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CONDENSED MATTER

The Influence of Hydrogen Loading Temperature on the Mechanical Strength of Optical Fibers

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Abstract The influence of hydrogen loading temperature on the mechanical strength of optical fibers is investigated. Fibers subjected to high-pressure hydrogen loading at different temperatures were submitted to bend tests, and the results compared with those for pristine fibers. The Weibull probability distribution function was used to analyze the data of the mechanical bending strength of the fibers. Fiber strength is reduced by the presence of hydrogen, and this decrease is greater for higher hydrogen loading temperatures. The mechanical properties of the polymers used to coat fibers are affected by the hydrogen loading process and also by the increase in temperature. However, there is no evidence of cracks formation that might allow water to penetrate to the surface of the glass. Observation using scanning electron microscopy revealed that the morphology of fractures in nonhydrogen-loaded fibers have distinct fracture characteristics to that of fibers that are hydrogen loaded at 90°C and 120°C.

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1 Introduction

In fiber optics, the term photosensitivity is used to refer to the possibility of permanent change in the refractive index in the core of an optical fiber as a result of radiation with light of a particular wavelength. The discovery of this phenomenon led to the emergence of a new class of fiber structures, of which the most important is the fiber Bragg grating [1].

The greatest advances in fiber sensor technology have been made in the fields of acoustic sensing, strain monitoring, chemical/biomedical sensors, and temperature sensing [2]. Measurement systems are currently expensive, particularly when Bragg filters are used as strain sensors. Thus, sensors that use Bragg filters to measure strain are recommended for use in situations where conventional extensometry is difficult to use, such as measurement of mechanical forces in cables carrying power, measurements where those involved must remain up to several kilometers away from the part or structure [3], measurements in a hostile environment or in inflammable fluids [2], and measurements in strong electromagnetic fields.

The ability to increase the photosensitivity of optical fibers is of great technological interest, as this allows Bragg grating to be written more efficiently without the need for high-power optical beams or long exposure times, lower cost lasers can also be used, thus increasing production efficiency. A number of techniques can be used to increase photosensitivity. These include increasing the Ge concentration in the core of the fiber, introducing hydrogen into the vitreous structure, using co-dopants such as boron together with Ge and using other dopants [4].

A relatively simple technique for increasing the photosensitivity of optical fibers is hydrogen loading. In this technique, the fiber is kept at a specific temperature (from 20°C to 70°C) in high-pressure hydrogen (from 20 to 750 atm) for several days [4]. This allows hydrogen molecules to diffuse to the core of the fiber so that Bragg grating can be written with greater modulation depth in optical fibers ($\Delta n \approx 10^{-3}$–10^{-2}) using lower-power optical writing beams and shorter exposure times. H_2 diffusion in optical fibers under high pressure and at ambient temperature causes the refractive index of the fibers to change by more than 0.01, with about all germanium forming vacancies after exposure to ultraviolet radiation while the Bragg grating is being written [4]. The fibers that have been made photosensitive by means of this technique remain photosensitive as long as the hydrogen is present and should be kept at low temperature (−15°C) to prevent the hydrogen from diffusing outside the fiber.

Menegotto [5] studied the influence of the increase of hydrogenation temperature on the grating Bragg-wavelength stability. The annealing of the gratings showed that fibers hydrogenated at 90°C had gratings more stables than those inscribed on fibers hydrogenated at room temperature. However, gratings inscribed in fibers hydrogenated at 120°C showed lower stability [5].

For the optical fiber to retain its mechanical strength after hydrogen loading, both the core and vitreous surface must be free of defects. The fatigue process that occurs in glass oxides as a result of microcracks in the material is well understood and is attributed to the combined effect of stress and a harsh environment, generally in the presence of humidity. In the chemical corrosion process proposed by Michalske and Freiman [6], defects grow as the bonds between oxygen and silicon atoms are broken one by one. The force resulting from broken bonds is transferred to the adjacent bonds in an accumulative process that ends in excess stress being concentrated at the end of the defect. If the stress is higher than the strength of the material, it results in a catastrophic rupture. The reduction in strength in the absence of external applied stress in an adverse environment, such as in water, is called zero-stress aging. The failure mechanism for glass in a state of static fatigue has been well documented [7], but the reason for the loss of strength by the vitreous part under zero stress is still the subject of study. One proposed explanation is that adsorption of water molecules at the surface causes the crack to grow during the strength test [7]; another explanation is that the corrosive reaction at the failure surface can act as a crack nucleus. Therefore, the mechanical strength of silica-based fibers depends on how their surfaces react in different environments, as the process by which a crack grows can vary according to the environment.

