COMBINATION OF DENSIFICATION AND SHEAR FLOW FOR AGED SILICA OPTICAL FIBRES

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Abstract - An aging study was performed on several silica optical fibres with standard epoxy-acrylate coating in hot water during several months. In hot water, the fibres were subjected to bending stresses by winding around alumina mandrel. Thereafter, the polymeric coating was removed by soaking fibres into dichloromethane at ambient temperature. The prepared fibres were submitted to a series of indentation tests using a microduremeter Matsuzawa equipped with a diamond Vickers indenter. The observation of the Vickers impression provided direct evidence of a pilling-up of the silica cladding submitted to the hydrothermal treatment. This indentation behaviour is consistent with a structural relaxation promoted by the water and the glass network interaction. A densification phenomenon by compression intervenes by rearrangement of the Si-O-Si atomic connections.

Keywords: Optical fibres, Bending test, Indentation test, Structural relaxation, AFM observations.

1. Introduction

Structural relaxation is a major characteristic of liquids and glasses. It relates to the structural transformations induced by temperature changes and its kinetics is governed by the viscosity [1]. The time required for such transformations becomes larger when temperature decreases. Below glass transition temperature T_g, the relaxation time is so large that vitreous materials appear rigid and consequently behave as solids.

In previous work, we observed a permanent deformation of aged fibre under bending in hot water at 85°C [2]. This is surprising because this temperature is far lower than the silica glass transition, and numerical simulation would lead to the conclusion the effect of such a relaxation is negligible. Then one may assume that external stress and water could promote structural relaxation at low temperature. This implies that relaxation time is different at surface and in the bulk. This hypothesis is consistent with the observations of Tomozawa et al. [3]. Water can exist in glass as hydroxyl attached to the glass as silanol groups (OH in Si-OH) and molecular water (H_2O). The molecular water can diffuse in the glass and react with the glass network to form hydroxyls by: $Si\text{-}O\text{-}Si + H_2O \leftrightarrow 2\ Si\text{-}OH$.

Since the mechanical strength of a glass is controlled by the surface characteristics of the glass, it is useful to determine the effect of such a structural surface relaxation on the mechanical behaviour of the fibre.

In this paper, the indentation hardness technique is presented and used to characterize the hardness and the deformation mode of the surface of optical fibres. Indentation tests use a Vickers diamond indenter.

This work leads to obtain AFM images of Vickers impressions when the fibre is submitted to different aging conditions. The purpose is to examine the influence of the structural relaxation on the indentation behaviour of the surface of silica optical fibre non aged and aged in hot water (at 65°C) during 27 and 30 months and subjected to bending stresses by winding around alumina mandrel of 40 mm in diameter.

2. Sample Preparations

The silica optical fibres used are made by an MCVD method with an epoxy-acrylate coating corresponding to an overall diameter of 125 µm. These fibres are commercial single mode silica fibres with a 62.5 µm thick epoxy-acrylate polymer coating (from Verrillon Inc.) doped with fluorine.

The fibres were heat-treated at 150°C for 48 hours under wet atmosphere using an autoclave. Part of the sample was rolled on a cylindrical mandrel. After the heat-treatment, the rolled samples exhibited a permanent deformation when the bending stress was removed. Then the coating of all samples was removed by soaking the fibres in dichloromethane at room temperature.

3. Bending Stress

Optical fibres were subjected to bending stresses by winding around alumina mandrel [2, 4] (Fig. 1). The constant level of the applied stress can be adjusted by the proper choice of the mandrel size. The applied stress on the fibre depends on the mandrel diameter according to the Mallinder and Proctor relation [2, 5] as follow:

$$\sigma = E_0.\varepsilon\left(1+\frac{\alpha'.\varepsilon}{2}\right) \qquad \alpha' = \frac{3}{4}\alpha \qquad \varepsilon = \frac{d_{glass}}{\phi + d_{fiber}} \qquad (1)$$

where σ is the applied stress (GPa), E_0 is the Young modulus (equal to 72 GPa for the silica), ε is the relative fibre deformation, α is the constant of the elastic nonlinearity (equal to 6).

ϕ is the mandrel diameter (40 10^3 µm); d_{glass} is the glass fibre diameter equal to 125 µm and d_{fiber} is the fibre diameter including the polymer coating and equal to 250 µm. This leads to the corresponding stress of 2.254 GPa.

