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Curing of polymer matrix composites
Fluorescence study of dansyl fluorophore labeled to glass fibers and DGEBA–ethylenediamine epoxy resin

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Curing process of diglycidyl ether of bisphenol A/ethylenediamine mixture in the presence of glass fibers was monitored by fluorescence in two ways: first, using dansyl labeled glass fibers and diglycidyl ether of bisphenol A (DGEBA)/ethylenediamine mixture and second, using unlabeled glass fibers and DGBA-dansyl labeled/ethylenediamine mixture. Integral fluorescence intensity was analyzed as a function of time. Results allow comparison between the curing process inside the bulk of the resin and at the glass fiber interface. It was concluded that for the system DGEBA/ethylenediamine the polymer matrix viscosity increases with the curing time faster inside the bulk than at the glass fiber interface.

Keywords Polymer composites; Monitoring curing; Fluorescence; Epoxy-amines; Glass fibers

1. Introduction

Glass fiber used as reinforcements of polymer matrix composite materials, are usually surface treated with ethoxy silanes having vinyl, epoxy or amino groups [1]. Such monomers react with the glass surface and also between themselves to form a graded cross-linked polymer layer [2,3] with a high surface density of reactive groups. In subsequent processes, such groups may react with the polymer matrix, coupling chemically and mechanically the constituents of the composite. The structure and properties of these interfacial regions has been extensively studied [2–7] although it remains as an open issue.

Of special interest are the competitive reactions that may occur at the interface during the curing process. In epoxy matrix composites, the epoxy component may react either with the hardener and/or with the amino groups located at the surface via the previous silanization process. Basic knowledge on this issue may help to optimize the mechanical properties at the interfacial level.

Fluorescence is a suitable non-destructive technique for monitoring the curing of composite materials. The technique sensitivity allows to study the glass fiber–matri interface when an adequate chromophore is located in the polymer matrix or in glass fibe surface. In this work we present a study of the interfacial reactions in DGEBA–ethylenediamine–glass fibe composites. We will demonstrate that fluorescenc is a potent technique to study the changes that happen at the interface during the curing process.

2. Experimental

Epoxy curing process of DGEBA/ethylenediamine mixture in presence of glass fiber supplied by Vetrotex (Spain) was studied in two ways: using dansyl (DNS) labeled glass fiber and DGEBA/ethylenediamine mixture and using unlabeled glass fiber DGEBA-DNS labeled ethylenediamine mixture.

In the firs experiment, glass fiber were subjected to Soxhlet extraction with dried toluene for 4 h and vacuum dried for 12 h to remove the soluble fraction of the unknown coupling composition. Well-dried glass fiber were put in contact with 5×10^{-4} M dansyl chloride solution in acetonitrile (AcN). Then, the fiber were subjected again to Soxhlet extraction with dried toluene for 4 h and vacuum dried for 12 h. After this preparation, the mixture DGBA/ethylenediamine was added over the fiber to monitor the curing process by fluorescence

In the second experiment, glass fiber were only subjected to Soxhlet extraction with dried toluene for 4 h and
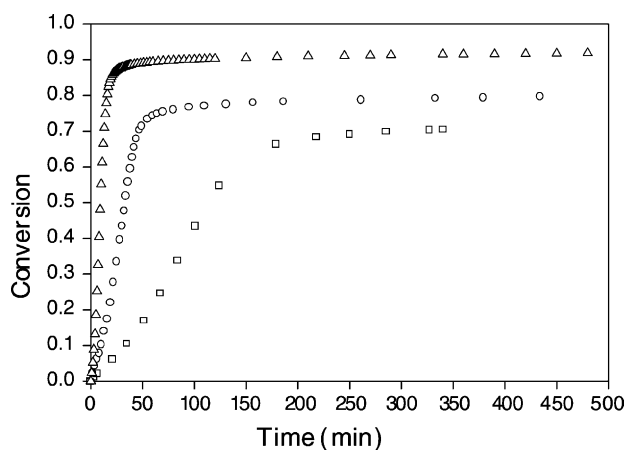
Fig. 1. Measurement system for solid samples.

