

Fluorescence-Labeled Pyrenesulfonamide Response for Characterizing Polymeric Interfaces in Composite Materials

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E-glass fibers were silanized using a 1% (v/v) aqueous solution of γ -aminopropyltriethoxysilane (APES). Pyrene-sulfonamide conjugates were formed by reaction of 1-pyrenesulfonyl chloride (PSC) in acetonitrile (AcN), with the amine groups immobilized on the glass fiber surface. These pyrene-sulfonamide conjugates were used as fluorescence probes, being a relatively simple analytical method to study the coating microstructure of polyorganosiloxane layer on glass fibers. The first aim of this work was to estimate possible interactions of the polyaminosiloxane coating with surrounding molecules of different solvents (solvent accessibility to the chromophore). For this study, the fluorescence response of pyrene-sulfonamide dye (PSA) was correlated with solvent polarity parameters. It was concluded that all the studied solvents were accessible to the chromophore, and they can gather in two groups, depending on their ability to swell the polyorganosiloxane layer. The second objective was to estimate the rigidity of the coating polymer from the temperature dependence of PSA emission. At about 180 K, a sudden change in the behavior of different photophysical parameters of PSA were observed. This phenomenon was interpreted as a density change in the polyaminosiloxane attached to the glass fibers.

KEY WORDS: Solvent accessibility; pyrenesulfonyl chloride; glass fibers; APES; exciplex emission.

INTRODUCTION

E-type glass fibers are usually employed as reinforcements in polymer matrix composites. For improving the interfacial adhesion, glass fibers are surface treated with coupling agents such as γ -aminopropyltriethoxysilane (APES), which react with both the glass surface and the polymer matrix. Reaction with the glass surface takes place by a condensation reaction in aqueous phase between the surface silanol groups and the hydrolyzed coupling agent. As a result, a functionalized polymer coating is formed. The structure of this polyorganosiloxane coating is not exactly known [1–5], although there

are some evidences of a gradient structure along the perpendicular to the surface.

Glass fibers surfaces treated in such a way become functionalized with amine groups, which may react with the polymer matrix during the curing stage of the composite; as a result, the mechanical properties of the composite are greatly enhanced [6,7].

The accessibility through the glass/coupling region and coupling region/polymer matrix interfaces and the structural flexibility of coupling regions are, among others, important features which determine the interfacial properties of the composite. To have some idea about the adhesion mechanism between the silane coupling agents and the polymeric matrices, as proposed by Plueddeman [8], it is necessary to know how the polymer matrix diffuses through the polysiloxane phase. The study of the diffusion and accessibility of small molecules through the coupling region may be a suitable way to model

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this phenomenon. In addition, careful selection of the diffusing molecules may help to study the chemical compatibility between the matrix polymer and the coupling region.

One method used in the determination of local properties in polymer systems is the measurement of some portion of the optical response of a molecule that is sensitive to a particular property of the local medium [9–11]. Pyrene and its derivatives are excellent probes or labels because they usually have long fluorescence lifetimes, form emissive excimers or exciplexes, and have a fluorescence spectrum sensitive to the polarity of the environment [10–12]. 1-Pyrenesulfonyl chloride (PSC) is a suitable chromophore that reacts easily with amine groups, yielding sulfonamide derivatives (PSA), which has a very high quantum yield, and it can form excimers [13] or exciplexes [11], depending on its concentration or the concentration of donor amine groups. In a previous work [11] it was concluded that the pyrene sulfonyl moiety attached to the amine-coated glass surfaces present an “excimer-like” band that arises mainly from exciplex emission. The presence of propylamine groups close to the PSA moiety allows exciplex formation between excited PSA (acceptor) and propylamine (donor). Since exciplex fluorescent emission is very sensitive to solvent polarity [14], it can be used to study solvent accessibility.

On the other hand, and since the mass fraction of the coating over the surface is small (less than 1%), temperature-dependent studies of the PSA emission may provide information on the thermal transitions at the coupling region. This photophysical approach has been used successfully with other fluorescent probes in different polymeric systems [15,16] to study polymer flexibility.

In this work, it is proposed to label an environmentally sensitive probe such as 1-pyrenesulfonyl chloride, to the surface of glass fibers. Solvent effects and accessibility of small molecules are studied as a function of exciplex-to-monomer emission (I_E/I_M) and I/V ratios. The temperature dependence of the fluorescent response of the probe is used to determine the thermal transitions of the polymer network in the coupling region.