The values recorded for rupture stress in optical fiber bending tests have less dispersion than those recorded in tensile tests, mainly because greater control can be exerted over the environment in which the sample is being tested and also because the area under test is smaller in bending tests, thus reducing the probability of preexisting cracks in the area under stress growing.

Considering the important applications of fiber optics in sensing and interest in increasing their photosensitivity, this study analyzes the influence of the temperature at which high-pressure hydrogen loading is performed on the mechanical strength of optical fibers by means of bending tests.

2 Experimental Procedure

2.1 Hydrogen Loading the Optical Fibers

The optical fibers used in this study are standard single-mode telecommunications fibers with a polyacrylate coating. The fiber diameter is 241 μm, of which 116 μm is polymer and 125 μm cladding/core (measurements taken with the aid of a Carl Zeiss/ZENA Neophot 32 microscope, increase of 200×).

The technique used to increase the photosensitivity of optical fibers is known as high-pressure hydrogen loading. This study examines the changes in the mechanical properties of fibers as a result of hydrogen loading using a constant pressure of 100 atm and duration 5 days in all the experiments. An EDGCON 3P oven was used to heat the optical fibers to temperatures of room, 90°C and 120°C during hydrogen loading. The hydrogenation occurs with the straight fibers. After the hydrogen load, the fibers were stored at a −15°C temperature to prevent the hydrogen from diffusing outside the fiber.

2.2 Bending Test

A bending test (Fig. 1) was carried out to calculate the mechanical strength of the fibers.

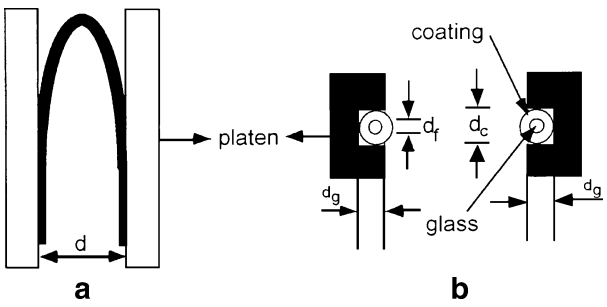

Fig. 1 Two-point bending device

In the bending test, the fracture stress σ_i is obtained by measuring the maximum final fracture strain ε_i, using the following equation [7]:

$$\sigma_i = \varepsilon_i E(1 + \alpha\varepsilon_i)$$

where, E is the elastic modulus of silica (72.2 GPa), and the factor α=2.125 is included to take into account the fact that the elastic modulus depends on tensile strain when the fiber is bent [7].

The two-parameter Weibull model was used to analyze the data for the distribution of stress in each fiber. The Weibull modulus is defined by the following relationship between cumulative failure probability at a particular applied stress [7]:

$$\ln(-\ln(1 - P_i)) = m \ln \sigma_i - m \ln \sigma_0$$

where, P_i is the cumulative failure probability at each level of stress, σ_i. The parameter m, known as the Weibull modulus, is a number that reflects the variability in the mechanical strength. Thus, a higher m value corresponds to less variability in strength. Typical values of m for pristine fibers are between 60 and 160 [7]. σ_0 is the strength at which 63.2% of samples fail within a set of fibers. These two parameters in the Weibull model were used to analyze the strength distribution of the optical fiber samples tested.

The test procedures and calculations to determine bending failure stress were carried out in accordance with international standard EIA/TIA-455-116.

The speed used in the bending tests was 1 μm/s, with an accuracy of ±10%. Fifteen samples 5 cm long were used for each test at a specific speed. The plates were initially positioned 10 mm apart. The laboratory temperature was 23°C, and the relative humidity 60%.

2.3 Hardness, Elastic Modulus, and Viscoelasticity Measurements

To analyze whether the polymer retains its mechanical characteristic after hydrogen loading, the hardness, elastic modulus, and viscoelasticity of the polymer fiber coating were measured. The hardness and elastic modulus of the polymers were measured using a Nanoindenter XP according to Oliver and Pharr's model, in a process similar to that used for measuring the properties of glass in fibers [8]. Viscoelasticity was measured by analyzing the variation in penetration over time under a constant force. An indenter with a 150 μm spherical tip was used, and the variation in penetration depth over time was measured. To obtain the viscoelasticity parameters, and the viscosity in particular, the four-parameter viscoelastic model was used to adjust the experimental curves [9, 10].

