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# Hydrolytic damage study of the silane coupling region in coated silica microfibres pH and coating type effects

D. Olmos\*, J. González-Benito, A.J. Aznar, J. Baselga

*Dpto. C. de Materiales e Ingeniería Metalúrgica, U. Carlos III de Madrid, Avda. Universidad, 30, 28911 Leganés, Spain*

## Abstract

Aqueous solutions of three silanes to cover silica microfibres were used, being the 3-aminopropyltriethoxysilane (APTES) and the 3-aminopropylmethyldiethoxysilane (APDES) the reagents for preparing them at the proportion of (APTES/APDES): 1/0, 1/1 and 0/1. The 1-pyrene sulphonyl chloride (PSC) fluorescent moiety was chemically attached to the silanised substrate via the sulphonamide formation. The hydrolytic degradation phenomenon of the silane coupling layer was studied as a function of: (i) temperature, (ii) coating layer type and (iii) pH (4, 7 and 10). The hydrolytic damage in the coupling region of the silica microfibres composite materials occurs under an equilibrium process. It was obtained the activation energies ( $E_a$ ) for the hydrolytic damage considering the rate to reach the equilibrium. The values of  $E_a$  depended on the type of coating and on the pH. As a consequence, the rate of hydrolytic damage could be related to the proportion of Si<sub>silane</sub>-O-Si<sub>silane</sub>, while the OH<sup>-</sup> groups were thought to catalyse the reaction.

## Keywords

Silane coating; Silica; Hydrolytic damage

## 1. Introduction

Highly crosslinked, highly functional polyorganosiloxanes can be obtained by polycondensation of trifunctional silane monomers with the general formula (R'-O)<sub>3</sub>-Si-R. R' usually corresponds to an alkoxy group (methoxy or ethoxy) and R can bear a great number of different chemical functionalities, as for example glycidoxo, vinyl, methacryloxy, aminopropyl, etc. These polymers have found very important applications in different industrial fields supports for catalysts [1] and biological molecules [2], synthesis of chromatographic supports [3] and advanced composite materials [4]. All these applications arise from the particular reactivity of the silane monomers since these molecules undergo two different types of chemical reactions. On one hand, they can be poly- or co-polycondensated via the alkoxy groups and, on the other; they can undergo addition reactions using the R-functionality. This "bi-functional" chemical character allows its use as "coupling agents" between two different materials.

Silanes usually are present in low concentration [5] (0.1–2%, w/w) in the sizing formulations used for coating the reinforcement components of reinforced advanced composite materials. For specific studies on the structure, prop-

erties and effects of silanes, the reinforcements are surface treated typically only with aqueous solutions of ethoxysilanes of varying concentration (0.1–5%, w/w). Ethoxysilanes hydrolyse rapidly in water to form isolated monomers, or a mixture with cyclic oligomers and intramolecular cyclics [6–8] (depending on the silane type, concentration, pH and storage time), bearing a large amount of silanol groups. In the case of  $\gamma$ -aminopropyltriethoxysilane ((CH<sub>3</sub>-CH<sub>2</sub>-O)<sub>3</sub>-Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>, APES), aqueous solutions of moderate concentration (around 1%, w/w) and at their natural pH (pK  $\approx$  8.5) are stable and it is reported that they are constituted by isolated hydrolysed trisilanol monomers and low molecular weight oligomeric cyclics [8].

Because of the acidic character of silanol groups of the silica surfaces (and also other M-O-H groups, where M refers to major impurities such as Al, B or Fe), condensation of hydrolysed monomer and oligomers takes place with the silica surface forming a more or less crosslinked coating layer. Careful surface free energy determinations on glass fibre coated with APES demonstrate that silanes not only impart chemical functionality to the surface but also hydrophobicity [9,10]. Typical values for the polar and dispersive components of the surface free energy are [9,11]  $\gamma_S^P = 3-8$  and  $\gamma_S^D = 32-35$  mN/m.