EXPERIMENTAL

Materials

E-type glass fibers were supplied by Vetrotex (Spain) and surface-treated according to the methods reported previously [11]. γ -Aminopropyltriethoxysilane (APES) and 1-pyrenesulfonyl chloride (PSC) were purchased from ABCR and Molecular Probes, respectively, and used

without further purification. Toluene was distilled over sodium just before use. Other solvents were high-quality products of fluorimetric grade. The list of solvents used, with their corresponding code for easy identification in the figures, is presented in Table I.

Labeling Procedure

Well-dried silanized glass fibers were put in contact for 10 min, at room temperature, with a PSC solution (10^{-4} M) in acetonitrile (AcN). Then the fibers were subjected to Soxhlet extraction with dried toluene for 16 h and vacuum-dried for at least 8 h.

Fluorescence Measurements

Silanized glass fibers labeled with PSC were immersed in 13 solvents for 12 min. After that period, steady-state fluorescence spectra were recorded on a Perkin Elmer LS-50B fluorimeter, using the standard front-face excitation accessory. The excitation wavelength was set at 340 nm and emission spectra were recorded from 360 to 600 nm.

For each pair sample/solvent, excitation spectra were also recorded at $\lambda_{em} = 400$ and 480 nm, respectively. In both emission and excitation spectra, the slits and scan rate were set at 3 nm and 120 nm/min, respectively.

Low-temperature measurements were performed in a SPEX fluorimeter with double monochromators in both the excitation and the emission paths. The sample was put in a refrigerated sample holder. Fluorescence spectra were recorded between -140 and 120°C (in steps of 5°C), waiting 5 min between each measurement before the spectrum was recorded.

Table I. Solvents Used and Identification Codes

Code	Solvent
1	Cyclohexane
2	1,4-Dioxane
3	Toluene
4	Tetrahydrofuran
5	Dichloromethane
6	<i>n</i> -Butanol
7	N-Propanol
8	Acetone
9	Methanol
10	Acetonitrile
11	Dimethylformamide
12	Dimethyl sulfoxide
13	Water

RESULTS AND DISCUSSION

 I_1/I_5 Band Ratio Variation

Fluorescence spectra of the labeled fibers as well as the fibers immersed in three solvents (H_2O , dimethyl sulfoxide, and cyclohexane) are presented in Fig. 1. Fluorescence spectra of the labeled fibers immersed in other solvents have the same profile but different band ratio values. Two regions can be observed in the spectra. The high-energy one, ranging between 360 and 420 nm, corresponds to the PSA monomer emission; the bands centered at 378 and 398 nm are assigned by analogy with pyrene with bands I and V, respectively, in the terminology used by Kalyanasundaram and Thomas [17]. It should be noted that band I corresponds to the 0-0 transition being shifted about 7 nm with respect to the 0-0 transition in pyrene. The second region (420 to 600 nm) consists of a structureless broad band, centered at about 470 nm. This broad band for the sample studied was assigned to "excimer-like" emission, in which exciplex is the main contribution [11]. Figure 1 clearly shows how the spectrum profile changes depending on the nature of the solvent.

Some condensed aromatic molecules, such as pyrene and its derivatives, show a room-temperature fluorescent spectrum in solution that is very well defined [18]. Changes in the solvent nature yield intensity variations in the vibrational bands without spectral shifting; this phenomenon was associated by Nakajima, due to its analogy, with the Ham effect in the benzene absorption spectrum [19]. Due to this effect, the vibrational bands in the pyrene molecule that are forbidden in weak electronic

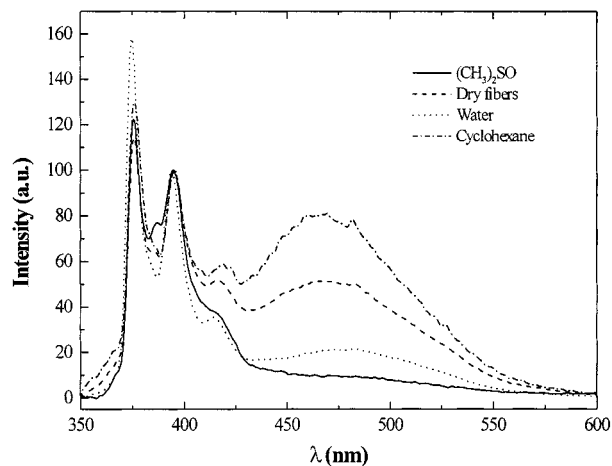


Fig. 1. Fluorescence spectra of labeled glass fibers as well as fibers immersed in three solvents (H_2O , dimethyl sulfoxide, and cyclohexane).

