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Microstructural and wettability study of surface pretreated glass fibres

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Commercial glass fibres were calcinated for the removal of organic matter, activated for surface silanol regeneration and silanized with γ -aminopropyltri-ethoxysilane. Two different activation methods were used: reflux with neutral water and reflux with 10% HCl aqueous solution. Acid treatments hydrolize Si–O bonds, greatly changing the composition of the glass and regenerating silanol groups, some of them being of intraglobular nature. Water treatment does not change appreciably the glass composition, but its surface free energy value is the lowest. The degree of silanization is the greatest for the acid activated samples and the lowest for the water activated one. The polar contribution to the total surface free energy, once the samples are silanized, is the highest for the fibres activated with boiling water whilst the dispersion component is about the same for all of them. SEM observations indicate that for the greatest degree of coating, debonding of the filaments may induce a peeling-out fractural mechanism.

Glass fibres; Surface tension; APES

1. Introduction

It is well known that to improve the properties of glass fibre reinforced polymer matrix composites it is necessary to form high-strength, chemically-stable interfaces between the reinforcement and the matrix. Surface treatments of fibres are usually carried out by reacting surface silanol groups with silane coupling agents [1–3].

Up to now the research in this field has been focused mainly on the characterisation of the substrate surface (acid-base properties and quantification of the number and distribution of surface silanol groups [1,4–6]) and on the characterisation of the silane coupling agent coating-structure of the polyorganosiloxane layer [7–14] and orientation of the silane organo-functional groups. To the best of the authors' knowledge, no work has been undertaken on the effects of surface treatments, prior to the silanization, on the structure and properties of the silane coupling agent layer.

There are many different methods for the surface characterisation of silane-treated glass fibres as well as for the interfaces with the polymer matrix [15]. Fourier transform infrared spectrometry (FTIR) is a particularly useful tech-

nique to study silane coupling agents adsorbed or bounded to glass surfaces [8–10,16]. However, the very small amount of coupling agent normally applied to the glass surface and the presence of strong bands from the substrate, often makes the IR detection of the silane characteristic bands difficult.

The measurement of dynamic contact angles (advancing and receding) and contact angle hysteresis is a complementary mean for macroscopic characterisation of coupling agent modified surfaces, allowing the surface free energy to be calculated, and the orientation of the organo-functional groups [7,12] to be estimated.

In this work the influence of different activation pretreatments of glass fibres on the structure of an aminosilane (γ -aminopropyltriethoxysilane) coupling agent layer is studied making use of SEM, FTIR and dynamic contact angle measurements.

2. Experimental part

The glass fibre was supplied by Vetrotex (Spain) and was calcinated at 450°C for 1 h for removing organic matter, prior to use. All reactives were of reactive grade.

The fibres were subjected to two different activation processes: treatment with boiling water and reflux with

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Table 1
Sample codes and activation procedures

Sample	Activation reagent	Activation time (h)
F-A	None	None
F-B	Water	1
F-C	HCl 10%	1
F-D		3

10% HCl aqueous solution. The activation times and samples codes are summarised in Table 1. After acid activation, all of the samples were washed repeatedly with distilled water until Cl removal. All the samples were dried at 110°C for 1 h and kept in a dessicator until silanization.

Silanization of activated fibres was performed using a 1% (v/v) γ -aminopropyltri-ethoxysilane (APES) aqueous solution for 10 min. Polymerisation of silanized fibres was performed at 110°C for 1 h in an oven and afterwards they were subjected to Soxhlet extraction with dried toluene for 16 h and vacuum dried for 12 h. The silanized samples were stored in a dessicator until use. The codes for silanized samples are the same as for activated, but with the addition of an S (F-x-S).

Microscopic examination and semiquantitative X-ray microanalysis were performed using a Philips XL30 scanning electron microscope (SEM) with an EDAX detector DX4i, on both activated and silanized samples (Au/Pt coated). Chemical analysis data are expressed as the average of four different measurements on different fibre samples.