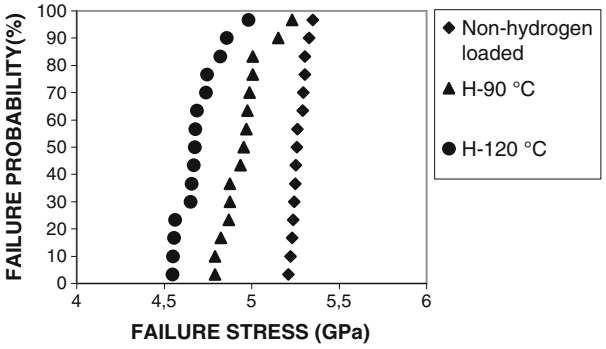

Fig. 2 Graph of fracture probability according to Weibull statistics: no hydrogen loading, H-90°C fibers hydrogen loaded at 90°C, H-120°C fibers hydrogen loaded at 120°C at a speed of 1 μm/s

3 Results and Discussion

3.1 Two-Point Bending Test

Figure 2 shows the curves of the fracture probability using Weibull statistics calculated for all the samples studied at a velocity of 1 μm/s.

Table 1 show the values of m and σ_0 obtained using Weibull statistical analysis of the results of tests carried out at a speed of 1 μm/s.

The mechanical strength of the fibers decreases as the hydrogen loading temperature increases. As the value of m is quite high for the pristine sample, it can be concluded that the flaws have very similar sizes without hydrogen loading and that the distribution of pre-existing flaws in the fiber must therefore be quite homogeneous. The heterogeneity of the flaws increases as the fiber hydrogen loading temperature increases. It can be observed that the fibers that were not hydrogen loaded have high Weibull "m" parameters, above the limit of 60 suggested for a good quality fiber [7]. This indicates that there is only a small dispersion of failure stresses and that the flaws on the surface must have very similar sizes. The "m" values in Table 1 can also be taken as indicating that there is only one family of flaws, from which the fractures originated. The fibers that were hydrogen loaded at 90°C and 120°C have an m value under 60, indicating that there is greater dispersion of failure

Table 1 Values of m and σ_0 obtained in the bending test for a speed of 1 μm/s

Hydrogen loading temperature	m	σ_0 (GPa)
No hydrogen loading	148	5.3
Hydrogen loaded at 90°C	45	5.0
Hydrogen loaded at 120°C	42	4.7

Table 2 Mechanical properties of the polymer before and after hydrogen loading

Fiber	H (GPa)	E (GPa)	Viscosity$\times 10^{11}$ (Pa s)
Nonhydrogen loaded	0.028±0.001	0.27±0.009	2.3±0.1
Hydrogen loaded at 90°C	0.034±0.002	0.26±0.004	2.2±0.1
Hydrogen loaded at 120°C	0.038±0.005	0.38±0.001	2.2±0.1

stresses. Thus, fracture in these fibers can be attributed to more than one family of flaws, than. Another parameter that should also be analyzed together with m is the parameter σ_0. Table 1 show that the value of the parameter σ_0 is greatest for nonhydrogen-loaded fiber, indicating that this is the strongest fiber. Taken together, Fig. 2 and Table 1 clearly show that the nonhydrogen-loaded fiber was the strongest and that the fiber that was hydrogen-loaded at 120°C was the weakest.

3.2 Polymer Coating Properties

The use of polymer as protection for glass optical fiber has been extensively studied [11]. Polymer protects the vitreous surface during handling, reducing the number of failures as a result of fatigue and leading to a significant increase in fiber lifetime and reliability. By acting as a barrier against moisture, polymer prevents the reduction in mechanical strength that exposure to moisture causes. Optical fibers exposed to moisture were analyzed by Matthewson et al. [12], who observed that two factors influenced their degradation. Although the polymer layer acts as a barrier, preventing external particles coming into contact with the vitreous surface, the reaction products cannot be eliminated from the surface. These internal reaction products can have a direct influence on the chemical environment at the vitreous surface and cause further degradation.

Examination of optical fiber after it has been submitted to hydrogen loading should also include an analysis of the degradation of the polymer layer. Visual inspection following hydrogen loading at 90°C and 120°C revealed that the fibers were yellowed. Therefore, it is important to investigate the polymer layer in order to establish whether it has degraded, as this could also cause a reduction in the mechanical strength of the fiber.

Table 2 shows the hardness (H) and elastic modulus (E) of the nonhydrogen- and the hydrogen-loaded fiber at temperature 90°C and 120°C, during 5 days and pressure of 100 atm.