Fig. 2. Dependence of the epoxy groups conversion on the curing time. Curing temperatures: 40 °C (○), 60 °C (△) and 80 °C (□).

pears. The conversion was obtained by FT-IR as:

$$C_t = \frac{A_0 - A_t}{A_0} \tag{1}$$

where A_0 and A_t are the initial and instantaneous area of epoxy group peak that appear to $4531\,cm^{-1}$, respectively, and C_t the conversion at the time t.

3. Results and discussion

In Fig. 3 the excitation and emission spectra for the glass fibe labeled with DNS and the emission spectra of glass fibe without DNS are presented. The excitation spectrum conditions were an emission wavelength of 460 nm on a 300–450 nm range and the emission scan on a 360–650 nm range with an excitation wavelength of 354 nm. These spectra show one excitation band centered at 354 nm and one emission band at 460 nm. The intrinsic emission of glass fiber without DNS and intrinsic emission of epoxy resin were very small compared with that of the emission of labeled fibers This characteristic allows to depreciate the glass fibe intrinsic signal in the curing process study.

The fluorescenc monitoring curing of diglycidylether bisphenol A and ethylenediamine was evaluated by intensity fluorescenc integral. The integral fluorescenc intensity is the most classical method to evaluate the chromophore flu orescent process.

3.1. Integral fluo escence intensity

DNS labeled glass fiber and DGBA/ethylenediamine mixture integral intensity versus curing time and epoxy group conversion are presented in Fig. 4. Unlabeled glass fiber and DNS labeled-DGBA/ethylenediamine mixture are presented in Fig. 5. Integral fluorescenc intensity increases highly at initial curing time until 200, 80 and 60 min in DNS labeled glass fiber and DGBA/ethylenediamine mixture at 40, 60 and 80 °C, respectively, and at higher
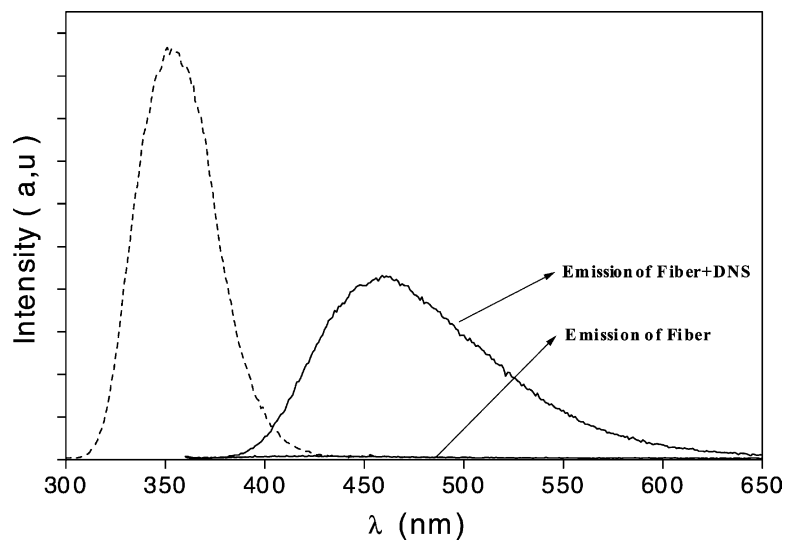
vacuum dried for 12 h. An amino derivative of dansyl was synthesized by reaction of dansyl chloride with excess of ethylenediamine for 12 h at 120 °C in chloroform. After washing several times the chloroform solution with saturated bicarbonate aqueous solution, chloroform was eliminated and the solid product was recrystallized from toluene. The reactive fluorophor was added to DGEBA/ethylenediamine to such an extent that its fina concentration was 5×10^{-4} mol of DNS over 1000 g of DGBA/ethylenediamine reaction mixture.

