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Kinetic study of the cure process at the silica microfibres/epox interface using pyrene fluorescenc response

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Abstract

In the present work, using the pyrene fluorescenc response, the kinetic of the cure process at the interface of a composite material is studied. Silica microfibre were surface coated with 3-aminopropyltriethoxysilane (APTES), labelled with the pyrene group and dispersed in a mixture based on diglycidylether of bisphenol A (DGEBA) and ethylenediamine (EDA). The fluorescenc of the pyrene was used to monitor, at different temperatures, the cure process at the epoxy/microfibre interface. A simple kinetic model was discussed from the fluorescenc data and an apparent activation energy was obtained ($E_a = 33$ kJ/mol). On the other hand, the cure process of the whole mixture was followed by FT-IR and by DSC and their results were compared with those obtained by fluorescence

Keywords:
Fluorescence; Curing; Epoxy; Kinetic

1. Introduction

The properties of composite materials are greatly influ enced by the type of adhesion between the reinforcement and the matrix [1–3]. If the adhesion takes place, the interface necessarily has to be controlled because composite materials depend on the ability of the interface to transfer stress between the matrix and the reinforcement [4].

Surface treatment of reinforcements has been a common method to improve general adhesion properties by increasing electrostatic interactions and facilitating chemical bonding between the constituents. Among others, coupling agents have a great effect on the interface structure and properties [1,5]. They have two different functionalities, which can chemically bond with both the reinforcement and the matrix. The most common used coupling agents are difunctional organosilicon compounds called silanes.

It is known that the mechanical properties of composite materials can be changed, because of the chemical and structural differences in this coupling agent interface layer [4,6,7]. There are different contributions trying to explain the mechanisms responsible for enhancing mechanical properties in composites [1,4,8]. Nevertheless, in many cases, the interface is not as well known as one would want. Due to this, for these systems it is necessary, among others, to know the extent of epoxy curing at the interface because it will be related to its rigidity and molecular structure. This aspect is essential for a better understanding of composite performance.

There are classical techniques used to investigate the cure processes, such as differential scanning calorimetry (DSC), dynamic dielectric analysis, dynamic mechanical thermal analysis and FT-IR. However, none of them have been revelled as very sensitive, non-destructive technique for monitoring in situ and in real-time polymerization processes. The most common methods for kinetic studies in the curing of the epoxy systems are FT-NIR and DSC showing some limitation of sensitivity at high extends of the curing process. In the FT-NIR studies, the decrease in the epoxy band at 4530 cm^{-1} is often used to monitor the curing process [9,10]. For DSC, the dynamic, isothermal and model-free isoconversional modes have been used to study the curing process of the epoxy systems [11–14]. Nevertheless, DSC methods are not suitable for monitoring real-time processes or for the non-destructive analysis of polymers.

The most common techniques used to investigate cure processes, such as DSC, dynamic dielectric analysis, dynamic mechanical thermal analysis and FT-IR, give information from the whole of the system. However, when composite systems are studied it will be of critical interest to monitor the curing just at the interface. It is very difficul to fin a very sensitive and non-destructive technique which can give microstructural information at the interface and big efforts have to be focused to this aspect.

Fluorescence is a very sensitive and non-destructive technique to monitor curing of different polymeric systems [15–24]. The use of fluorescen response from labels and probes has become a very powerful tool to follow changes in its surroundings such as polarity and/or rigidity [15–27]. Some works propose that an enhancement in the microviscosity of the medium leads to a decrease in the non-radiative decay rate and consequently an increase in the fluorescenc quantum yield [19]. Others use the increase of the fluores cence intensity that comes from chemical changes of the fluorophor [20,23].

Pyrene and its derivatives are excellent fluorescen probes or labels because they usually have long fluorescenc life times, form emissive excimers or exciplexes, and have a fluorescenc spectrum sensitive to the polarity of the environment [25,26]. 1-Pyrenesulphonyl chloride (PSC) is a suitable chromophore that reacts easily with amine groups, yielding sulphonamide derivatives (PSA); which has a very high quantum yield, and it can give a "excimer-like" band that arises mainly from exciplex emission when propylamine groups are close enough to the PSA moiety [26].