The hardness and elastic modulus of the polymer in the hydrogen-loaded fiber increased. An increase in hardness and elastic modulus can be observed in polymer materials that degrade when exposed to UV radiation [10]. This increase is associated with changes in the polymer structure and the increase in hardness is also usually accompanied by surface cracks. Thus, although not visible at the surface with an optical microscope, small fractures that could allow water to permeate to the vitreous surface may be occurring in the polymer. As previously described, there is a reduction in fiber strength in the presence of moisture. This phenomenon is caused by corrosion of the silica surface, leading to surface roughness and the formation of dimples that can act as new sources of defect concentrations [13]. There was no a significant change in viscosity. This indicates that the polymer maintains its viscoelastic behavior. Thus, while the mechanical strength of the polymer changed, there is no clear evidence of increased water permeability in hydrogen-loaded fibers compared with nonhydrogen-loaded ones. It can thus be concluded that the polymer, although modified, remains intact, and that the changes of the mechanical properties are associated

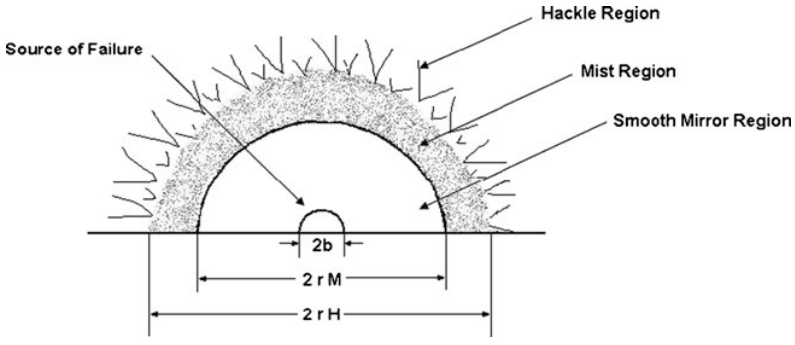

Fig. 3 Drawing showing the characteristic types of vitreous surface during failure [23]

with the formation of defects formed in the hydrogenation (species of OH) [14].

3.3 Fractography

Inspection of the surface of a fiber after failure in a tensile or bending test can reveal much about the fracture process. Fractography of an optical fiber after failure thus allows the mechanisms by which failure stress in a bending test decreases with increasing hydrogen loading temperature to be analyzed. In an ideal glass fracture, a pre-existing flaw propagates quickly to form four distinct neighboring regions, as shown schematically in Fig. 3.

These regions are given the following names: first a smooth region, commonly known as the mirror fracture region; then a region next to the mirror region, known as mist; then a rough region after the mist region, known as the hackle region; and lastly, the formation of two or more primary cracks, called crack branching. At first, the crack front produces a smooth mirror region. As the crack grows and its speed of propagation increases, it becomes unstable, and dimples form on the surface known as the mist region. This instability can sometimes cause crack branching, leading to the formation of the rough hackle region. The hackle region is characterized by long hackle marks in the direction of propagation, in the opposite direction to the source of the failure. The mirror region is greatly influenced by residual stresses arising from thermal or chemical treatment [15]. Compressive stresses can also affect the direction in which a crack propagates [16]. When a fiber is submitted to a bending test, the propagation of the crack may be deviated along the length of the section and reach the compression area. This phenomenon can frequently be identified by the presence of a rough hackle region, which can act as a reference to distinguish between tensile and compression areas in bending tests. In general, fractures with a rough region are indicative of tensile and compressive loads acting simultaneously and denote the presence of compressive stress.

The size of a preexisting flaw in the fiber, and hence the strength of the fiber, can be forecast from the size of the mirror region (r_m). It has been shown that the product of failure stress in fiber and the square root of the radius of the r_m is a constant in silica glasses [17]:

$$\sigma = A_m (r_m)^{-1/2}$$

where, A_m is known as the mirror constant. In any case, the mirror region is inherent to tensile tests where a precrack propagates until the tensile strength is reached. This region cannot be identified in any of the fibers shown in Fig. 4. However, different fracture modes can be observed in samples nonhydrogen loaded, hydrogen loaded at 90°C, and hydrogen loaded at 120°C. There is no mirror region in nonhydrogen-loaded fibers, but the mist and hackle regions can be clearly observed (see Fig. 4a). In hydrogen-loaded fibers at 90°C and 120°C, the fracture has multiple nucleation points generating multiple fragments (see Fig. 4b and c).

