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Influence of time and temperature of hydrothermal treatment on glass fibers surface

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Abstract

Leaching appears to be a suitable method of obtaining a high hydroxyl population at the surface of borosilicate fibers. Several procedures were investigated and the treated fibers have been characterized by Fourier transform infrared spectroscopy (silanol band), and elemental analysis (carbon content) after trimethylsilylation. The texture of leached fibers was examined by scanning electron microscopy and the result was compared to that of original fibers. The modified fibers which exhibited the highest hydroxyl population with minimum alteration of the texture, as could be seen by scanning electron microscopy, were characterized by using nitrogen, krypton and water adsorption techniques in order to get information on surface area and porosity. The procedure revealed textural modifications: the surface area was increased and a micropore volume was formed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

A great deal of studies on inner wall capillaries treatment have been performed and the topic is well documented [1–11], particularly on open tubular gas chromatography (GC) columns. Most of these studies have been devoted to deactivation of the wall surface to prevent undesirable adsorption effects. Metal impurities are carefully removed prior to stationary phase coating in GC. Conversely, bonding of a chemical moiety onto the capillary wall requires attachment sites. Si–OH is convenient for that purpose since it may be directly involved in a Si–O–Si bond. The hydride pathway as proposed by

Sandoval and Pesek [12] also requires the availability of silanols. The goal is thus to increase the surface concentration of silanols on the inner wall. Etching or leaching is the most popular treatment; pros and cons of both methods have been described [13]. Borosilicate glass is generally treated by leaching with the aim of removing metal ions from glass surface and also to ensure the increase of the silanol surface density [14].

Wright et al. [1] have shown that a 20% HCl solution is as efficient as H₃PO₄ or NaOH but much less damaging to the surface. Moreover, Grob et al. [15] have proposed rinsing the fibers with a 2% hydrochloric acid solution prior to deionised water to prevent extracted metal salt from settling on the microfibers surface. Pyrex glass from acidic leaching

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may contain as much as 2.8 hydroxyl groups per square nanometer (this value can be compared to that of fully hydroxylated porous silica, i.e., 4.6 accessible groups per square nanometer) [16]. Disc membranes for sample pretreatment consist of a set of glass fibers. These disc membranes are made out of borosilicate with percentage of silica around 58%. Grafting chemical moieties onto the surface of the fibers will permit the achievement of different and selective sample pretreatment. Grafting is tedious due to both the fragility of the membranes and the low number of reaction sites.

The purpose of this work was first to evaluate whether the Wright et al. method is applicable to increase hydroxyl groups density onto borosilicated fibers and then to obtain, by appropriate modification of the procedure, the maximum yield of surface hydroxyl groups together with the minimum alteration of the texture. We report here some preliminary results.

Fourier transform infrared spectrometry (FT-IR) was used to monitor the increase of silanol number. However, the method is not fully quantitative and to confirm the result of the leaching treatment, silanization has been carried out with monochlorosilane. Similarly to the end-capping procedure in preparation of reversed-phase material, we used chlorotrimethylsilane (TMCS) as silylating agent. TMCS is a monofunctional silane and polymerization does not occur. The reaction consists of substituting the proton of the silanol by trimethylsilyl groups.

The texture of the fibers before and after treatment has been examined by scanning electron microscopy (SEM). The Brunauer–Emmet–Teller (BET) specific surface areas of both the native and the hydroxylated fibers derived from adsorption isotherms, which were determined either by gravimetric (water) or by volumetric (nitrogen and krypton) techniques.

2. Experimental

2.1. Materials

Glass microfiber filters (GF/D) were purchased from Whatman (Maidstone, UK). Trimethylchlorosilane was from Aldrich (Saint Quentin Fallavier,

France). The 25% hydrochloric acid, water, toluene and tetrahydrofuran (Merck, Darmstadt, Germany) were of analytical-reagent grade. Toluene was dried over calcium hydride overnight and distilled before use.

2.2. Apparatus

Elemental analyses were performed at the “Laboratoire de Microanalyses, Faculté St. Jérôme” (Marseille, France).

Infrared spectra were obtained with a Nicolet 20 SXB FT-IR instrument (WI, USA). Surface area measurements were carried out at the “Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S.” (Marseille, France). The BET specific surface areas were obtained from nitrogen, krypton and water adsorption isotherms. Adsorption of water by gravimetry was performed at 25°C with equipment constructed around a vacuum microbalance already described [17].