Transmission Fourier transform infrared spectra were performed on a Mattson Galaxy 3000 instrument (4000–400 cm^{-1} range, 100 scans, 4 cm^{-1} resolution): the fibres were ground, diluted up to 3% with KBr and press moulded in an evacuated press at 9 atm to form disks of 12 mm diameter.

Dynamic wettability was measured using a Krüss K14 dynamic contact angle analyser. A single glass fibre was fixed to the electrobalance by means of adhesive tape and the force on the fibre was measured as the liquid container was raised and withdrawn at a stage velocity of 50 $\mu\text{m s}^{-1}$. The liquids were water, ethylenglycol and α -bromonaphtalene at 24°C. The fibre perimeter was measured for each fibre with an optical microscope immediately before each wettability measurement. The cosines of the advancing contact angles were calculated by the wetting force extrapolated to zero depth. Up to 10 different fibres were measured and the contact angle was taken as the average value of them.

Surface free energy was calculated according to the method of Owens–Wendt [17]. The polar, γ_s^p , and dispersion, γ_s^d , contributions to the total surface free energy of the solid, γ_s , were calculated from the slope and intercept of Eq. (1):

$$(1 + \cos \theta)A = B\sqrt{\gamma_s^p} + \sqrt{\gamma_s^d} \quad (1)$$

where:

$$A = \frac{1}{2} \frac{\gamma_L}{\sqrt{\gamma_L^d}}$$

$$B = \sqrt{\frac{\gamma_L^p}{\gamma_L^d}}$$

γ_L , γ_L^p and γ_L^d are the surface tension and the polar and dispersion contributions of the testing liquids. In the Owens–Wendt approximation, the solid surface tension is the sum of these two contributions.

3. Results

3.1. SEM observation and chemical analysis

The fibre morphology and surface texture, as revealed by SEM, do not change when calcinated fibres are subjected to activation treatments. A representative image of the ‘as received’, calcinated or activated glass fibres, irrespective of the activation treatment, is presented in Fig. 1. Long cylinders with smooth surfaces and average diameters of between 12 and 17 μm . are the common morphological characteristics of these fibres.

Silanized fibres look very similar to activated fibres, but some differences can be observed as a consequence of the silanization treatment. For samples F-B-S, Fig. 2, where the silane covering degree is low, as will be shown below, an adherence following the mayor fibre axis can be observed. This protuberance resembles the trace that a debonded fibre may leave as a consequence of the silanization treatment. In the case of more extensively silanized fibres, samples F-D-S, it is possible to find surface regions in which glass seems to be peeled from the bulk of the fibre, as shown in Fig. 3. It seems, therefore, that the fibres become bonded one to another when they are silanized. For preparing the fibres for SEM inspection, the fibres may debond leaving the fibre trace, if the coating degree is low. If the coating degree is high then the adhesive joint strength becomes high enough to induce a peeling-out fracture mechanism. More work is being done for elucidating the exact origin of these SEM observations.

Table 2 shows the semi-quantitative chemical analysis of activated and silanized fibres, expressed as atomic ratios between silicon and the other main elements: Na, Ca and Al: boron was excluded from analysis because the instrument cannot detect it. Si has been selected as a reference element because its relative content does not change with any activation procedure.

It can be observed in Table 2 that the activation treatment by water reflux does not significantly change the glass composition, at least within the volume from which X-rays are emitted, which has been roughly estimated as 1 μm^3 . For acidic activation treatments the content on Al, Ca, and Na

