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EFFECT OF SILANE TREATMENT OF E-GLASS ON THE CROSS-LINKING KINETICS OF AN EPOXY RESIN

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SUMMARY

The primary focus of this study was to demonstrate that conventional reinforcing E-glass fibres can be used for *in-situ* monitoring of cross-linking reactions using evanescent wave spectroscopy. The effect of silane treatment on the cross-linking kinetics of a thermosetting resin is also presented.

Keywords: Cure monitoring, Silane coupling agent, Cure kinetics, Evanescent wave spectroscopy

INTRODUCTION

Silane coupling agents are used to improve the interfacial bonding between the reinforcing glass fibres and the matrix [1]. Silane coupling agents can be represented by the general formula (R'-Si-(OR)$_3$). R' is a reactive functional group, such as, vinyl, epoxy, methacryl, amino or mercapto that can react with the matrix. OR is another reactive functional group, for example, methoxy or ethoxy that can hydrolyse to form a silanol group in aqueous solution. These silanol groups can react with the hydroxyl groups on the glass fibre surface to form covalent bonds [1]. The interphase region between the fibre and matrix was reported to have a thickness in the range of 100 to 900 nm depending on the concentration of the silane coupling agent [2]. A number of previous studies have concentrated on characterising the molecular structure of the interphase region and its contribution to mechanical properties [3-6]. However, the focus of the current study was on investigating the effect of silane treatment of glass fibres on the cross-linking kinetics. The following section presents a general overview of selected papers that have addressed this issue.

González-Benito used Fourier Transform infrared (FTIR) imaging technique to monitor the change of hydroxyl (OH) absorption and found that there was an increase in the hydroxyl group absorption from the fibre surface to the bulk of the resin system [7]. He proposed that the cross-linking rate increased with distance from the fibre within the interphase region, which was proposed to be due to the existence of a concentration gradient in the active-amine/epoxy ratio. The greater proportion of the amine group near the glass fibre surface was expected owing to the following possible reasons: (i) favorable reaction between amine and OH groups; and (ii) since the hardener molecule is smaller than the resin, it diffuses at a faster rate through the silane coating. González-

Benito *et al.* also studied the cross-linking kinetics of an epoxy/amine resin system using the fluorescence response of dansyl (5-dimethylaminonaphthalene-1-(2-aminoehyl) sulfonamide (DNS-EDA)) [8]. In order to follow the curing process by fluorescence in the epoxy bulk and at the interface formed between the epoxy matrix and the silanised glass coating, the matrix and the glass fibre coating were labeled with dansyl. The cross-linking rate was found to be higher at the interface than in the bulk, which is in accordance with results obtained previously [7]. They also found that the cross-linking behaviour at the interface changed with the type of silane coupling agent. When 3-aminopropylmethyldiethoxysilane (APDES) was used, the activation energy was lower than when the fibres were coated with 3-aminopropyltrimethoxysilane (APTES). They suggested that this could be explained by the more open structure for APDES coating. Culler *et al.* used FTIR spectroscopy to characterise the reaction at the silane/matrix resin interphase and found that the reaction was most affected by the thickness of the silane interphase and the degree of condensation of the silane interphase [9]. If the silane interphase was less condensed, the diffusion of the resin into the silane interphase was said to be easier and thus the extent of the reaction was observed to increase.

The above-mentioned spectroscopic methods often involved the fabrication of a model composite followed by fracture of the sample at or near the interphase. Brill and Palmese used attenuated total reflectance (ATR) to study the cross-linking behaviour of DGEBA-based vinyl ester (VE) and styrene (ST) resin system [10, 11]. In order to investigate the effect of the silane coupling agent on the cross-linking rate of VE and ST, the ATR crystal was treated with Z-6032 which has an amine functional group. The solution with 3% Z-6032 and methanol (pH = 4.5) was prepared to coat the ATR crystal surface by spin-coating method. The observed fractional conversion of the vinyl ester double bond was 0.2 and 0.65 with and without surface treatment, respectively. On comparing the conversion of the styrene double bond for the un-treated and silane-treated ATR crystal, the fractional conversion was similar up to 0.4, but the final conversion was 0.85 and 0.7, respectively. They speculated that this could be due to the interphase near Z-6032 which was rich in homopolymerised styrene.