Nitrogen adsorption was performed at 77 K with a batch volumetric apparatus (Omnisorb 100, from Coultronics). Krypton adsorption was carried out at 77 K by using a quasi-equilibrium adsorption procedure [18]. To perform reproducible gas adsorption experiments, reversible adsorbed water was removed by a thermal treatment at 150°C under vacuum. Surface morphology was determined by SEM on a JSM-6320 F scanning microscope.

Samples of activated fibers were mounted on aluminum stubs using silver print and were sprayed with gold (100 Å) to enhance conductivity.

2.3. Leaching

General procedure: glass fibers were placed in a 250-ml three-necked round bottom flask equipped with a thermometer and a condenser. One hundred ml of 20% HCl solution was added and the mixture was gently stirred for different times at different temperatures.

The modified fibers were washed with 2% HCl solution and with deionised water. The remaining water was evaporated in an oven at 170°C during 15 h to produce the activated fibers.

2.4. Silanization

A 1.0-g sample of dried fibers was placed in a 250-ml three-necked round bottom flask equipped with thermometer and condenser. Dry toluene (30 ml) was added and refluxed under nitrogen with continuous stirring. To the boiling solvent (111°C), was added 3.0 ml of TMCS through a septum by means of a syringe.

The mixture was maintained at reflux for 24 h. The modified glass fibers were successively washed with toluene, a mixture of tetrahydrofuran–water (90:10, v/v), deionised water then dried in vacuum at 100°C for 5 h to give the final sample of hydroxylated fibers.

3. Results and discussion

In order to study the influence of temperature on silanol content, first, the fibers were treated by leaching at temperatures of 40, 60, 80 and 100°C during 24 h and then dried in an oven at 170°C during 15 h to produce the activated fibers.

Treatment at 170°C may be questionable. Removal of water on a silica surface has given rise to a large amount of literature [19]. Transition between the departure of physisorbed water and the dehydroxylation (removal of the surface OH groups) occurs around 150°C [20]. According to Lange [21] removal of strongly physisorbed water (in very narrow micropores) requires a temperature approaching 180°C. Zhuravlev [22] stated that 200°C is necessary. However in the comprehensive textbook from Gregg and Sing [23] differences in the surface concentration of hydroxyl groups of silica as function of temperature of dehydration between 170°C and 200°C is small whatever data from authors were considered.

“The aim of acidic leaching is to produce a glass surface consisting of almost pure silica” [14]. Data of silica dehydration are available for borosilicate glass treated by leaching. We thus kept our operating conditions at 170°C to eliminate most of physisorbed water (which amounts to a tenth of a monolayer) without damage to the fibers.

The samples have been characterized by FT-IR. Fig. 1 shows the evolution of FT-IR spectra with the temperature of the treatment. The hydroxyl stretch

region exhibits a broad band at 3700–3200 cm^{-1} from silanol groups. From these results, we observe that the modification of the surface (i.e., the silanol content) by hydrothermal treatment becomes more efficient at higher temperatures. However, when compared to the original fibers, those treated at high-temperature and especially at 100°C seem to be seriously altered as seen by SEM. In view of these results, experiments at higher temperature were not carried out.

The leached fibers have been reacted with TMCS and the extent of modification was monitored by carbon determination. Due to low carbon percentage and uncertainty of accurate determination no quantitative data can be given but we can observe a good correlation between FT-IR spectra and carbon percentage. It turns out that the carbon content increases when the temperature varies from 40°C to 100°C (Table 1). Since TMCS readily reacts with surface silanols to form a siloxane bond, it confirms that the hydrothermal treatment generates reactive sites at the surface.

If TMCS reacts with residual water, the resulting hydroxylated compound is washed out. It does not lead to a false positive result. It only can be a false negative if water is present within the pores with the consequence of a lower percentage of carbon.

Second, to prevent structural damage to glass fibers during long-term exposure to hydrochloric acid, we performed the same experiments by modifying the duration of experiment on that the leaching at 80°C and 100°C was made for 4, 6 and 8 h. The infrared spectra of these samples provide evidence for a time dependent hydroxylation yield (Figs. 2 and 3). The maximum content of surface hydroxyl is obtained with the following conditions: $t=100^\circ\text{C}$, reaction time=8 h. From visual observation, the fiber treated at 100°C for 8 h are deeply damaged. This observation was confirmed by SEM.

