

## CETYLTRIMETHYLAMMONIUM CHLORIDE INFLUENCE ON SILICA OPTICAL FIBER STRENGTH

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The evolution of silica optical fibers strength aged in cetyltrimethylammonium chloride solution (CTAC) are investigated. The mechanical behaviour of silica coated and naked fibers in contact with CTAC solution at different concentrations is studied. Result analysis proves that the immersion in CTAC drastically decreases the fiber strength and specially near the critical micelle concentration point (CMC). Beyond CMC point, a small increase of fiber strength is analyzed and commented. Based on analysis of aged fiber surface morphology obtained from Scanning Electron Microscopy, the damage extent on fiber core and polymer coatings is observed.

**Keywords:** *optical fiber, critical micellar concentration point, cetyltrimethylammonium chloride solution surfactant, fiber strength, Weibull distribution.*

Surfactants are used as detergents, dispersants or pharmaceutical adjuvants and industry uses enormously the chemical activity of surfactant for example for lubricants of machinery. This relies on the fact that a solution containing surfactants presents high changes at critical micelle concentration (CMC). These changes affect the physical and chemical solution properties such as electrical conductivity, surface tension, and detergent activity [1, 2]. At the CMC point, the water surface tension is reduced by the surfactant which adsorbs the liquid-gas interface. Above this point, stable aggregates are spontaneously formed.

On the other hand, for example and for cleaning industries, it is economically important to find the CMC point because the detergent activity does not effectively change after this point.

To find the CMC point, different techniques are used such as fluorimetry, anisotropy probe, spectrophotometry [3], ion-selective electrode, light scattering, conductometry, fluorescence anisotropy probe, and polarography.

Based on the measurement of evanescence wave adsorption [4, 6], the optical fiber sensors are used more and more. The fast implantation of optical fiber probes which are adapted for in situ measurements leads to an increasing interest and does not need reference electrode or several samples [4]. But near the CMC point, surfactants adsorb at solid/water interfaces (particularly at the surface of hydrophilic oxide of silica fiber) and lead to a significant decrease of the mechanical fiber structure as the fiber strength and the polymer coating can be seriously damaged.

Using dynamic tensile test and Weibull's statistic, the evolution of mechanical fiber properties (as fiber strength and fiber damage) versus the surfactant concentration is analyzed. Fibers are aged during 7 days in cationic CTAC surfactant at 25°C and their behaviour is particularly analyzed near the CMC point.

**Experimental. Surfactant used.** Cetyltrimethylammonium chloride solution (CAS number 112-02-07) is a cationic surfactant used as an antiseptic very toxic especially against aquatic bacteria but can also be used as a phase-transfer catalyst under con-

ditions which avoid emulsions. The adsorption of this surfactant on solid / liquid interfaces is important in different processes. The analysis of this adsorption helps to understand the biological phenomena, the detergency effects and the control of the pollution. CTAC was purchased from Sigma Aldrich Co. (France) (25 wt. % in H<sub>2</sub>O). Table gives CTAC properties and detailed formula. Fig. 1 shows the toxicity of CTAC against aquatic bacteria. Even for a lower concentration (0.5 mmol/l), all bacteria were destructed (Fig. 1b) after an aging of an optical fiber in CTAC solution during 7 days.

#### Physical and chemical CTAC solution properties

Product	Formula	Molecular weight, g/mol	pH at 20°C (C = 20 g /l)	CMC at 25°C, mm/l	Boiling point, °C	$\rho$ , g/cm <sup>3</sup>
CTAC	C <sub>19</sub> H <sub>42</sub> ClN	320	6..7	1.3	100	0.968

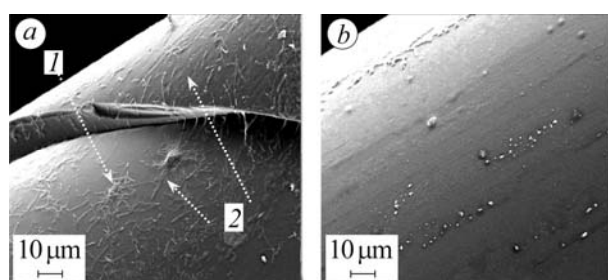


Fig. 1. Optical fiber immersed in distilled water (a) (1 – aquatic bacteria; 2 – coating) and optical fiber aged in CTAC solution (0.5 mmol/L) during 7 days (b) bacteria extermination.