The properties and structure of such a coating layer has been extensively studied [5,8,12–15] using a number

\* Corresponding author.

E-mail address: dolmos@ing.uc3m.es (D. Olmos).

of different techniques (FTIR, NMR, Raman, SEM, XPS, AFM and SIMS). Nevertheless, it remains as an open issue at least with respect to the relation between coating structure, resistance to hydrolysis degradation and interfacial properties of composite materials.

It has been observed experimentally that the APTES coating layer is not uniformly distributed over the glass surface. The polysiloxane coating is not continuous but forms instead the so-called microscopic “sea-islands” [16] with characteristic dimensions that can be easily observed by SEM.

Inside such islands, the structure of the polysiloxane is also non-uniform. It is generally agreed that this structure can be described by a 3D-graded network model [12]. According to this model, the crosslinking density is graded along the thickness of the layer. The inner part is formed by a layer of silane monomers condensed both with the substrate and between them; it is therefore a highly crosslinked monolayer network with very small fraction of uncondensed silanol groups. The outer part, which is exposed to the environment, has an open structure with low crosslinking density; higher fraction of uncondensed residues and contains a fraction of purely adsorbed monomer. The total thickness of the coating is usually expressed as an *effective number of monomer monolayers* that covers the silica surfaces. For glass fibres assuming that they are perfect cylinders; although it is an increasing function of the initial monomer concentration and some other reaction conditions [17], typical values range between 3 and 8 monolayers.

From the technological point, one of the most important properties that polyorganosiloxanes impart to composites and adhesive joints is a relatively large protection against the effects of water either in the liquid or in vapour state. Excellent papers and reviews [9,18–20] can be found showing the benefit of polyorganosilanes in the durability and peeling strength of adhesive joints and flexural strength and interfacial shear strength of glass reinforced composites. In the presence of water, the mechanical properties of all the studied systems decrease with exposure time; when polyorganosiloxanes are present, the rate of variation is greatly reduced. Nevertheless, up to the author’s knowledge there are no works trying to explain from a fundamental basis the chemical mechanism of water action on the interfacial properties of composites or adhesive joints. Probably, the origin of this lack of information lies on the great difficulty of characterising interfaces and chemical reactions at the molecular level.

Few authors have faced the problem but using a different approach, that is to say, trying to characterise and to measure the effects of water on simple surfaces coated with polyorganosiloxanes. The earliest works correspond to Schrader et al. [21] who applied radio tracer techniques for the measurement of remaining poly(3-aminopropylsiloxane) coating over a glass surface as a function of exposure time to water. They discovered that hot water was able to remove very quickly a first layer of coating but cold water was not efficient. They proposed a first-order kinetic scheme for

this hydrolysis process. In the light of the actual knowledge about the structure of these coating networks and taking into account that hydrolysis is always a bimolecular process; their results should be reinterpreted.

Verdu and co-workers [22] measured the weight gain and loss of APTES coatings exposed to water in either liquid and vapour state. For the first time, a hypothetical chemical mechanism for the hydrolysis process was proposed although: (i) it is not easy to find in their paper the experimental evidences supporting their hypothesis, (ii) the purely adsorbed remaining monomer was not extracted prior to the kinetic study, (iii) hydrolysis conditions were not controlled.

In this paper, the hydrolysis under controlled conditions (different pHs and temperatures) of carefully prepared poly(3-aminopropylsiloxane) coatings is studied. Three different 3-aminopropylsilane aqueous solutions are used for preparing the samples: triethoxy (APTES), diethoxy (APDES) and triethoxy + diethoxy in the ratio 1/1 (APTES-50%), yielding coatings with different structure. The technique of fluorescence labelling is used for detecting extremely small concentration of the hydrolysis products. According to the results obtained and to some theoretical assumptions a kinetic mechanism for the hydrolytic damage is proposed.

