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# *In-situ* monitoring of cross-linking reactions using E-glass fibres and evanescent wave spectroscopy

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ABSTRACT

E-glass fibres are used in products such as printed circuit boards, wind turbine blades, pipes, marine vehicles and pressure vessels. With reference to the production of fibre reinforced composites, the reinforcement (E-glass) is impregnated with a resin system, consolidated and generally processed by the application of heat. This results in the resin system being converted from a liquid or semi-solid to a highly cross-linked and infusible solid. There is significant interest in monitoring the progression of these cross-linking or chemical reactions and a number of optical and electrical, ultrasonic-based techniques have been developed and demonstrated. The current paper reports on the use of the reinforcing E-glass fibres to track the cross-linking of commercially available epoxy/amine resin systems. The mode of interrogation was based on using the E-glass fibres as evanescent wave sensors thus enabling Fourier transform infrared spectroscopy to be conducted. This enabled the cross-linking reactions at the glass/resin interface to be monitored. Conventional transmission Fourier transform infrared spectroscopy experiments were also conducted. The cross-linking kinetic data from the two methods were modelled and compared. A good correlation was obtained between the experimental and predicted data using a single rate constant.

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## 1. Introduction

E-glass fibres are used extensively as the reinforcement in the production of high-volume and high-value fibre reinforced composites. The prefix "E" in E-glass is used to describe its primary area of applications (electrical grade) and composition (predominantly oxides of boron, sodium, calcium, aluminum and silicon). The filaments are produced by drawing the molten material through bushings that contain a multitude of fine orifices [1]. The array of molten filaments is spray-cooled to prevent crystallization. A "binder" solution is applied before the filaments are gathered into a bundle and wound to produce a creel. The term "Tex" is used to describe the bundle; Tex is defined as the mass in grams of 1000 m of the fibre bundle. A characteristic feature of E-glass is its low dielectric strength and as such, it is used extensively in the manufacture of printed circuit boards and applications where electrical insulation is required. The mechanical properties of E-glass fibres and its relative cost are key drivers in its extensive utilisation in the chemical, construction, wind energy, recreation, aerospace and marine industries.

With reference to the production of thermoset-based composites, the E-glass preform (fibre bundle or fabric) is impregnated with a resin system (for example, epoxy/amine, vinyl ester, polyester), stacked, with the fibres in the required direction, and consolidated. The cross-linking reactions are generally initiated when the resin and hardener is mixed, and they are accelerated by the application of heat. Since the focus of the current paper is on epoxy/amine resin systems, Fig. 1 presents generalised reactions involving these two classes of functional groups [2]. In Fig. 1, reaction scheme (i) represents the predominant reaction pathway between the epoxy and primary amine functional groups whilst reaction scheme (ii) shows the generalised reaction between the secondary amine that is formed as a consequence of reaction (i). Side-reactions (iii) and (iv) are also known to occur under certain conditions. For example, as illustrated in (iii), hydroxyl groups are known to catalyse the epoxy ring opening reactions [3]. Techniques such as differential scanning calorimetry [4] and Fourier transform infrared spectroscopy [5–8] continue to be used extensively to characterise thermoset-

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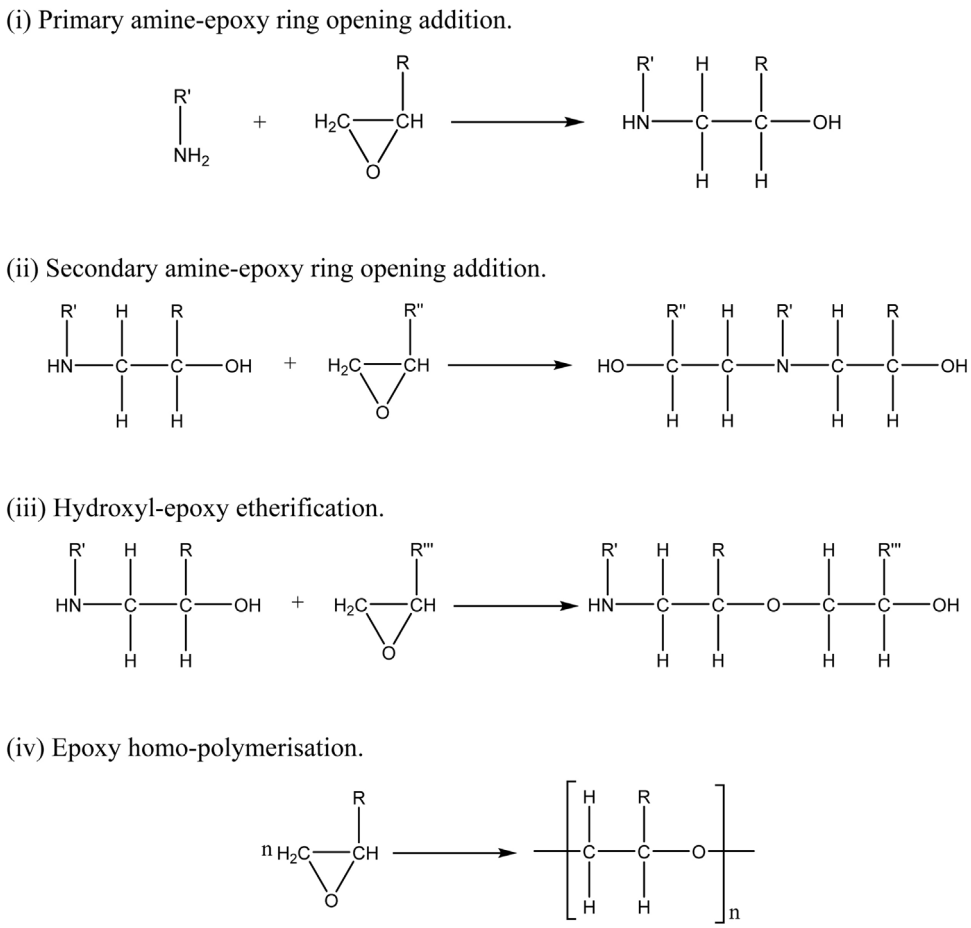