Connell *et al.* used evanescent wave spectroscopy to monitor the interaction between an epoxy resin system and coupling agent, γ-aminopropyltrimethoxy silane (γ-APS), which being absorbed on silica fibre, in real-time [12]. The reactivity of the primary amine in the silane was found to decrease when the concentration of the coupling agent was increased. They proposed that this could be as a result of the entrapment of the silane molecules and making them unavailable for reaction with epoxy when the density of γ-APS was increased. The fibres used in their study were silica fibres, which consisted of a 100 μm diameter fused silica core, a 10 μm thick, fluorine-doped fused silica cladding and a 10 μm thick polyamide buffer. Johnson *et al.* used thin-clad optical fibres, consisting of 25 μm diameter flint-glass core with a 1 μm thick soda-lime cladding, to perform the evanescent wave spectroscopy [13]. One of the reasons stated for using this type of fibre was that the composition of the cladding was said to be similar to that of E-glass. However, that paper only demonstrated the ability to monitor the interphase chemistry; only the spectra of the resin before and after cross-linking were shown.

This current paper presents evidence to demonstrate that evanescent wave spectroscopy can be used to study the cross-linking kinetics of epoxy/amine resin systems *in-situ* and in real-time using the reinforcing E-glass fibres. Evanescent wave spectroscopy was used to study the effect of silane treatment on the cross-linking kinetics on the surface of E-glass fibres.

EXPERIMENTAL

Materials, sample preparation and silane treatment

The glass fibres used in this study were supplied by PPG Industries (UK) Ltd in the form of continuous un-sized E-glass fibre bundles containing approximately 2500 filaments with an average individual fibre diameter of 15 ± 3 μm. The refractive index of the E-glass preform was measured to be 1.56 at 589.6 nm and 20 °C. The ends of the glass fibre bundle were potted into sub-miniature A-type (SMA) connectors using EPO-TEK® 314 (Promatech Ltd) and polished using an APC 8000 polisher (SENKO Advanced Components Ltd) to maximise the collection and transmission of light. A photograph of a short length of an E-glass fibre bundle with SMA connectors is shown in Figure 1.

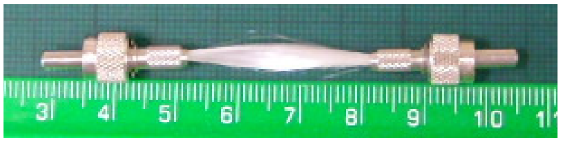

Figure 1 Photograph of an E-fibre bundle with a pair of polished SMA connectors.

The coupling agent used in this study was 3-glycidoxypropyltrimethoxysilane (GPS) (Sigma-Aldrich, UK) and was used as-received. A 0.1 wt% GPS solution was prepared using a mixture of ethanol and distilled water (4:1) and the pH was adjusted to 4 using acetic acid. The exposed portion of fibre bundle (see Figure 1) was immersed in this solution for one hour at room temperature. After this period, the solution was drained and the fibre bundle was dried at room temperature for two hours. Subsequently, the silane-treated fibre bundle was dried in the oven at 100 °C for three hours. 0.5, 1 and 3 wt% silane solutions were also prepared in a similar manner and applied to the E-glass fibre bundles.