Steady-state of fluorescenc measurements were performed on an Edinburgh fluorimete , composed by a xenon lamp Xe900 and double monochromators for excitation and emission pathways. A bifurcated optical fibe was employed for both excitation and emission. Spectral conditions were 2 mm for excitation and 1.5 mm for emission slits. The excitation wavelength was fi ed at 354 nm and spectra were recorded in the range of 360–650 nm at 5 nm/s. The curing temperature was controlled at 40, 60 and 80 °C with a thermostatic bath. The measurement system for solid samples is presented in Fig. 1.

Glass fiber were located longitudinally between two Teflo film with a section of 1 mm and supported over a glass platform. The optical path was kept constant on all samples with this method. Optical fibe temperature was controlled at 20 °C in all measurements.

Curing process of DGBA/ethylenediamine mixture was followed by FT-IR in near IR region. Epoxy group conversion was evaluated as the area variation on the epoxy group peak that appears at $4531\,cm^{-1}$ (Eq. (1)). The dependence of the epoxy groups conversion on the curing time at 40, 60 and 80 °C is shown in Fig. 2. The conversion increases strongly until the conversion limit at 200 min–70%, 50 min–80% and 25 min–92% for 40, 60 and 80 °C, respectively. Starting from these temperatures, a constant area appears.

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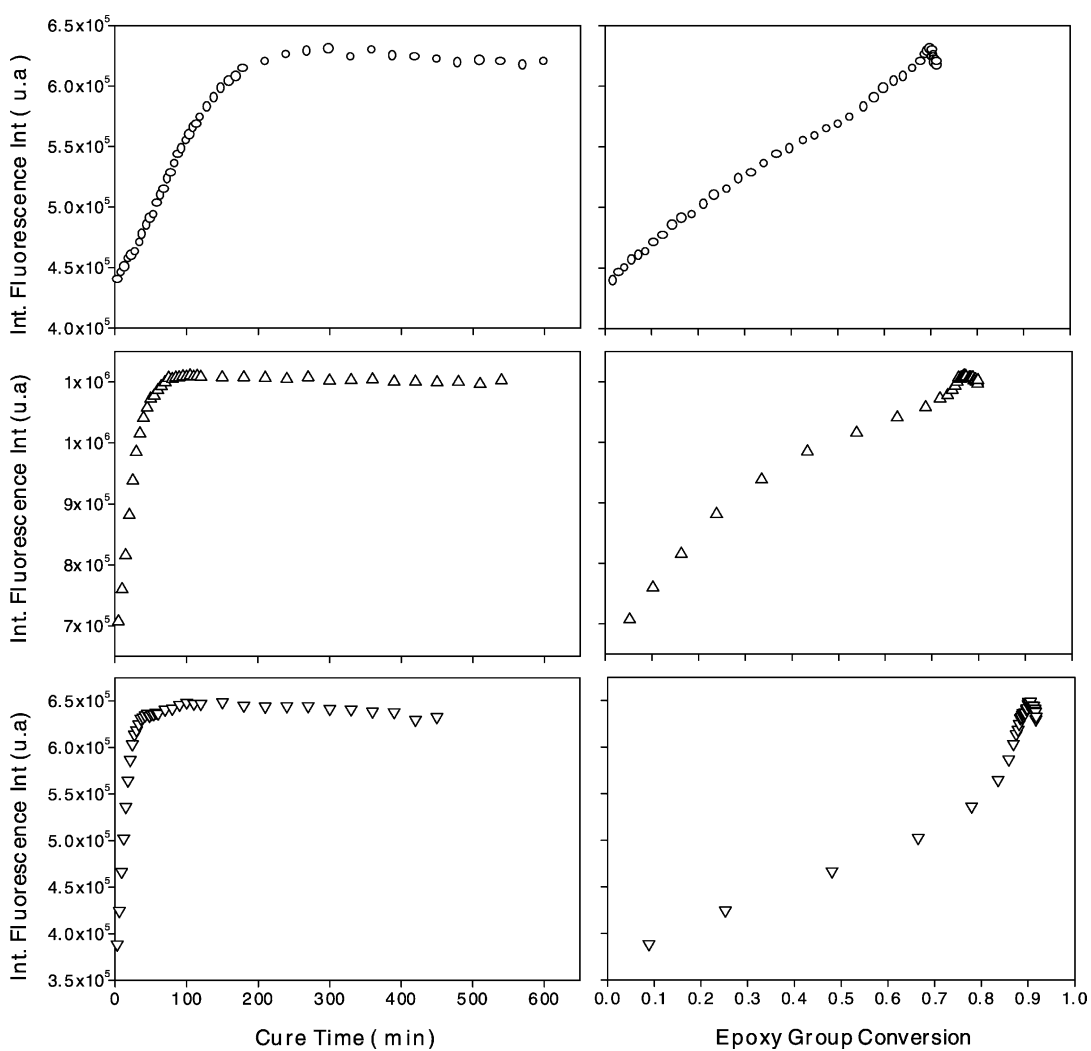Fig. 3. Excitation and emission spectra for the glass fibe labeled and unlabeled with DNS.

