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Kinetic study of epoxy curing in the glass fiber/epox interface using dansyl fluorescenc

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Abstract

The fluorescenc response of the dansyl chromophore has been used to study the kinetic of epoxy curing processes. With this new method, comparison between the curing at the interface of a glass fiber/epox and in the epoxy bulk of a composite material was studied. The effect of two glass fibe surface treatments was investigated. Commercial E-glass fi ers were surface coated with 3-aminopropyltriethoxysilane (APTES) and 3-aminopropylmethyldiethoxysilane (APDES). Fluorimetry (using fluorescen labels) and FT-NIR (Fourier transformed infrared spectroscopy in the near range) techniques were used to monitor the curing process in these composite materials. From the analysis of the data obtained, different simple kinetic models were discussed and apparent activation energies were obtained. Furthermore, from those techniques the respective results were compared to obtain complementary information. Independently of the sample and the technique used for the kinetic analysis, no variation of the activation energy of the epoxy curing reaction was found, which suggests that there are no changes in the mechanism of the reaction along the process. Fluorescence from dansyl located at the glass fiber/epox interface reflecte that the kind of reinforcement treatment clearly affects the epoxy curing process exactly in that region. However, when analytical response comes from the whole system the mechanism of the reaction does not seem to change with the silane coating used although is quite different in comparison with the process at the interface.

Keywords
Fluorescence; Interfaces; Composites; Epoxy

1. Introduction

During the last century the use of composite materials has increased sharply. Most of the composites are designed for very specif c applications. For this reason, in many occasions, these materials are referred to as high-performance composite materials. Nowadays, glass-fibe -reinforced composites are very important because of their widespread applications in the automotive and aerospace industries.

It is well known that the physical properties of cured epoxy resins depend on their structure, the extent of cure, the curing conditions, and the time and temperature of cure. For this reason, the knowledge and understanding of the relationships between the structure of the networks and the f nal properties are very important for obtaining suitable resins for these high-performance applications. To optimize the processing conditions of thermosetting materials it would be very helpful: (i) to monitor nondestructively and in situ the chemical conversion during the curing process and (ii) to model the kinetics of the reaction. Great efforts are being made to attain these objectives, particularly in the case of epoxy resins. Several techniques have been used to monitor the cure process in epoxy-based materials. Although FTIR [1–4] and DSC [4–7] have been the most widely used, they show some limitations. First, they seem to have low sensitivity at high conversions [4]. Secondly, although DSC experiments in the dynamic mode are very simple and fast to carry out [5,6], this method is not recommended when in situ and nondestructive monitorization is required. Finally, FTIR and DSC provide information from the whole system and it is not possible to monitor the curing process in specifi sites of interest, for instance, to get information from the interfacial regions. It is well known that the properties of composites are greatly dependent on the interface, since many of the catastrophic failures in this kind of material occur due to bad adhesion between the reinforcement or the f ller and the polymer matrix. Therefore, a deeper knowl-

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edge of the cure process exactly at the interface and its effect on the final properties of the composite in this kind of materials is required. To overcome these difficulties, the use of fluorescent response from probes or labels is being revealed to be a very easy and feasible tool [8–10].

The fluorescent emission from many molecules is so sensitive to changes in its immediate surroundings that very small amounts of chromophores are enough to obtain the information required. The advantage of using such a small amount is that no perturbation is introduced into the system. In general, the fluorescent emission changes when polarity and/or rigidity variations occur in the system where the chromophore is immersed [11–15]. Some studies propose that an enhancement in the microviscosity of the medium leads to a decrease in the nonradiactive decay rate and consequently an increase in the fluorescence quantum yield [13]. Other authors use the increase of the fluorescent intensity that comes from the chemical changes of the fluorophore [14,15]. However, this method does not eliminate the effect of intensity variations arising from external factors such as lamp intensity, optical alignment, probe location, and excitation area. Due to these limitations, new methods have been proposed. Neckers and co-workers [16,17] reported the use of fluorescence probes to monitor the curing process of polyacrylate monomers with an intensity ratio method and more recently Lemmetyinen and co-workers [18,19] have developed a new intensity ratio method, where ratios of the low- to high-intensity changes (LHIC) in the emission bands were used to determine the degree of the curing processes. More recently, González-Benito and co-workers [20] reported a new method to accurately monitor polymerizations. This method is based on the first moment of the fluorescence band. This parameter is used to follow the progress of the polymeric reactions.

Furthermore, using an adequate functional group it is possible to label either the bulk or the interface of the composite with a fluorescence molecule. This allows the obtaining of information either on the overall material, similar to that obtained by FTIR or DSC, or exactly at the interface of the composite material [8–10]. Using the fluorescence from labels, some attempts have been made to model the epoxy curing at the interface of glass/epoxy matrix composites [9,10]. However, those works only show the potential utility of the method and deeper studies should be carried out. For instance, it is necessary: (i) to perform the studies with real systems, glass fibers instead of glass plates; (ii) to find dyes whose fluorescent response is stable at the temperature used for curing and at the wavelength used for its excitation—for example, the nitrostilbene moiety has been demonstrated to be not very stable when used to monitor cure processes [21]; (iii) to find specific photophysical parameters whose values perfectly correlates with epoxy conversion; and (iv) to understand the relation between surface characteristics of the reinforcement and curing at the interface.

