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Mechanical and chemical damage of optical fiber polymer coating

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Systematic measurements have been implemented on commercial optical silica fibers in which the polymer coating has been damaged, either chemically or mechanically. Dynamic fatigue has been studied using a two point bending bench at different stress rates. Small mechanical flaws, subsequently controlled by SEM observations, were created on the polymer coating surface using a micro-hardness indenter, without reaching the glass surface. Chemical damage was implemented by methylene chloride either as a gel or as a liquid. In this later case polymer could be removed just after a few minutes. Fiber strength was altered when polymer – silica interface was affected.

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1. Introduction

Optical fibers have been intensively developed [1] and they make now a key component in telecommunication networks. Accordingly, their long-term stability, even in severe environmental conditions, appears as an important requirement. The reliability and the expected lifetime of the optical fibers are closely related to the chemical action of the environment on silica that in turn, influences fiber strength.

To ensure the long-term mechanical strength of the optical fibers, a polymer coating is applied onto fiber surface during fiber fabrication [2-4]. This external coating is vital for the optical fiber lifetime. Its protective action includes several functions, such as: to protect glass fiber from any external damage, to limit chemical attack of water and to ensure fatigue protection and bending insensitivity [5-7], especially during handling and in-service installation.

It has been emphasized that failure of fibers is ruled by two major factors that are micro-crack growth from the glass surface, "Griffith flaws" [8,9], and water activity at glass surface [10-13]. Different fatigue behaviors of silica optical fibers have been reported as a function of glass adhesion, water absorption, water permeability and mechanical strength properties of the polymer coating [14,15]. In order to assess the influence of flaw generation during fiber processing, some indentation tests have been implemented on silica surface [16,17]. They have revealed several fatigue mechanisms, in particular crack tip blunting [18-20], and structural relaxation under static stress [17, 21]. Silica is very sensitive to environmental action, through the well-known stress corrosion phenomenon, and it is of practical importance to assess the protection ensured by the polymer and the long-term mechanical stability. As this external coating may be damaged during handling or normal use, the question arises to assess to what extent fiber strength is influenced by mechanical and chemical damages.

In order to find an answer, fiber polymeric coatings were damaged mechanically and chemically, then tested to dynamic fatigue and finally compared to the as-received commercial fibers. While one could expect that nay large coating degradation enhances fiber failure, experiments have drawn some unexpected conclusions.

2. Experimental

2.1 Fibers used for testing

Fibers used in this study are Alcatel commercial single mode silica fibers, 125 μm in diameter with a 62.5 μm thick epoxy-acrylate two layers polymer coating. This type of coating is the most largely used one in standard optical fibers. It offers a good protection to external mechanical damage, but it remains permeable to water, playing a role of diffusion barrier. The internal layer is soft with a low glass transition temperature and is applied onto the glass fiber surface. It ensures protection against micro-bending and damping of the external stresses. The external layer has a higher T_g and protects the fiber against physical aggressions. To comply with process requirements, the UV-polymerization of the acrylate resins is rapidly performed, in line, offering an excellent adhesion to glass surface and a large range of elasticity (Young modulus).

2.2 Dynamic fatigue measurement using a two-point bending testing apparatus

As-received fiber samples and as-damaged ones (see procedure described below) were subjected to dynamic fatigue measurements using a two-point bending testing device [4, 22]. Samples, 10 cm in length, are bent and placed between the grooved faceplates of the testing apparatus, in order to avoid the fiber slipping during the faceplates displacement and to maintain the fiber ends in the same vertical plan. Several series of 30 samples were tested with faceplates constant velocities of 80, 150, 500 and 800 μm/s respectively. All measurements were performed in the laboratory environment (temperature 19°C±1ºC and relative humidity 35%±2%). The stress to fracture applied to the fiber was calculated from the distance separating the faceplates, using the Proctor and Mallinder relation, improved by Griffioen [23]. The failure stress was measured for each fiber, and then the results were treated through a statistical approach using the Weibull theory [24].