**Fig. 1.** Generalised reaction schemes for an epoxy resin and amine hardener system: (i) primary amine reaction; (ii) secondary amine reaction; (iii) reaction between hydroxyl and epoxy leading to an ether link; and (iv) homo-polymerisation of the epoxy functional group.

ting resins. More recently, a number of optical fibre-based sensing techniques have been developed to track the progression of the cross-linking reactions [9,10]. With reference to optical fibre-based Fourier transform infrared spectroscopy, quantitative and real-time data can be acquired on the relative depletion of reactive functional groups as a function of the processing temperature and time. The feasibility of using the reinforcing fibres as a sensor for chemical process monitoring and damage detection has also been demonstrated [11]. The advantages of using reinforcing glass fibres as the sensing device are as follows: (i) they can provide *in-situ* information on the cross-linking kinetics of thermosetting resins; (ii) the sensors can be interrogated in the intensity or evanescent modes where qualitative and quantitative data respectively can be obtained; (iii) the sensor does not cause any perturbation to the reinforcing fibres since there is no diameter mismatch; and (iv) uniquely, they provide a means for obtaining cross-linking data in the vicinity of the interface between the reinforcing fibres and the matrix [12]. In addition to transmission and reflection Fourier transform infrared spectroscopy, attenuated total reflections (ATR) spectroscopy is a long-established method for identifying specified functional groups [13,14]. ATR spectroscopy is based on the absorption of the evanescent field by the medium. The theoretical aspects of evanescent wave spectroscopy are presented in Section 2.5.

The aim of the present paper is to demonstrate that conventional E-glass fibres can be used as pseudo-optical fibres to monitor the progression of cross-linking reactions using evanescent wave spectroscopy. The primary advantage of this approach is that the reinforcement itself is used as the sensing element thus providing a representation of the cross-linking reactions occurring at the glass fibre/resin interface. Furthermore, since the surface composition of the "sensor" in this instance is similar to the reinforcing fibres, the cross-linking reactions as a function of specified surface-treatments can be investigated.

## 2. Materials and methods

### 2.1. Sensor

Commercially produced E-glass fibres were used as the sensor for monitoring the cross-linking reactions. E-glass fibres are generally supplied with a proprietary binder system that secures the individual filaments together. However, in this instance, water-sized E-glass fibres were supplied by PPG Industries (UK). These bundles consisted of approximately 2500 individual filaments with a diameter of $15 \pm 3\ \mu m$. The refractive index of the E-glass preform (disks) was 1.56; these measurements were conducted on an Abbe refractometer at 589.6 nm and 20 °C using bromo-naphthalene as the contact liquid. Approximately 8 cm of the bundle was cut from the creel using a razor blade. In order to enable efficient coupling of light into and out of the ends of the bundle, they were potted into sub-miniature A-type (SMA) connectors using an epoxy resin (EPO-TEK® 314, Promatech Ltd). The refractive indices at the start and end of the cross-linking reactions were measured to be as 1.4917 and 1.5162 respectively. The protruding ends of the bundle were ground and polished using an optical fibre polishing unit (APC 8000 polisher, SENKO Advanced Composites Ltd). A photograph of a polished section of the E-glass fibre bundle with a pair of end-connectors is shown in Fig. 2. The length of the sensing area was

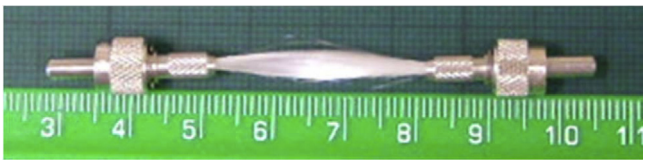

**Fig. 2.** Photograph showing a length of the water-sized E-glass bundle potted in a pair of SMA connectors.

approximately 6 cm. In other words, in addition to the un-potted region seen in Fig. 2, the sections of the bundle inside the SMA connectors also serve as the sensing region. This was possible because only the protruding regions of the SMA connectors contained the potting resin. Thus, when the sensing region is impregnated with the resin, it can wick into the SMA connector.

### 2.2. Resin systems

The epoxy/amine resin system used in this study was EPO-TEK 310M® (Promatech Ltd, UK). The refractive indices of this resin system as a function of temperature was described by $Y_{(refractiveindex)} = -0.0006X_{(temperature)} + 1.5504$ [15]. Thus, it was possible to track the cross-linking reactions to completion using E-glass fibres as the evanescent wave sensor. The stoichiometric ratio for this epoxy/amine resin system was 1:0.55. The two components were mixed manually and then degassed in a vacuum chamber for 15 min. The mixed resin systems were cured isothermally at 35 °C, 45 °C, 55 °C and 65 °C for specified periods. An industrial epoxy/amine resin system (LY3505/XB 3403, Huntsman Advanced Materials, UK) was also used to demonstrate that the cross-linking reactions could be monitored using E-glass fibre bundles and evanescent wave spectroscopy. It is known that the refractive indices of thermosetting resins generally increase as a function of the cross-link density [2,8,9]. The refractive indices of the LY3505/XB3403 resin (measured at 25 °C) at the start and after isothermal cross-linking at 70 °C were 1.525 and 1.562 respectively. Since the refractive index of the E-glass preform (disk) is 1.56, evanescent wave spectroscopy can be used in conjunction with E-glass fibres up to the point where the refractive index of the resin system (cladding) approaches and exceeds that of E-glass fibres (core). The rationale for the selection of the second resin was to demonstrate that partial data acquisition during processing could be used to predict the cross-linking kinetics.

