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# A fluorescence method to estimate the distribution of stresses in polymer materials

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## Abstract

It is very important to control the distribution of stresses in order to prevent catastrophic failures during working life of polymer materials. At the present moment, there are several methods to test the distribution of stresses in materials. In the last years, many numerical methods have been proposed, but they have limitations. On the other hand, experimental methods are difficult to perform in all cases, for example when “in situ” determinations are required. In the present work, the use of environmentally sensitive fluorescence molecules (fluorophores) to estimate the tensile state in polymers is discussed. Pyrene, p-quaterphenyl, 1,6-diphenyl-1,3,5-hexatriene (DPhHT), 1,4-bis(5-phenyloxazol-2-yl)benzene and dansyl derivatives, whose fluorescences are sensitive to different types of changes (polarity, microviscosity, etc.), were immersed in one epoxy mixture. After that, the epoxy mixture was cured in a mould to prepare size controlled samples. The specimens were uniaxially loaded. In most of the cases the fluorescence suffers small variations with the epoxy deformation. To evaluate these changes, two photophysical parameters were used: (i) the integrated intensity and (ii) the first moment in the wavenumber of the emission band,  $\langle \nu \rangle$ . Related to the fluorescence intensity, the dansyl moiety seems to be the most sensitive; however, for  $\langle \nu \rangle$  the DPhHT showed the highest changes.

## Keywords

Fluorescence; Tensional state; Epoxy resins

## 1. Introduction

The epoxy resins are very important thermosetting commonly used as structural adhesives, coatings and matrices for composite materials. When they are used as the matrix in composite materials, the appearance of residual stresses after curing process is very well known. This behavior is interpreted in terms of the difference in the thermal expansion coefficient between the matrix and the reinforcement. In addition, the small defects such as microcracks, inclusions, etc., can generate an accumulation of stresses in specific sites as to induce mechanical failure from those places. The study of that residual stresses distribution is very important in order not to prevent desired failures. In the last years, many numerical methods have been proposed, but they have limitations [1,2]. Photoelasticity offers a good method for the analysis of stress in polymeric matrices, such as epoxies and polyesters, which exhibit artificial birefringence [3,4]. Nevertheless, all of these methods do not allow realizing the analysis non-destructively, in situ and when the material is in service. If the last point said were possible, it could be prevented catastrophic failures at any time.

The use of fluorescence probes and labels has revealed a good method to study specific sites at a molecular level in different kinds of materials. Depending on the fluorescence molecule used, it is possible to study the characteristics of its immediate surroundings as polarity [5–8], rigidity [9–12], etc. and its potential changes, when environmental conditions have been modified.

Optical methods to measure molecular orientation are birefringence [13], optical dichroism [14] and fluorescence based methods [14–18]. The first two methods require the probing light to be transmitted through the material, but fluorescence measurements can be carried out via excitation and detection from the same surface. The polarized fluorescence [16,17] and fluorescence anisotropy [15] have been commonly used to measure molecular orientation caused by shear and extensional stresses applied to the material. Nevertheless, they have shown some difficulties to interpret the results because of the low accuracy of the data. Therefore, keeping the advantages that the fluorescence offers, it would be interesting to find an easier method to monitor the tensional state on polymers even when they are in service.

It is well known that the fluorescence quantum yield of several probes changes as a function of the degree of stretching and this behavior is assigned to conformational changes or restrictions of internal motion of the probes. Therefore,

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among others, the simple use of this photophysical parameter could be of great interest.

The aim of this work is to select fluorescence probes to monitor in situ and in real time, changes in the tensional state of the epoxy resins. Conventional photophysical parameters as fluorescence intensity and the energy of the emission band were used to check deformation created under a load applied to the material. A model epoxy formulation based on diglycidyl ether of bisphenol A (DGEBA) cured with ethylenediamine (EDA) was used.