The classical Weibull plots showing the logarithm function of the cumulative failure probability $\boldsymbol{ln(-ln(1-F_k))}$, where F_k (in %) represents the cumulative probability to failure for each stress to fracture σ (in MPa), related to the logarithm of the stress to fracture ln(σ, in MPa), has allowed to find the statistical parameters, namely: the medium stress value σ_{med}, the median stress $\sigma_{(50\%)}$, corresponding to a probability to fracture F_k=50%, the Weibull slope m_d, and the Weibull parameter σ_0.

The slope p of the curve ln(σ, in MPa) as a function of ln(stress strain, μm/s) is related to the stress corrosion parameter n_d, by the following relation [25]:

$$n_d=(1/p)-1 \qquad (1)$$

So, from the experimental failure stress for the four testing speeds, by linear regression one may calculate the straight line slope p, that finally leads to the stress corrosion parameter, n_d, to be compared to that of the as-received fibers.

2.3 Aging testing

The fibers subjected to aging were plunged into a tank containing de-ionized cold water for one hour. Eight series of 30 samples, 10 cm in length, were carefully arranged to float into the water tank, in zero stress conditions during the aging treatment. The number of series was adjusted in order to carry out the dynamic fatigue testing measurement at the four different testing velocities in order to calculate the $\boldsymbol{n_d}$ factor.

After aging, fibers were removed from water and four series were subjected immediately to dynamic fatigue testing at the four selected speeds. The other four series were simply laid to dry into the laboratory environment on absorbent paper for one day (20-24 hours) prior to similar testing.

The $\boldsymbol{n_d}$ factor was calculated using the linear regression slope that interpolates the stress to fracture $\boldsymbol{\sigma}$ corresponding to a cumulative failure probability of 40%. The different group of fibers behavior was compared.

2.4 Mechanical damage through Vickers indentation

The optical fiber surface may be easily damaged through abrasion or indentation, and handling bare fibers currently creates enough flaws on the fiber surface to reduce significantly the fiber strength. As already mentioned, polymer coating plays a major role to protect the fiber surface against mechanically induced aggressions.

In order to investigate the influence of mechanical damage on fiber strength, controlled indentations using a Vickers micro-hardness indenter (Digital Matsuzawa Seiki Co. MXT 70) were applied on the polymer coating in such a way that indenter does not reach glass surface. Different combinations of loads (10 and 25 gf) and durations (5, 10, 15 and 20 s) were chosen. The resulting mechanical flaws were observed by SEM [22].

The indented samples were carefully placed between the two point testing bench faceplates, so that the small indented flaw should initiate fracture, which means that it is centrally oriented on the sample external curvature. Dynamic fatigue tests were performed at a speed of 150 μm/s and the medium stresses to fracture were determined.

Another indented series was aged into de-ionized water for one hour (same procedure § 2.3), then dried in air for one day prior to dynamic fatigue measurement at the testing velocity of 150 μm/s. Results of different groups of fibers were subsequently compared.

2.5 Chemical damage through methylene chloride etching

The chemical etching of the polymer coating was performed using liquid and gel based methylene chloride.

In the first step, a methylene chloride based gel was used, etching the polymer coating on 1 cm in length in the sample’s central part for durations of 3, 5, 10, respectively, 15 minutes. The gel was removed by de-ionized water abundant rinsing followed by acetone rinsing. Dynamic tests were performed after drying for 70 hours in ambient environment, at a testing speed of 150 μm/s.

In the second step, a more severe etching was implemented: the methylene chloride based gel etched the polymer coating for 15 minutes, subsequently, for 30 minutes. Then the gel was removed through paper sweeping (without any friction) and dynamic fatigue tests were performed immediately. The etched region of the fiber was carefully inserted between testing bench faceplates to be located on the curvature to be fractured. The four selected speeds were applied. Some measurement problems were encountered, in particular for low speeds, because gel residues paste over bench faceplates. Therefore frequent cleaning was required.

In the third step, the most severe etching was applied, using liquid methylene chloride. Etching for 5 min. allowed the polymer to be removed to obtain pristine glass fibers. These fibers were carefully separated prior to dynamic fatigue measurements at the four selected stress rates. Practical handling difficulties were encountered due to pristine glass fibers brittleness.