### 2.3. Conventional transmission FTIR spectroscopy

Spectra were collected during the cross-linking reactions from 1100 to 4000 cm$^{-1}$ *via* a Bruker MATRIX™ -F Duplex FT-NIR spectrometer (Bruker Optics Ltd, UK) operating at a resolution of 4 cm$^{-1}$ over 64 scans. A CUV-TLC-50 F temperature-controlled cuvette holder (±0.02 °C) from Ocean Optics Inc., Netherlands, housed a demountable optical glass cuvette with a path length of 1 mm (Starna, UK). RTV silicon rubber (3 M) was used to seal the two halves of the demountable cuvette. A syringe was used to dispense the mixed and degassed resin system into the glass cuvette. With reference to Fig. 3(a), two low-OH optical fibre probes were used: one to deliver light from the spectrometer to the cuvette and the other to collect the light that is transmitted through the cuvette and direct it to the InGaAs detector of the spectrometer.

### 2.4. Cross-linking kinetics

The cross-linking kinetics of thermosetting resin have been investigated widely and a variety of kinetic models have been proposed [16–20]. In a previous study [21], the authors used

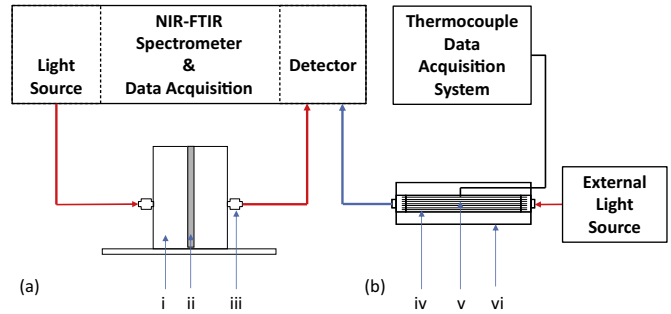


**Fig. 3.** The experimental set-ups for: (a) conventional transmission spectroscopy; and (b) evanescent wave spectroscopy. The details of the coded items are as follows: i—temperature regulated transmission FTIR spectroscopy cuvette holder with integral SMA connectors for linking to the spectrometer *via* a fibre optic cable; ii—demountable 1 mm path length quartz cuvette; iii—SMA connector enabling optical connection to the spectrometer; iv—impregnated E-glass bundle attached to a pair of SMA connectors; v—thermocouple; and vi—purpose-built oven.

an autocatalytic model to cross-correlate the cross-linking data from a conventional differential scanning calorimeter (DSC) and a hyphenated analytical technique based on simultaneous DSC/FTIR spectroscopy [21]. The autocatalytic model can be described as:

$$\frac{d\alpha}{dt} = k\alpha^m \times (1-\alpha)^n \tag{1}$$

where k is the rate constant, α is the conversion of a specified functional group, t is time, and m and n represent the reaction orders. In this current study involving EPO-TEK® 310M, equation 10 was elaborated to model the cross-linking kinetics under isothermal conditions using reaction orders of m = 0.35 and n = 1.65:

$$\frac{d\alpha}{dt} = k\alpha^{0.35} \times (1-\alpha)^{1.65} \tag{2}$$

$$\int \frac{d\alpha}{\alpha^{0.35} \times (1-\alpha)^{1.65}} = kt \tag{3}$$

$$t = \frac{1}{k}\frac{20}{13}\left(\frac{\alpha}{1-\alpha}\right)^{0.65} \tag{4}$$

The degree of epoxy conversion (α) was calculated from the evanescent wave and transmission FTIR spectra using Eq. (5):

$$\alpha = 1 - \left[\frac{\frac{A_{Epoxy,t}}{A_{Reference,t}}}{\frac{A_{Epoxy,t=0}}{A_{Reference,t=0}}}\right] \tag{5}$$

where $A_{Reference,t=0}$ and $A_{Reference,t}$ refer to the areas of the "inert" or reference peak (4620 cm$^{-1}$) at the start of the reaction (t = 0) and after time (t) respectively. $A_{Epoxy,=0}$ and $A_{Epoxy,t}$ are the areas of the epoxy peak (4530 cm$^{-1}$) for the uncured and partially cured resin at a specified time respectively.

### 2.5. Evanescent wave FTIR spectroscopy

The following section set out the background theory for evanescent wave spectroscopy. Consider an interface of an optically denser and rarer media with refractive indices $n_1$ and $n_2$ respectively. When light is incident from the denser medium at the interface of the denser-rarer media with an angle of incidence greater than the critical angle, defined as,

$$\theta_c = sin^{-1}\left(n_2/n_1\right) \tag{6}$$

the beam is totally reflected back into the denser medium. Interestingly, light is not instantaneously reflected when it reaches the interface instead of this the superposition of incident and reflected beams results in the formation of a standing electromagnetic wave