Fig. 4. Dependence of integral fluorescenc intensity on curing time for DNS labeled fiber plus DGBA/ethylenediamine. Curing temperatures: $40\,^{\circ}$C ($\bigcirc$), $60\,^{\circ}$C ($\triangle$) and $80\,^{\circ}$C ($\triangledown$).
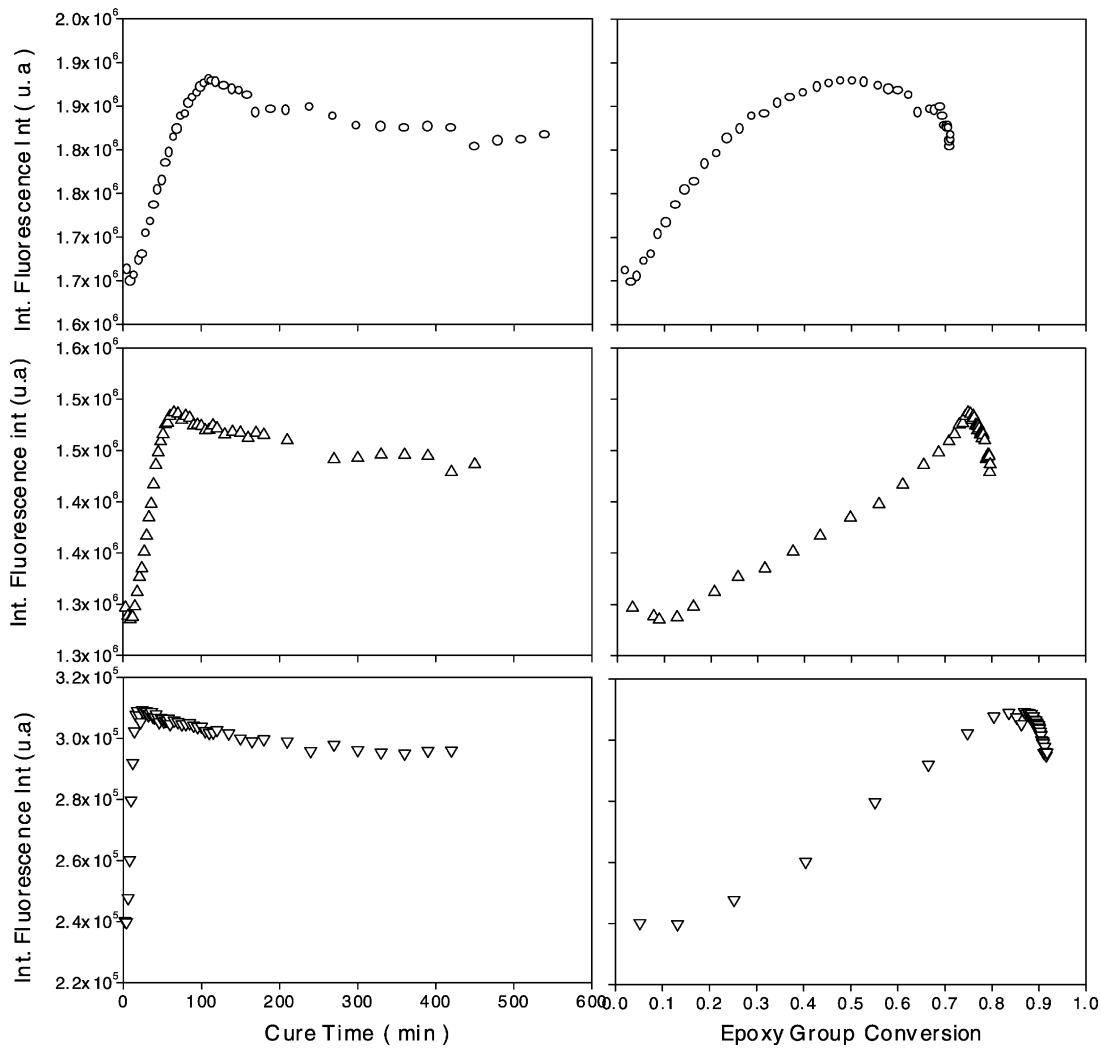
Fig. 5. Dependence of firs moment of frequency on curing time for pure fiber plus DGBA/dansyl labeled-ethylenediamine. Curing temperature: $40\,^{\circ}$C ($\bigcirc$), $60\,^{\circ}$C ($\triangle$) and $80\,^{\circ}$C ($\triangledown$).