## 2. Experimental

### 2.1. Materials

One epoxy system based on poly(bisphenol A-co-epichlorohydrin) glycidyl end-capped (average  $M_n = 348$  g/mol) and EDA supplied by Aldrich Chem. (Madrid, Spain) was prepared. This epoxy system was doped with the fluorescence probes: pyrene (Py), *p*-quaterphenyl (QPh), 1,6-diphenyl-1,3,5-hexatriene (DPhHT) (Aldrich Chem., Madrid, Spain), 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) (Lancaster Synthesis), and 5-dimethylaminonaphthalene-1-*[N*-(di-*n*-butyl)]sulfonamide (DANDBS) and 5-dimethylaminonaphthalene-1-*(N*-propylamine)sulfonamide (DANPAS) that were synthesized in our lab; the former by reaction of 5-dimethylaminonaphthalene-1-sulfonylchloride (Lancaster Synthesis) with and excess of di-*n*-butylamine and the later by carrying out the method already reported

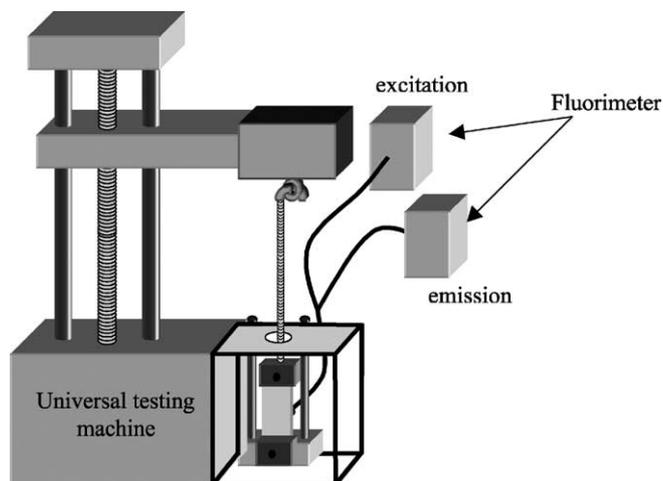


Fig. 2. Schematic view of the system used for coupled strain-stress.

[11]. All the chemicals were used without further purification. In Fig. 1, the chemical structure of the fluorescence probes used in this work are grouped.

### 2.2. Insertion of the fluorescence molecules

The fluorophore were physically inserted (probes), except for DNSPA that was chemically bonded to the DGEBA. The fluorophore used as probes were mechanically mixed with the DGEBA using a magnetic stir bar for 20 min, while the DNSPA was labeled by reacting its amine group with the epoxies in the DGEBA formulation [19].

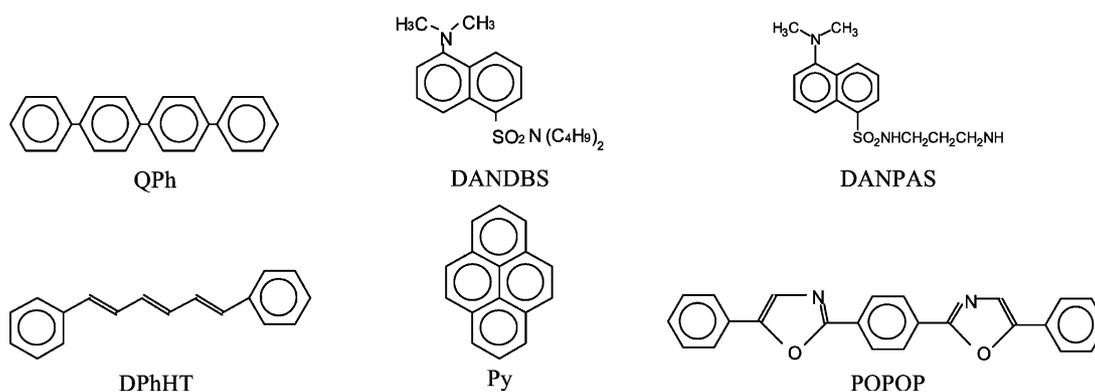


Fig. 1. Chemical structure of the fluorescence probes.