Comparison of the FT-IR spectra obtained at 100°C during 6 h and 80°C during 24 h (Fig. 4) shows that hydroxyl content is higher in the second experiment.

The images (Figs. 5 and 6) of the native fibers (untreated fibers) and of treated fibers confirm the visual observation: the intense leaching effects on the fiber texture. Differences in the texture and resulting damage caused by acidic treatment to the fibers can

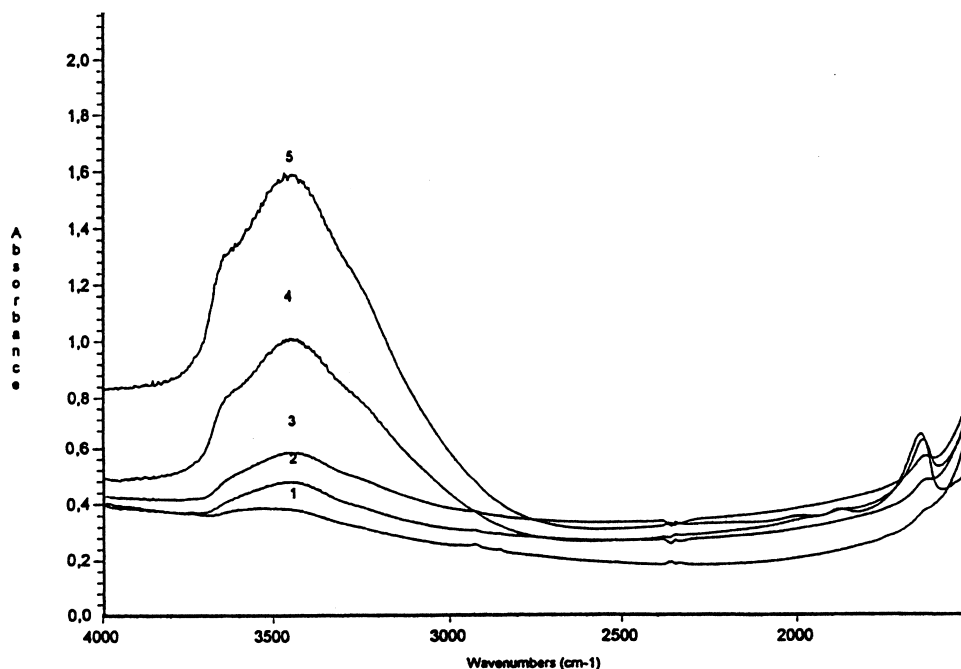


Fig. 1. Silanol bands absorption as a function of temperature during acidic treatment for 24 h of glass fibers. Spectra: 1=Native fibers, 2=40°C, 3=60°C, 4=80°C, 5=100°C.

easily be observed. Image 5 displays some fibers with smooth and regular surface.

Then, surface analyze on micrograph 6 revealed that those fibrillar bundles surfaces seem to be irregular and rough. The best conditions for significant increase of hydroxyl groups while preserving an unaltered fiber texture is the acidic treatment at 100°C during 6 h.

Another way to evaluate the modification of fibers texture is to determine their surface area and pore size distribution before and after treatment. For that purpose, adsorption isotherms of various gases have been determined. Analysis of these adsorption isotherms by the BET equation in the P/P_0 range

Table 1
Results of silanization of treated fibers by leaching during 24 h

| Leached samples | Blank (native fibers) | 40°C | 60°C | 80°C | 100°C |
|-------------------------------------------------------|-----------------------|------|------|------|-------|
| % C | ≤0.04 | 0.14 | 0.34 | 0.46 | 1.03 |
| mol g ⁻¹ (·10 ⁻⁴) ^a | | 0.39 | 0.95 | 1.29 | 2.95 |

^a Mole of bonded silane per gram of stationary phase.

0.05–0.35 allows calculation of the surface area [23]. In this mode, calculation was performed considering that an adsorbed nitrogen molecule covers a surface of 16.2 Å².

Conversely from the results of Jelinek and Kováts [24] a surface coverage of 13.5 Å² is also claimed. As those are preliminary results the 16.2 Å² value was only considered and a subsequent paper will focus on the difference. The pore size distribution is more difficult to obtain.