times for unlabeled glass fiber and DNS labeled-DGBA/ethylenediamine mixture.

The integral fluorescenc intensity increases with the curing time because of the increase of medium local viscosity, that are related with the epoxy and amines conversion, therefore the slopes are related to reaction rates. Differences between the two studies show characteristics in the interface between glass fibe and epoxy resin. Slopes at low curing times of normalized integral fluorescenc intensity appear in Table 1.

Table 1
Slopes at low curing times of normalized integral fluorescenc intensity

Temperature (°C)	Slopes in labeled glass fiber +DGBA/ ethylenediamine	Slopes in unlabeled glass fiber +DGBA/ ethylenediamine-DNS
40	0.618	1.145
60	1.852	2.357
80	2.758	9.129

These values show that the polymeric rates increase with temperature and a very important date: the reaction rates are higher when the chromophores are labeled on the matrix than when they are labeled on the glass fibe . These results show that the polymer matrix cures faster than the interface matrix–glass fibe , therefore, the adhesion is harmed for the DGBA/ethylenediamine curing. The polymer matrix viscosity increases with the curing time faster than the interface with the glass fibe , so it is difficul the epoxy group diffusion to the interface and therefore the adhesion matrix–fibe is also being harmed. The optimal mechanical behavior would happen when the curing interface speed was higher than the one inside the matrix.

4. Conclusions

Fluorescence techniques are very sensitive for the monitoring curing study of epoxy resin and interface matrix–glass fibe adhesion. The reaction rates are higher when the

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chromophore are labeled on the matrix than when are labeled on the glass fibe . The polymer matrix faster than the matrix–glass fibe interface, therefore, the adhesion are harmed for the DGBA/ethylenediamine curing. The polymer matrix viscosity increase faster than the interface with the glass fibe therefore are harmed the epoxy group diffusion to the interface and therefore the adhesion matrix–fibe is also being harmed. The optimal mechanical behavior would happen when the curing interface speed was higher than the one inside the matrix.

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