muller, L. Quantitative determination of unsaturation in photocured halogenated acrylates and methacrylates by FTIR and Raman-spectroscopy and by thermal analysis. *Polymer*, 1999, **40**, 3631–3640.
- 30 Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd edition, 1975 (Chapman and Hall, Wiley, New York).
- 31 Williams, D. H. and Fleming, I. *Spectroscopy Methods in Organic Chemistry*, 5th edition, 1995 (McGraw-Hill, London).
- 32 Fouchal, F., Knight, J. A. G., Garrington, N. and Cope, B. Optical fibre sensor for an on-line monitoring of epoxy resin/amine reaction. 28th Annual Review of *Progress in Quantitative Non-destructive Evaluation*, Iowa State University, 2001, pp. 961–968.