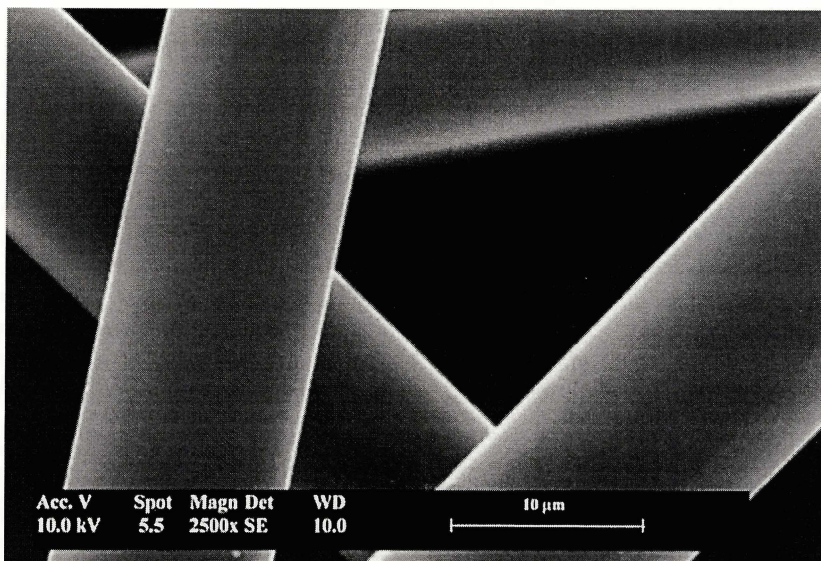


Fig. 1. SEM image of glass fibres activated with HCl 10% (w/w) for 3 h (F-D).

decreases and the effect is more pronounced for the highest activation time.

For silanized samples, since the silanization time is low enough to alter the chemical composition within the measured volume, the content on Al, Ca and Na should remain constant. A slight increase in Si content due to APES incorporation to the surface can be expected, increasing therefore the atomic ratios from Table 2. This effect is observed clearly only for sample F-D-S, suggesting that, for this sample, the polyorganosiloxane content is the greatest. Composition changes at the surface level cannot be observed with the analysis method employed, but its associated effects on fibres wettability will be studied below.

3.2. FTIR spectra

Fig. 4 shows two regions of the FTIR spectra of activated samples. Although the detailed assignment of the IR bands can be found in [14], the main IR observations can be summarized as follows. As can be observed at about 3425 cm^{-1} the tension band of bounded water increases in a parallel way as the intensity of activation treatments: none < water < HCl(1 h) < HCl(3 h). The free water band, which appears at 3250 cm^{-1} , follows the same trend. The O-H stretching band from silanol groups appears at 3650 cm^{-1} only for samples F-C and F-D. The position of the band suggests that the silanol groups are of intraglobular nature rather than surface groups [4].

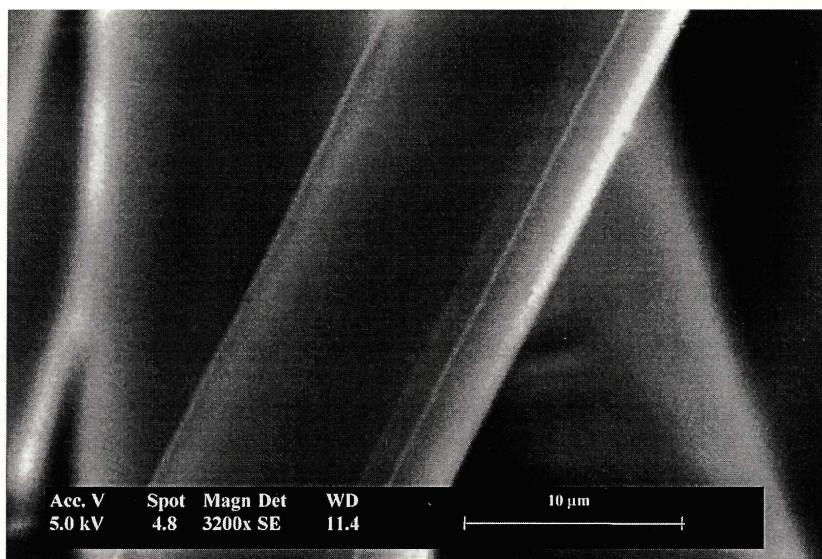


Fig. 2. SEM image of a silanized glass fibre sample, activated previously with boiling water for 1 h (F-B-S).