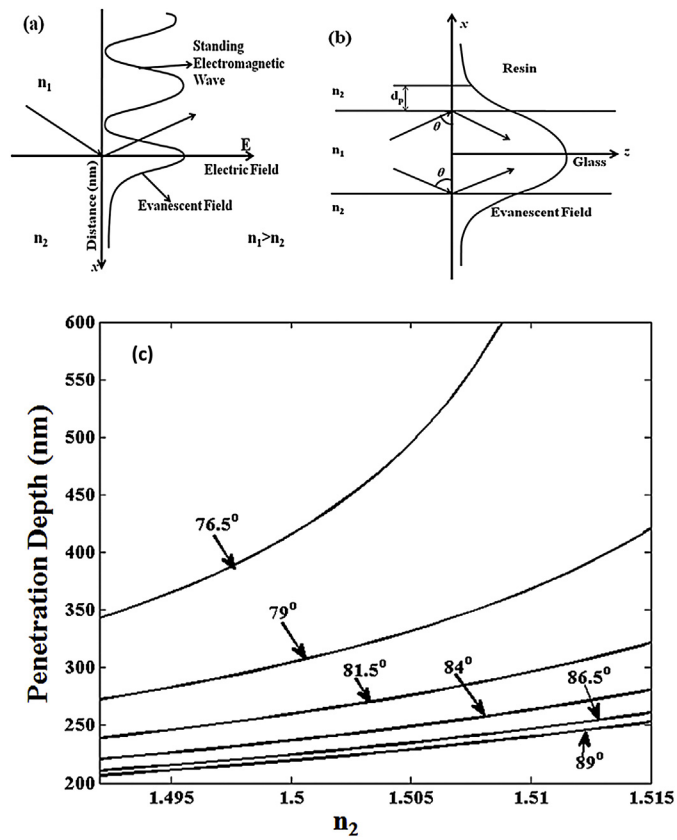


**Fig. 4.** Schematic illustration of: (a) production of evanescent wave at an interface; (b) evanescent wave phenomenon at the core-cladding interface in an optical fibre; and (c) penetration depth as a function of refractive index of rarer medium ($n_2$) for different values of angle of incidence of the ray with $n_1 = 1.56$ and $\lambda = 589.6$ nm.

at the interface as shown in Fig. 4(a). The electric field amplitude is maximum at the interface and it decays exponentially along the outward normal to the interface. The decaying field in the rarer medium is called the evanescent field whilst the electromagnetic wave associated with it is called the evanescent wave, and it propagates along the interface [22]. The electric field amplitude (E) along the normal to the interface at a distance $x$ is given by:

$$E = E_0 \exp\left(-x/d_p\right) \tag{7}$$

where $E_o$ is the electric field amplitude at the interface and $d_p$ is the penetration depth whose magnitude is given by:

$$d_p = \frac{\lambda}{2\pi\left(n_1^2 sin^2\theta - n_2^2\right)^{1/2}} \tag{8}$$

where $\lambda$ is the wavelength of light in vacuum and $\theta$ is the angle of incidence of the ray with the normal to the interface. Fig. 4(b) shows the presence of an evanescent field in an optical fibre with $n_1$ as the refractive index of the core and $n_2$ as the refractive index of the cladding region. The energy distribution in the core has its peak on the axis of the fibre whilst the evanescent field in the cladding decays exponentially in the direction normal to the core-cladding interface. The existence of an evanescent field is used extensively for chemical sensing. If the fibre cladding is replaced by an absorbing medium, the evanescent field is absorbed by the medium giving rise to a reduction in the power transmitted through the fibre. The absorption of the evanescent field by the cladding medium has been exploited for the development of a large number of chemical and biological sensors. The larger the absorption, the greater the sensitivity of the sensor. For a given absorbing medium, the amount of absorption depends on the penetration depth of the evanescent field. An increase in the penetration depth increases the absorption and hence the sensitivity of the sensor. For a given light source and fixed refractive index of the core of the fibre, the penetration depth depends on the refractive index of the absorbing cladding medium, and the angle of incidence of the beam at the core-cladding interface. Fig. 4(c) shows the variation of penetration depth with the refractive index of the cladding medium for different values of the angle of incidence greater than the critical angle. It may be noted from Fig. 4(c) that for a given angle of incidence, as the refractive index ($n_2$) of the cladding medium increases, the penetration depth increases. It may also be noted that, for a given refractive index of the cladding medium, the penetration depth increases with the decrease in the angle of incidence. Since the refractive index of the resin around the E-glass fibre increases during cross-linking the penetration depth will also increase during cross-linking and hence the absorption of the evanescent field by the resin. In addition to this, the critical angle also increases during the cross-linking. Thus the absorption of light transmitted through the fibre will change during cross-linking. This will further be affected if the absorption coefficient of the resin changes during cross-linking. In the case of an optical fibre, a large number of reflections of a ray occur at the core-cladding interface as it propagates. For a ray with θ as the angle of incidence, the number of reflections per unit length of the fibre of core radius ρ is given by [23]:

$$N = \frac{\cot\theta}{2\rho} \tag{9}$$

The larger is the number of reflections, the greater the absorption. If $P_o$ is the power transmitted by the fibre in the absence of resin around the core, then the power transmitted in the presence of resin is given by:

$$P = P_o exp\left(-\gamma L\right) \tag{10}$$

where $L$ is the length of the fibre with resin around it and $\gamma$ is the evanescent absorption coefficient of resin and is written as:

$$\gamma = NT \tag{11}$$

where T is the Fresnel transmission coefficient of the light at the interface of a lossless core and lossy cladding. If $n_2 - ik$ is the refractive index of resin, then T can be written as:

$$T = \frac{\alpha\lambda n_2 cos\theta}{\pi n_1 cos^2\theta_c\left(n_1^2 sin^2\theta - n_2^2\right)^{1/2}} \tag{12}$$

where $\alpha = 4\pi k/\lambda$ is the bulk absorption coefficient of the resin at wavelength $\lambda$. The evanescent absorption coefficient for a given angle θ and refractive index of resin ($n_2$) is given by:

$$\gamma\left(\theta, n_2\right) = \frac{\alpha\lambda n_2 \cos\theta cot\theta}{2\pi\rho n_1 cos^2\theta_c\left(n_1^2 sin^2\theta - n_2^2\right)^{1/2}} \tag{13}$$

If all the guided rays are launched into the fibre, then the effective evanescent absorption coefficient of resin is given by [24]:

$$\gamma_{eff}\ n_2 = \frac{\int_{\theta_c}^{\pi/2} p\ \theta\ \gamma\ \theta, n_2\ d\theta}{\int_{\theta_c}^{\pi/2} p\ \theta\ d\theta} \tag{14}$$

where $p(\theta)$ is the power distribution of the rays. Since during cross-linking the refractive index of the resin changes, the limit of integration in the above equation will also change because of the change in the critical angle. Thus the progress of cross-linking reactions can be monitored through the monitoring of change in effective evanescent absorption coefficient.