Table 1  
Sample codes, fluorophore used and their concentrations

| Sample code | Fluorophore    | [Fluorophore] ( $\times 10^4$ mol/kg) | $\lambda_{exc}$ (nm) | $\Delta\lambda_{em}$ (nm) |
|-------------|----------------|---------------------------------------|----------------------|---------------------------|
| A           | Py (probe)     | 1.13                                  | 340                  | 360–650                   |
| B           | QPh (probe)    | 0.99                                  | 310                  | 320–420                   |
| C           | DPhHT (probe)  | 4.78                                  | 350                  | 365–650                   |
| D           | POPOP (probe)  | 1.00                                  | 365                  | 380–650                   |
| E           | DANDBS (probe) | 1.02                                  | 350                  | 360–650                   |
| F           | DANPAS (label) | 0.99                                  | 340                  | 360–650                   |

### 2.3. Sample preparation

Seven samples of the epoxy resin were prepared. The codes, the fluorophore inserted in each sample and their concentrations are summarized in Table 1. The samples were obtained by curing the doped epoxy component (DGEBA) with EDA (used as the hardener). The epoxy component was first degassed under vacuum for 2 h and then stoichiometrically mixed with the amine. After that, the mixture was injected in a homemade mould, cured at 60 °C for 24 h and post-cured at 110 °C for 2 h. Finally, the completely cured samples (98% of conversion, checked by FTIR) were carefully cut to get specimens with a size of 10 mm × 65 mm × 0.5 mm.

### 2.4. Measurements

Two types of experiments were done: (i) the change in the fluorescence of the doped specimens were in situ monitored as a function of deformation and (ii) the stress distribution around a hole, which was made by purpose, was estimated by mapping the fluorescence of the specimen subjected to a certain load or deformation. The dispositive used for the first experiment is schematically showed in Fig. 2. The epoxy specimens were subjected to a sequential deformation test with the aid of a Microtest universal testing machine (load cell of 50 N) and using a special program done for that purpose. This program allows to elongate the specimen a finite length with an accuracy of 0.001 mm being able to read the strength hold by the sample at any moment. Therefore, the tensile tests were realized by steps of controlled deformations. In addition, as it can be seen in Fig. 2, an optical fiber cable to both excite and collect in

situ fluorescence was located close and perpendicular to the samples surface. Fluorescence was recorded on an Edinburgh fluorimeter using the excitation and emission conditions required for each fluorophore (see Table 1). The excitation and emission slits were 2.3 and 3.6 nm, respectively.

In the second experiment, a circular hole with a diameter of 5 mm created in one specimen of the epoxy resin labeled with DPhHT moiety. Subsequently, a map of its fluorescence response was recorded when the sample was uniaxially loaded.

## 3. Results and discussion

Fig. 3 represents the strain–stress plots for all of the samples with fluorescence probe or label. In every case straight lines are observed, which is in accordance with the elastic region that only was tested. In addition, it can be observed nearly the same slope in every case. In fact, after linear fitting and doing the average of the Young's modulus we obtained the value of  $E = 0.44 \pm 0.03$  GPa; where the small error confirms that the addition of the chromophores at concentrations less than  $10^{-3}$  M does not seem to change the mechanical properties of the epoxy resin. This aspect is of relevant importance in order to propose the use of fluorescence moieties to monitor tensional changes in materials.