## 2. Experimental part

### 2.1. Materials

The silica SMF2 were supplied by Tolsa S.A. (Madrid, Spain) with SiO<sub>2</sub> content over 95% and the specific surface area of 500 m<sup>2</sup>/g. In order to obtain different surface coatings of the silica microfibres two aminosilanes (Aldrich Chem. Co.) were used without further purification 3-aminopropyltriethoxysilane (APTES) and 3-aminopropylmethyldiethoxysilane (APDES). 1-Pyrene sulphonyl chloride (PSC) (Molecular Probes) was used as a fluorescence label. All the experiments were carried out at controlled pH by using standard solution of pH 4.0 (pH = 4.0 ± 0.02, 20 °C), 7.0 (pH = 7.0 ± 0.02, 20 °C) and 10 (pH = 10.0 ± 0.05, 20 °C), respectively (Panreac Química, S.A., Barcelona, Spain). The solvents used (Aldrich Chem. Co.) were HPLC grade without further purification except toluene that was distilled over sodium to remove the water.

### 2.2. Sample preparation

As received silica microfibre (1 g) were introduced in a 2% (v/v) silane aqueous solution for 15 min to silanise them. After that, silanised samples were filtered polymerised at 110 °C for 1 h, Soxhlet extracted during 4 h to remove any physisorbed residue and vacuum dried for at least 8 h. Three solutions of silane were used to obtain three different coatings: (i) 2% (v/v) aqueous solution of APTES, (ii) 2% (v/v) aqueous solution of APDES and (iii) 2% (v/v) aqueous

solution of a 50% mixture between APTES and APDES. The three types of samples were named APTES, APDES and APTES-50%, respectively. Taking into account the different functionality of the silanes used in this work, it is expected an increase in the degree of crosslinking in the following order: APTES > APTES-50% > APDES. After the silanisation process was finished 0.4 g of each sample were immersed in  $10^{-4}$  M PSC solutions 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 samples were exhaustively washed with acetonitrile and vacuum dried for at least 8 h.

### 2.3. Measurements

Inside a small paper bag, the labelled microfibre of each sample were introduced in a quartz cell with a standard pH solution. The paper bag was carefully haggled in the upper part of the cell to allow the free pass of a light beam through the centre of the cuvette. The solution in the cuvette was continuously thermostatised and stirred with a magnetic bar. In these conditions, the hydrolytic damage of the silane coatings was monitored by measuring the fluorescenc of the solution as a function of time. As the hydrolysis progresses, pyrene labelled fragments of the siloxane coating are incorporated to the solution giving it fluorescence which increase with the immersion time. Using a homemade programme, fluorescenc spectra were recorded automatically as a function of time in a Perkin Elmer LS-B50. The excitation wavelength was set at 340 nm, the excitation and emission slits were of 5 nm and the scanned speed  $120 \text{ nm min}^{-1}$ . Finally, to obtain the integrated intensity for all of the spectra in each experiment (at least 200 spectra), another homemade programme was used.

## 3. Results and discussion

### 3.1. Effect of the temperature and the silane coating

As an example, in Fig. 1 a whole and representative experiment of hydrolysis is plotted. In this figure the emission spectra of pyrene moiety is represented as a function of immersion time. It can be observed how the fluorescenc intensity increases as the reaction of hydrolysis is taking place.

In order to study the kinetic of the hydrolytic damage on the silane coupling region of silica microfibre composite, the degradation process was monitored at different temperatures (Fig. 2). In Fig. 2, the integrated fluorescenc intensity of the pyrene moiety in the aqueous solution is represented as a function of the silica immersion time for different silane coatings of the silica surface. It is important to underline that normalisation was done with respect to the intensity reached at equilibrium. Therefore, the plots of Fig. 2 represent the hydrolytic equilibrium degree,  $\alpha$ , in