Monitoring the cross-linking reaction

A two-component resin system, EPO-TEK® 310M (Promatech Ltd, UK) was used in this study. The refractive index of this cross-linked resin was 1.52. A fresh batch of the resin and hardener were weighed in the required stoichiometric ratio 10:5.5 (epoxy : amine) and mixed thoroughly. The resin was processed at four isothermal temperatures: 35 °C; 45 °C; 55 °C; and 65 °C. A schematic illustration of the experimental setup that was used for monitoring the cross-linking kinetics is presented in Figure 2. With reference to the conventional transmission FTIR spectroscopy experiments, a Bruker MATRIX™-F duplex FT-NIR spectrometer (Bruker Optics Ltd, UK) was used for monitoring the cross-linking reaction. The spectrometer was operated in the near-infrared region from 11000 to 4000 cm^{-1} and spectra were collected at a resolution of 4 cm^{-1} and with 64 scans. The mixed resin was injected via a syringe into a demountable optical glass cuvette with a path-length of 1 mm (Starna, UK). The cuvette was housed in a CUV-TLC-50F temperature-regulated cuvette holder (± 0.02 °C) (Ocean Optics Inc., Netherlands). With reference to Figure 2a, two low-OH optical fibre probes (Ocean Optics Inc., Netherlands) were used to illuminate the cuvette and to deliver the transmitted light to the detector port of the spectrometer. The spectrometer was equipped with an InGaAs detector. The experimental setup for the evanescent wave spectroscopy experiments is illustrated in Figure 2b. The same spectrometer was used for evanescent wave spectroscopy experiments but in this instance, the spectra were acquired over 128 scans (Figure 2b). An external white light source, WLS100 (Bentham Instruments Ltd., UK) was used instead of the internal light source of the spectrometer. The fibres were impregnated manually and then cross-linked in a custom-designed oven (± 0.2 °C). A thermocouple was used to monitor the temperature of the resin system during processing.

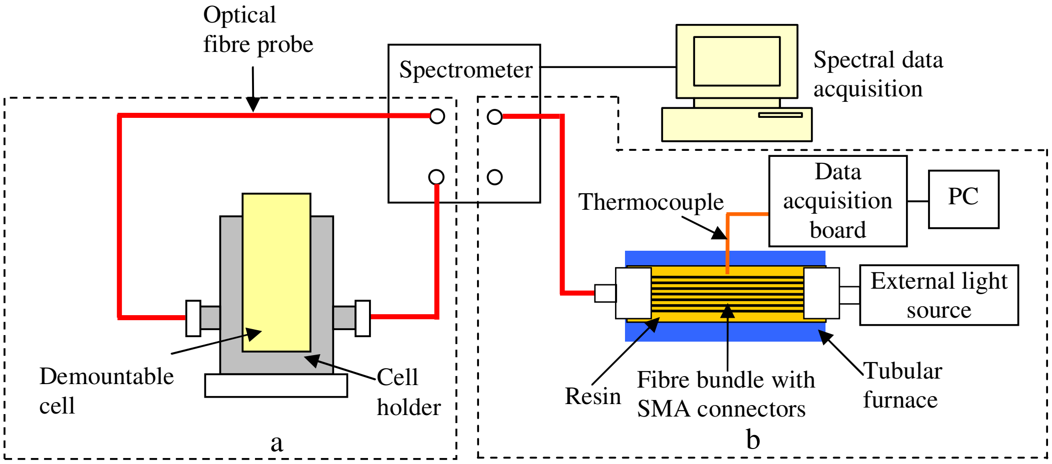

Figure 2 Schematic illustration of the experimental set-up used for: (a) conventional transmission and (b) evanescent wave spectroscopy.

RESULTS AND DISCUSSION

Conventional transmission spectroscopy

The near-infrared transmission spectra of the EPO-TEK® 310M resin system cross-linked at 35 °C as a function of time is shown in Figure 3a. The absorbance peak at 6500 $\mathrm{cm^{-1}}$ was attributed to the primary and secondary amine overtones. During the cross-linking reaction, this peak area was observed to decrease due to the consumption of the primary amine followed by the reaction and depletion of the secondary amine as the reaction proceeded. The peak at 4935 $\mathrm{cm^{-1}}$ was associated with the fundamental vibrations of the primary amine groups [14]. The rapid decrease in this peak area is caused by the epoxy-primary amine reaction. The peak at 4600 $\mathrm{cm^{-1}}$ is generally attributed to the combination bands of the C-H stretching vibration of the aromatic ring [14]. This peak area does not change as a function of curing time because this functional group does not participate in the cross-linking reaction. The peak at 4530 $\mathrm{cm^{-1}}$ is attributed to the epoxy CH_2- and C-H deformation bands [14] and it is seen to decrease as a function of cross-linking. Since the aromatic C-H group at 4600 $\mathrm{cm^{-1}}$ does not participate in the cross-linking reaction, the peak area corresponding to this absorbance was used to normalise that of the epoxy absorbance bands. With reference to Figure 1, the conversion was calculated using Equation 1:

$$\alpha_x = (1 - \frac{(A_x / A_{C-H})_t}{(A_x / A_{C-H})_0}) \times 100 \qquad [1]$$

where α is the conversion of the reacting group (amine or epoxy), A_x is the area of the absorption peak, A_{C-H} represents the area of the reference C-H peak, *t* and *0* are the cross-linking time in minutes and the start of cross-linking respectively.

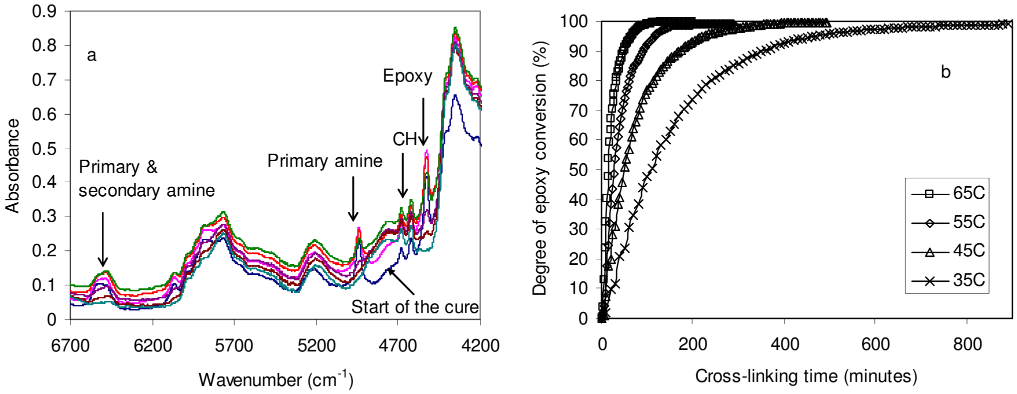

Figure 3 (a) Conventional transmission FTIR spectra of EPO-TEK 310M resin at different stages of cross-linking at 35 °C and (b) conversion plots of epoxy functional groups in EPO-TEK 310M as the resin was cross-linked at 35, 45, 55 and 65 °C.

Figure 3b shows representative plots of epoxy conversion calculated using Equation 1. On inspecting Figure 3b, it can be seen that epoxy functional groups are consumed at a faster rate at the higher cross-linking temperatures. For this resin system, the final epoxy conversion was observed to be slightly higher when the resin was cross-linked at higher temperatures.

Evanescent wave spectroscopy

As-received and silane-treated fibre bundles were to monitor the cross-linking of the resin system at 35, 45, 55 and 65 °C. Comparing the transmission and evanescent wave spectra, it was observed that the relative positions of the absorbance peaks for the epoxy and amine functional groups were similar. Although the quality of the evanescent wave spectra was lower due to a low signal throughout, the characteristic peak positions of the reactive functional groups were the same.

The epoxy peak was chosen to enable comparison of the conventional transmission and evanescent wave spectroscopy data. Figures 4 (a-d) show the epoxy conversion for the EPO-TEK 310M resin system cross-linked at 35, 45, 55 and 65 °C. The data for the silane-treated E-glass fibres corresponds to 1 % GPS. The differences between the three datasets can be seen in the cross-linking rate and the degree of conversion. The final degree of conversion of the epoxy group via evanescent wave spectroscopy using as-received fibre is slightly lower than that observed for the conventional transmission

FTIR spectroscopy experiments. However, the final epoxy conversion via evanescent wave spectroscopy using silane-treated fibres is approximately 3 % lower than that observed for the as-received E-glass fibres. On comparing the epoxy conversion obtained from these three datasets, the conversion rates were similar up to approximately 60 %. After this period, the silane-treated fibres showed a lower rate of conversion. At all the cross-linking temperatures investigated, the silane-treated E-glass fibres showed a lower degree of conversion when compared to the conventional transmission and the as-received E-glass fibres.