Another series of dynamic fatigue testing were performed on stripped fibers (liquid methylene chloride for 5 min. followed by polymer detachment) subjected to ageing by immersion into de-ionized water for 30 min., then drying in air for 70 hours prior to testing. The samples etched in methylene chloride were SEM examined. The polymer damage and related viscosity change were observed, sometimes even with naked eye, but evidenced clearly through SEM observations.

3. Results and discussion

3.1 Aging treatment

The comparison between the Weibull plots drawn for the four dynamic testing velocities in the case of the as-received fibers, as-aged fibers in water for one hour, tested immediately after aging and the fibers aged and dried for one day prior testing was given in Fig. 1. This comparison has emphasized some differences.

By comparison to non-aged fiber, the immediate fiber strength slightly decreased (below 10% average) following aging treatment into de-ionized water. A broader dispersion was noticed, too. Drying in air prior to testing has lead to fiber strength increase to slightly higher values than the non-aged fibers (below 2%). Broader dispersion in the case of low stress rates, but slightly steeper for high rates may be noticed. The stress corrosion coefficient $\mathbf{n_d}$, and the corresponding regression coefficients (R^2) are the followings: as-received fibers 13.16 (0.983), as-aged immediate tested 12.83 (0.985), finally, aged/dried prior to testing 12.66 (0.992). The decrease in strength may be explained simply by the variation in water activity at glass surface level following aging and drying. While stress corrosion coefficient rather decreases for aged fibers, this evolution is hardly significant.

3.2 Mechanical damage of polymer coating through Vickers micro-indentation

In order to create small flaws on the polymer coating surface, controlled indentations were applied. The indentation load and duration were increased step by step, taking care not to reach the glass surface.

Using a faceplate velocity of 150 μm/s, dynamic fatigue testing was performed placing the indentation centrally, on the external curvature of the tested sample, so that the small flaw should act as fracture initiator. The fiber strength is not affected by the mechanical indentation, as this appears in Table 2.

Table 2. Vickers micro-indentation.

Vickers load, gf	As-received fiber	10	10	10	10	25
Duration, s		5	10	15	20	10
Medium strength, MPa	5980	5998	5937	5941	5949	5995

There is no significant difference between the fiber strength of the indented fiber and that of the as-received one. This suggests that the polymer coating efficiently protects against external mechanical aggressions as long as the surface of the glass fiber is not reached. Neither the stress at the interface induced by indentations, nor superficial coating mechanical damage through Vickers indentation seems to affect fiber strength.

SEM observations, previously reported [22], confirmed the Vickers flaws size, the absence of any fracture associated to indentations (neither to diagonals, nor upon the indentation surface) and the “sink-in” plastic behavior of the polymer coating [25].

The indented fibers were subsequently aged into de-ionized water for one hour, then dried in ambient environment for one day and subjected to dynamic fatigue measurement at the speed of 150 μm/s, as-seen in Fig. 2. A slight strength increase (below 2%) may be noticed in the case of indented fibers aged and dried. This increase is notable for Vickers indentations applied with a load higher than 10 gf and longer than 10-15 s.

3.3 Chemical damage of polymer coating through gel-based etching

Fiber samples have been etched by methylene chloride (CH_2Cl_2) based-gel for a few minutes, then abundantly rinsed in water, then in acetone, and finally dried for 70 hours prior to mechanical testing. Testing were performed in order to directly subject the treated zone (approx. 1 cm in length) to the stress, locating the etched area centrally between the testing faceplates. Weibull plots for the selected speeds are shown in Fig. 3. As it may be seen, no significant differences were observed between these fibers and the as-received fibers at the testing speed of 150 μm/s.

The gel action on the polymer coating appeared clearly in a second set of experiments. After etching for longer durations (15-30 min), gel was removed by sweeping fiber surface with absorbent paper. Dynamic tests were performed immediately after etching and sweeping. The Weibull distribution for the different fibers – etched and as-received - is shown in Fig. 4. A slightly steeper dispersion is noticed for the 30 min. etching duration.

Although some manipulation problems were encountered due to gel residues pasted on testing bench faceplates, the dynamic fatigue tests were performed for the four selected stress rates, so the stress corrosion coefficient $\boldsymbol{n_d}$ of 11.8 was determined, with a regression coefficient R^2 of 0.99.