The presence of mesopores (apertures ranging between 2 and 50 nm) is generally indicated by a closed hysteresis loop in the adsorption–desorption isotherm. From the desorption branch a mesopore size distribution can be derived by the BJH method [25] which uses the Kelvin equation for the capillary condensation. The presence of micropores (pore size lower than 2 nm) is more difficult to assess. In a micropore, the adsorption potential is generally higher than on a non-porous surface, which leads to a shift of adsorption isotherms towards low pressures. Highly microporous samples give a type I adsorption isotherm, however for the general case a

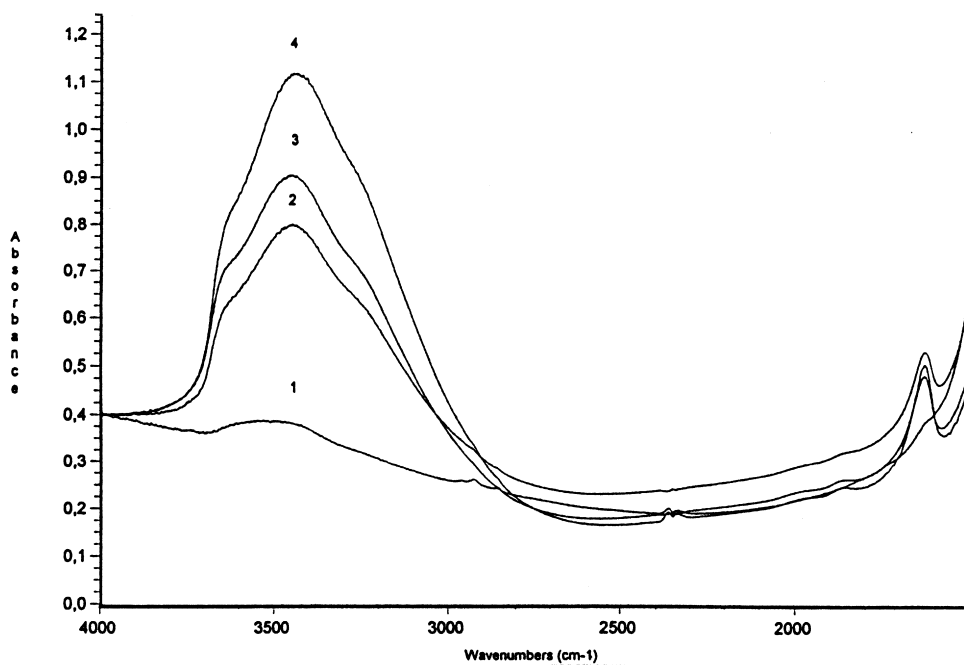


Fig. 2. Silanol bands absorption as a function of reaction time during acidic treatment at 80°C of glass fibers. Spectra: 1=Native fibers, 2=4 h, 3=6 h, 4=8 h.