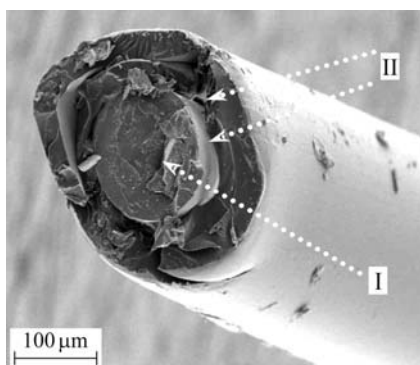


Fig. 2. Morphology of broken silica optical fiber. I – glass fiber; II – two polymer coatings.

protects the fiber from mechanical and chemical damages, stress and water cause microscopic flaws in the glass to propagate resulting in fiber failure. Fig. 2 gives the morphology of a broken optical fiber.

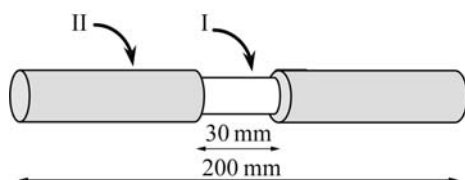


Fig. 3. Naked fibers. I – silica glass; II – coating.

**Fiber used.** The used multimode fiber has two acrylate coatings (primary and outer coatings). This fiber has a numerical aperture of 0.2 (NA value). A soft, primary coating has a low module of elasticity, adheres closely to the glass fiber and forms a stable interface. It protects the fragile glass fiber against microbending and attenuation. The outer coating protects the primary coating against mechanical damage and acts as a barrier to lateral forces. It has a high glass temperature and Young's modulus. It has a good chemical resistance and serves as a barrier against moisture.

The fiber core is made of silica and is hydrophilic. If the acrylate polymer coating

protects the fiber from mechanical and chemical damages, stress and water cause microscopic flaws in the glass to propagate resulting in fiber failure. Fig. 2 gives the morphology of a broken optical fiber.

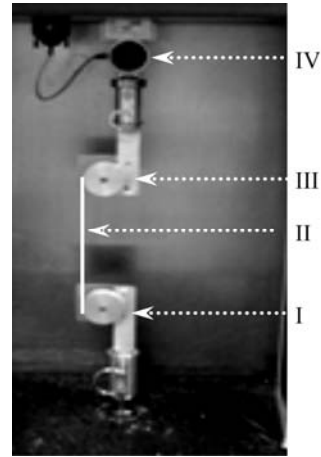
Fibers with and without coatings are analyzed. The coating was removed on 30 mm length (the overall length of tested fiber being equal to 200 mm) using an air blower at high temperature.

The naked fibers are very delicate to be tested and cannot be in the contact with impurities such as the dust particles or the manipulator hands. Therefore, only a part of coated fiber was stripped (Fig. 3).

When the naked fibers are removed from the solution surfactant, they are dried under a drying oven where the air has been filtered to protect the fibers from the environment impurities. As soon as the fibers have been removed from the drying oven, the manipulator (with rubber gloves) performs very fast the tensile tests.

**Test bench used.** The dynamic tensile test consists of subjecting fibers to a deformation under a constant velocity until rupture. The fiber is rolled three times around two pulleys (Fig. 4); the lower pulley is fixed and the upper pulley is movable with different velocities (20; 50; 200 and 500 mm/min). These strain rates, expressed as a percentage of the initial sample length (200 mm), correspond to  $1.67 \cdot 10^{-3} \text{ s}^{-1}$ ;  $4.17 \cdot 10^{-3} \text{ s}^{-1}$ ;  $1.67 \cdot 10^{-2} \text{ s}^{-1}$ ;  $4.17 \cdot 10^{-2} \text{ s}^{-1}$ .

Fig. 4. Dynamic tensile set-up. I – fixed pulley; II – optical fiber; III – movable pulley; IV – sensor load.



Tensile testing was performed in a controlled environment with 46...52% relative humidity with a maximum of 5% humidity variation for each series of the tensile tests.