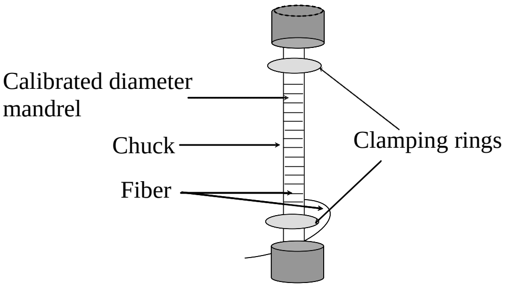

Figure 1: Alumina mandrel with calibrated diameter

4. Indentation Experiments

The indentation hardness technique is a very useful method to characterize the hardness and the deformation mode of the surface of a material. When a sharp indenter such as Vickers indenter is loaded onto a glass, a residual surface impression is observed after unloading and the material hardness is generally estimated from the projected area of the impression. The deformation is dependent on the applied load, temperature and load time. It is assumed the deformation is caused by compression and/or shear.

Glasses can be classified in two groups, according to whether the glass shows “normal” or “anomalous” mechanical behaviour [6]. Silica-rich glasses are known to exhibit anomalous behaviour under load since volume densification has occurred while in normal glasses shear lines due to shear flow have been observed [7]. Fused silica is known to densify relatively easily during indentation owing to its open three-dimensionally coordinated structure [8]. Peter [7], in microscopic observations of the indentation topography, detected a transformation from essentially radial (“sink-in”) to lateral (“pile-up”) displacement of material about the indenter as the modifiers content in silica glass was increased, suggesting a corresponding transformation from densification to shear flow in the deformation mechanism. The role of the modifying ions in the structure is to provide “easy-slip” paths through another rigid, strongly covalent network [9]. Correlation between surface modification and mechanical resistance of soda lime glasses has been studied by Sorarù [10, 11]. These works emphasize the effect of various surface treatments on indentation response of this kind of glasses.

In this paper, we present indentation experiments which are performed on a Matsuzawa apparatus equipped with a Vickers diamond indenter. Concerning the curved sample, indentations were performed on the compressive side and on the tensile side. 25 grams load was applied during 10 s in air at room temperature. Vickers diamond pyramid hardness is determined in practice by measuring the diagonal length of the indentation produced by the penetration of a square-based pyramid having an angle of 136° between opposite pyramid faces. The hardness number *HV* is given by the relation:

$$HV = \frac{2.P.sin(\theta/2)}{d^2} \qquad (2)$$

where *P* is the applied load, *d* is the average value of the impression diagonals d_1 and d_2:

$$d = (d_1 + d_2)/\,2 \qquad (3)$$

and the angle θ is equal to 136°. Although the diagonals, d_1 and d_2, are obtained by measurement after the removal of the load, it is known that the change in the lengths of the diagonals upon unloading is very small [12] and almost insignificant when compared to the diagonal length itself. Thus, the Vickers hardness number is given by:

$$HV = 1854.4P/d^2 \qquad (4)$$

HV is in kg/mm², where *P* is in kilograms and *d* is in millimetres [13].

It is interesting to know the indenter penetration depth *h*, in the material:

$$h = d/2.\sqrt{2}.tan(68°) \qquad (5)$$

- ***Residual impression***

Observation of indenter impressions was carried out using the atomic force microscope to have the diagonal size and the depth of each indentation impression. Vickers hardness of each sample is calculated from relation (4) and uses the measurement of each diagonal impression which the length is considered not affected during the indenter unloading.

The indenter penetration depth at maximal load was calculated using the relation (5). This makes possible to define vertical elastic covering after unloading.

Vertical elastic recovery of glass can be defined as:

$$e^v = | h - h_i | \qquad (6)$$

where h_i is the residual impression depth and h is the depth of the indenter at maximum load [14].

The average hardness of every sample is obtained from the average of five measurements of residual indenter impressions.

- ***Behaviour of aged fibres after indentation loading***

After aging period, fibres left hot water and the polymeric coating was removed by soaking fibres into dichloromethane. Thereafter, the stripped fibre was submitted to indentation load of 25 grams during 10 s at ambient temperature. During the unloading phase, a residual impression was observed using electronic microscope which equipped the microduremeter.

During the indentation test, several phenomena related to the glass surface deformation could be observed:

1/ during the loading phase, glass undergoes a hydrostatic compressive stress and a shear stress,

2/ during the unloading phase, one observes more or less important elastic return of the compressed silica. After the unloading, the resulting impression is the consequence of two distinct phenomena:

  i/densification obtained after compression loading,

  ii/ and plastic rearrangement obtained from shear stresses.