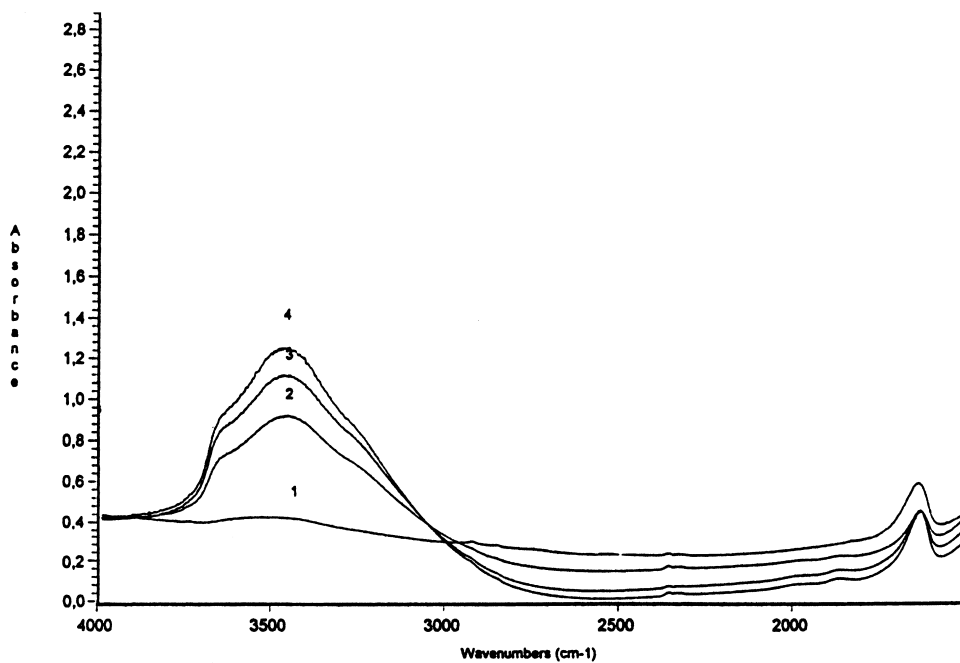


Fig. 3. Silanol bands absorption as a function of reaction time during acidic treatment at 100°C of glass fibers. Spectra: 1=Native fibers, 2=4 h, 3=6 h, 4=8 h.

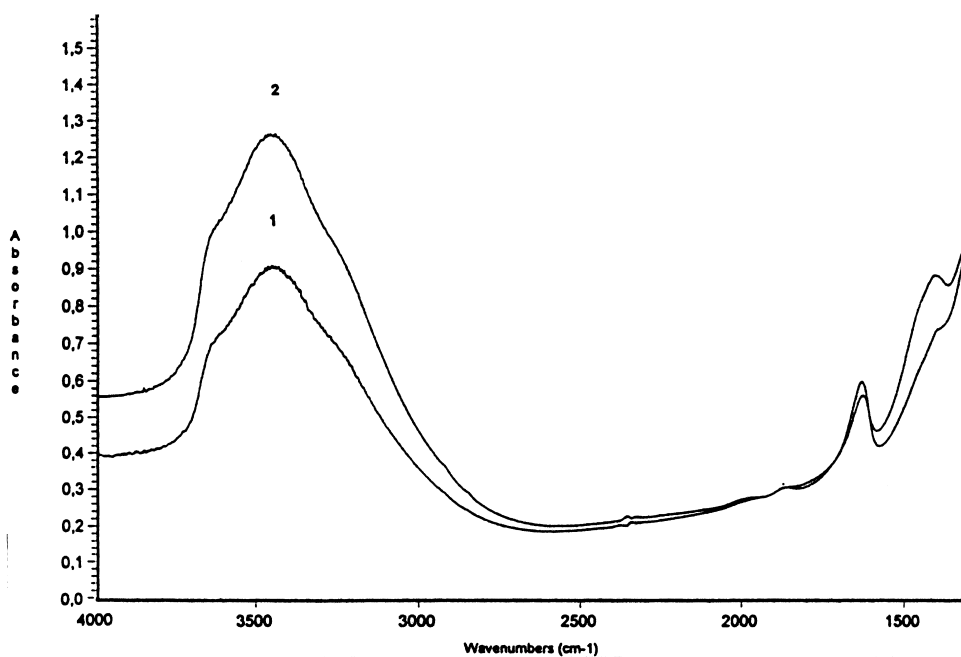


Fig. 4. Silanol bands of glass fibers treated by leaching at 80°C during 24 h (1), and 100°C during 6 h (2).

careful analysis is needed to conclude to their presence. The simplest way is to use the t -plot or the Sing's α_s methods that consists in comparing the adsorption isotherm to that of a nonporous reference [23]: a pore volume and an external surface area can be calculated. If the presence of micropores is

ascertained, a model like Horváth–Kawazoe (HK) [26] can be used to give a pore size distribution.

In the present work, we have determined the adsorption isotherms of nitrogen and krypton at 77 K on one side and of water at 25°C on the other side.

Nitrogen adsorption is the standard method, but on low-surface-area samples (which are the case of the native fibers) krypton adsorption is more accurate.

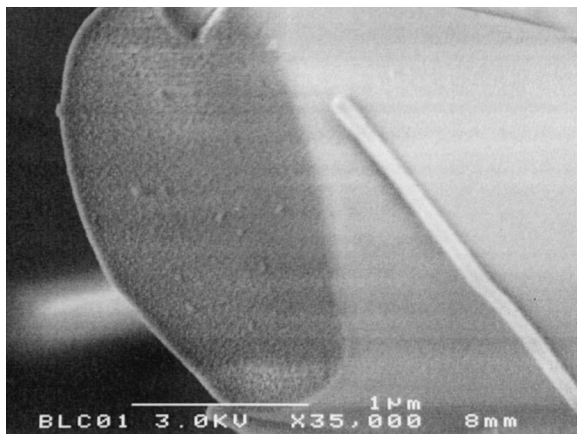


Fig. 5. SEM micrograph of surface texture of the untreated glass fibers.