The previously mentioned near-infrared FTIR spectrometer was used to acquire evanescent wave spectra during the cross-linking of the two resin systems. Spectra were obtained at a resolution

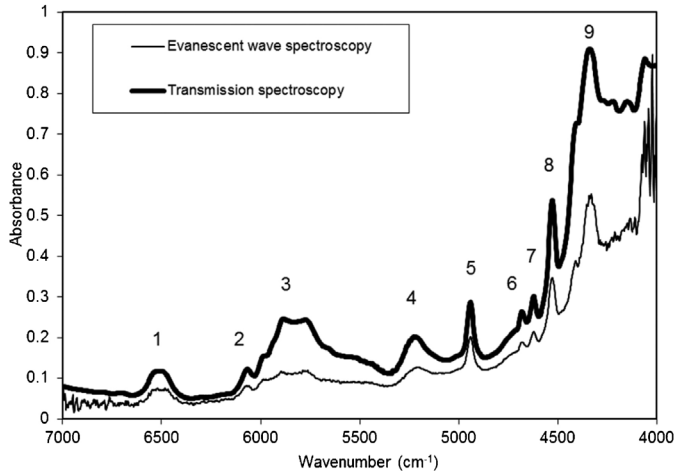


**Fig. 5.** Transmission and EWS FTIR spectra for EPO-TEK® 310M resin systems.

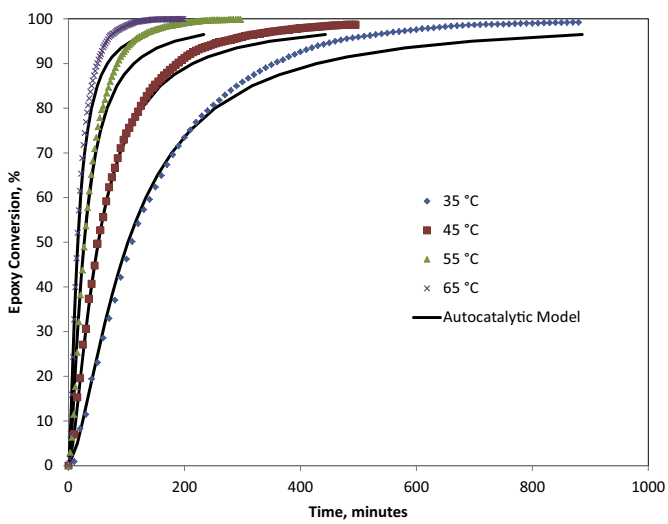


**Fig. 6.** Combined plots for the transmission FTIR spectroscopy-based epoxy conversion data at 35, 45, 55 and 65 °C for the EPO-TEK® 310M resin system. The curve-fit using the autocatalytic model is also represented for each temperature.

of 2 $cm^{-1}$ over 128 scans. An external white-light source, WLS100 (Bentham Instruments Ltd., UK) was used to illuminate the glass fibre bundle. The fibre bundle with the SMA connectors (Fig. 2), were impregnated manually with the degassed resin system. The fibre bundle was secured in a custom-made oven and maintained at the required isothermal temperature (±0.2 °C). Prior to any experiments being undertaken, the oven was calibrated using a thermocouple; the thermocouple was then used to monitor temperature and provide temperature control during the curing of the resin system. A schematic illustration of the experimental set-up for evanescent wave-based monitoring of the cross-linking reactions is shown in Fig. 3(b).

## 3. Results

Fig. 5 shows typical FTIR and EWS spectra for the EPO-TEK® 310M resin system. The associated peak assignments are summarised in Table 1. With reference to Fig. 5, good correlation is observed between the absorbance bands of the various functional groups of the resin system using conventional transmission FTIR spectroscopy (bold line) and E-glass-based evanescent wave FTIR spectroscopy (thin line).

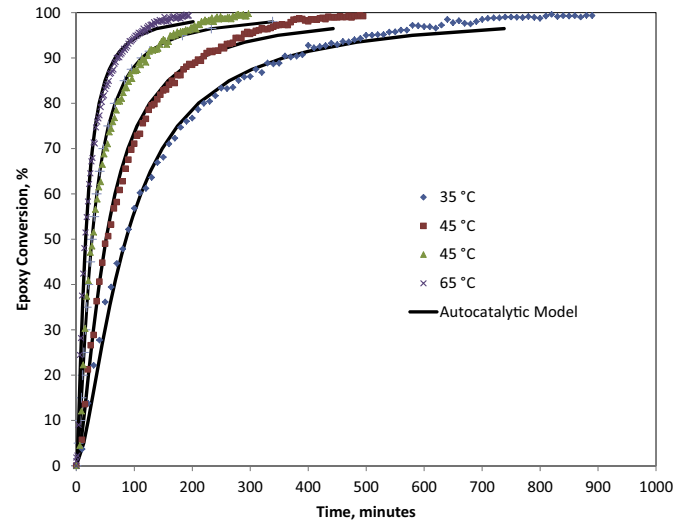


**Fig. 7.** Combined plots for the evanescent wave FTIR spectroscopy-based epoxy conversion data at 35, 45, 55 and 65 °C for the EPO-TEK® 310M resin system. The curve-fit using the autocatalytic model is also represented for each temperature. The predicted trend using the autocatalytic model is also represented.