After the compression loading, the silica densification is the consequence of the atom's rearrangement. One notes an angle reduction of the atomic connection Si-O-Si. These can be regarded as a simple loss of volume.

The rearrangement by sliding does not influence the material volume. It is the result of the connection rupture and of the connection formation. According to the prevalence of one or the other of these two mechanisms, glasses were divided into two categories: "normal" glasses, where the sliding is prevalent, and "abnormal" glasses, where the densification phenomenon prevails.

The analysis of a normal glass indentation shows a lateral displacement of the material (pill-up) around the impression zone (fig. 2a) and a package of sliding lines comparable to steps under the indenter contact surface.

For abnormal glasses such as silica, it is the tetrahedral network which will be rearranged under the stress. Indenter application produces a large strain, induces a deformation of the angle Si-O-Si and leads to a material densification. One observes the phenomenon of "sink-in" under the indenter contact surface which corresponds to a material radial displacement (fig. 2b).

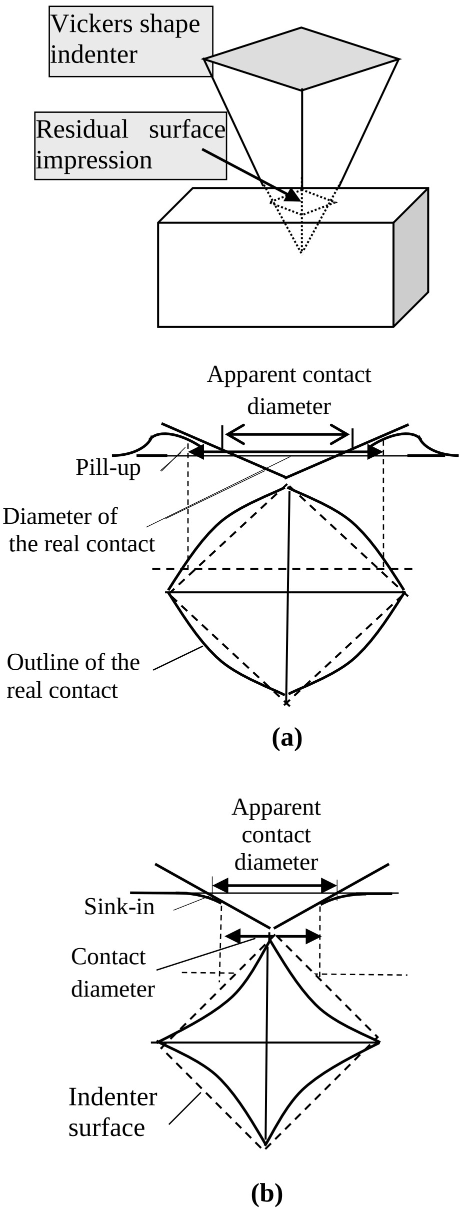

Figure 2: Used Vickers indenter, pill–up (a) and sink-in (b) effects from lateral material displacement.

Thus, silica and glasses with a silica high percentage are known for their abnormal behaviour indentation. The silica densification phenomenon under loading is attributed to its open SiO_4 tetrahedrons which are connected together at the vertex. The densification is characterized by a radial displacement of the material under the indenter.

5. AFM Observations

The AFM principle is to measure the various indentation forces between a point fixed at the end of a lever arm and the material surface (ionic forces, repulsion forces, Van der Waals's forces, electrostatic forces, friction forces, forces magnetic forces, etc...). The cantilever deflection is followed while positioning a laser beam on the higher cantilever surface; the beam is reflected on a mirror then pointed on photodetectors which record the light signal. Displacements x, y, z are done thanks to a piezoelectric ceramic.

- ***Indentation observations***

An Atomic Force Microscope was used to profile the residual indentation. The observations were performed in tapping mode. The AFM has proven to be a helpful experimental technique for studying the impression topography.

Photographs were collected using Digital Instruments Nanoscope III Atomic Force Microscopy equipment. The photography acquisition was carried out in "tapping" mode. In tapping mode, the cantilever oscillates close to its resonance frequency with sufficiently high amplitude. The microscope sensor tip comes periodically in contact with the sample and the forces of friction are thus avoided.

Figure 3 shows an AFM image of the residual impression obtained on the surface of optical fibre 1 aged in hot water (65°C) during 27 months and indented under a load of 25 grams during 10 seconds. The topographic image and the representation of the profile of the residual impression (a cut according to the two perpendicular diagonals), show the fibre surface is prone to the "pilling-up" phenomenon (fig. 4 and 5).