During the test, the deformation and the tensile load are measured using a dynamometric cell while the fiber deformation is deduced from the displacement between the fixed lower pulley and the mobile higher pulley (Fig. 4).

The testing procedure uses 20 samples for each surfactant concentration and for each velocity.

Before the dynamic tensile tests, fibers are plunged in a container with a distilled water-surfactant solution and aged at different surfactant concentrations. This container itself is deposited in water at 25°C. An adiabatic enclosure maintains a constant temperature during the ageing duration of 7 days (Fig. 5).

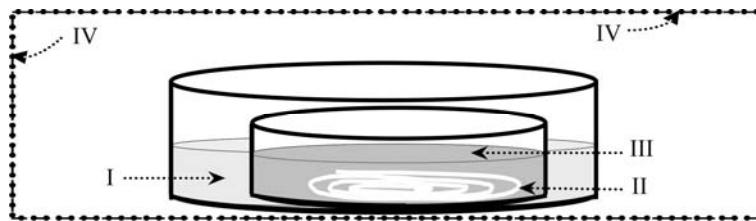


Fig. 5. Fiber aging in CTAC solution. I – hot water (25°C); II – optical fibers; III – CTAC solution; IV – adiabatic enclosure maintained at constant temperature.

**Weibull theory.** Optical fiber strength reliability which is analyzed before various engineering applications is commonly characterized by Weibull strength distribution. Weibull distribution [6] function  $F$  based on simple fitting of experimental data obtained from a uniaxial homogeneous tensile stress state of an amplitude  $\sigma$  is given by:

$$F(V, \sigma) = 1 - \exp \left[ -\frac{V}{V_0} \left( \frac{\sigma}{\sigma_0} \right)^m \right], \quad (1)$$

where  $\sigma_0$  is the characteristic strength and represents the stress for which the cumulated rupture probability of the fiber  $F$  is equal to 50%,  $V$  is the sample volume,  $V_0$  is a

chosen normalising volume (with a normalising length  $\ell_0$ ),  $m$  is the size parameter which characterizes the defect size dispersion and measures the scatter of strength data.

From Eq. (1), one can obtain:

$$m[\ln \sigma - \ln \sigma_0] = \ln \left[ \frac{V_0}{V} \ln \left( \frac{1}{1-F} \right) \right]. \quad (2)$$

For a uniaxial homogeneous tensile stress state, by replacing  $V_0/V$  by  $1/\ell$  ( $\ell$  is the specimen length), one can obtain the statistical Weibull relationship between the probability  $F$  of fiber rupture and the applied stress  $\sigma$ :

$$\ln \left[ \frac{1}{\ell} \left\{ \ln \left( \frac{1}{1-F} \right) \right\} \right] = m[\ln \sigma - \ln \sigma_0]. \quad (3)$$

**Results and discussion.** For coated and naked aged fibers, Weibull plots for four different strain rates are given in Fig. 6. The failure stress increases with velocity values. For each velocity, one can deduce the average failure stress  $\sigma$ . For example, for a strain rate  $V$  equal to 200 mm/min, the average failure stress  $\sigma$  for coated fibers is equal to 5.024 GPa ( $\ln \sigma = 1.61$ , see Fig. 6a). For each velocity, this average stress for naked fibers is lower than the one of coated fibers. One might notice that the surfactant damage leads to different microcrack kinds for naked fibers: different slope curves are obtained (Fig. 6b), but the protective function of the polymer coating leads to one slope curve (a linear regression for each velocity can be obtained (Fig. 6a)).

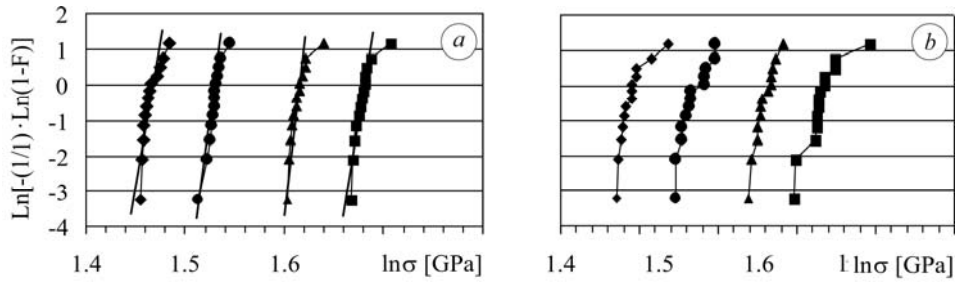


Fig. 6. Weibull plots for different tensile velocities (in mm/min) for aging at CMC concentration during 7 days: *a* – aged coated fibers; *b* – aged naked fibers.