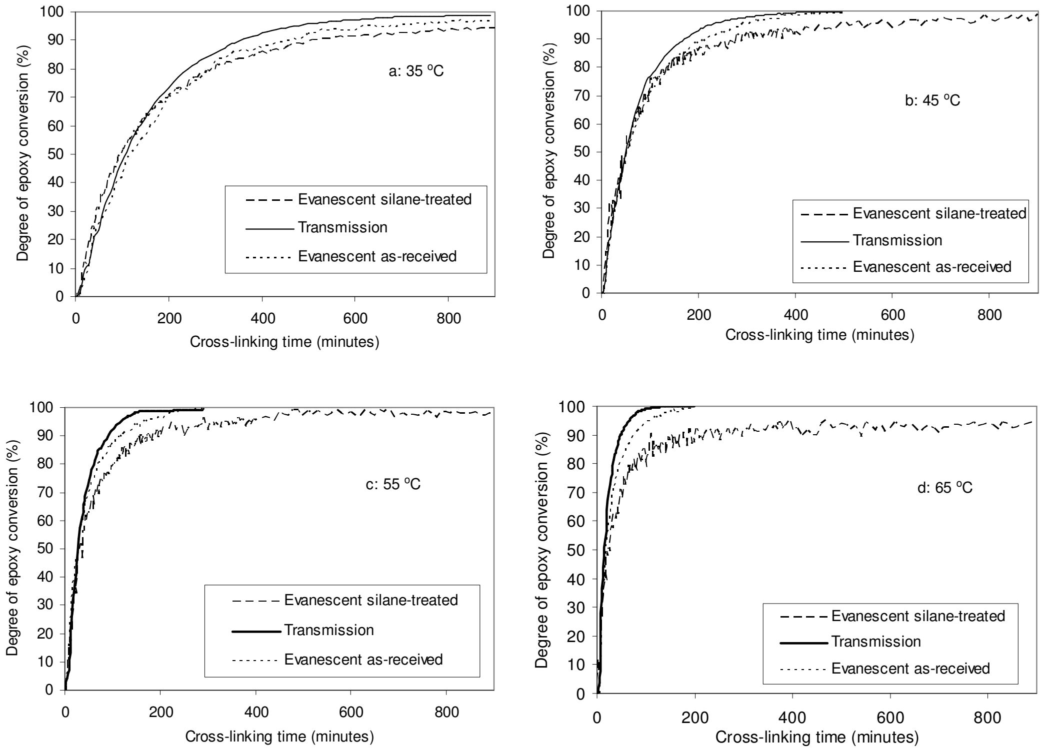

Figure 4 Conversion of epoxy groups for the EPO-TEK 310M resin system cross-linked at different temperatures using transmission FTIR and evanescent wave spectroscopy.

In order to enable comparison of the conventional transmission and evanescent wave spectroscopic data, the data were fitted to a phenomenological model; Equation 2 is generally referred to as the modified Kamal model and is represented as [15]:

$$\frac{d\alpha}{dt} = k\alpha^{m}\left(1-\alpha\right)^{n} \qquad [2]$$

where $d\alpha/dt$ is the rate of reaction, α is the conversion, k is the rate constant and m, n represent the reaction orders. Table 1 presents a summary of the kinetic parameters for the transmission and evanescent wave spectroscopy measurements. The activation energy was calculated using the Arrhenius relationship. As seen in Table 1, the activation energy obtained from the two cross-linking monitoring techniques and surface treatments are different.

Table 1 Kinetic parameters obtained from the autocatalytic model for isothermal cross-linking experiments for EPO-TEK 310M using conventional transmission FTIR and evanescent wave spectroscopy.