Such behaviour is also seen on figures 6, 7, 8 for optical fibre 2 aged during 30 months in hot water at 65°C. Around the indented zone, a lateral material displacement with an overflow is noted.

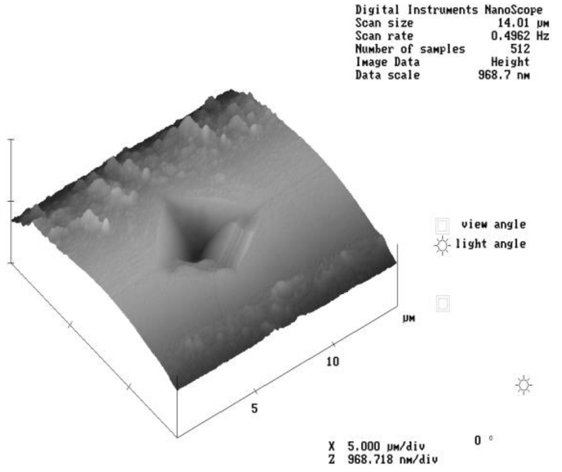

Figure 3: AFM photography of Vickers indentation residual impression on surface of fibre 1 aged during 27 months in water at 65°C.

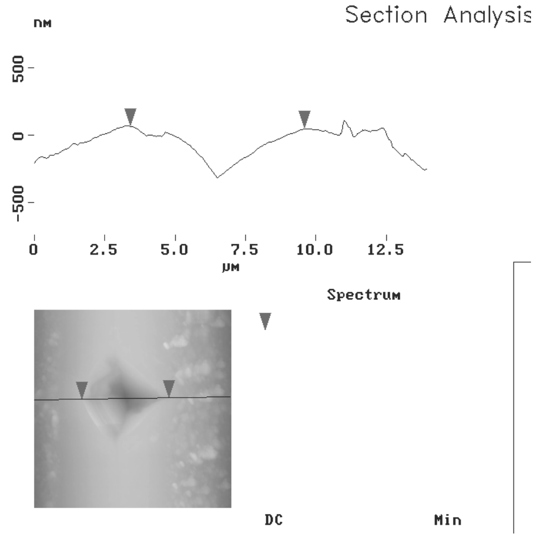

Figure 4: Profile of residual impression for fibre 1 across horizontal diagonal.

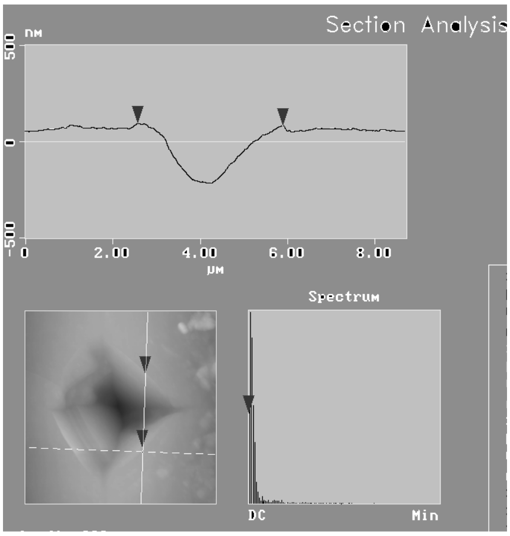

Figure 5: Profile of residual impression for fibre 1 across vertical diagonal.

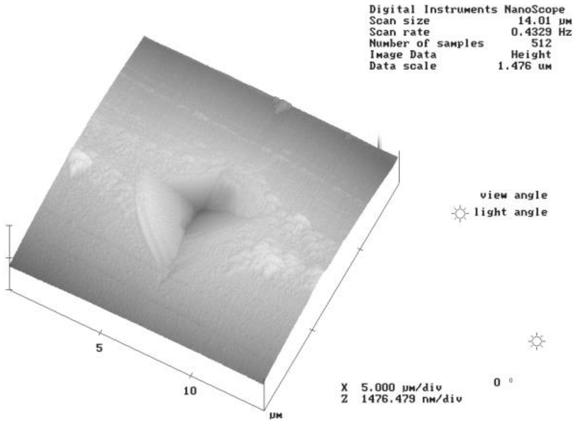

Figure 6: AFM photography of Vickers indentation residual impression on surface of fibre 2 aged during 30 months in water at 65°C.