The other aspect of optimizing the curing processes is to know the kinetics of the reactions under study. To do this kind of study, different techniques have been used, such as FTIR [1–4], DSC [4–7], DEA [22,23], and rheometry [24]. All of them, at least, allow the obtaining of a global kinetic equation and the apparent kinetic parameters such as the activation energy of the processes. However, none of them allow the carrying out of local kinetics studies, that is to say, the studying of the kinetics of the curing process in specific sites.

One of the first attempts to study the kinetics of epoxy curing was made by Horie et al. [25], studying the curing of DGEBA with different diamines by DSC. The determination of a kinetic mechanism is extremely difficult. In general, different kinetic models are used to explain different aspects of the reaction. An approach to study the kinetics of a reaction is to consider the curing reaction formed by an nth-order and by an autocatalytic reaction. It seems reasonable to think that at the first stages the nth-order term dominates, while as the reaction progresses the autocatalytic term becomes more and more important. This is attributable to the formation of hydroxyl (OH) groups during the curing, since donor groups such as OH have been proven to be catalysts of these reactions [25,26]. This model, first proposed by Horie et al. [25], has been used by several authors to explain different diepoxy–diamine systems, showing good results. Nevertheless, the scientific literature offer many other approximations for studying the kinetics of the epoxy curing reactions [27–29].

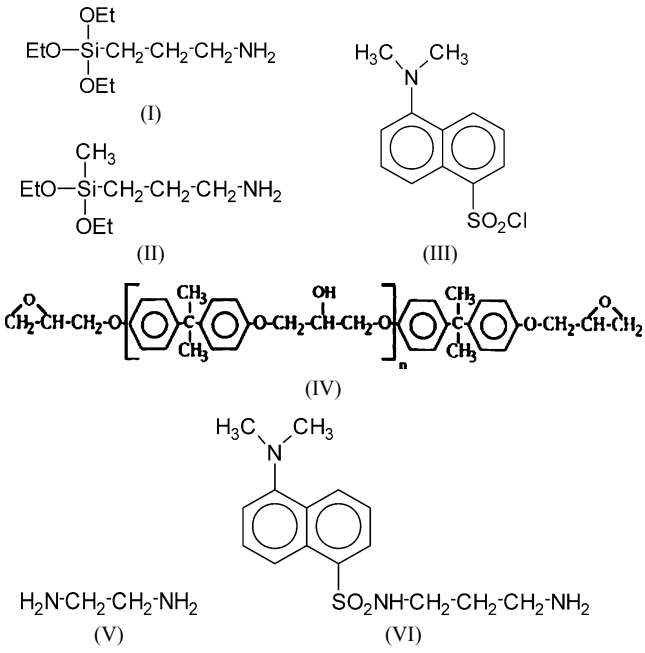
In this work, the use of the fluorescent response from the dansyl moiety is proposed to monitor the curing process of an epoxy system based on diglycidyl ether of bisphenol A (DGEBA) and EDA. The epoxy polymer is the matrix in a composite in which the reinforcement is E-glass fibers coated with silane coupling agents. The dansyl fluorophore will be introduced into the system as a label either in the bulk polymer or in the silane-coupling layer. From the fluorescence data, a new kinetic study will be done and the cure processes in the polymer bulk and in the interface will be compared. Furthermore, the glass fiber will be silane-coated differently to study the effect of the glass fiber surface treatment on the kinetics of the epoxy cure at the interface. Finally, the results obtained from the kinetic studies carried out using two techniques, Fourier transform infrared spectroscopy in the near region (FT-NIR) and fluorescence, will be also discussed. From this comparison, this work tries to understand exactly what information fluorescence gives concerning the changes that the epoxy system suffers during the curing process (chemistry, rheology, etc.).

2. Experimental

2.1. Materials

E-glass fibers were provided by VETROTEX (Spain). The silane coupling agents, 3-aminopropyltriethoxysilane (APTES) (I), 3-aminopropylmethyldiethoxysilane (APDES)

(II), and the reactive chromophore, 5-dimethylamino-1-naphtalenesulfonyl chloride (DNS) (III), were supplied by Fluka-Kemika Co. and Lancaster Inc., respectively. The components of the polymeric system, poly (bisphenol A-co-epichlorohydrin) glycidyl end-capped (DGEBA) (IV), $M_n = 348$ g/mol ($n = 0.03$), and ethylenediamine (EDA) (V), were purchased from Aldrich Co. A reactive dansyl derivative, 5-dimethylaminonaphthalene-1-(2-aminoehyl)) sulfonamide (DNS-EDA) (VI), was synthesized in our laboratory to label the epoxy resin. Toluene was dried over molecular sieve (4 Å) for 24 h before use. Other solvents were used with at least HPLC quality.



2.2. Sample preparation

Commercial E-glass fibers were burned at 450 °C for 1 h to remove the organic matter from the surface. After that, two sorts of treatment were carried out: (i) activation with boiling HCl 10% (v/v) aqueous solution and (ii) no activation. Then, the fiber were silanized with APTES and APDES by immersion of 1 g in 50 ml of a 2% silane aqueous solution (v/v) for 15 min. In order to follow the curing process by fluorescence in the epoxy bulk and at the interface formed between the epoxy matrix and the silanized glass fibers, the polymeric matrix in one case and the glass fiber coating in the other were labeled with the dansyl moiety. The epoxy matrix was dansyl-labeled, treating the DGEBA with the reactive DNS derivative DNS-EDA following the procedure already described [8]. To label APTES and APDES with the dansyl group, 0.4 g of silanized fibers were immersed into 10^{-4} M solution of DNS in dimethylformamide (DMF) for 15 min. After that, the fibers labeled with DNS were washed several times with DMF. We can assume that the chromophore is not physically adsorbed onto the fibers because the last fraction of DMF used for washing did not show any fluorescence signal. The photophysical characterization of the resulting labeled E-glass fibers has already been described [11]. Samples codes and conditions for their preparation are presented in Table 1.