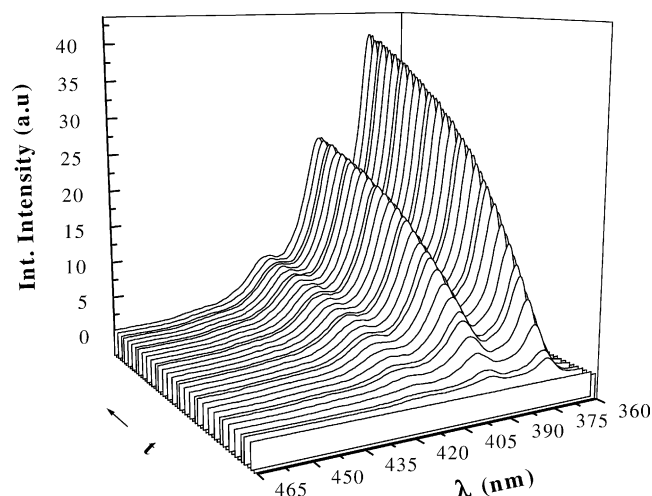


Fig. 1. Emission spectra of pyrene moiety as a function of the silica microfibre immersion time in a standard solution of pH = 7 (APTES silane coating).

percentage, as a function of time or, in other words, the rate to reach the equilibrium. As can be seen, all the samples show the same behaviour at different temperatures. During the first stage of the reaction, there is a nearly linear and fast increase in the fluorescenc intensity while, at longer

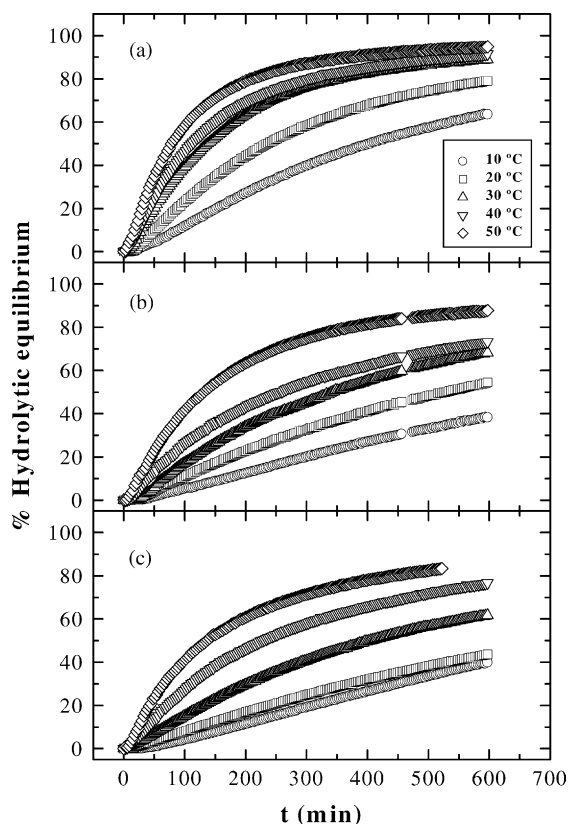


Fig. 2. Integrated fluorescenc intensity of the pyrene moiety in one aqueous solution as a function of the silica immersion time for different silane coatings of the silica surface: (a) APTES, (b) APTES-50% and (c) APDES.

times, the curves level off. Comparing the graphs for the different samples (Fig. 2a–c), it is possible to establish a qualitative order in the rate for the hydrolytic damage of the coatings: APTES > APTES-50% > APDES.

Let us assume that the hydrolytic rate to reach the equilibrium follows a typical kinetic equation of the form:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where  $k$  is a kinetic-like constant only dependent on temperature. By integration of Eq. (1) it is obtained

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = kt \quad (2)$$

Since

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = f(\alpha)$$

is a constant for each value of  $\alpha$  and  $k$  could be described as a typical Arrhenius expression ( $k = A e^{-E_a/RT}$ , where  $A$  is the preexponential factor and  $E_a$  the activation energy of the process), taking logarithms in Eq. (2) results in

$$\text{Ln } f(\alpha) = \text{Ln } A - \frac{E_a}{RT} + \text{Ln } t \quad (3)$$

which should be a straight line if one represents  $\text{Ln } t$  versus  $1/T$  for each value of  $\alpha$ . This kind of plots (Method A) was done for the three samples studied in this work (Fig. 3) and from their slopes the  $E_a$  values were obtained (Table 1). It is observed that the  $E_a$  is independent on the value of  $\alpha$  indicating that the hydrolytic mechanism does not change along the whole hydrolysis process. In addition,  $E_a$  values change depending on the silane coatings, showing an increase when the silanol functionality of the silane is higher. These results are in accordance with the qualitative observation above mentioned.