It is known that fluorescenc from species that have a clear charge separation in the excited state, shows appreciable shift in their fluorescenc emission band depending on the polarity and/or rigidity of their surroundings. Therefore, their spectral shifts seem to be good photophysical parameter to monitor whatever change appearing in the polymeric systems [28].

In this work, it is proposed to use the fluorescen response of PSA groups directly attached to the coupling region between a silica reinforcement and a epoxy matrix, to follow the curing process of the polymer just at the interface.

2. Experimental part

2.1. Materials

The silica SMF2 was supplied by Tolsa S.A. (Madrid, Spain) with SiO_2 content over 95% and the specifi surface area of 500 m^2/g. The silica microfibre were silanized with 3-aminopropyltriethoxysilane (APTES) (Aldrich Chem. Co.) without further purification 1-PSC (Molecular Probes) was used as a fluorescenc label. The solvents used (Aldrich Chem. Co.) were HPLC grade without further purificatio except toluene that was distilled over sodium to remove the water. One epoxy system based on poly(bisphenol A-co-epichlorohydrin)glycidyl end-capped (DGEBA) (average M_n = 348 g/mol) and ethylenediamine (EDA) supplied by Aldrich Chem. Co. (Madrid, Spain) was used as the matrix.

2.2. Sample preparation and curing

As received silica microfibre (1 g) were introduced in a 2% (v/v) silane aqueous solution for 15 min to silanize them. After that, silanized samples were filtered polymerized at 110 °C for 1 h, Soxhlet extracted during 4 h to remove any physisorbed residue and vacuum dried for at least 8 h. After the silanization process was finished 0.4 g of the silanized silica were immersed in 10^{-4} M PSC solution in acetonitrile. To label the silica surface with the fluorescenc moiety, the reaction of the sulphonyl group with the amines of the siloxane coating was carried out to yield the sulphonamide derivative. Finally, the pyrene labelled sample were exhaustively washed with acetonitrile and vacuum dried for at least 8 h.

The curing procedure was carried out at different temperatures by mixing the stoichiometric epoxy-amine mixture with the silanized silica in a proportion of 20% (w/w) for the reinforcement.

2.3. Measurements

For fluorescenc and FT-NIR measurements the mixtures were placed between two glass plates controlling their thickness with a Teflo spacer (0.6 mm). The curing processes were monitored at fi e temperatures (40, 45, 50, 60 and 70 °C) introducing the samples in a SPECAC temperature controller:

(a) *Fluorescence*. Fluorescence spectra were recorded as a function of curing time using an Edingburg fluorimete . The excitation and emission slits were 2.3 and 3.6 nm, respectively, the excitation wavelength was 340 nm and an optical fibr cable was used to excite and collect in situ fluorescence

(b) *FT-NIR*. The extent of reaction α_{IR} at any time t is calculated from the initial areas of epoxy, $A_{E,0}$, and reference, $A_{R,0}$, peaks and their corresponding values at time t, $A_{E,t}$ and $A_{R,t}$, according to the following equation:

$$\alpha = 1 - \frac{(A_{E,t})(A_{R,0})}{(A_{E,0})(A_{R,t})} \quad (1)$$

The peak at 4530 cm^{-1} was used to monitor the disappearance of the epoxy group, while the peak due to C–H stretching vibration of the benzene ring was used as the reference absorption.

(c) *DSC*. The DSC measurements were done by placing the samples on a Perkin Elmer DSC7 in the dynamic mode and using three heating rates (2, 5 and 10 °C/min).