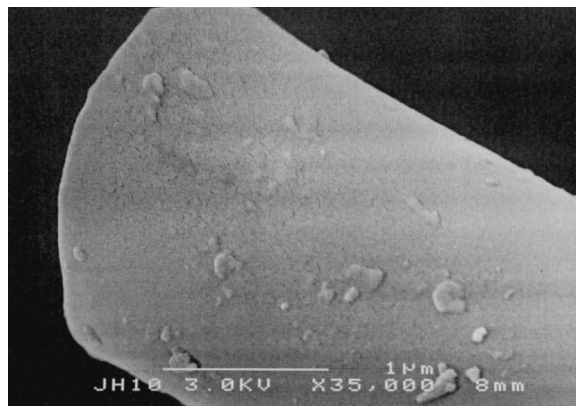


Fig. 6. SEM micrograph of glass fibers leached at 100°C during 6 h.

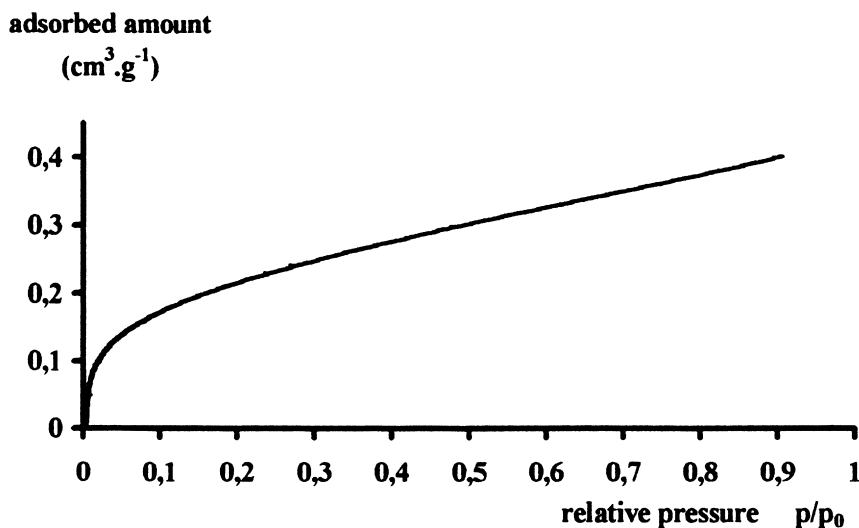


Fig. 7. Adsorption isotherm of krypton on untreated fibers.

The adsorption of water is interesting at two levels. First, this is the medium of corrosion, which means that the surface area derived from water adsorption isotherm seems to be a real reflect of the extent of modification. Secondly, the comparison of nitrogen and water adsorption is a good way to evidence the presence of very narrow pores that are accessible to water.

The adsorption isotherms of the native fibers and treated fibers at 100°C during 6 h are presented respectively in Fig. 7 (krypton) and Fig. 8 (nitrogen). Water adsorption isotherms of the two types of fibers are illustrated in Figs. 9 and 10.

The BET surface areas calculated for the three gases are presented in Table 2. Whatever the probe molecule (water, nitrogen or krypton), the compari-

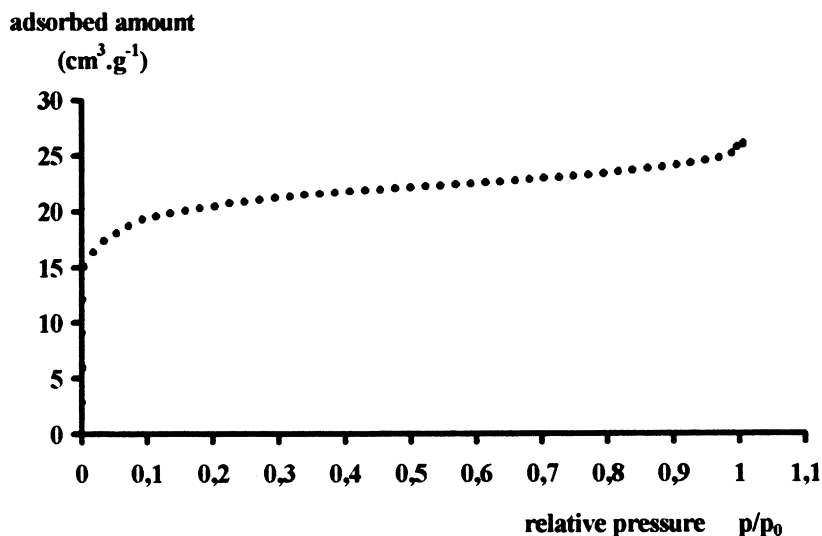


Fig. 8. Adsorption isotherm of nitrogen on leached fibers during 6 h at 100°C.