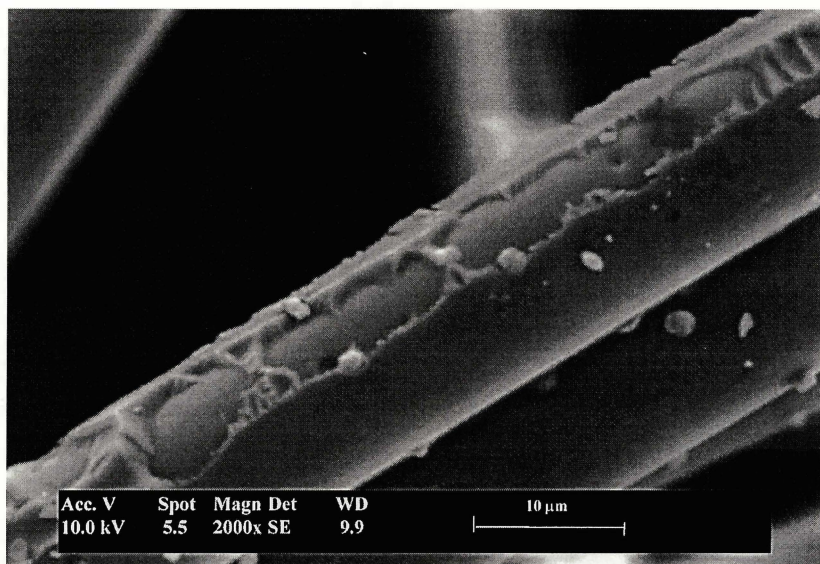


Fig. 3. SEM image of a silanized glass fibre sample, activated previously with HCl 10% (F-D-S).

In the low energy region of the IR spectrum (Fig. 4(b)), acidic water bending bands can be observed at 1620 cm^{-1} only for samples activated with reflux of HCl (F-C and F-D). A progressive change of the band centered at 1000 cm^{-1} can be observed also. This band results from the contributions from Si-OH, Si-OSi, Si-OAl and Al-OSi stretching bands. Vibrations in which Al(III) is involved appear at 978 cm^{-1} , and decrease as the intensity of the activation treatment increases; therefore, it can be concluded that Al(III) is leached out when activation takes place under acidic conditions. This result is in accordance with the chemical analysis results.

Fig. 5 shows the infrared spectra from silanized glass fibres. In the high energy region of the spectra, the water signal is reduced, in comparison with Fig. 4, mainly for the F-A-S and F-B-S samples. The presence of residual silanol groups can be observed for F-C-S and F-D-S. The characteristic stretching bands from methyl and methylene groups can be observed between $2960\text{--}2850\text{ cm}^{-1}$ for all of the samples, being more intense for samples F-C-S and

F-D-S; this result suggests that the coating degree seems to be the highest for samples activated under acidic conditions at longer times.

Fig. 5(b) shows the low energy portion of the spectra. At about 1385 cm^{-1} , bending bands of methylene groups can be observed clearly for sample F-D-S. The presence of these bands is due to either the propyl residues from APES or the uncondensed ethoxy residues: The latter can also be observed as indicated by a shoulder at about 900 cm^{-1} .

Table 2
Atomic ratios between Si and the main constituent elements of E-glass fibres

Sample	Si/Al	Si/Ca	Si/Na
F-A	3.6 ± 0.2	3.1 ± 0.2	27 ± 7
F-B	3.7 ± 0.5	3.1 ± 0.6	32 ± 7
F-C	5.2 ± 0.6	5.1 ± 0.7	39 ± 9
F-D	8.3 ± 0.6	11 ± 3	60 ± 13
F-A-S	3.7 ± 0.4	3.0 ± 0.3	36 ± 8
F-B-S	3.8 ± 1.1	2.5 ± 1.2	—
F-C-S	5.7 ± 0.8	6.1 ± 1	56 ± 17
F-D-S	12 ± 3	17 ± 7	—