◆ – 20; ● – 50; ▲ – 200; ■ – 500 mm/min.

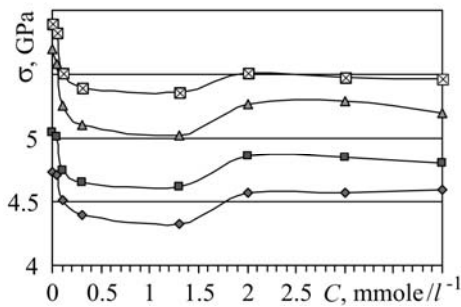


Fig. 7. Mean failure stress change versus CTAC concentration for coated fibers:

⊠ – 500 mm/min; ▲ – 200; ■ – 50; ◆ – 20 mm/min.

Fig. 7 gives the changes of the average failure stress for aging duration of 7 days in CTAC solution at various concentrations and for different velocities.

As in Weibull plots, the mean failure stress decreases when the velocity decreases. According to surfactant concentration, the failure stress decreases until reaching a minimum value at CMC critical concentration (1.3 mmol/l). Beyond the CMC point, a small failure stress increase is observed. The stress decrease is due to the combined effects of water and surfactant.

**Water effect.** The silica fiber strength degradation in distilled water is controlled by increasing the surface roughness due to the dissolution of silica on the surface of the fiber by water corrosion [7, 8]. Flaws in glass optical fibers subjected to stress in the presence of moisture grow in a critical way prior to failure. That is due to the combination of stresses at the crack tip and the effect of reactive species, especially water, in the environment.

When a water polar species ruptures the silicon-oxygen bond, dissolution occurs controlled by the following equation:



Silicon-oxygen bonds are slowly broken progressively advancing the crack and the fiber is weakened.

If one can segregate the water effect from the silica surface, the fiber strength cannot present a notable decrease (perhaps a minor decrease can be observed and will be due to the residual moisture inserted between the silica surface and the polymer during the coating application). The fiber strength change after aging depends thus on the permeability of the used coatings, only hermetic coatings are considered to be capable of completely preventing water from reaching the glass surface [9] and the used acrylate coating shows a small permeability to water diffusion.

**Adsorption effect.** Surfactant molecules comprise heads and tails. Heads are hydrophilic components and tails are hydrophobic components (Fig. 8). These molecules have a component which is water insoluble and another component which is water soluble and thus can diffuse in water and adsorb at the interface between water and air. For cationic surfactants as CTAC solutions, the hydrophilic part is positively charged and releases a positive charge (cation) in aqueous solution (Fig. 8).

At 25°C, the hydrophilic groups of the CTAC molecules dissolve in water before the adsorption onto the silica surface which comprises hydrophilic hydroxide groups OH (Eq. (4)) and onto the hydrophilic polymer coating. When the concentration is below the CMC point, surfactant molecules are scattered in the solution, a small adsorption is initiated onto the optical fiber and the molecule hydrophobic parts are attracted onto the surface of the interface between the air and the surfactant solution [10]. At the CMC, all the surfaces of optical fiber are covered with the monolayers of surfactant molecules. Beyond the CMC point, several surfactant molecules, after adsorption onto fiber surfaces, wrap the fiber surface with lasting layers of surfactant aggregates, leading to an increase in fiber thickness, preventing or slowing down the water effect and causing a weak increase of the fiber strength (Fig. 7).

The same behaviour is observed for naked fibers but the harmful effect of distilled water and the surfactant leads to severe fiber damage and to a stress decrease higher than for the coated fibers (without coating, fibers are not protected against water and surfactant solution effects). The minimum failure stress value is obtained when the surfactant concentration reaches the CMC point and a small increase is observed beyond CMC concentration (Fig. 9).