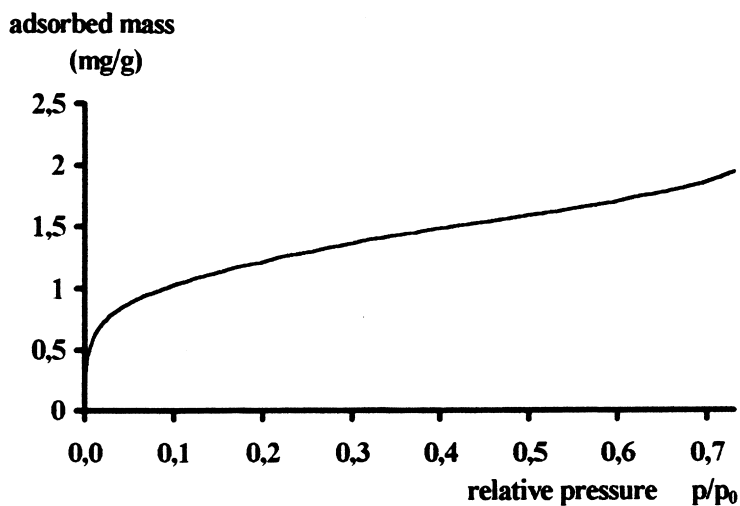


Fig. 9. Adsorption isotherm of water on untreated fibers.

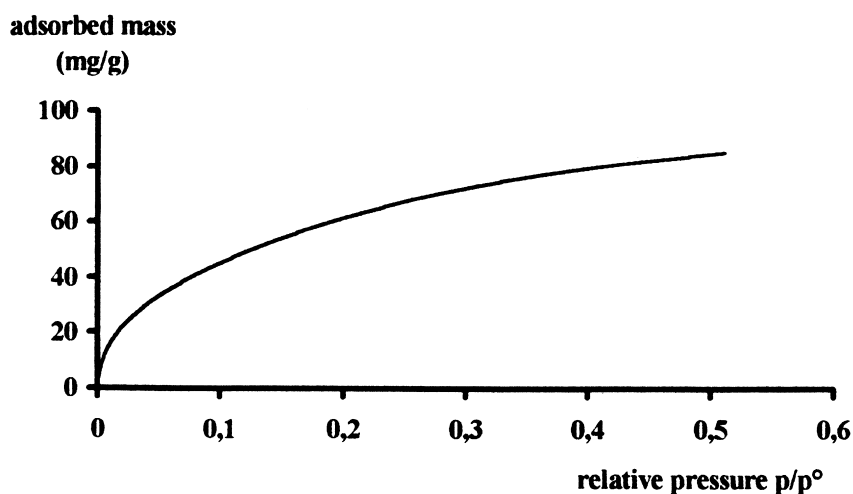


Fig. 10. Adsorption isotherm of water on leached fibers during 6 h at 100°C.

Table 2
Surface area measurements

| | Volumetric measurements | | Bonded TMCS ($\mu\text{mol m}^{-2}$) | Gravimetric measurements | | Bonded TMCS ($\mu\text{mol m}^{-2}$) |
|----------------|----------------------------------------------|------------------|-------------------------------------------|----------------------------------------------|------------------|-------------------------------------------|
| | Surface areas ($\text{m}^2 \text{g}^{-1}$) | C_{BET} | | Surface areas ($\text{m}^2 \text{g}^{-1}$) | C_{BET} | |
| Native fibers | 0.97 _(krypton) | 43.52 | 0 | 3.47 | 129.98 | 0 |
| Treated fibers | 76.31 _(nitrogen) | 928.57 | 1.84 ^a | 203.81 | 21.13 | 0.69 ^a |

^a Values obtained with 0.5% C from elemental analysis.