Table 1
Conditions for the glass surface treatments and sample codes

Sample code	Activation treatment	Chromophore location	Techniques
APTES-B	No	DGEBA	FTIR, fluorescence
APDES-B	No	DGEBA	FTIR, fluorescence
APTES-F	Yes	APTES	Fluorescence
APDES-F	Yes	APDES	Fluorescence

The curing process was followed using two different techniques: Fourier transformed near infrared spectroscopy, FT-NIR, and fluore cence spectroscopy. In the case of the samples with the chromophore chemically bonded to the glass fber surface (chromophore located at the interface of the composite) only fluorescence was used to monitor the cure process. In every case, the samples were prepared by mixing the stoichiometric epoxy–amine mixture with the silanized glass fbers in a proportion of 20% (w/w) for the reinforcement and placed between two microscope-glass slide plates with an optical path of approximately 0.6 mm thickness determined by the thickness of a Teflo spacer. The curing reaction was monitored at 40, 50, 60, and 70 °C using a SPECAC temperature controller. The temperature in the sample holder of the oven (SPECAC) used to cure was checked with a thermocouple and variations higher than 1 °C were not observed. A Perkin–Elmer GX FTIR (Perkin–Elmer) were recorded in a FTIR Spectrum GX (Perkin–Elmer) using a homemade program to collect spectra as a function of time.

Fluorescence spectra were recorded in an Edinburgh Instruments Co. fluorimete using an optical fibe cable for both excite and collect the fluorescence of the sample in situ. The excitation and emission slits were set at 2.3 and 3.6 nm, respectively. All the spectra were recorded between 360 and 650 nm, setting the excitation wavelength at 350 nm.

3. Results and discussion

3.1. FT-NIR measurements

The extent of reaction, α_{IR}, at any time, t, obtained from the FT-NIR spectra is calculated in terms of the epoxy group absorption according to the equation

$$\alpha = 1 - \left[(A_{E,t})(A_{R,0})\right] / \left[(A_{E,0})(A_{R,t})\right], \quad (1)$$

where $A_{E,0}$ and $A_{R,0}$ refer to the initial areas of epoxy and reference bands, respectively, and their corresponding values at a given time t, $A_{E,t}$ and $A_{R,t}$. The area of the band centered at 4530 cm^{-1} was used to monitor the disappearance of the epoxy group, while the band at 4623 cm^{-1} due to a

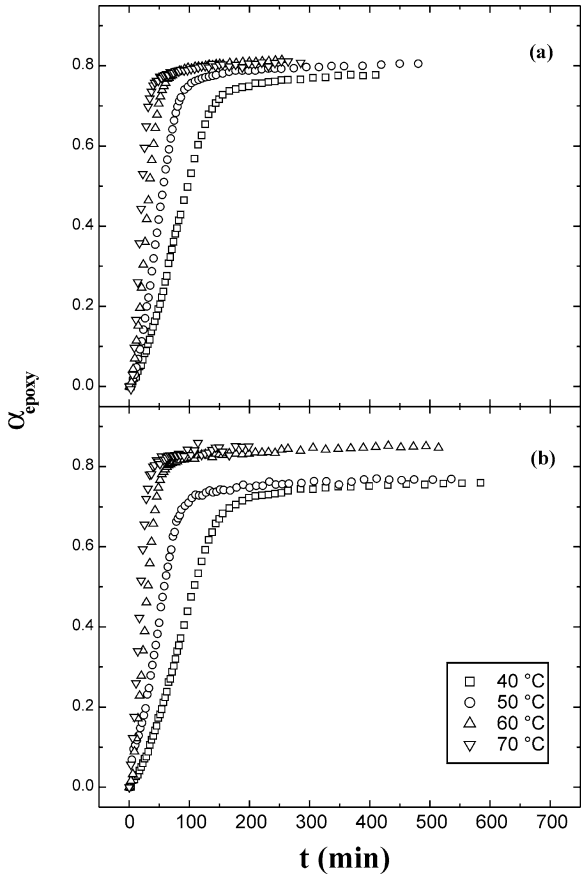


Fig. 1. Epoxy group conversion versus time at different temperatures for (a) APTES-B and (b) APDES-B samples.

combination band C–H stretching vibration of the benzene ring was used as a reference [2,3].

In Fig. 1 the plots of epoxy group conversion versus time at different temperatures for the APTES-B and APDES-B samples are shown.

Probably the most common kinetic analysis (isoconversional method, method A) considers a general rate equation and, for a given conversion, it is possible to write

$$d\alpha/dt = kf(\alpha) \tag{2}$$

and after integration

$$t = B/k, \tag{3}$$

where B is a constant for a particular choice of conversion and k is the apparent kinetic constant with an Arrhenius-like behavior. Taking the natural logarithm, the following expression is obtained:

$$\ln t = C + E_a/RT. \tag{4}$$

Therefore, plotting $\ln t$ versus $1/T$, straight lines should be obtained and from their slopes apparent activation energies should be able to be calculated. The results obtained using this method (method A) are listed in Table 2. In Fig. 2 an example of this kind of plots is shown. In this fi ure it can be seen that nearly parallel lines are obtained, which from

Table 2
Isoconversional method (method A): Apparent activation energies (kJ/mol) obtained from linear fit of the plots in the Fig. 2 for the APTES-B and APDES-B samples