Cross-linking temperature (^{o}C)	Transmission spectroscopy			Evanescent wave spectroscopy: as-received fibre			Evanescent wave spectroscopy: silane-treated fibre		
	m	n	k	m	n	k	m	n	k
35	0.35	1.65	$2.3x10^{-4}$	0.35	1.75	$2.4x10^{-4}$	0.35	1.65	$2.3x10^{-4}$
45	0.35	1.65	$4.2x10^{-4}$	0.25	1.85	$4.1x10^{-4}$	0.35	1.65	$4.6x10^{-4}$
55	0.35	1.65	$9.0x10^{-4}$	0.25	1.85	$8.0x10^{-4}$	0.35	1.65	$7.0x10^{-4}$
65	0.35	1.65	$1.7x10^{-3}$	0.35	1.75	$1.5x10^{-3}$	0.35	1.65	$1.0x10^{-3}$
Activation energy (kJ mol^{-1})	58.48			53.29			47.77		

m, n = reaction order and k = reaction constant.

Whilst the actual reasons for the observed discrepancy between the cross-linking monitoring techniques and surface-treatments were not established conclusively at the time of writing, the following issues are being investigated further [14]. (i) Temperature control: The temperature control in the conventional cuvette-based transmission FTIR spectroscopy and oven-based evanescent wave spectroscopy were ±0.02 °C and ± 0.2 °C respectively. (ii) Evaporation: The relative surface area of the impregnated fibres is significantly higher than the open-top of the cuvette. Therefore, the rate of evaporation from the surface of the impregnated glass fibres is likely to be more significant. The data summarised in Table 1 indicates that the discrepancy in the reaction constant between the datasets are higher at the higher processing temperatures. (iii) Surface-area of treated and un-treated fibres: Previous researchers have found that silane-treatment of E-glass fibres results in a modification of the surface morphology [2, 16]. There is evidence in the literature to suggest that the surface area of the silane-treated fibres increases. This is not the case with conventional transmission experiments where the cross-linking of the bulk resin is monitored over the path-length of the cuvette. The effect of the surface chemistry of the silane-treated and un-treated fibres also needs to be taken into account. (iv) Background spectra: In the case of evanescent wave spectroscopy, the background spectrum can be taken using the as-received or silane-treated fibres. The selection of the background spectra will have an effect on the apparent rate and extent of the reaction. With reference to Figure 4 and Table 1, the spectrum of the as-received fibre bundle was used as background. (v) Penetration depth of the evanescent field. The penetration depth of the evanescent field into the lower index medium (resin) can be expressed as:

$$d = \frac{\lambda}{2\pi(n_{glass}^2 \sin^2 \theta - n_{resin}^2)^{1/2}} \qquad [3]$$

where n_{glass} and n_{resin} are the refractive indices of E-glass fibre and epoxy-amine resin system respectively; λ and θ are the wavelength of light and the angle of incidence at the fibre/resin interface. From Equation 3, it is apparent that the penetration depth depends on indices of E-glass, resin system, wavelength of light and the angle of incidence at the interface. When the resin-impregnated fibre bundle is subjected to isothermal cross-linking conditions, the refractive index of the resin initially drops due temperature rise and gradually increases and approaches a steady state. The penetration depth of the evanescent field also initially decreases with the drop in index of resin and increases with the resin index until the resin index approaches that of the fibre. When the resin index is equal to that of the fibre, the interaction between the light in the fibre and surrounding resin is no longer evanescent in nature and the light is lost to the absorbing cladding. As the resin index exceeds the fibre index, the light is no longer guided by total internal reflection but governed by the Fresnel equations at oblique incidence at the interface. A simulated graph of the refractive index of isothermally cross-linked resin system and penetration depth of the evanescent field against time is presented in Figure 5. Here the E-glass index is taken to be 1.56, wavelength corresponds to the centre of epoxy band (4530 cm^{-1}) and the angle of incidence of the bound rays at 88.5°. The effect of evolving penetration depth on the bulk evanescent absorption coefficient is being investigated.