As compared to the as-received fibers, the $\boldsymbol{n_d}$ factor decreases following chemical damage through gel-based etching. In the meantime, the distribution of the Weibull plots is broader and appears nearly bi-modal, meaning that an increasing number of extrinsic defects are present and active on the fiber surface. While overall fiber strength is not significantly affected by gel-based etching, especially at short exposure times and further drying, direct observations – visual and SEM - revealed coating modifications.

After fracture, the coating surface exhibits striae expressing its brittle character. Handling fibers may damage coating, as seen in Fig. 5. In some areas the polymer coating, already stressed and inflated, exhibits large cracks while, in other ones, it becomes more plastic and viscous. This leads to changes in diameter, especially after pinching fibers for sampling before observation. All over fiber length, fiber surface appears irregular with frequent flakes and variations in diameter. Taking into account the polymer fracture in some inflated zones and diameter variations one may assume that this chemical treatment induces locally some residual stresses.

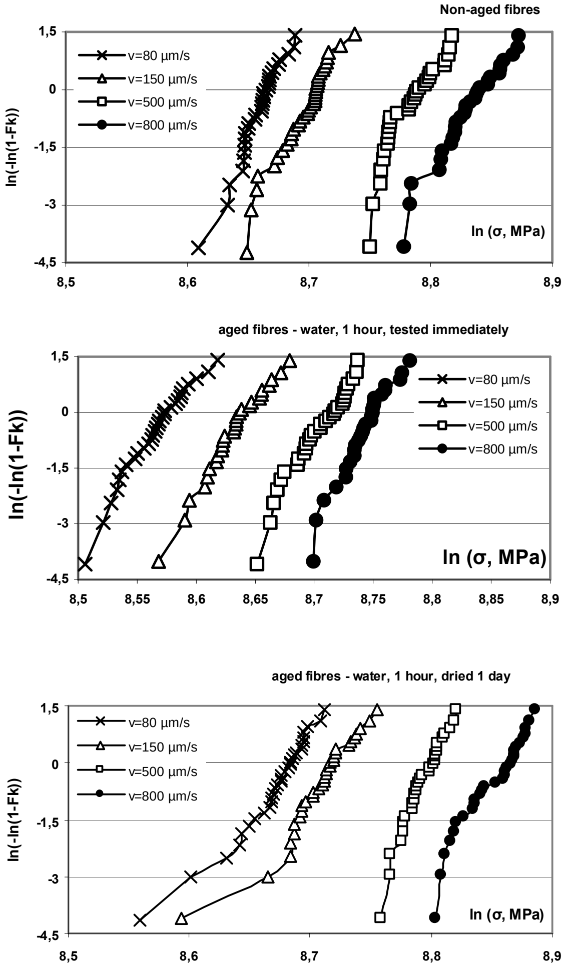

Fig. 1. Weibull plot of two-point bending testing for different faceplate velocities v, in µm/s (in axes: Fk cumulative failure probability, in % and σ stress, in MPa).

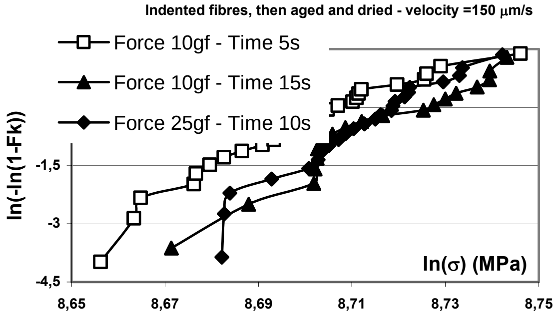

Fig. 2. Vickers indented fibres, testing velocity 150 µm/s; for clarity reasons, the abscise scale was enlarged and the non-aged fibre strength was not reported.

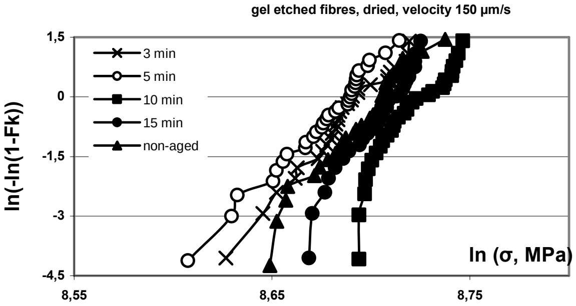

Fig. 3. Fibres etched with gel for different durations, in min. (see legend), for clarity reasons, the abscise scale was enlarged.