α	APTES-B	APDES-B
0.1	37 ± 2	54 ± 14
0.2	41 ± 2	54 ± 7
0.3	43 ± 1	52 ± 1
0.4	43.3 ± 0.5	53 ± 1
0.5	45.0 ± 0.1	52 ± 1
0.6	45.2 ± 0.5	52 ± 1
0.7	43 ± 1	55 ± 2
Average	42 ± 3	53 ± 1

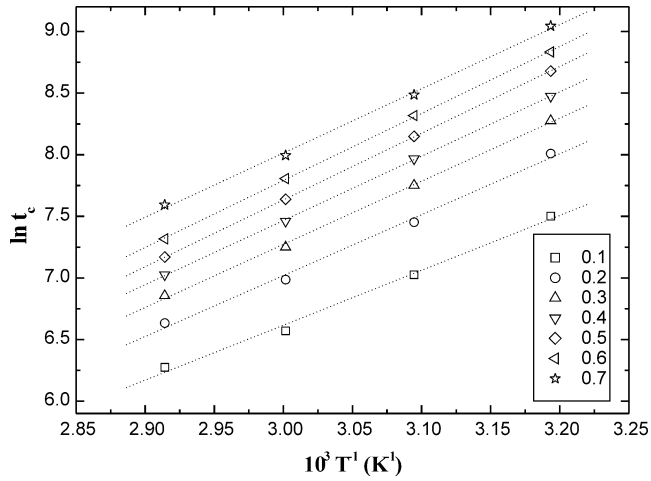


Fig. 2. Representation of natural logarithm of the curing time versus inverse of temperature for constant values of epoxy group conversion (APTES-B sample).

a mechanistic point of view can be interpreted in terms of a constant mechanism. The values for $\alpha = 0.1$ may differ from the rest due to inefficie t thermostatization at the very fi st stages of the reaction.

Horie et al. [25] reported an activation energy of 12.9 kcal/mol (53.9 kJ/mol) for the system DGEBA-EDA determined by DSC. Gupta and Varma [30] found a value of 56 kJ/mol, observing that the activation energy hardly changes with the hardener used. Furthermore, the kinetic study for the epoxy model system DGEBA + EDA (without f bers) has been done using FT-NIR and similar activation energy to the literature values were obtained. The values in Table 2 suggest that the composite with glass f bers treated with APTES has lower activation energy than that with fi ers modifie with APDES, which values are closer to that of the system without reinforcement.

When the maximum rate of a reaction appears after some consumption of the reactive species it may indicate an autocatalytic mechanism [25]. To study the autocatalytic behavior of this kind of systems a second kinetic model has been used [31] method B. The analysis consists in considering a rate equation,

$$\frac{d\alpha}{dt} = \left(K_1' + K_1\alpha^m\right)(1-\alpha)^n, \tag{5}$$

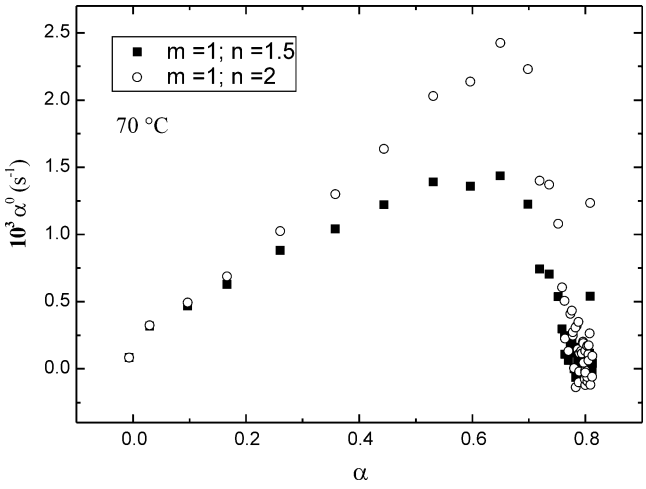


Fig. 3. Variation of the reduced rate, α^0, as a function of the FT-NIR epoxy group conversion, α, for the APTES-B sample at 70 °C.

where K_1' is the kinetic constant for an nth order process and K_1 the kinetic constant for the autocatalytic one; m and n are the partial orders of the reaction, being adjustable parameters depending on the system studied. The reduced rate is def ned as

$$\alpha^0 = \frac{d\alpha/dt}{(1-\alpha)^n} = \left(K_1' + K_1\alpha^m\right). \tag{6}$$

In order to conf rm the validity of this method the α^0 versus α plots were represented. As a f rst approximation the analysis was done for $m = 1$ and $n = 1.5$ and 2. Figure 3 shows, as an example, the plot of α^0 versus α for the APTES-B sample at 70 °C.

A very fast increase is observed from the beginning of the reaction until a conversion of approximately 0.6. When this conversion is reached, a sudden decrease in the reduced rate is then observed. According to the Flory–Stockmayer theory, the gel conversion is the critical conversion at which an inf nite network of the polymer has been formed. In the case of a diepoxy–diamine system the gel conversion can be estimated with a value of 0.6. From this point, the reaction rate starts to be controlled by the diffusion of the reactants, due to the high viscosity of the system. However, there are several examples [25] in which this phenomenon does not occur. Horie et al. [25] explained this fact in terms of the different structure of the network formed depending upon the components of the polymeric system; when more f exible networks are formed the onset of the diffusion-controlled reaction can be delayed in comparison with the formation of the infi ite network.