On the other hand, it is possible to analyse the data from Fig. 2 in terms of the hydrolytic rate to reach the equilibrium (Method B). If the logarithm of the hydrolytic rate is

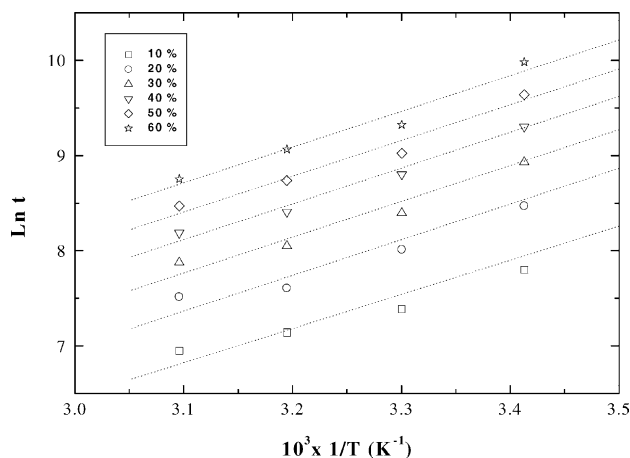


Fig. 3. Arrhenius plots at different hydrolytic equilibrium degrees for the APTES sample.

Table 1  
Activation energy values

Method of analysis	$\alpha$	$E_a$ (kcal/mol)		
		APTES	APTES-50%	APDES
Method A	0.1	7.1 ± 1.0	8.6 ± 0.3	9.2 ± 0.5
	0.2	7.5 ± 0.9	8.3 ± 0.3	9.3 ± 0.8
	0.3	7.5 ± 0.7	8.5 ± 0.2	9.0 ± 0.9
	0.4	7.5 ± 0.4	8.3 ± 0.5	8.7 ± 1.0
	0.5	7.5 ± 0.6	–	–
	0.6	7.5 ± 0.6	–	–
Method B		8.9 ± 0.8	9.8 ± 0.7	9.6 ± 1.2

represented as a function of the  $\text{Ln}(1 - \alpha)$ , it should be obtained a straight line with the slope equal to  $n$  and a zero intercept equal to  $\text{Ln } k$ . As an example, Fig. 4 shows these straight lines for the APTES sample. After fitting the data to the straight lines, it was obtained nearly the value of 1.5 for  $n$  in any case. Furthermore, taking the values of  $k$  at the different temperatures, the typical Arrhenius plots were drawn. From their slopes it is possible to obtain the apparent activation energy for each sample (Table 1), which are in complete agreement with those obtained with the previous method. These results reflect that the hydrolytic damage mechanism does not change with the type of the silane coupling agent used in this work for the coatings. Nevertheless, they suggest that, under the effect of aqueous media, the difficult to break the siloxane bonds between the silica surface and the silane ( $\text{Si}_{\text{silica}}\text{-O-Si}_{\text{silane}}$ ) is higher than to break the siloxane bonds between silane and silane ( $\text{Si}_{\text{silane}}\text{-O-Si}_{\text{silane}}$ ).