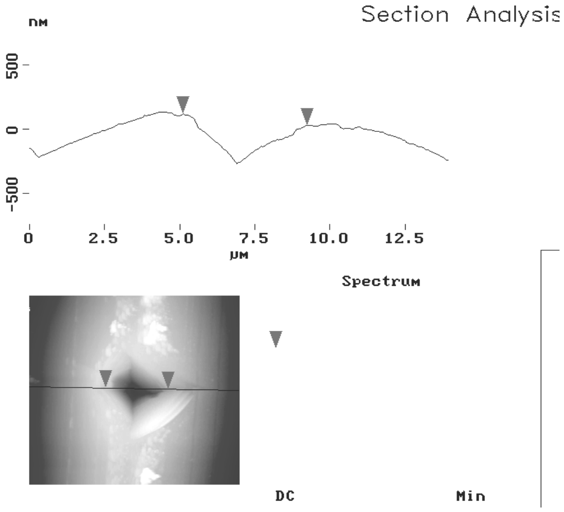

Figure 7: Profile of the residual impression for fibre 2 across horizontal diagonal.

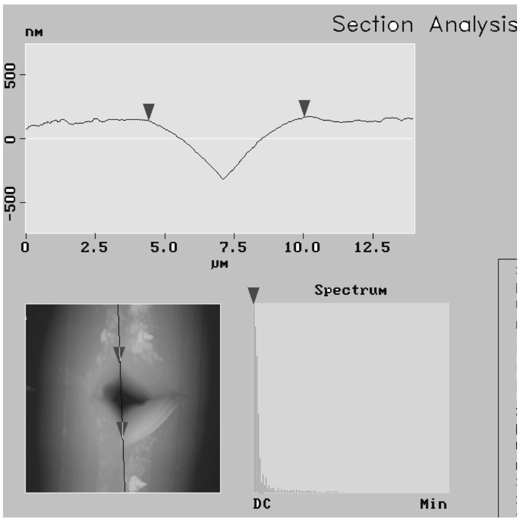

Figure 8: Profile of the residual impression for fibre 2 across vertical diagonal.

Fig. 9 shows an AFM image of a Vickers impression produced on the surface of non-aged optical fibres. The AFM topographic image and the cross section of the indentation made across the indentation following one of the diagonals of the indentation show that this indent was subjected to a sinking-in phenomenon.

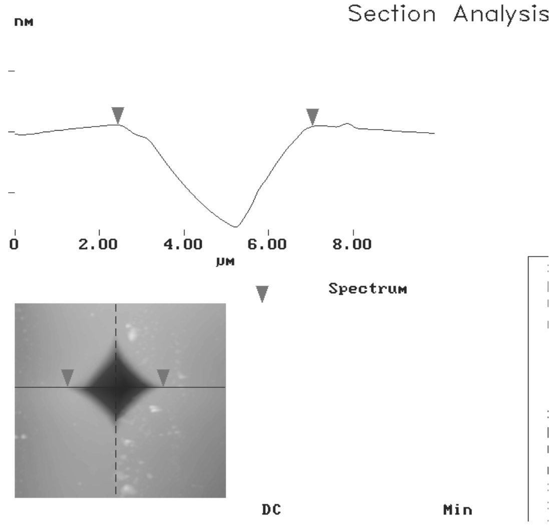

Figure 9: AFM topographic image and cross section of indentation on as-received silica optical fibre (non-aged fibre) showing sinking-in of material.

Aging led to a fibre surface hardening (smaller diagonal, decreasing indenter penetration and higher hardness) (Table 1).

The pill-up phenomenon is noted whatever the fibre aging period may be but not for non-aged fibres.

Table 1. Results for fibres submitted to indentation load of 25 grams during 10 s.

Sample	Average diagonal d (μm) (±0.001μm)	Maximal depth h (nm)	Vickers Hardness HV (GPa) (±0.05 GPa)	Observed behaviour	Aging time (months)
Non aged fibre	7.88	1125	8.04	Sink-in	
Fiber 1	6.17	881	12.14	Pill-up	27
Fiber 2	5.96	851	12.33	Pill-up	30

Due to the difficulty to observe the state of fibre 1 surface, one could not have clear residual indenter impressions. Table 2 presents residual impression depths for non-aged fibre and for fibres 1 and 2. The non-aged fibre presents a less marked elastic return (a larger residual impression depth) than for the aged fibres.

The aging period makes fibres more resistant to the indenter penetration (the maximum penetration depth decreases when the aging time increases). On the other hand, and whatever the aging period, the percentages of the vertical elastic recovery (e^v) remain almost constant (around 42 %).