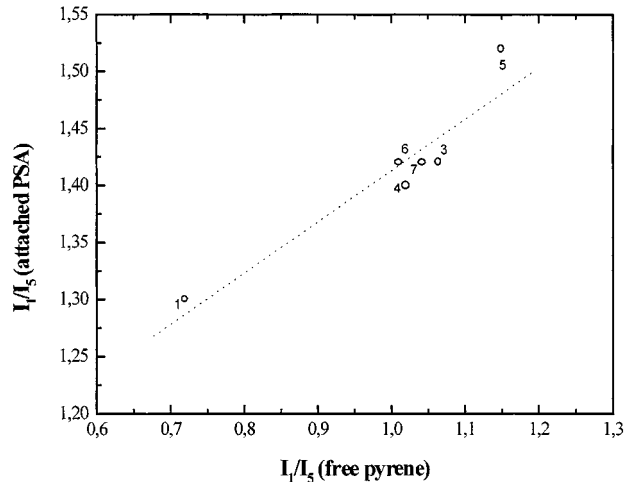


Fig. 2. The band ratio I_1/I_5 for free pyrene [17] versus the I_1/I_5 ratio in the attached pyrenesulfonamide for a selection of solvents.

transitions show a large increase in polar solvents [17,20,21]. The sulfonamide group in position 1 does not alter the symmetry of the molecule very much, and therefore, solvent effects in pyrene should also operate in the sulfonamide derivative, although the extent of variation in the band ratios may be different. In Fig. 2, the band ratio I_1/I_5 for free pyrene [17] versus the I_1/I_5 ratio in the attached pyrenesulfonamide is presented for a selection of solvents. This figure qualitatively confirms that the I_1/I_5 ratio in the pyrenesulfonamide conjugate is also sensitive to the solvent polarity, at least if the solvent can effectively swell the polymer coating.

The band ratio I_1/I_5 was studied as a function of different solvent polarity parameters: dipole moment, dielectric constant, Kosower parameter, and Dimroth parameter. All of these plots, because they present similar tendencies, are summarized in Fig. 3, which represents

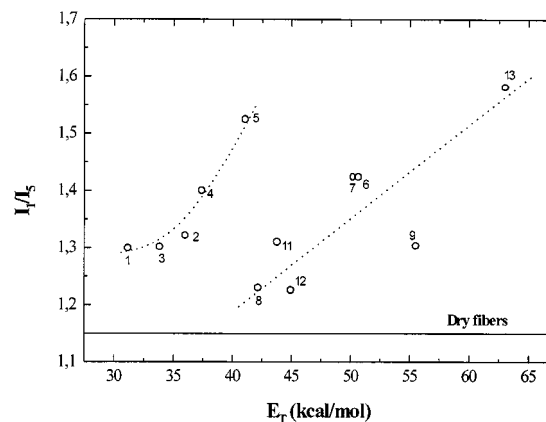


Fig. 3. Fluorescent I_1/I_5 ratio versus the Dimroth parameter, E_T , for the solvents studied.

only the I_1/I_5 ratio versus the Dimroth parameter, E_T . Several observations can be made from this figure.

- For all solvents, irrespective of their polarity, the I_1/I_5 ratio is higher than for the dried fibers.
- For nonpolar aprotic solvents the I_1/I_5 ratios increase with E_T from solvent 1 (cyclohexane) to solvent 5 (dichloromethane) and can be grouped together.
- A similar tendency is observed for polar solvents, either protic or aprotic. Recent studies have demonstrated that the S_2-S_1 vibrational coupling in pyrene is not affected by the hydrogen-bonding tendency of the solvent [20].

These observations allow us to conclude that the chromophore in this sample is accessible for the studied solvents. The fact that the solvents present two different tendencies derives from the different swelling capacity for the two groups of solvents. Polar solvents solvate only the surface of the polymer, while apolar ones can arrive at inner layers. The explanation of this behavior lies in the thermodynamically favorable interaction between the polymer and some of the solvents. The solubility parameter calculated for the polymer is $17 \text{ MPa}^{1/2}$, which is very similar to the solubility parameters of the apolar solvents used in this work.

I_E/I_M Band Ratio Variation

In accordance with the classical thermodynamic analysis of exciplex emission [22], the free energy for the exciplex formation has four contributions: (i) the reduction potentials of the acceptor (PSA) and of the donor (amine), (ii) the correction due to PSA excitation, (iii) the radical ion solvation, and (iv) the electrostatic potential from the ion interaction. For the same couple donor/acceptor in different solvents, contributions i and ii are constant, and only contributions iii and iv may change. Comparing contributions iii and iv, the latter must predominate because (a) the electrostatic interaction distance is bigger than the ion-dipole one and (b) the radical ion solvation attached to the surface is always imperfect.