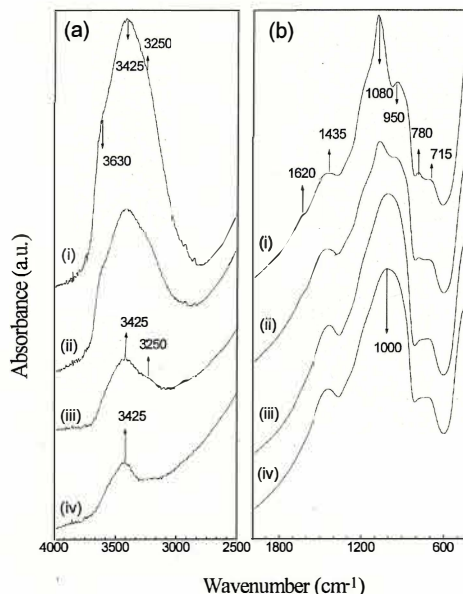


Fig. 4. Showing: (a) high and (b) low; energy regions of FTIR spectra from activated samples ((i): F-D; (ii): F-C; (iii): F-B; (iv): F-A).

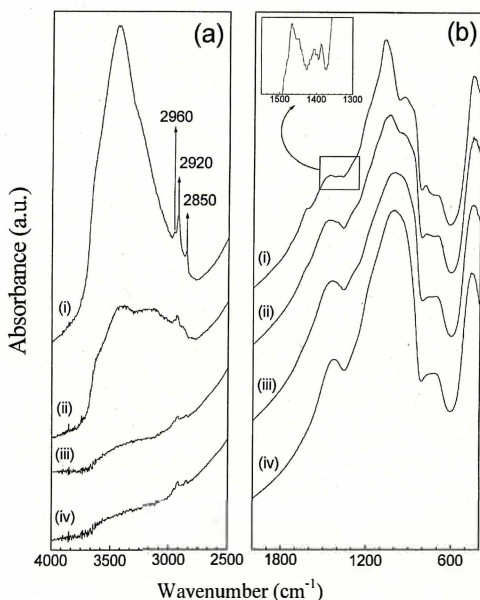


Fig. 5. Showing: (a) high and (b) low; energy regions of FTIR spectra from silanized samples ((i): F-D-S; (ii): F-C-S; (iii): F-B-S; (iv): F-A-S).

3.3. Dynamic contact angles

In Table 3, the results from wettability studies are presented. The first column shows the difference between the advancing and receding contact angles (hysteresis) for each sample when water is employed as the test liquid. Within the activated sample set (F-A to F-D), the hysteresis is minimum for the non-activated sample. It seems that the different activation treatments do not change the surface morphology very significantly, except for fibres activated with boiling water for 1 h, for which the hysteresis is maximum.

For silanized fibres, hysteresis is about 200% greater than for activated fibres, except for sample F-A-S, where the hysteresis increases by about 400%. That the hysteresis is higher for all the samples shows that the silanization process changes the surface structure. Some effects that may contribute to this change are [18]: the adsorption of water through the polyorgano-siloxane layer, surface roughness

Table 3
Hysteresis ($(\theta_a) - (\theta_r)$) and surface free energy values

Sample	$(\theta_a) - (\theta_r)$ (°)	Surface free energy (Owens-Wendt) (mN m^{-1})	
		γ_s^p	γ_s^d
	H_2O		
F-A	9.2 ± 3.2	111.8 ± 1.5	0.2 ± 0.01
F-B	17.3 ± 5.1	98.5 ± 3.1	0.1 ± 0.1
F-C	11.4 ± 4.1	130.6 ± 2.5	2.2 ± 0.4
F-D	14.3 ± 5.4	138.9 ± 5.5	3.7 ± 3.3
F-A-S	37.8 ± 4.7	5.0 ± 0.5	32.6 ± 1.3
F-B-S	31.5 ± 6.1	8.3 ± 1.2	31.9 ± 2.1
F-C-S	34.4 ± 6.7	3.2 ± 0.6	34.7 ± 1.5
F-D-S	35.6 ± 4.1	3.8 ± 0.7	32.2 ± 1.8

and orientation of surface polar groups (amino-propyl residues). This result is also in agreement with the well known tendency of APES to polymerize, forming isolated islands or aggregates. Since SEM observations do not show any imperfection at 2000x magnification, it must be concluded that aggregates must have a characteristic length of less than $0.1 \mu\text{m}$.