To monitor mechanical changes of an epoxy specimen during a tensile test, two photophysical parameters were used: (i) integrated fluorescence intensity and (ii) the first moment in the wavenumber of the emission band,  $\langle \nu \rangle$ :

$$\langle \nu \rangle = \frac{\int \nu I(\nu)}{\int I(\nu)} \quad (1)$$

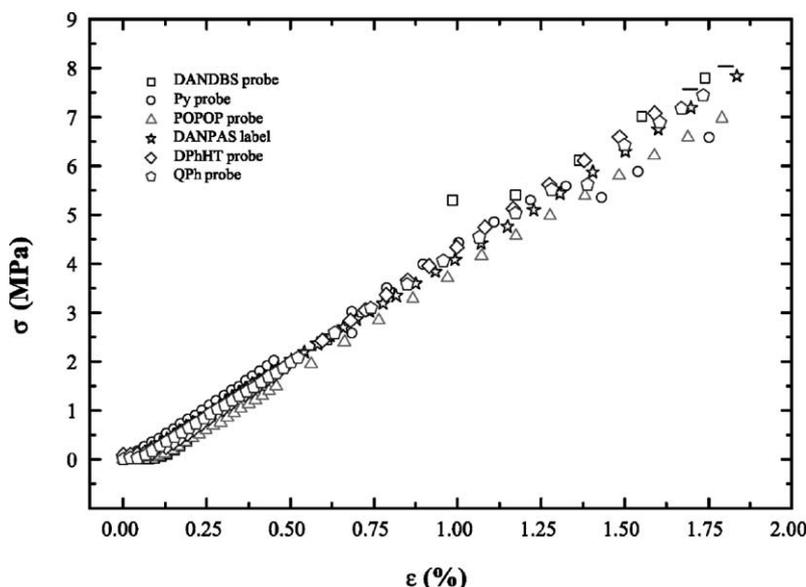


Fig. 3. Elastic region for the strain–stress plots of the epoxy resins doped with fluorescence probes.

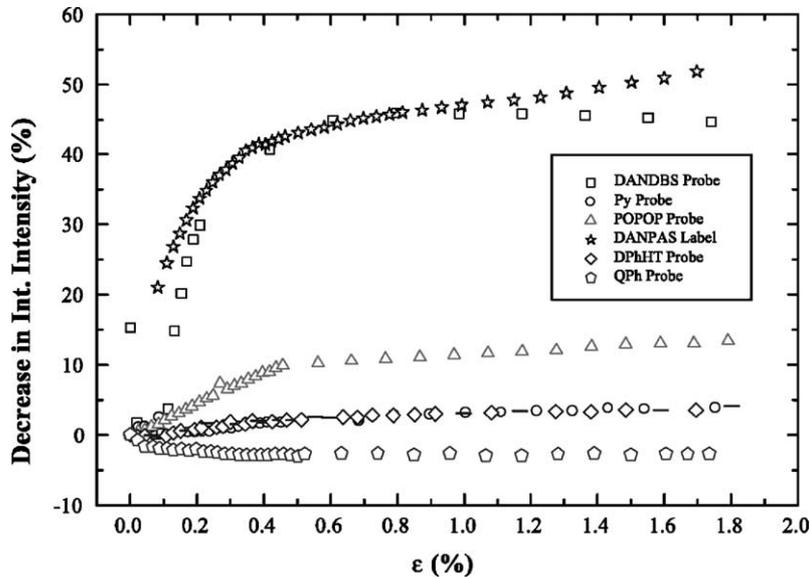


Fig. 4. Variation of the integrated intensity (decrease) as a function of the specimen deformation for several fluorescen moieties.

Fig. 4 shows the variation of the integrated intensity as a function of the specimen deformation for several fluorescen moieties. The objective of analyzing the fluorescenc for different fluorophore is to fin which one offers the biggest change in their photophysical parameters, hence these experiments are focused to select the best system to analyze changes in the tensional state of epoxy polymers. Due to this, the integrated intensity has been represented as its change (in percentage) with respect to that obtained for the relaxed system (without application of load, Fig. 4). For all the samples there is a nearly linear variation of the intensity when the deformation is low, while it almost level off for bigger deformations. In order to prove that these changes observed, among others, are not due to degradation of the fluorophor it was checked the reversibility of the process, obtaining exactly the same firs spectra when the load is retired.