3. Results and discussion

3.1. Fluorescence measurements

In Fig. 1 is presented, as an example, the fluorescenc spectra of PSA label for different curing times when the reaction takes place at 40 °C. It is observed two regions for all the spectra: (i) the monomer region (350–420 nm), in where it is observed the typical vibrational structured band

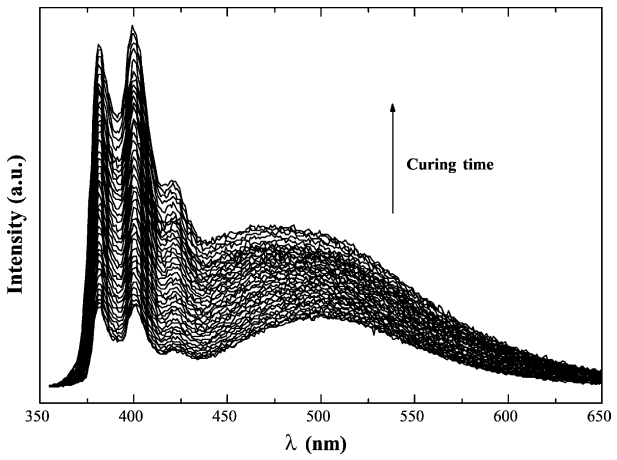

Fig. 1. Fluorescence emission spectra of PSA label during the curing of the epoxy system at 40 °C. The vertical arrow indicate the order of the spectra during the curing process.

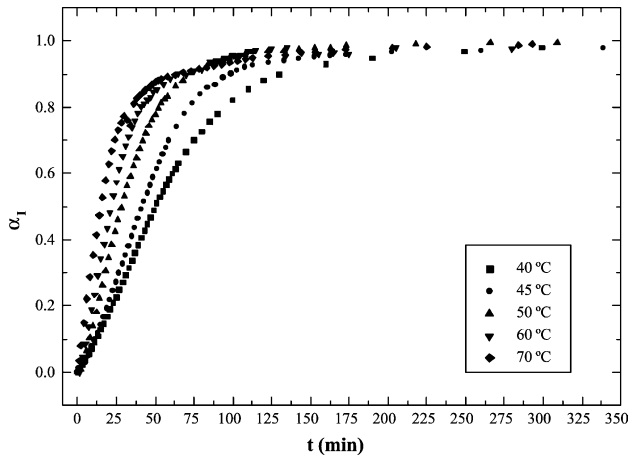

Fig. 2. Fluorescence intensity conversion as a function of curing time at 40, 45, 50, 60 and 70 °C.

that arise from the pyrene monomer emission and (ii) the exciplex region that correspond to a broad band assigned to the emission coming from the complex formed between the amine groups of the silane coating and the pyrene moiety in the excited state [26]. The exciplex band undergoes a blue shift when curing of epoxy mixture proceeds. In addition, the intensity clearly increase as a function of curing time.

From the spectra obtained at each curing temperature, it was calculated the integrated intensity being plotted as a function of curing time. Normally, to do a kinetic study it is more convenient to use the relative extent of one change instead of the absolute values. Due to this, we use the fluo rescence intensity conversion define as

$$\alpha_{\mathrm{I}} = \frac{I_t - I_0}{I_\infty - I_0} \tag{2}$$

where I_t, I_0 and I_∞ are integrated intensities at time $t = t$, $t = 0$ and $t = \infty$, respectively, during the curing process.

Fig. 2 shows the fluorescenc intensity conversion as a function of curing time at 40, 45, 50, 60 and 70 °C. In every case, it is observed similar profile as to those obtained for chemical conversion in epoxy cured systems [9–14].

Assuming that the intensity increase with curing is only due to an enhancement of the viscosity, one may conclude that the stabilization of this parameter could inform about vitrificatio of the system. When vitrificatio is reached in a curing process, there must not be large changes in the mobility of the system and therefore in the intensity.

The general kinetic equation can be described as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{3}$$

where α is the conversion and k the rate constant.

Since, conversion of the epoxy systems at the vitrificatio time use to be constant independently of the cure temperature. It is possible to integrate Eq. (2) to obtain:

$$t = \frac{B}{k} \tag{4}$$

where B is the constant $\int_0^\alpha \mathrm{d}\alpha/f(\alpha)$.