By fitti g the linear part of the curve to a straight line it is possible to obtain values for K_1' and K_1 from the intercept and the slope respectively. The values thus obtained are listed in Table 3.

Considering that these constants follow an Arrhenius-like behavior, the apparent activation energies for the nth-order and autocatalytic processes can be calculated from the slope of the plots $\ln K$ versus the inverse of temperature. These

Table 3
Kinetic constants and apparent activation energies obtained with method B (reduced rate method), using the FTIR data

T (°C)	n	$10^5 K_1'$ (s^{-1})	$10^4 K_1$ (s^{-1})	E_a (nth order)	E_a (auto)
			APTES		
40	1.5	4.32	4.47	54 ± 5	46 ± 2
50		7.04	8.64		
60		12.69	13.8		
70		27.27	21.5		
40	2	1.96	6.59	58 ± 9	49 ± 2
50		6.10	11.14		
60		8.97	19.22		
70		15.12	33.79		
			APDES		
40	1.5	2.82	4.53	66 ± 12	42 ± 4
50		–	–		
60		17.57	12.77		
70		23.81	18.98		
40	2	2.41	5.87	64 ± 13	42 ± 7
50		–	–		
60		14.96	17.22		
70		18.99	25.94		

energies are also included in Table 3. From the values in the table, it can be seen that in every case the activation energies corresponding to the autocatalyzed process are lower than those from the nth reaction, as was also observed by Nuñez et al. [31]. According to these results the reaction seems to have an order between 2.5 and 3. Horie et al., Nuñez et al., and Cook and co-workers [25,31,32] reported an order of 3 for similar curing reactions.

Taking into account the error associated with the results, when the effect of surface treatment is compared, no clear differences between the samples are found independent of being the nth-order or the autocatalyzed reaction. However, the values in Table 3 seem to reflec the same tendency in the nth-order activation energies as obtained with the method A for its apparent activation energies.

The last method of analysis used in this study (method C) is the one purposed by Cook and co-workers [32]. Taking natural logarithms in the rate equation (1) and considering an Arrhenius dependence of k with temperature yields

$$\ln(d\alpha/dt) = \ln A f(\alpha) - E_a/RT. \tag{7}$$

Thus, plotting the natural logarithms of the curing rate versus the inverse of temperature for a given value of conversion (α = constant), another apparent activation energy of the process can be obtained. These data are included in Table 4.

Figure 4 illustrates these plots for conversions ranging from 10 to 80% and shows how the slopes and therefore the E_a values do not change with conversion. This result suggests again that the curing mechanism is not changing with the progress of the curing reaction.

On the other hand, the E_a values obtained for the two samples studied suggest that the mechanism of the reaction is the same and independent of the surface treatments studied (APTES and APDES). Although the results are very close to

Table 4
Activation energies obtained with method C from FTIR data

α	E_a (kJ/mol), APTES	E_a (kJ/mol), APDES
0.1	50 ± 1	47 ± 13
0.2	53 ± 7	48 ± 4
0.3	52 ± 5	51 ± 4
0.4	51 ± 6	50 ± 3
0.5	49 ± 8	53 ± 6
0.6	51 ± 4	53 ± 5
0.7	47 ± 7	54 ± 18
Average	50 ± 2	51 ± 2

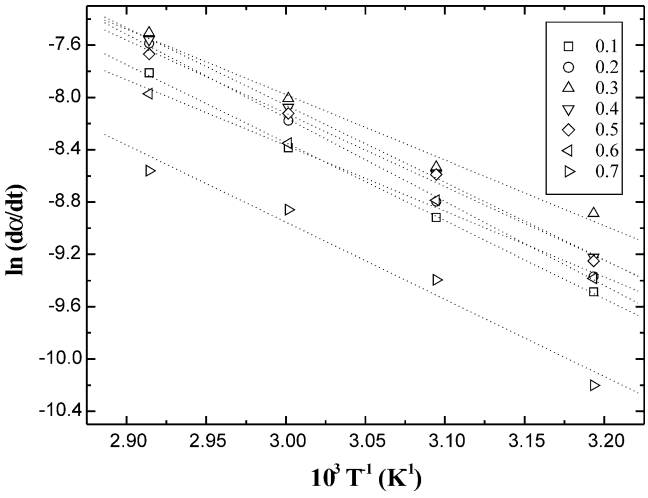


Fig. 4. Natural logarithm of the polymerization rate versus the inverse of temperature at specif c conversions for the APTES-B sample.

those obtained with methods A and B, the comparison re- f ects an apparent controversy. At this point, it is necessary to emphasize that the results of E_a obtained with method C come from real experimental data, while with methods A and B extrapolated values of curing time were used. Therefore, the results from the analysis with the method C are considered more reliable.

In principle, results from method C would be in accordance with those expected if one considered that FT-NIR information comes from the whole system and the mass fraction of the interface region is so low that the different coating should not greatly inf uence the average behavior of the reactive system.

4. Fluorescence measurements

In Fig. 5, plots at different curing times of the f uorescence emission of dansyl moiety are shown; particularly this graph belongs to the APTES-B sample at 40 °C. It is possible to appreciate how the f uorescence intensity increases as the curing reaction progresses. As the reaction proceeds, the viscosity of the environment surrounding the chromophore increases and therefore the number of nonradiative processes decreases, indicating an enhancement of the radiative contribution.