Activated fibres show a high surface free energy with a practically zero dispersion component. It is noteworthy that the F-B sample shows the lowest surface free energy, whereas acidic activation treatments lead to more hydrophilic surfaces, in agreement with a high silanol content as observed by FTIR.

Silanization with APES decreases the solid surface tension as compared with the untreated glass fibres. All of the samples show approximately the same value of the dispersion component, about 33 mNm^{-1} , which agrees with other reported values [7]. This component is the main contribution to the total solid surface free energy, showing the non-polar character of the coating. Slight differences can be found in the polar contribution, the highest value of which corresponds to the F-B-S sample; this result can be explained in terms of a partial coating of the fibre surface, which is in accordance with the low surface silanol concentration found for this sample. Samples C and D have about the same polar contribution, showing that the testing liquid interacts with the surface in the same way.

4. Discussion

Calcination of commercial fibres at 450°C to remove organic matter oxidizes the surface, creating a generally homogeneous layer of amorphous silica with a low surface silanol concentration. A higher surface free energy value with respect to the commercial fibres should be expected but not so high as that of the hydrated fibres, and this is observed in Table 3. Regeneration of silanol groups on silica is not an easy process [1] when neutral aqueous solutions are employed; accordingly, activation with boiling water for 1 h at least may hydrate the surface but without appreciable silanol regeneration. Although hydration is observed by an enhancement of the free water band at 3250 cm^{-1} , a similar or slightly higher surface free energy value should be expected, but the values from Table 3 for samples F-A and F-B show that this is not the case. It seems that hydration of calcinated fibres with boiling water and a subsequent drying process at 120°C reduces the surface free energy of the fibres. At the present moment the unique possible explanations can be associated to a surface dehydroxylation during the drying process, as well as to a selective leaching of boron oxide from the surface.

The acid activation of glass fibres greatly changes the surface composition and the hydration state of the glass. It seems that an acid media hydrolyzes Si-O and Al-O bonds, allowing water diffusion through the bulk and generating a

great number of silanol groups; some of them can be of an internal nature and, therefore, not accessible to APES, as the presence of residual silanol bands in the FTIR spectra of silanized samples (F–D–S and F–C–S) reflect. The presence of acid water, that is to say, hydrogen bonded water, revealed by the IR band at 1620 cm^{-1} , after drying at 120°C may confirm that a substantial amount of it is located inside the internal micropores of the fibre.

The greater amount of surface silanol groups for samples C and D may explain the higher silane content found for these samples, as revealed by their FTIR spectra. When the fibres are activated under less vigorous conditions the silane content is lower. In fact, the higher polar contributions to the total surface free energy of silanized samples A and B is in accordance with a lower coating degree: amongst these two sample sets, the higher polar contribution corresponds to fibre activated with boiling water, suggesting a lower coating degree. This may be explained in terms of a lower number of surface silanol groups, which is in accordance with the low surface free energy value found for these samples.

5. Conclusions

Boiling water pretreatment at neutral pH, does not increase the reactivity of glass fibres, with respect to simply calcinated fibres. Under acidic conditions, a great number of silanol groups are generated: although a substantial number of these silanols are of internal character, greater coating degrees can be achieved.

The different experimental techniques used in this work show that as a consequence of the different activation treatments, the silane coating degree increases in the following order: water activated < non-activated < acid treated for 1 h < acid treated for 3 h.

Finally, SEM observations reveal that when the fibres are silanized as fibre bundles and not as isolated filaments, the silane coating bonds the fibres one-to-another. If the coating

degree is high enough, debonding may induce surface peeling on the fibres. This peeling mechanism should be investigated in more detail.

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