Table 2. Residual impression for non-aged fibre and for fibres 1 and 2.

Sample	Residual impression depth h_i (nm) (±1nm)	Maximal depth h (nm)	Vertical elastic recovery e^v (nm)	Percentage of the vertical elastic recovery (%)	Aging time (months)
Non aged fibre	675	1125	450	40	
Fiber 1	494	881	387	44	27
Fiber 2	501	851	350	41	30

- ***Discussion***

Since a permanent impression is left after indenter removal for all samples, and considering that sample mass remains unchanged, a small volume of the glass should reorganize during indentation process.

It is well established that the structure of silica glass having only bridging oxygens is not compact, but very open, and the strength of the Si-O bonds is large, giving the high glass transition temperature of around 1200°C. For this reason, it is considered that structural units (SiO_4) can be reorganised without bond breaking but by changing the angle of the Si-O-Si bond during loading. Therefore, we observed a densification and a sinking-in of the material as shown in Figure 9. The Vickers value (HV= 8.04) and the large elastic recovery of around 40% were found to be in accordance with the literature [6, 7].

On the other hand, the indentation topography of aged fibres exhibited a pilling-up of the material. This pilling-up phenomenon is usually caused by a lateral displacement of material, hardly imaginable without flow. A difference in deformation mechanism is likely to account for the differences between the non-aged and aged fibres. It is generally considered that modifying ions located in the interstices of the Si-O network are responsible to such indentation behaviour (Fig.10). Typical modifiers are cations that interact with the bridging oxygens to depolymerise the network. Small molecules - e.g., hydrogen - may diffuse in silica glass as this glass is far from being compact. Hot water molecules may act in the same way. They fill voids in the network constructed by the SiO_4 tetrahedra. As they are neutral molecules, they appear different from modifying cations. However, they are polarized units and may react with the bridging oxygens of the network according to the chemical reaction: $Si\text{-}O\text{-}Si + H_2O \leftrightarrow 2\ Si\text{-}OH$. These non-bridging anions are weak points in the network that enhance shear flow in the same way as modifiers. Thus, water molecules can also be considered as modifiers.

Thus, water molecules can also be considered as modifiers. The results concerning the bent fibre exemplify this idea as the elastic recovery of the internal side of the curvature (i.e., the compressive side) was found to be higher than that of the external side. The combined effect of water and tensile stress are supposed to accelerate the surface relaxation while water and compressive stress would decelerate the relaxation [15, 16]. This acceleration of the surface relaxation should lead to the increase of the Si-O-Si angle and therefore should increase water diffusion in glass. Thus, the concentration of water diffused in the tension side should be much higher than that in the compressive side. This would lead to a more important contribution of the shear flow process during indentation and also to a smaller elastic recovery [17]. It should be noted our observations that relate to silica in hot water liquid water are consistent with the behaviour of silica exposed to high water vapor pressure [18].

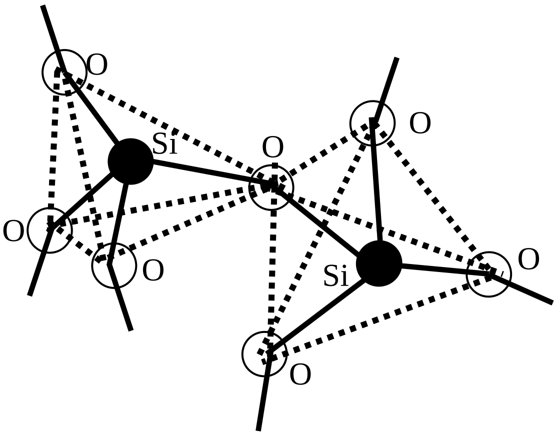

Figure 10: Representation of SiO_4 network

6. Conclusion

Effects of the surface structural relaxation on the indentation behaviour of silica optical fibre aging in hot water during large periods were investigated.

Due to the hydrothermal hot water action on the glass surface, the silica optical fibre behaviour was analysed. Using AFM image of the residual impressions and after measurement of the indenter depth after loading, the evolution of the Vickers hardness was obtained. The aging period makes fibres more resistant to the indenter penetration. For the non-aged fibre, the glass surface exhibited an anomalous behaviour under load as sinking-in and densification were observed. For aged fibres, one can observe a lateral displacement of material which leads to a pill-up phenomenon.

It suggested that the water could act as a modifier since the deformation was found to be due to the combination of the densification and the shear flow of the material.

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