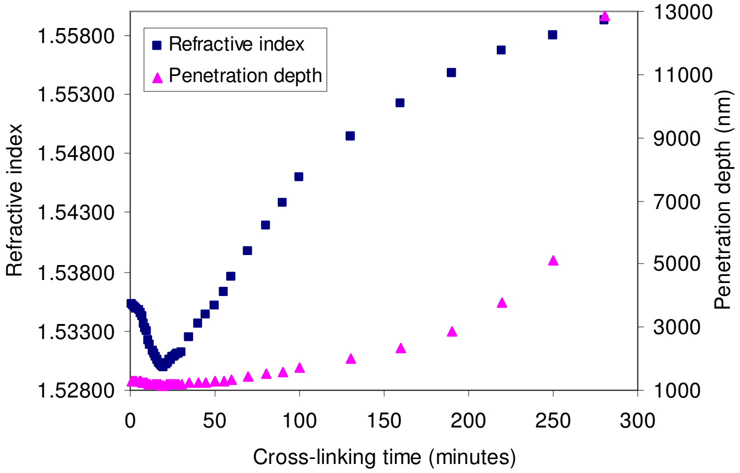

Figure 5 Measured refractive index (Abbe refractometer) and the change in the penetration depth (simulated) with time during isothermal cross-linking.

In the case of silane-treated fibres, the net field interaction with the resin system would be influenced by the index of silane coating and its thickness. Investigations are currently underway to investigate these factors further. The thickness of the silane coating was not available at the time of writing. However, the thickness of 1 % APS was reported to be around 0.2 µm [2]. Therefore, the silane coating is thin enough to allow extension of the evanescent wave into the resin system.

Figure 6 shows the epoxy conversion plots for the E-glass fibres that were untreated and treated with 0.1, 0.5 and 1% GPS solution. The conversion of the epoxy functional group was found to decrease as the concentration of silane was increased. The rate of consumption of the epoxy functional group was also affected by silane treatment. The observed trends in Figure 6 may be attributed to the following: Since the as-received fibre was used as the background spectrum, the effect of surface-treatment with GPS would be to increase the concentration of the epoxy functional group on the surface of the glass fibres. Therefore, the rate of conversion of the epoxy, as inferred by evanescent wave spectroscopy, is likely to be faster. As the relative concentration of the GPS increased, the surface concentration of the epoxy functional group is also likely to increase on the surface of the glass fibres until saturation is achieved. The morphology and penetration depth of the evanescent filed would then dictate the "apparent" extent of reaction. Further research is needed before convincing conclusions can be reached.

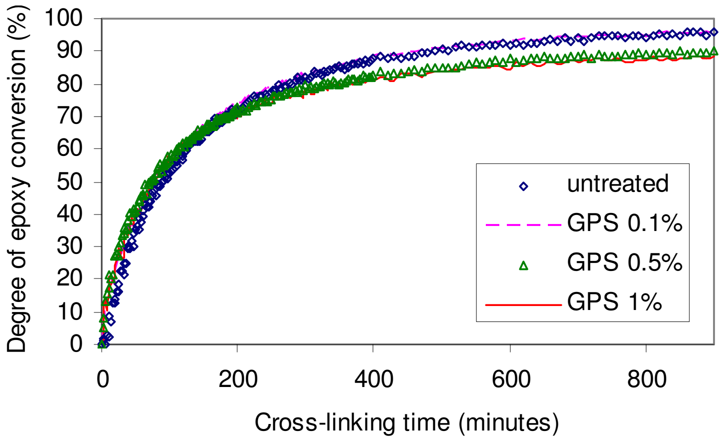

Figure 6 Conversion plot for EPO-TEK 310M resin systems cross-linked at 35 °C using un-treated and silane treated E-glass fibres.

CONCLUSIONS

This study has successfully demonstrated that conventional reinforcing E-glass fibres can be used as a chemical sensor for *in-situ* and quantitative monitoring of cross-linking reactions. The technique developed in this study has also shown that evanescent wave spectroscopy can be used to study the effect of a silane treatment on the cross-linking behaviour of thermosetting resins on the surface of glass fibres. A good correlation was observed between conventional transmission infrared spectroscopy and evanescent wave spectroscopy until the degree of epoxy conversion reached around 60 %. The reasons for this discrepancy between as-receive fibres and silane-treated fibres need further investigation.

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