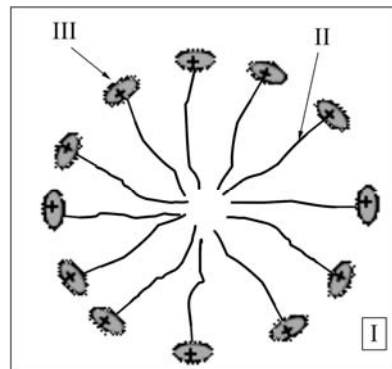


Fig. 8. Micelle of cationic surfactant in aqueous solution. I – aqueous solution; II – hydrophobic part; III – hydrophilic part.

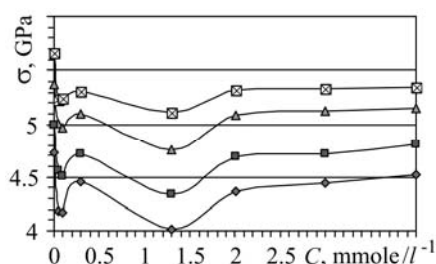


Fig. 9. Mean failure stress change versus CTAC concentration for naked fibers for different velocities:

- – 500 mm/min;
- ▲ – 200; ● – 50;
- ◆ – 20 mm/min.

**SEM observations.** As the fiber surface has determined fracture to a large extent, the external coating appears critical. This coating is polymeric in most cases, and modern optical fibers are coated by two different layers, a soft coating at the glass surface and a hard coating at the external surface (Fig. 2). The coating fills the surface flaws gluing in some way the two sides of the micro cracks and finally, it reduces water and surfactant activities at the glass surface. A non-aged broken fiber is shown in Fig. 10a and a brittle fracture of the fiber core and coating is observed.

For the coated and aged fibers in a low surfactant concentration (0.5 mmol/l) (Fig. 10b), the crack propagation is not perpendicular to the fiber axis but the micro-crack is propagated with an angle of 45° and this indicates a pronounced brittle fracture of the fiber core, but the polymer resistance remains efficient.

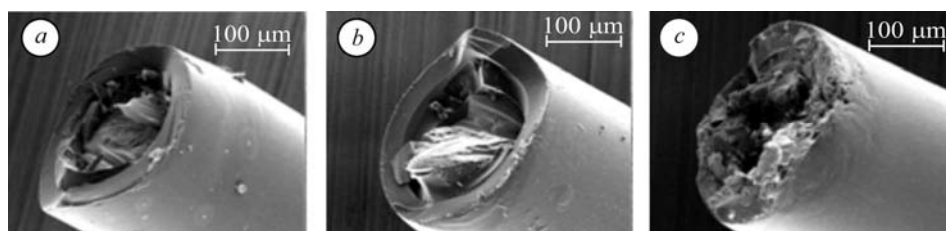


Fig. 10. Fracture morphology of coated fibers (tensile test velocity of 200 mm/min):  
*a* – non-aged fibers; *b* – aged fibers during 7 days in surfactant concentration of 0.5 mmol/l;  
*c* – aged fibers during 7 days in surfactant concentration of 1.3 mmol/l.

When the surfactant concentration reaches the CMC critical point (Fig. 7), the surfactant damage becomes severe for the silica and leads to high fiber resistance decrease, but no microscopic crack is on the external surface of the fiber coating (Fig. 10c).

For naked fibers aged at the CMC concentration, a high coating damage is observed (Fig. 11). The fiber core is broken and the two polymer coatings are separate after a severe attack from CMC solution. On the polymer external surface (Zooms of Fig. 11), a dense and continuous network of microscopic cracks appears and quickly weakens the fiber resistance.

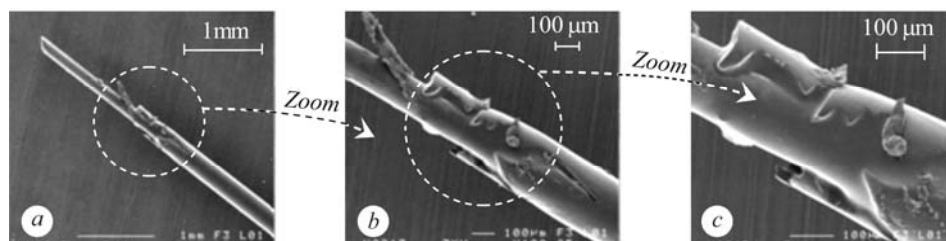


Fig. 11. Fracture morphology for aged naked fibers. Surfactant concentration 1.3 mmol/l (CMC) (aging period = 7 days) (tensile test velocity of 200 mm/min).