Since the exciplex/monomer ratio is proportional to the negative exponential of the Gibbs' free energy variation for the exciplex formation, and since the electrostatic contribution depends inversely on the dielectric constant of the medium, a logarithmic plot of the I_E/I_M ratio versus $1/\epsilon$ should be linear.

Figure 4 confirms this analysis. It can be observed that the studied solvents can be arranged in two groups: (i) nonpolar solvents, grouped in a straight line with a

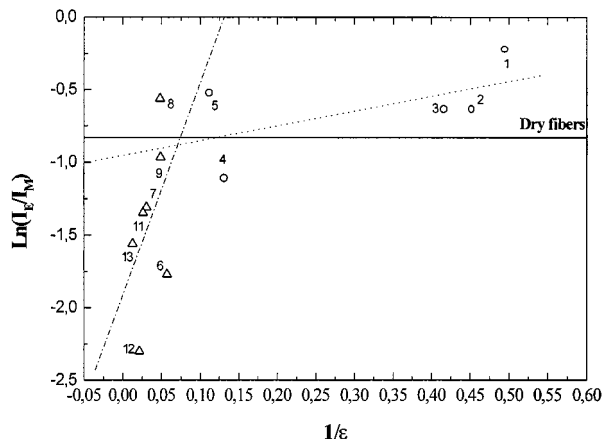


Fig. 4. Logarithm of the I_E/I_M ratio versus the reciprocal dielectric constant, $1/\epsilon$.

slope of 1; and (ii) polar solvents, for which the straight line has a slope 14 times greater. The slopes of these lines should be inversely proportional to the donor-acceptor distance if coulombic interaction dominates exciplex emission.

These results can be explained taking into account that the donor and acceptor are both attached to the polymer coating and are not free to diffuse. Nonpolar solvents swell the polymer, isolating the fluorophore, and as a result, a larger donor-acceptor separation is observed. On the other hand, polar solvents are not able to swell the polymer, giving rise to a shorter donor-acceptor distance.

Temperature Effects

The temperature-dependent spectral shifts for absorption processes in apolar molecules in nonpolar solvents normally can be interpreted taking into account the balance between two opposite effects [16]: (i) when the temperature increases, the population of some vibrational levels can be perturbed, changing the shape of the transition band and shifting it to low energies; and (ii) at the same time, the solvent density can decrease, increasing the equilibrium molecular separation distance, decreasing the stabilization effects from dispersion forces (induced dipole-induced dipole), and yielding a shift toward higher energies. We can assume that in emission processes the same predictions can operate.

Figure 5a shows the variation of the emission wavelength for the 0-0 transition (λ_{0-0}) as a function of the reciprocal temperature. When the temperature increases from 146 to 156 K, a slight red shift is observed, which is interpreted as an increase in the population of the vibrational levels. From 156 to 186 K this bathochromic

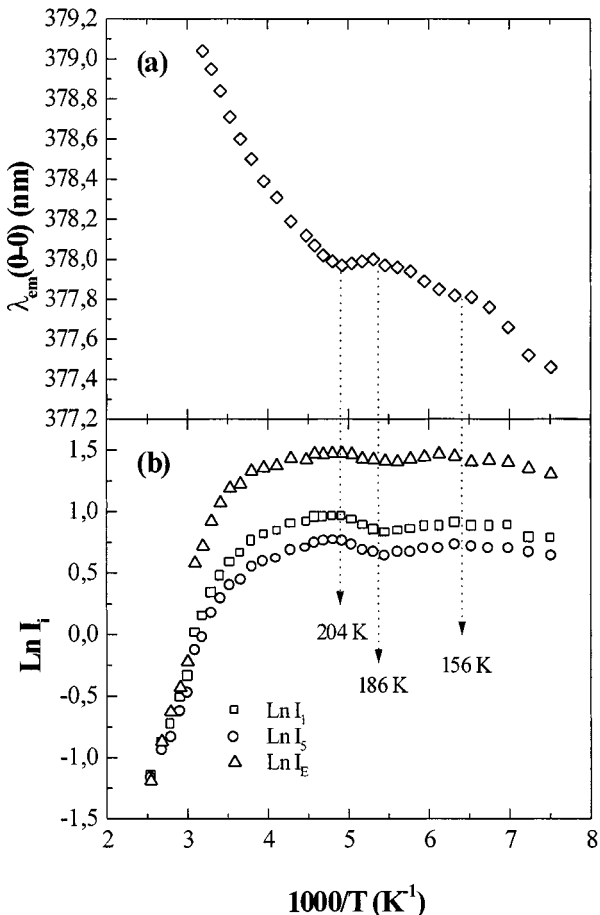


Fig. 5. (a) Variation of the emission wavelength for the 0-0 transition (λ_{0-0}) and (b) logarithmic plot of the fluorescent intensity for bands I, V, and "excimer-like," as a function of the reciprocal temperature.