Thus, the vitrificatio time, t_{v}, can be related to the apparent kinetic constant k according to Eq. (4). From Fig. 2, it was obtained the vitrificatio times as the points in where the slopes of the curves change. Assuming an Arrhenius behaviour for k ($k = A\,\mathrm{e}^{-E_{\mathrm{a}}/RT}$), Eq. (4) can be converted in

$$\ln t_{\mathrm{v}} = C + \frac{E_{\mathrm{a}}}{RT} \tag{5}$$

where C is a constant and E_{a} the apparent activation energy.

Therefore the activation energy could be obtained from the slope by plotting $\ln t_{\mathrm{v}}$ vs. $1/T$ (Table 1). The good correlation factor for the straight line ($r = 0.99$) suggest the goodness of the method.

Assuming that the curing reaction in terms of fluorescenc intensity variation can be described by an Arrhenius-like process with only one activation energy (one reaction or several with very close activation energies), a master curve should be obtained by a time–temperature superposition of the α_{I} vs. $\ln t$ data at an arbitrary reference temperature [29]. In Fig. 3a is represented α_{I} vs. $\ln t$ from isothermal curing at different temperatures, while in Fig. 3b is plotted the master

Table 1
Apparent activation energies obtained by using different methods

Methods	E_{a} (kJ/mol)
Fluorescence	
Vitrificatio time	32 ± 2
Shift factor	35 ± 3
FT-NIR	
Shift factor	58 ± 8
DSC	
Barrett's method	68 ± 3
Kissinger's method	67 ± 8

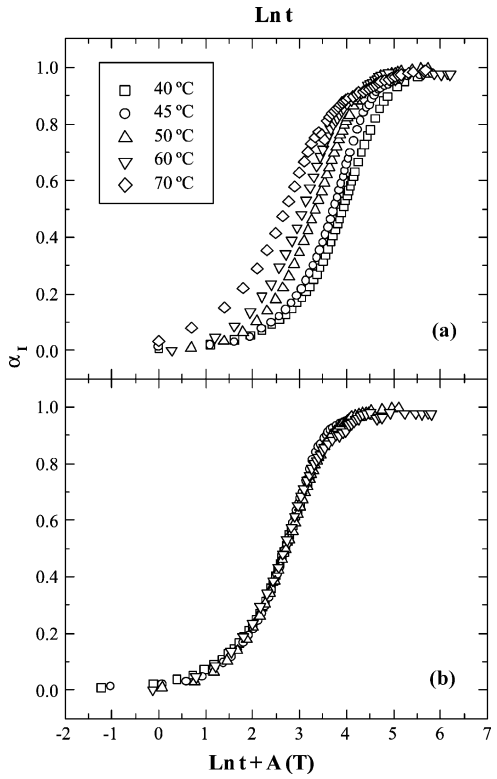

Fig. 3. (a) α_I vs. $\ln t$ from isothermal curing at different temperatures and (b) master curve at 70 °C after shifting each curve in (a) with a constant factor $A(T) = \ln(t_{70\,^\circ C}) - \ln(t_T)$.

curve obtained after shifting each curve in Fig. 3a with a constant factor, $A(T) = \ln(t_{70\,^\circ C}) - \ln(t_T)$, along the $\ln t$ axis.

The successful superposition in Fig. 3b confirm the Arrhenius behaviour and therefore the possibility of obtaining an apparent activation energy (Table 1) by plotting the shift factor, $A(T)$ vs. $1/T$.

3.2. FT-NIR measurements

The time–temperature superposition can also be applied to the FT-NIR data, and therefore another apparent activation energy can be obtained (Table 1).