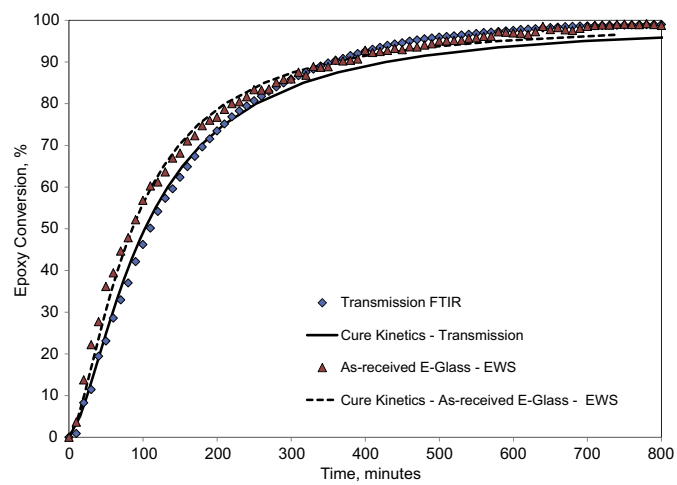


**Fig. 8.** Epoxy conversion α (%) for EPO-TEK® 310M, cross-linked at 35 °C.

The effect of isothermal cross-linking of the EPO-TEK® 310M resin, using conventional FTIR spectroscopy, at 35, 45, 55 and 65 °C is shown in Fig. 6 where as expected, the rate of initial conversion of the epoxy functional group increases with increasing temperature. A higher initial extent of conversion is also observed as the isothermal curing temperature is increased. On inspecting Fig. 7, which represents the corresponding datasets for the isothermal cross-linking of the EPO-TEK® 310M using E-glass fibres as the evanescent wave sensor, an excellent correlation is observed between the experimental and predicted data sets up to in excess of 90% epoxy conversion. A comparison of the epoxy functional group consumption using the data from conventional transmission and evanescent wave spectra, at each isothermal condition, is presented in Figs. 8–11. Fig. 12 shows an Arrhenius plot of ln(k) against 1/T for the evanescent wave sensor and conventional transmission FTIR spectroscopy. Error bars of 5 percent were added to data obtained for the transmission FTIR dataset as shown in Fig. 12. As stated previously, evanescent wave spectroscopy of epoxy resins involving E-glass fibre bundles can be conducted until the refractive index of the cross-linking resin approaches that of E-glass. This means that the cross-linking kinetics of other classes of resins, other than EPO-

**Table 1**
Summary of functional groups and peak assignments for the EPO-TEK® 310M resin system before cross-linking.

| Peak Number | Wavenumber($cm^{-1}$) | Characteristic Functional Group |
|---|---|---|
| 1 | 6498 | First overtone of primary and secondary amine |
| 2 | 6044 | Aromatic band |
| 3 | 5830 | First overtone of $CH_2$ |
| 4 | 5189 | Overtone of $CH_3$ |
| 5 | 4917 | Primary amine |
| 6 and 7 | 4630 | Aromatic band |
| 8 | 4522 | Oxirane ring |
| 9 | 4327 | Overtone of unsaturated CH |

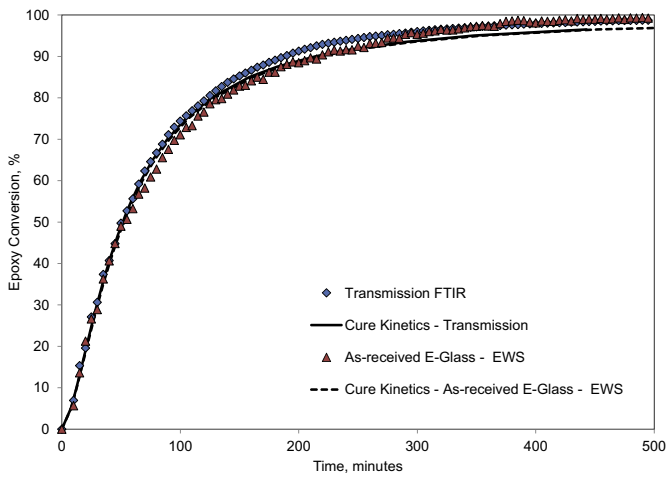


**Fig. 9.** Epoxy conversionα (%) for EPO-TEK® 310M cross-linked at 45 °C.

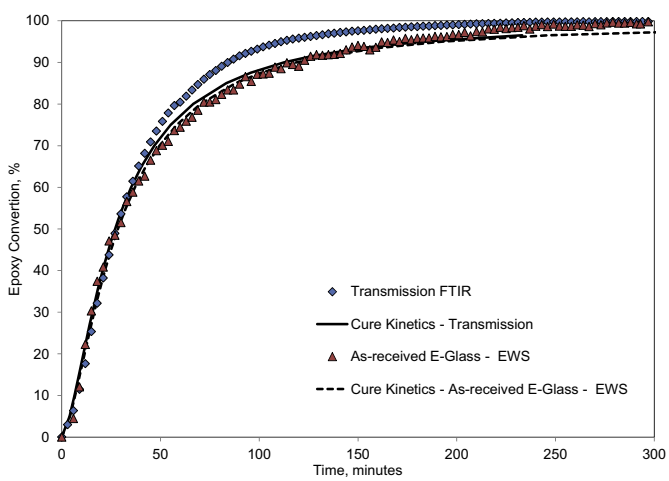


**Fig. 10.** Epoxy conversion α (%) for EPO-TEK® 310M cross-linked at 55 °C.

TEK® 310M, can be tracked in real-time up to a point. This is shown in Fig. 13(a) and (b) and for a commercial epoxy/amine resin system (LY3505/XB3404, Huntsman) where E-glass fibres were used as the sensor for cross-linking of the resin at 60 and 70 °C.