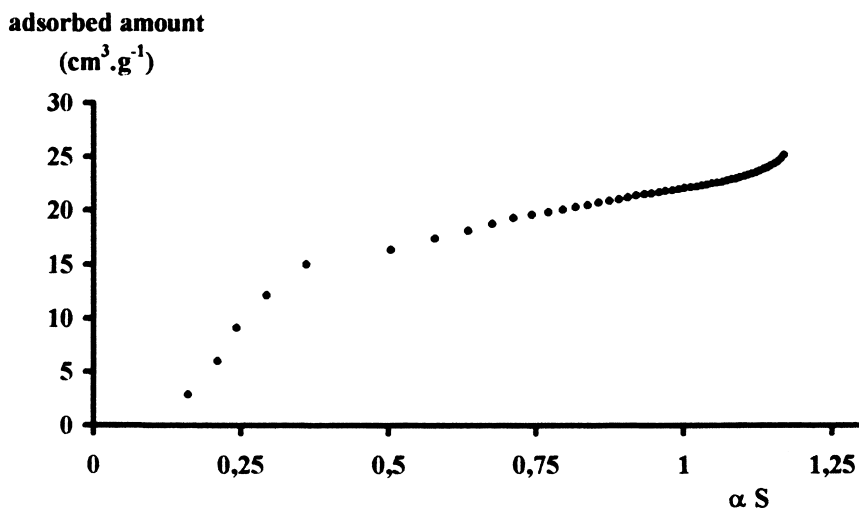


Fig. 11. α plot on leached fibers during 6 h at 100°C.

son of the values before and after treatment shows a large increase of accessible surface area (surface areas are multiplied by a factor of at least 70).

The effect of the hydrothermal treatment primarily increases the roughness (which can be observed on SEM images) but also probably creates a porosity (non visible on SEM images) that can explain the very high surface area. The nitrogen adsorption isotherm on the treated sample is of type I of the BDDT [27] classification that is often an indication of microporosity. The C values (Table 2), which are

the energetic parameter of the BET model, are also very high for this sample. In order to confirm the presence of micropores, we have applied the α_s method to this sample by using standard silica as reference [23]. The α_s curve is plotted in Fig. 11. The interpolation at the origin of the linear part confirms the presence of micropores. By applying the HK model, a microporous size distribution is calculated (Fig. 12). This distribution is centered on 0.6 nm, but this is only an order of magnitude since any models have some approximations. TMCS

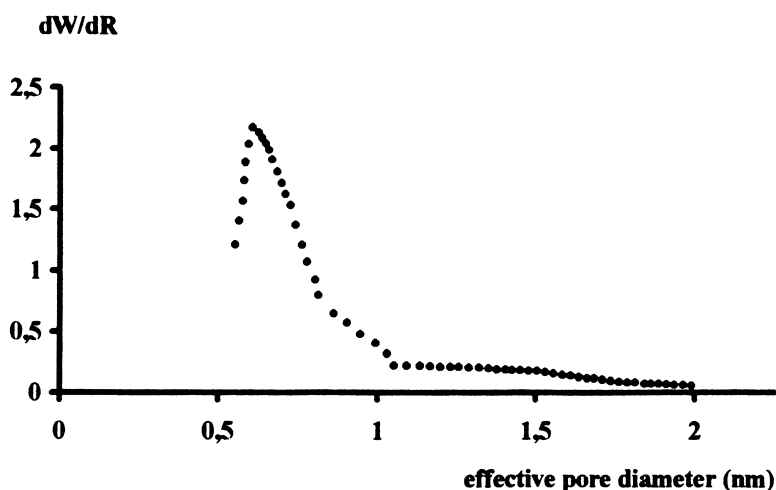


Fig. 12. Microporous size distribution on leached fibers during 6 h at 100°C.

groups have a surface requirement of 0.38 nm^2 [28] and then can enter most of them.

Now, if we compare water adsorption to both the nitrogen and the krypton molecules, a large difference is observed in surface areas. This could be interpreted by the existence of very narrow pores which are accessible to water and not to the other molecules.

4. Conclusions

The results obtained indicate that the compromise for high hydroxyl content and minimum deterioration of the fibers surface, the leaching should be 20% HCl during 6 h at 100°C .

The procedure modifies the texture and the structure of the fibers in increasing the reactive silanol amount and specific surface area. However, use of hydrochloric acid for the hydrothermal treatment results in the formation of micropores.

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