3.3. DSC measurements

Fig. 4 shows the DSC thermograms recorded for the system under study at 2, 5 and 10 °C/min heating rates, in the temperature range 40–150 °C. The apparent activation energy was estimated using the Barrett's relation [30]:

$$k = \frac{\mathrm{d}H/\mathrm{d}t}{H_\mathrm{T} - H} \tag{6}$$

where $\mathrm{d}H/\mathrm{d}t$ is the heat fl w (J/min), H_T the total heat recorded over all the reaction and H the heat recorded up to time t. The Barrett method assumes that the temperature dependence of the reaction rate follows a relationship of Arrhenius type ($k = A\,\mathrm{e}^{-E_\mathrm{a}/RT}$). Therefore, E_a can be obtained from the slope of the curve $\ln k$ vs. $1/T$ (Table 1).

The E_a determined taking into account all the three heating rates was evaluated by means of the Kissinger equation [31]:

$$\ln\frac{\beta}{T_\mathrm{p}^2} = \ln\frac{k_0}{\beta} - \frac{(E_\mathrm{a}/R)}{T_\mathrm{p}} \tag{7}$$

where β is the scan rate (°C/min), T_p the peak temperature in the DSC trace and k_0 the Arrhenius pre-exponential factor (min^{-1}).

3.4. Comparison between the different kinetic methods

Attending the E_a values shown in Table 1 it can be possible to separate the results in two groups of methods: (i) methods based on fluorescenc data and (ii) methods based

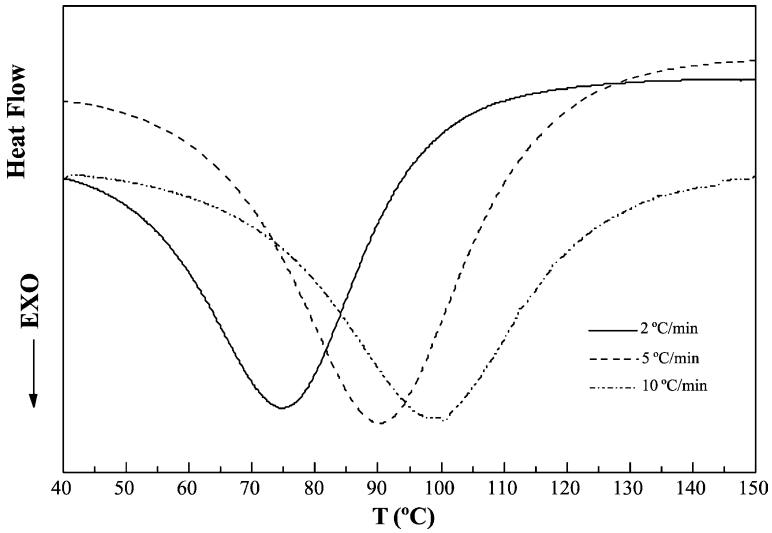

Fig. 4. DSC thermograms recorded for the system under study at 2, 5 and 10 °C/min heating rates.

on FT-NIR and DSC data. The E_a values obtained using FT-NIR and DSC are very similar and correspond to typical values for these kind of epoxy systems [14]. On the other hand, they are nearly two times higher than those obtained by fluorescence This apparent controversy could be explained taking into account that fluorescenc reflect the curing process just at the interface. In this region, there must be several factors affecting the curing process, such as the variation in the local stoichiometry. The presence of the amine groups associated to the silane coating may change its local concentration. Therefore, this results suggest that the kinetic of the epoxy reaction is different in the bulk of the polymer than in the filler/matri interface.

4. Conclusions

The use of fluorescenc response from pyrene label is revelled as a good method to monitor the curing of epoxy systems at the silica/epoxy matrix interface and even to study its kinetic.

Using fluorescence FT-NIR and DSC it was obtained different apparent activation energies, 33, 58 and 68 kJ/mol, respectively. Since the pyrene is directly bonded in the interface region its fluorescenc response has to give information about the curing just at the interface. The different values of the apparent activation energies reflec that the kinetic of the epoxy reaction must be different in the bulk of the polymer than in the filler/matri interface.

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