### 3.2. Effect of pH

Fig. 5 shows the influence of pH on the hydrolytic damage rate at 50 °C for each sample. In any case, the hydrolysis rate increases at higher pH. This confirms that hydroxyls

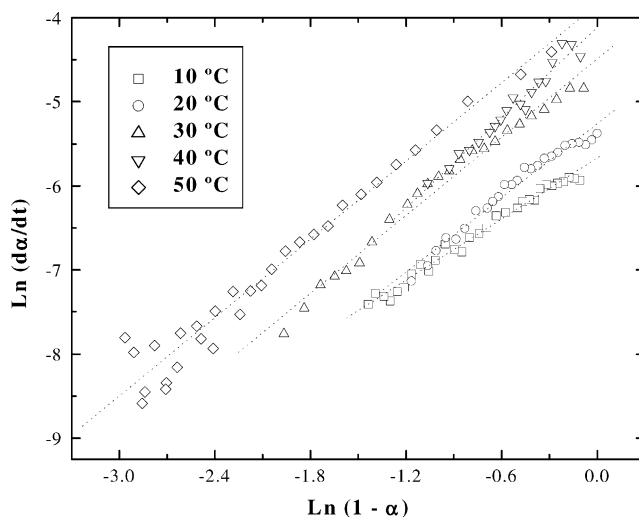


Fig. 4. Representation of the hydrolytic damage rate logarithm as a function of  $\text{Ln}(1 - \alpha)$  for the APTES sample.

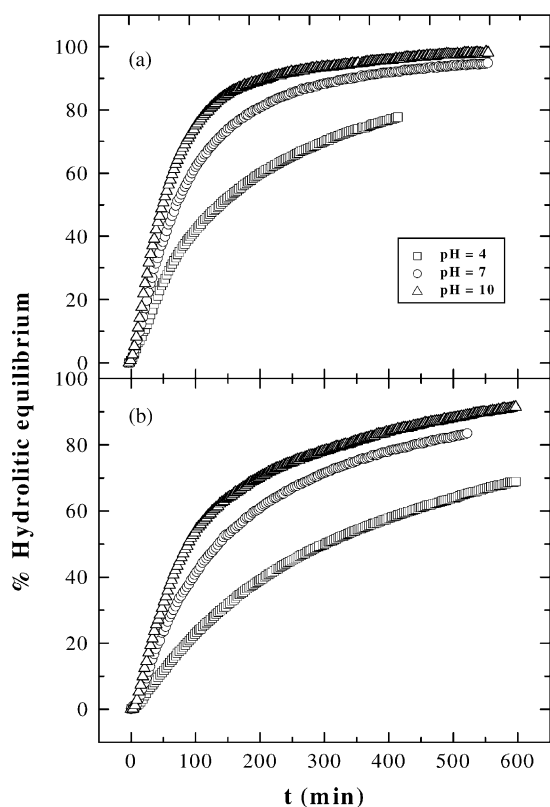


Fig. 5. Influence of the pH on the hydrolytic damage rate at 50°C for the samples: (a) APTES and (b) APDES.

groups catalyse the hydrolysis reaction in these systems. In addition it was possible to use Eq. (3) independently on the pH to obtain the consequent straight lines. This suggests that the catalytic constants and the concentration of  $H_3O^+$  and  $OH^-$  groups must take part in the kinetic-like constant.

On the other hand, comparing Fig. 5a and b it can be concluded that the effect of pH is strongest as the functionality of the silane increase. Therefore, in order to improve the silane coatings on silica surfaces for composite materials respect to the hydrolytic damage in aqueous media, our results suggest that it is necessary to reduce as much as possible the functionality of the silane coupling agent, even at any pH.

#### 4. Conclusions

It has been demonstrated that the use of the fluorescence response of pyrene moiety is a good method to monitor the

hydrolytic damage in crosslinked polymers. The hydrolytic damage in the coupling region of silica microfibre composite materials occurs under an equilibrium process. Considering the rate to reach the equilibrium and a very simple kinetic mechanism it is possible to obtain the activation energy of this process,  $E_a$ . The values of  $E_a$  depend on the type of coating and on the pH. As a consequence, the rate of hydrolytic damage depends on the proportion of  $Si_{silane}-O-Si_{silane}$ , while the  $OH^-$  groups seem to catalyse the reaction.

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