## 4. Discussion

With reference to the data presented in Fig. 5, the relative amplitude for the evanescent wave spectra is lower when compared to the conventional transmission experiments because of the relatively short length of the E-glass fibre bundle. In this instance, the length of the senor was limited by the length of the custom-made oven for heating the impregnated E-glass bundle.

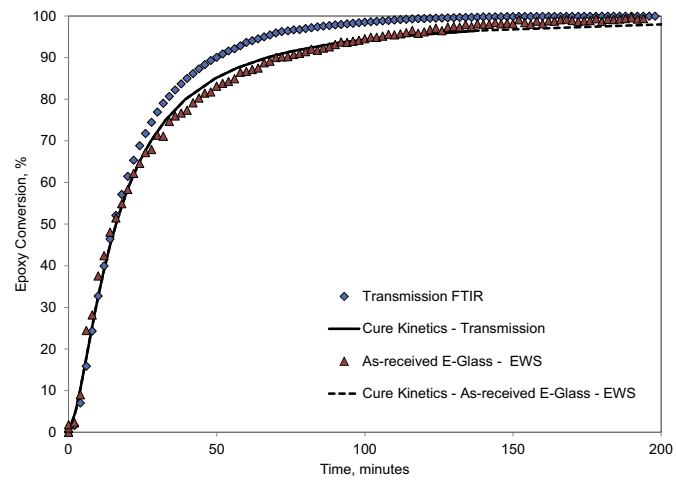


**Fig. 11.** Epoxy conversion α (%) for EPO-TEK® 310M cross-linked at 65 °C.

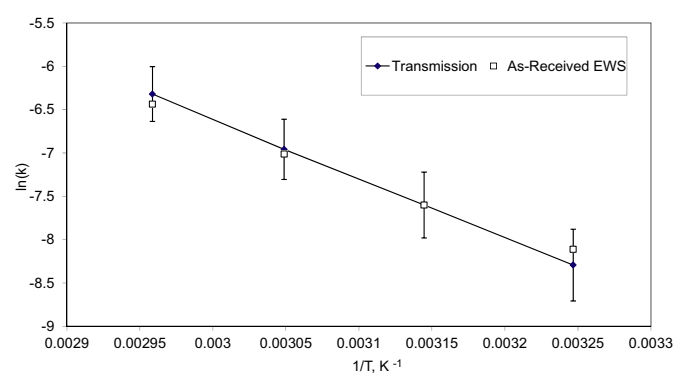


**Fig. 12.** Arrhenius plots for the EPO-TEK® 310M resin system when using conventional transmission and evanescent wave spectroscopy in conjunction with as-received E-glass fibres.

In Figs. 6 and 7, the predicted epoxy functional group conversion, calculated from the autocatalytic model, was fitted to the experimental results from the conventional transmission and evanescent wave FTIR spectroscopy experiments respectively. The rate constants and activation energies for the two sets of experiments are summarised in Table 2. It is apparent from Fig. 6 that the autocatalytic model can be used to predict the cross-linking of the EPO-TEK® 310M resin up to approximately 80% of epoxy conversion. However, a deviation is observed between the experimental and the predicted epoxy conversion after 80%, where the model over-predicts the depletion of the epoxy functional group. The discrepancy between the measured and predicted rate of depletion is generally attributed to: (i) a change in the reaction mechanism from chemical-controlled to diffusion-controlled reactions towards the latter stages [10]; (ii) the fact that the rate constants for the primary and secondary amine reaction rates may be different (a single rate

**Table 2**
Rate constant k for the EPO-TEK® 310M resin system when using transmission and evanescent wave Fourier transform infrared spectroscopy at specified processing temperatures.

| Temperature (°C) | Transmission FTIR Spectroscopy | | Evanescent wave FTIR Spectroscopy | |
|---|---|---|---|---|
| | k | Ln(k) | k | Ln(k) |
| 35 | 0.00025 | −8.29405 | 0.0003 | −8.11173 |
| 45 | 0.0005 | −7.6009 | 0.0005 | −7.6009 |
| 55 | 0.00095 | −6.95905 | 0.0009 | −7.01312 |
| 65 | 0.0018 | −6.31997 | 0.0016 | −6.43775 |
| Activation Energy, kJ mol$^{-1}$ | 56.8 | | 48.5 | |