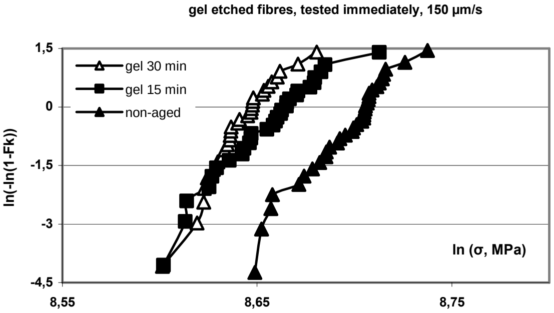

Fig. 4. Fibres etched with gel removed by wipe drying with absor bent paper prior to testing (the abscise scale enlarged for clarity reasons).

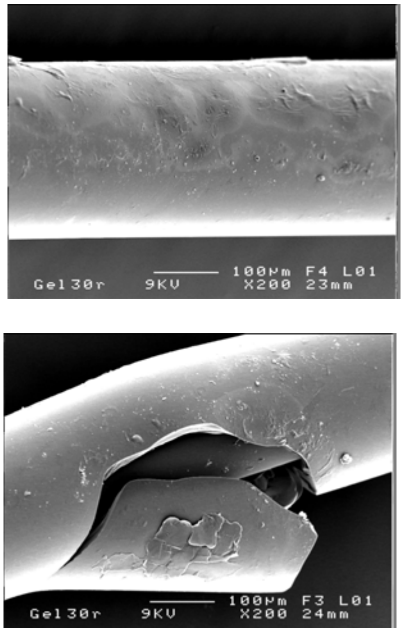

Fig. 5. Polymer coating irregular viscous surface of gel-etched fibres; inflated-stressed polymer coating cracks during handling.

3.4 Chemical damage of polymer coating through liquid methylene chloride etching

The etching reaction was quite more severe in liquid methylene chloride. As a result, coating could be entirely removed after etching for just a few minutes and pristine glass fiber carefully extracted from the liquid reagent. The first series of pristine glass were subjected immediately to dynamic fatigue testing (Fig. 6) while the other series were aged into water for one hour and dried in air for 70 hours prior dynamic testing. The Weibull distributions are shown in Fig. 7.

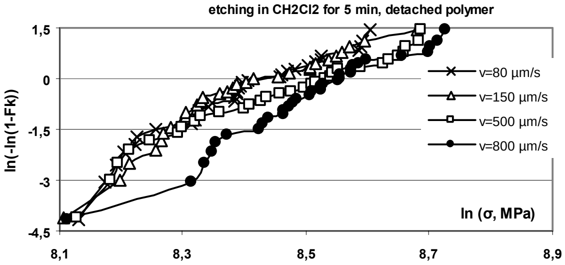

Fig. 6. Fibres etched in concentrated liquid CH_2Cl_2, polymer coating removed, pristine fibres immediately tested.

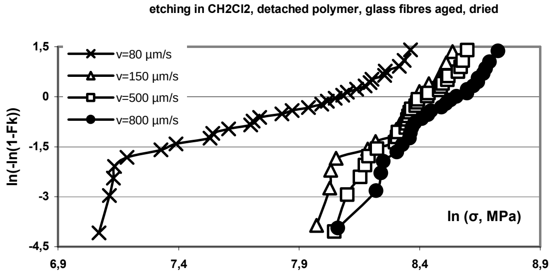

Fig. 7. Fibres etched in concentrated liquid CH_2Cl_2, polymer coating detached, pristine fibres aged for 1 hour and dried for 70 hours prior to testing.

The fiber strength decreased after polymer removal following chemical etching: the medium strengths, ranging between 5800 and 6800 MPa in the case of as-received fibers, decrease to values of 4400 to 5000 MPa in the case of etched and stripped fibers. A quite broader dispersion is noticed, too. An even larger decrease was observed for fibers etched for a longer time: in this case strength values range from 2700 to 4800 MPa. In all cases, failure strength of Weibull plot had a broader distribution than non-aged ones.