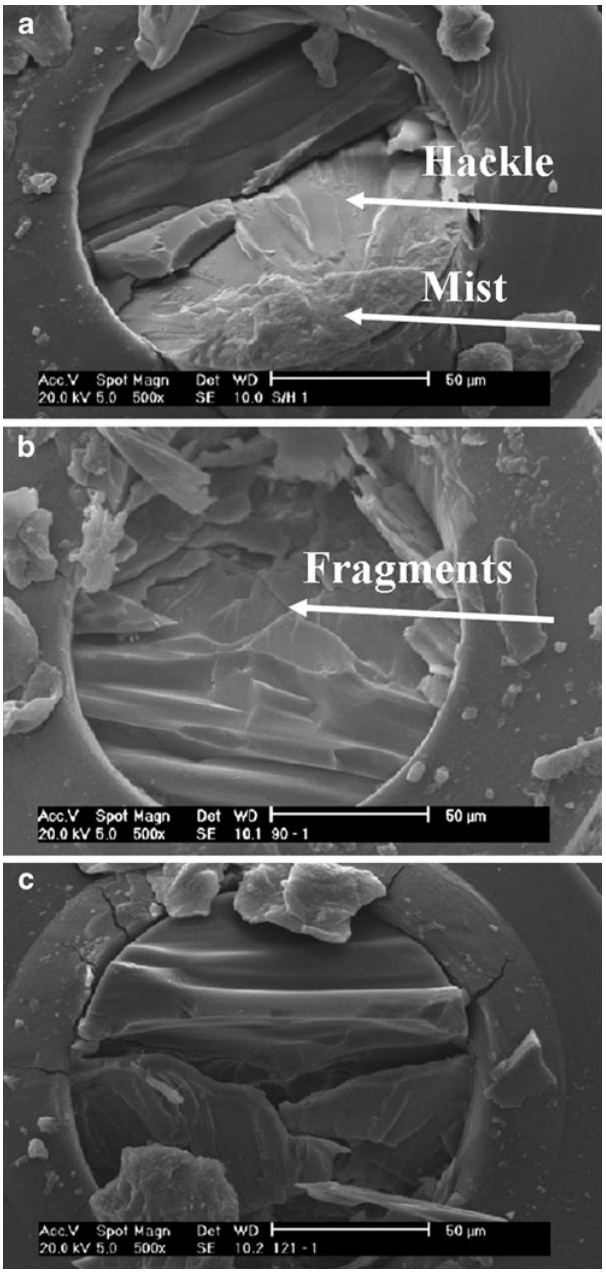

Fig. 4 SEM photographs of fracture regions in **a** nonhydrogen-loaded fibers, **b** fibers that were hydrogen loaded at 90°C, and **c** fibers that were hydrogen loaded at 120°C

Hydrogen diffuse quickly inside silica-based glass, both at ambient temperature and higher temperatures [18]. At temperatures below 500°C, interstitial diffusion takes place, and there is no chemical interaction with the host material [19, 20]. However, there is evidence that drawing-induced defects in silica-based fiber can result in chemical interaction, with H_2 molecules dissociating even at much lower temperatures [21].

These defects have sufficient activation energy to dissociate the H_2 molecule into active hydrogen atoms, which can react with the atoms present in the defects at ambient temperature. Incorporation of hydrogen atoms in the vitreous lattice weakens the glass and reduces its rupture stress [22]. As shown in this study, fibers hydrogenated at 90°C and 120°C had reduced mechanical strength. This indicates that the hydrogen molecules must be interacting with the pre-existing defects to make the fiber more fragile. However, direct analyses to determine how hydrogen reacts with the defects or it is incorporated into the vitreous lattice were not carried out.

4 Conclusion

In view of the importance of optical fibers in sensing applications, it is essential to increase their photosensitivity. Increased photosensitivity can be achieved by hydrogen loading at high pressure and temperature up to 90°C. But this study has shown that the mechanical strength of fibers decreases as the hydrogen loading temperature increases. A high degree of uniformity was observed in defects in fibers that were not hydrogen loaded. However, this uniformity was found to decrease as the hydrogen loading temperature increased.

A slight change in the mechanical properties of the polymer covering the fiber was observed, but this was not sufficient to indicate severe degradation caused by the temperature and the hydrogen. The increase in the hardness of the material may have been the result of hydrogen loading together with the high temperature. No cracks that might indicate that water could penetrate to the surface of the glass were observed on the outside of the polymer cladding.

The analysis of the fracture regions in fibers that were not hydrogen loaded exhibit a region from which the crack might have propagated. However, the fibers that were hydrogen loaded at 90°C and 120°C show that fractures were not clearly defined and that could have had more than one nucleus.

It is believed that the hydrogen dissociates and interacts with the pre-existing defects to make them larger, leading to a reduction in rupture stress after hydrogen loading.

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