In most of the cases there is a decrease in the fluorescenc intensity as a function of deformation, except for the DPhHT probe that show a weak increase. It is well known that the fluorescenc quantum yield (or intensity) of several probes increases as a function of the degree of stretching of thermoplastics, being this behavior assigned to the conformational changes or restrictions of internal motion of the probes. Nevertheless, this argument cannot be used in our case because it was obtained practically the opposite except for the DPhHT probe. A possible explanation is to consider that in this work a thermosetting polymer is studied instead of a thermoplastic and there must not be big changes of the mobility in a molecular level. The changes observed for the intensity could be interpreted in terms of variations in the diffraction index or due to quenching of the fluorescence. However, a deep study of these aspects will be done in another work.

Comparing the curves of Fig. 4 it can be observed that the biggest change in the intensity occurs for the dansyl moi-

ety, nevertheless it is the firs one to level off. Furthermore, the use of label instead of probe does not produce appreciable changes in the fluorescenc as can be seen for dansyl moiety (Fig. 4). On the other hand, the POPOP probe is the fluorophor that shows the highest sensitivity at higher deformations. This result suggests that the POPOP chromophore may be a good candidate to monitor tensional state of thermosetting polymers by using fluorescenc intensity measurements.

Nevertheless, when optical measurements are being used, the intensity of light does not seem to be the best parameter to monitor changes in the properties of the materials, since it depends, among others, on sample thickness and fluorophore concentration. Due to this, new parameters for this purpose are continuously being looking for. One of these parameters, which has been demonstrated to be very useful to monitor reactions of polymers is the so-called firs moment of the fluorescenc  $\langle \nu \rangle$  [20]. When rigidity and/or viscosity increases there is always a blue shift in the fluorescenc band that, in some cases, only can be observed by calculating the  $\langle \nu \rangle$ . Therefore, if there are small changes of rigidity for the epoxy specimens when they are under stress, it should be reflecte by changes in  $\langle \nu \rangle$ .

Fig. 5 shows the variation of the firs moment as a function of epoxy specimen deformation. In all cases the variation of  $\langle \nu \rangle$  is very low, being practically zero for DANDBS, DANPAS, QPh. For the rest of the fluorophore there is a small increase of  $\langle \nu \rangle$  with the elongation, being the highest change observed for the DPhHT. This result suggests that the DPhHT is placed on special sites where there are observable changes of rigidity. In fact, this is the unique fluorophor that presents an increase of the fluorescenc intensity when the epoxy specimen is under stress. Therefore, from the group of fluorophore studied the DPhHT should be the best one to monitor the tensional state in epoxy

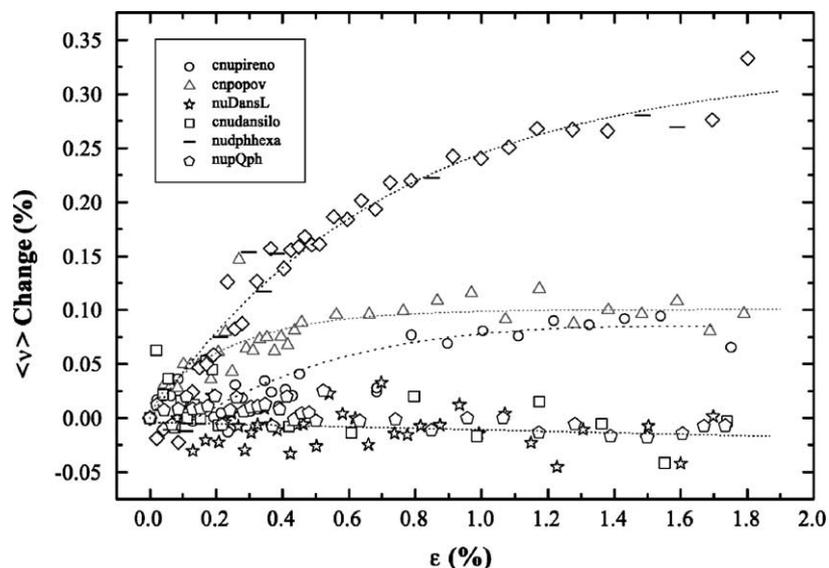


Fig. 5. Variation of the first moment (as a percentage of change) as a function of epoxy specimen deformation.