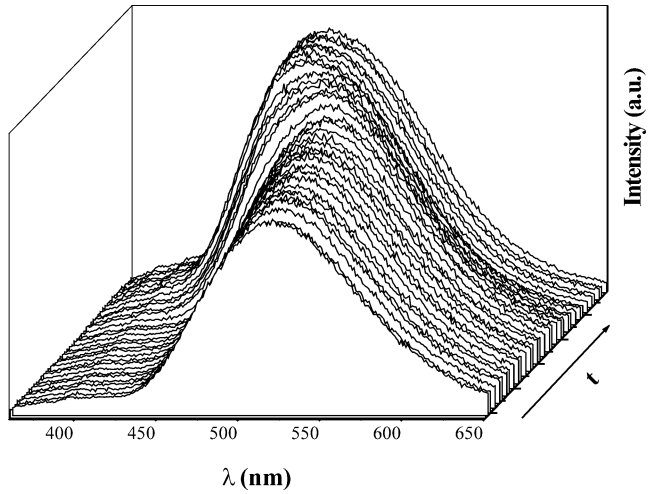


Fig. 5. Evolution of the fluore cence emission band of dansyl derivative with curing time.

Furthermore, the emission maximum shifts to the blue. This behavior can be explained by taking into account the dipolar-coupling model [33–37]. As the rigidity of the medium progresses the coupling between the dipole moment of the excited state of the chromophores and the dipoles of their immediate surrounding is less effective. Therefore, the stabilization for the excited state of the dansyl f uorophore should be smaller [9].

Although variation in f uorescent intensity can be used to monitor the curing reaction, other photophysical parameters are preferred, as mentioned in the Introduction. In this work, the average wavenumber, of the f uorescence emission bands, $\langle \nu \rangle = \sum I_F(\nu_F)\nu_F / \sum I_F(\nu_F)$, has been selected, where $I_F(\nu_F)$ is the f uorescent intensity at a specif c wavenumber. This parameter has been demonstrated to be a good parameter to monitor the curing processes [8,20]. In Fig. 6 is represented, as an example, the average wavenumber, $\langle \nu \rangle$, as a function of curing time for the samples APTES-B and APDES-B. Similar plots were obtained for those samples with the chromophore located at the interface region (APTES-F and APDES-F).

In every case the $\langle \nu \rangle$ parameter continuously increases with curing time. First, in the very early stages of the reaction $\langle \nu \rangle$ increases slowly; after that, its variation is considerably faster and at longer times it levels off. This variation of $\langle \nu \rangle$ associated with the dipolar coupling mentioned above is similar to the variation in the epoxy group conversion with curing time obtained by FT-NIR (Fig. 1). This result suggests that there must be an easy relationship between the chemical conversion (FT-NIR data) and the value of $\langle \nu \rangle$ (f uorescence data) in these processes. Therefore it seems to be reasonable to take the $\langle \nu \rangle$ parameter to carry out a simple kinetic study, considering now the variation in $\langle \nu \rangle$ instead of the variation in the epoxy IR absorption band.

The variation in the average wavenumber, $\Delta\nu = \langle \nu \rangle_t - \langle \nu \rangle_0$ was used to calculate an apparent activation energy using method A (Eq. (3)), where $\langle \nu \rangle_t$ and $\langle \nu \rangle_0$ are the average

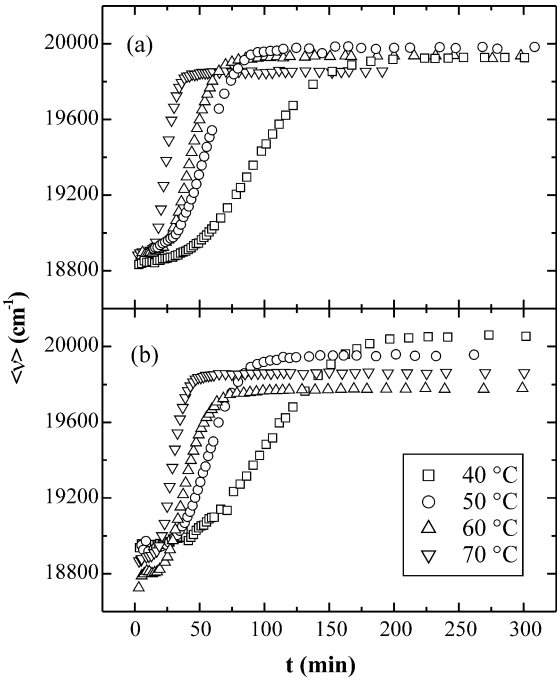


Fig. 6. Representation of $\langle\nu\rangle$ vs curing time for (a) the APTES coating and (b) the APDES coating.

Table 5
Apparent activation energies obtained from the fluore cence experiments using method A

$\Delta\nu$ (cm^{-1})	E_a (kJ/mol)			
	APTES-B	APDES-B	APTES-F	APDES-F
100	–	28 ± 4	34 ± 7	23 ± 9
200	33 ± 4	32 ± 4	36 ± 6	26 ± 7
300	34 ± 3	35 ± 4	36 ± 6	26 ± 7
400	36 ± 3	36 ± 4	35 ± 6	26 ± 7
500	37 ± 3	37 ± 4	34 ± 6	24 ± 8
600	37 ± 3	37 ± 3	–	–
Average	35 ± 2	34 ± 4	35 ± 1	25 ± 1

wavenumber values at curing times t and 0, respectively. Representing the $\ln t$ versus $1/T$ for a group of $\Delta\nu$ values, from the plots apparent activation energies were obtained (Table 5).