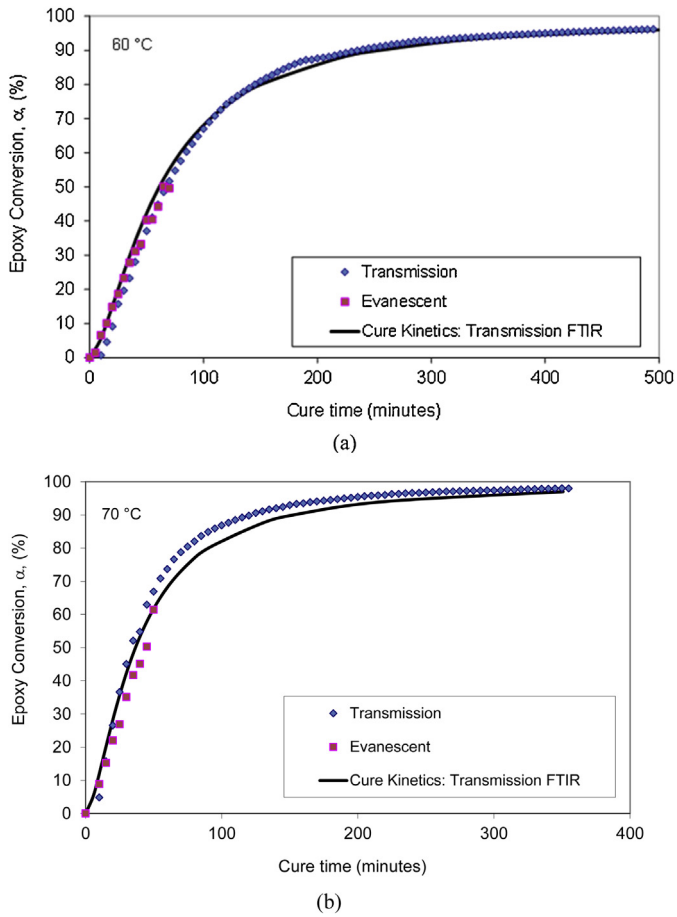


**Fig. 13.** Epoxy conversion α (%) for a high-performance epoxy/amine resin system (LY3505/XB3403) as a function of cross-linking time at (a) 60 °C and (b) 70 °C. The data were generated using conventional transmission FTIR and EWS.

constant is assumed in the auto-catalytic model) [21]; (iii) the sum of the reaction orders, *m* and *n*, being forced to equate to an integer (2 in the current case) in the curve fitting routine; (iv) the observation that when the epoxy conversions are greater than 80%, the signal-to-noise decreases progressively.

In contrast to Fig. 6 (transmission FTIR spectroscopy), an excellent correlation is observed in Fig. 7 (evanescent wave spectroscopy) between the experimental and the predicted trends for the cross-linking characteristics as a function of processing temperature. Possible reasons for the superior correlation observed with the evanescent wave spectroscopy data maybe due to: (i) the large surface area that is available when using 2500 individual E-glass filaments with an average diameter of 15 um diameter with an effective length (including the region inside the SMA connector) of approximately 40 mm; and (ii) as discussed previously, the penetration of the evanescent field increases as a function of refractive index or cross-link density.

With reference to Fig. 8, the cross-linking reactions that were carried out at 35 °C, the rate of epoxy conversion is higher for the evanescent wave spectroscopy dataset when compared with that obtained from conventional transmission spectroscopy. However, after approximately 80% of epoxy conversion, the reaction rates were similar up to near-complete depletion of the epoxy functional group. As the isothermal cross-linking temperature was increased from 35 to 45, 55 and 65 °C (Figs. 8–11), the rate of epoxy conversions were similar for the two cross-linking monitoring methods up to approximately 55%. After this point, the epoxy conversion rate conventional transmission FTIR spectral datasets for the conventional transmission FTIR spectral dataset increased at a faster rate until the depletion of the epoxy functional group. Likely reasons for these observations were discussed previously. A summary of the rate constants at the specified isothermal temperatures are summarised in Table 2.

In Fig. 12, it is apparent that the Arrhenius plots for evanescent wave sensor are similar to those obtained for transmission FTIR spectroscopy data. The conclusion that can be reached on inspecting Fig. 12 is that the cross-linking kinetics of the EPO-TEK® 310M resin system can be monitored effectively using transmission and evanescent wave FTIR spectroscopy; in the latter case, the reinforcing glass fibres were used as the sensor.

The feasibility of monitoring a high-performance thermosetting resin using E-glass fibres as the sensor was presented in Fig. 13(a and b), where the processing was carried out at 60 and 70 °C. With this high-performance resin, it is seen that the modelling of the cross-linking kinetics, using the equations cited previously, match the experimental data for the conventional transmission FTIR spectroscopy and E-glass-based evanescent wave spectroscopy. In this instance, data were obtained up to approximately 50% and 60% conversion of the epoxy functional group. This is because, after these points, the refractive indices of the resin approaches and exceeds that of the E-glass fibres. Thus light guiding in the E-glass is not possible beyond this point. It is proposed that since excellent correlation is seen between the kinetic model and the experimental data, when using evanescent wave spectroscopy to monitor the cross-linking reactions (see Fig. 13(a) and (b)), the partial epoxy conversion data up to 50–60% conversion will suffice for assessing if the cross-linking kinetics are proceeding as expected.

## 5. Conclusions

This study has demonstrated that E-glass fibres can be used as the sensing device to derive the cross-linking kinetics in conjunction with evanescent wave spectroscopy. The theoretical basis for the mode of operation of the evanescent-based "optical fibre" sensor was presented. Two commercially available epoxy/amine resin systems were investigated. In the first case, the refractive index of this resin system, after cross-linking to near-depletion of the epoxy functional group was below that of the refractive index of E-glass. In the second case, the final refractive index of the cross-linked resin was higher than that of E-glass. The impregnated E-glass bundles were conditioned isothermally at

35, 45, 55 and 65 °C whilst conducting *in-situ* evanescent wave spectroscopy *via* a fibre-coupled near-infrared FTIR spectrometer. Conventional transmission FTIR spectroscopy experiments were also conducted in a separate temperature-regulated cuvette at the above-mentioned isothermal conditions. An auto-catalytic cross-linking model was used to predict the cross-linking characteristic of the epoxy/amine resins.

Excellent correlation was observed between the evanescent wave spectroscopy experiments and the auto-catalytic models. In the case of conventional transmission FTIR spectroscopy, the correlation between the measured and experimental data were excellent up to 80% of epoxy conversion; a small deviation was observed after this point. Possible reasons for this discrepancy were discussed.

With reference to the resin system that had a final refractive index that was higher than that of E-glass, as expected, it was only possible to monitor the depletion of the epoxy functional group up to between 50 and 60%. However, it was proposed that since the datasets for the transmission and evanescent wave spectral analyses in this instance match, the previously derived rate constants can be used to track and predict the progression of the cross-linking reactions. The advantage of evanescent wave spectroscopy is that *in-situ* cross-linking kinetic data provides real-time information on specified chemical reactions taking place on the surface of the reinforcing glass fibre.

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