Following CH_2Cl_2 etching, the stress corrosion parameter $\boldsymbol{n_d}$ increased to 16 (with R^2 of 0.959) as compared to as-received fibers (13.2), suggesting either that methylene chloride adsorbed onto fiber surface could act as a barrier against water corrosion, or it is less efficient than water as a stress corrosion reagent. Due to aging into water, pristine glass fibers stress corrosion coefficient $\boldsymbol{n_d}$ decreased drastically to a low value of 5.9 calculated from a plot with a poor regression coefficient (0.86 *vs* 0.96). This lower stress corrosion coefficient could indicate that water is much active, due to the larger water diffusion into the crack tips. This observation confirms that polymer coating reduces the diffusion of the water molecules toward glass surface.

SEM observations have evidenced some features of polymer removal, namely: the dissolution tendency and drop withdrawal, the viscosity change leading to an easily removed plastic layer (Fig. 8) and finally, some longitudinal polymer residues in areas under stress (cracks on polymer drops). The pictures also show a few detached glass fragments and fracture surfaces that underline brittleness of pristine fiber.

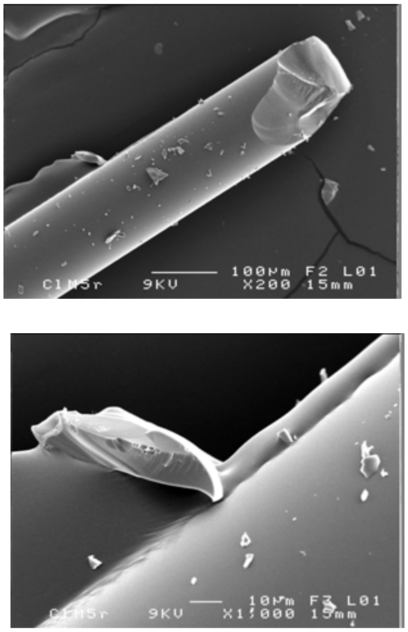

Fig. 8. Polymer coating during removal – change of viscosity, brittle pristine glass.

5. Conclusions

During handling or in use, the external coating of the optical fibers may be damaged, naturally raising the question of the correlation between fiber strength and coating mechanical / chemical damage. Various dynamic fatigue testing on damaged fibers have been carried out, using a two-point bending bench at different stress rates.

Mechanically induced flaws in the coating do not significantly alter fiber strength. Surprisingly enough mean strength slightly increases following aging in water and drying in air. However, more systematic studies are required to confirm this observation. Nevertheless the epoxy-acrylate polymer appears to offer a good mechanical protection of the fiber when induced flaws do not reach glass surface. The stresses at the interface level induced by flaw indentations do not affect fiber strength, nor does superficial polymer coating mechanical damage through Vickers indentation. Microscopic observations confirm the “sink-in” polymer coating plastic behavior and the absence of flaws-associated cracks.

The extension of the chemical damage depended on the reagent and the etching duration. The methylene chloride gel-based affected fiber strength when etching was prolonged and testing performed immediately after gel removal by paper sweeping. But fiber strength did not change when gel was removed by abundant water rinsing and fibers were dried in air, even though SEM observations showed surface damage and polymer coating viscosity modifications. The chemical damage was more severe in liquid methylene chloride that led to polymer dissolution and a quite drastic decrease of fiber strength. The polymer removal process arising from the chemical etching may be exemplified by SEM observations.

The stress corrosion coefficient slightly decreased following aging in water and drying in air. Chemical etching in liquid reagent increased the n_d factor, in the case of pristine glass fibers tested immediately after etching and polymer removal. But this factor drastically decreases after aging in water and drying.

In summary, this study shows that optical fiber strength has been altered only if damage affected the polymer – glass interface so that polymer coating is delaminated, cracked or stripped. This appears quite positive for reliability assessment. Insofar as residual stresses are not high enough to affect interface, the fiber strength is not significantly changed. Then, superficial coating damage should not influence average fiber strength.

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