As expected, the apparent activation energies for the curing process when the fluore cence label is located in the polymer bulk is the same independently on the glass surface treatment, indicating that this silane treatment does not seem to affect the curing process of the epoxy mixture in the whole system. However, at the interface level the silane treatment seems to affect appreciably the curing process, being more favored when APDES is used since the activation energy is lower for the sample APDES-F (Table 5). This result may be explained in terms of interpenetration. When APDES is used to modify the glass surface it is expected a more opened structure for the coupling region since crooss-linking is not possible (the APDES silane only has two hydrolyzable groups susceptible of subsequent condensation). Therefore,

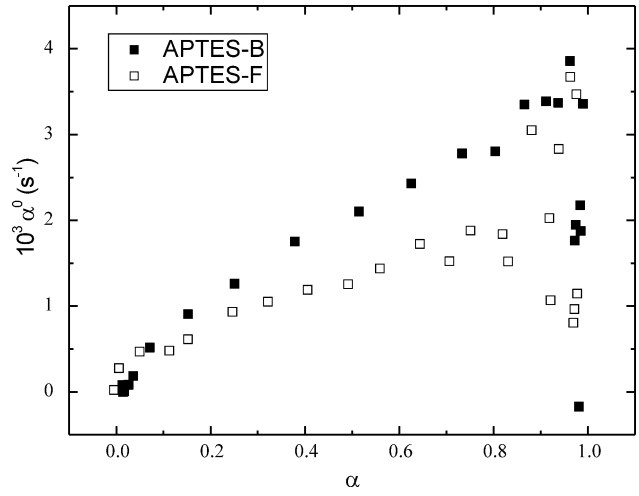


Fig. 7. Reduced f uorescence rate, α_ν^0, versus f uorescence conversion, α_ν.

the epoxy mixture should more easily penetrate the coupling region [38], increasing the local amine concentration, which might affect the mechanism of the reaction.

A f uorescence extent of reaction, α_ν, was define in terms of $\langle\nu\rangle$ as

$$\alpha_\nu = \frac{\langle\nu\rangle_t - \langle\nu\rangle_0}{\langle\nu\rangle_\infty - \langle\nu\rangle_0}, \tag{8}$$

where $\langle\nu\rangle_t$, $\langle\nu\rangle_0$, and $\langle\nu\rangle_\infty$ are the averaged wavenumber at curing times t, 0, and infinit , respectively. Therefore, it could be possible to calculate a reduced rate in terms of the fl orescence extent of reaction. Plotting the fl orescence reduced rate, α_ν^0, versus f uorescence conversion α_ν (Fig. 7), plots similar to those of FT-NIR are obtained. Making a similar treatment as we did in the case of FT-NIR data, it is possible to obtain the results summarized in Table 6.

The values of the corresponding constants K_1' and K_1 (obtained from f uorescence data) for all the samples are listed in Table 6 for all of the samples studied. Again apparent activation energies are calculated from the corresponding Arrhenius plots. These values are also listed in Table 6.

Similar comments can be extracted from the data obtained using this method as in the case of using method A. However, with this method there is more evidence for different curing kinetics in the epoxy bulk and at the interface, since the respective E_a values are clearly different. The activation energies in the f rst kind of samples, named silane-B (Table 6, top) are clearly higher than those from the samples named silane-F (Table 6, bottom).

In the case of f uorescence, the analysis with the method C has also been used to calculate different activation energies. These results are listed in Table 7.

Although the values obtained (f uorescence data) with method C (Table 7) are close to those calculated with method A (Table 5), much care must be taken because the conversion in terms of f uorescence was calculated estimating the values of $\langle\nu\rangle$ at infinit curing time. Therefore this

Table 6
Kinetic constants and apparent activation energies obtained with method B (reduced rate method), using the fluorescence data

Sample	T (°C)	$10^5 K_1'$ (s^{-1})	$10^4 K_1$ (s^{-1})	E_a (nth order)	E_a (auto)
			Bulk		
APTES-B	40	1.19	6.27	70 ± 17	46 ± 7
	50	7.93	1.34		
	60	–	–		
	70	20.0	2.92		
APDES-B	40	2.18	6.65	79 ± 3	46 ± 7
	50	3.96	15.0		
	60	5.81	18.3		
	70	27.4	35.0		
			Interface		
APTES-F	40	10.4	5.16	42 ± 2	34 ± 9
	50	11.7	9.11		
	60	29.6	7.47		
	70	31.2	21.1		
APDES-F	40	13.4	5.87	38 ± 3	29 ± 2
	50	20.2	8.62		
	60	32.8	11.4		
	70	30.0	23.5		

Table 7
Activation energies obtained with method C from fluorescence data

α	APTES-B	APDES-B	APTES-F	APDES-F
0.1	51 ± 16	46 ± 16	28 ± 6	28 ± 6
0.2	48 ± 7	40 ± 6	44 ± 6	36 ± 3
0.3	50 ± 3	53 ± 9	41 ± 3	32 ± 4
0.4	48 ± 5	47 ± 5	38 ± 5	40 ± 9
0.5	46 ± 5	50 ± 5	35 ± 5	39 ± 2
0.6	46 ± 6	42 ± 8	39 ± 6	37 ± 6
0.7	44 ± 5	44 ± 6	30 ± 8	37 ± 3
Average	47 ± 2	46 ± 5	36 ± 6	36 ± 4

may be why similar values of E_a have been obtained for samples APTES-F and APDES-F.