trend slows down, and in the temperature range 186–204 K the wavelength remains constant. At temperatures above 204 K, the bathochromic trend is recuperated. In accordance with the above-mentioned interpretation, these changes reflect that in the temperature range 156–204 K the polymer matrix, to which the pyrenesulfonamide is labeled, decreases abruptly in density. This volume transition can be associated with a secondary relaxation of the polymer coating, although from Fig. 5a it is not very clear if a single transition operates.

In Fig. 5b a logarithmic plot of the fluorescent intensity for bands I, V, and "excimer-like" versus the inverse temperature is presented. In the high-temperature range in this plot the fluorescence intensity increases linearly when the temperature decreases. This is the typical expected behavior associated with the decrease in the nonradiative rate constants. It is possible to calculate the activation energy for the emission processes of both the monomer

and the exciplex, 4 and 6 kcal/mol, respectively; these values are very similar to those found in the literature [23].

In the low-temperature region in Fig. 5b some changes in the fluorescent intensity can be observed in the same temperature range in which polymer secondary relaxations appear. A better understanding of the low-temperature processes can be achieved from the Arrhenius plot of the exciplex band ratio, as presented in Fig. 6.

Figure 6 shows the presence of two maxima for the I_E/I_M band ratio in the low-temperature region. The presence of a maximum for the exciplex ratio usually indicates a change in the driving force for exciplex formation: from enthalpy control at high temperatures to diffusion control at low temperatures. The temperature at which the maximum is found should depend strongly on the properties of the medium in which the exciplex is formed since the medium determines the mobility of the acceptor/donor couple. The presence of two maxima suggests that there are two sites in the polymer matrix in which an exciplex is formed. According to the model proposed by Wang and Jones [24], the polyorganosiloxane layer over a silica substrate has heterogeneous structure; the portion of the layer near the silica surface is rigid and closed, while the outer portion of the layer is more flexible and has an open character. Taking this model into account, it is possible to assign the two maxima to exciplexes formed in these two sites which differ in mobility. Therefore, the maximum appearing at the lowest temperature should correspond to exciplexes

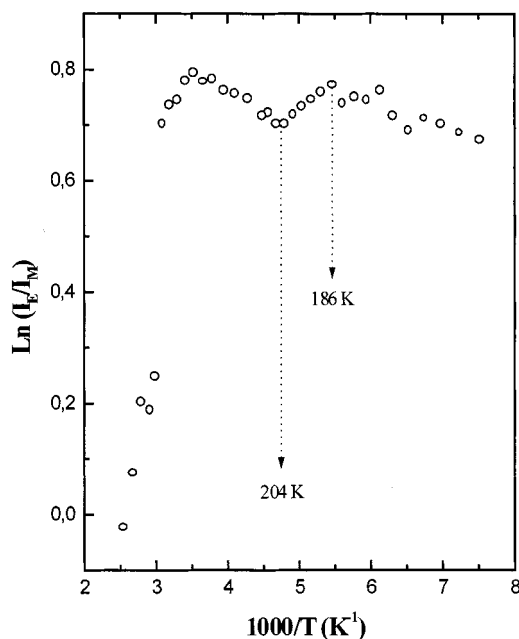


Fig. 6. Arrhenius plot of the exciplex band ratio (I_E/I_M).

formed in the outer sites, while the maximum that appears at the higher temperature should correspond to exciplexes formed in a more rigid environment.

CONCLUSIONS

Small molecules such as the solvents used in this work are able to penetrate and swell the polyorganosiloxane layer used as the coating for glass fibers. Favorable thermodynamic interactions between the polymer and apolar solvents explain their behavior. Although polar solvents cannot penetrate the polymer network, pyrene fluorescence reveals its presence at the surface of the layer.

Exciplex emission is also sensitive to the presence of solvents of different polarities. Apolar solvents give rise to large donor–acceptor distances since they are able to penetrate and swell the polymer coating. On the contrary, polar solvents give rise to small donor–acceptor distances since they are not able to swell the polymer matrix.

Finally, fluorescence temperature dependence has revealed the presence of low-temperature secondary relaxations in the polymer and has provided some evidence of two sites for chemical reaction at the coating surface: flexible outer sites and rigid inner sites.

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