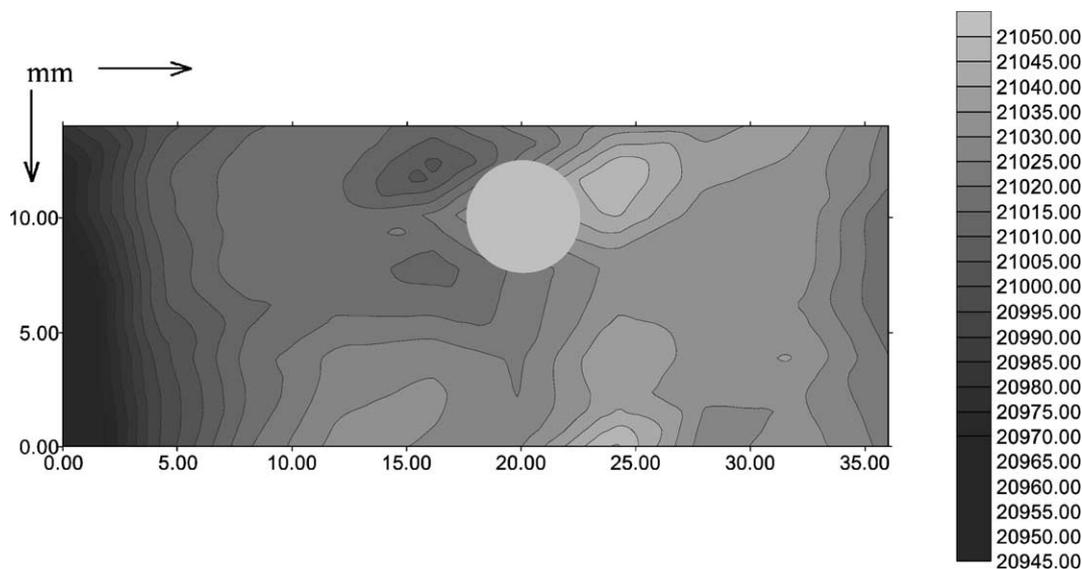


Fig. 6. Fluorescence mapping of an uniaxially stressed (11% of elongation) epoxy specimen with a hole. Representation of the  $\langle \nu \rangle$  values (DPhHT probe) as a function of the coordinates in the sample.

resins and even to estimate the distribution of stresses of the material.

Fig. 6 shows the fluorescence mapping of an uniaxially stressed (11% of elongation) epoxy specimen with a hole. The value of  $\langle \nu \rangle$  (DPhHT probe) as a function of the coordinates in the sample was represented. As can be seen, a particular distribution of the  $\langle \nu \rangle$  values appears in the figure. Taking into account that  $\langle \nu \rangle$  increases at higher deformations for the DPhHT probe (Fig. 5), Fig. 6 suggests that there is an accumulation of stresses in the center of the specimen along the load axis. This result, although non-conclusive, reveals that the fluorescence method seems to be a simple experiment to estimate the distribution of stresses in polymer materials.

#### 4. Conclusions

The use of typical photophysical parameters, although not very sensitive, has been demonstrated to be a very easy method to monitor tensional state of thermosetting materials. POPOP probe is the fluorophore that shows the highest sensitivity of its emission intensity at bigger deformations, therefore it must be a good candidate to monitor the tensional states by using fluorescence intensity measurements. The DPhHT shows the highest change in the first moment with specimen elongation. It seems to be placed on special sites where there are observable changes of rigidity. Therefore, among the fluorophores studied, the DPhHT must be the best one to monitor the tensional state

in epoxy resins by using the average energy of the emission band.

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