5. Comparison between the epoxy curing in the epoxy bulk and at the glass fiber/epoxy matrix interface

Figure 8 shows the correlation in terms of the fluorescent extent of reaction, α_ν, between the epoxy curing exactly at the interface (fluorescent label localized at the interface), α_ν^i, and the epoxy curing in the epoxy bulk (fluorescent label localized in the epoxy bulk), α_ν^B. Independent of the surface coating, two regions can be observed. At the first stage of the reaction, the curing rate is higher at the interface than in the bulk (the slopes of the curves are higher than 1); after that there is another region in which the slopes decrease and are lower than 1, which may indicate that a similar process is being monitored. One possible explanation of this result may be that when the epoxy resin penetrates the interface the increase in the viscosity is faster because of a higher local concentration of the amino groups.

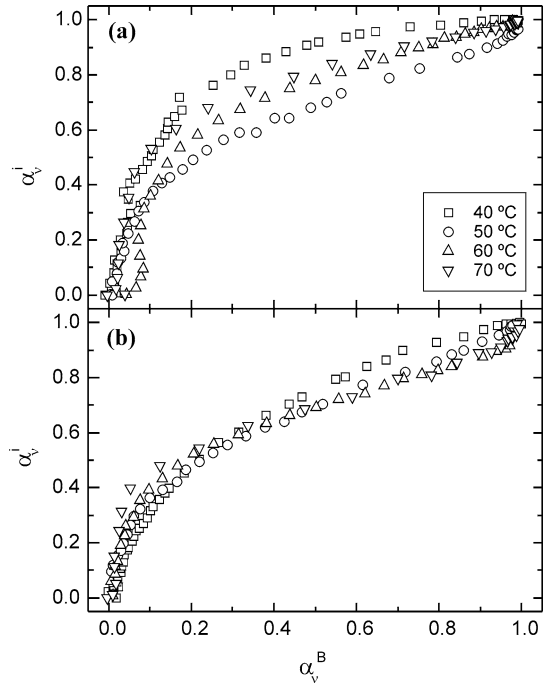


Fig. 8. Fluorescent extent of reaction when fluorescent label is localized at the interface, α_ν^i, as a function of fluorescent extent of reaction when fluorescent label is localized in the epoxy bulk, α_ν^B: (a) APDES and (b) APTES coatings.

Additionally, comparing the cure behavior as a function of the silane coating, it is observed that when APDES is used (Fig. 8a), the region with the higher slope is more extended than when the fibers are coated with APTES (Fig. 8b). This result can be explained in terms of a more opened structure for the APDES coating, which would be in accordance with the interpretation given from the kinetic analysis (Table 5).

6. Comparison FTIR-fluorescence

Finally a comparison between FT-NIR and fluorescence data is shown in Fig. 9 in which the fluorescent conversion is represented as a function of the epoxy group parameter $\langle\nu\rangle$. Only at 40 °C is a nearly linear trend observed. As temperature increases the plots deviate from linearity as can be seen in the graph for 70 °C. With FTIR a chemical reaction is followed, so higher changes in conversion are observed from the beginning until the gel conversion is reached. At this point, the viscosity of the system is very high and small changes in the chemical reaction will increase the viscosity of the system highly until its vitrification is reached. For this reason, higher variations in $\langle\nu\rangle$ than in epoxy conversion are observed. As we mentioned before, the fluorescence during cure seems to give more information about changes in the viscosity of the system than real chemical changes.

However, a key aspect to be considered is that there must be a relationship between the α_{epoxy} and $\langle\nu\rangle$, which means that a change in $\langle\nu\rangle$ corresponds to a specific change in

Fig. 9. Correlation plots of $\langle \nu \rangle$ versus epoxy group conversion for (a) APTES-B and (b) APDES-B samples.

chemical conversion. In Fig. 9, two different parts are observed: in the first one, at low conversions, the plots present a moderate slope, and in the second one, at higher conversions, the plots have greater slope.

These results suggest that FT-NIR and fluorescence actually can be considered as a complementary technique to study epoxy-curing processes. The FT-NIR seems to be more useful when the first stages of the curing reaction are concerned because bigger changes are observed with curing time, while the fluorescence should be recommended to follow the curing processes at the last stages of the epoxy cure reactions due to its higher sensibility. However, both of them allow the obtaining of kinetic parameters that could help in designing curing conditions for preparing epoxy materials.

On the other hand, only fluorescence technique can be used to monitor the curing process at the interface in a composite material and, additionally, it allows carrying out the kinetic studies of the process.

7. Conclusions

Two different techniques have been used to monitor the curing process in a composite material, FT-NIR and fluorescence. FT-NIR and fluorescence actually can be considered as complementary techniques to study epoxy-curing processes. The FT-NIR, seem to be more useful when the first stages of the curing reaction are concerned because bigger changes are observed with curing time, while the fluorescence should be recommended to follow the curing processes at the last stages of the epoxy cure reactions due to its higher sensibility. Independent of the sample and the technique used for the kinetic analysis, no variation of the activation energy of the epoxy curing reaction was found, which suggests that there are no changes in the mechanism of the reaction along the process. Fluorescence from dansyl located at the glass fiber/epoxy interface reflected that the kind of reinforcement treatment clearly affects the epoxy curing process exactly in that region. When APDES is used to modify the glass surface instead of APTES, a more opened structure is expected and, therefore, the epoxy mixture should more easily penetrate the coupling region, increasing the local amine concentration, which might affect the mechanism of the reaction. However, when the analytical response comes from the whole system (using FT-NIR and the fluorescence of dansyl when it is chemically bonded to the epoxy bulk), the mechanism of the reaction does not seem to change with the silane coating used.

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