One observes a disintegrating of the inner coating. The external coating is much deteriorated (several pieces are removed), the polymer is torn with large cracks: the fiber is very damaged.

On the other hand, for the naked fibers (Fig. 9) a small stress increase is observed for a surfactant concentration of 0.3 mmol/l. Fig. 12 shown a zoom of the stress change when the velocity is equal to 50 mm/min.

When the surfactant concentration is equal to 0.1 mmole/L, a polymer ungluing is obtained and a circular crack appears and weakens the optical fiber (Fig. 13). During the tensile test, a decrease of the failure stress occurs.

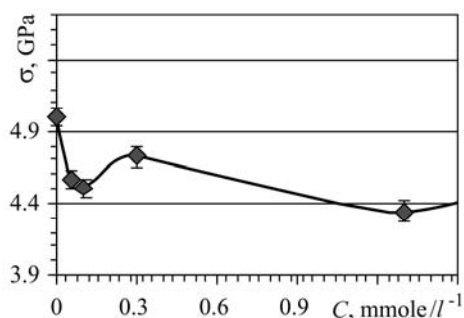


Fig. 12.

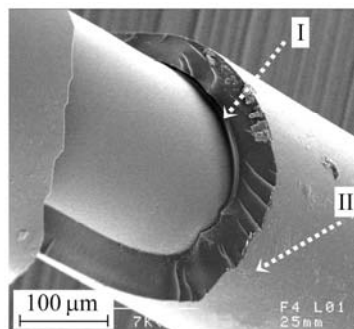


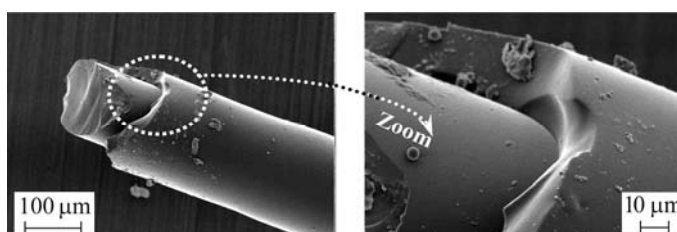
Fig. 13.

Fig. 12. Mean failure stress change versus CTAC concentration for naked fibers for velocity of 50 mm/min.

Fig. 13. Fiber morphology for a naked fiber for surfactant concentration of 0.1 mmol/l. I – circular crack; II – coating.

When the surfactant concentration increases from 0.1 mmol/l to 0.3 mmol/l, the crack closes, and the polymer joins again the fiber (Fig. 14) and the failure stress increases again to 4.72 GPa (Fig. 12). This phenomenon does not occur for the coated fibres (Fig. 7) where coatings protect the fiber against mechanical and chemical damages preventing the diffusion of water to the glass surface [11] and minimizing the mobility of water at the glass-coating interface. When the concentration increases beyond 0.3 mmol/l, the surfactant effect weakens again the fiber (Fig. 12).

Fig. 14. Fiber morphology for a naked fiber for surfactant concentration of 0.3 mmol/l.



## CONCLUSION

Fiber mechanical behavior immersed in the cetyltrimethylammonium chloride solution is analyzed. The experimental results illustrate the change of the strength curve at the point of the critical micelle forming molecules. The use and the quality of the fiber coating are determining factors for the strength change for fibers immersed in the surfactant solution. Near the critical CMC point, the CTAC adsorption leads to the formation of a CTAC monolayer on the fiber surface and beyond this point the adsorption amount remained unchanged as the fiber strength. Since the whole surface of the optical fibers is covered with surfactant molecules as soon as the surfactant concentration reaches the CMC, the water effect is reduced, the fiber thickness increases and a small increase of fiber strength is obtained. The adsorption of CTAC depends on the silica and coating surfaces and the decrease of the fiber strength can be prevented if a hermetic coating is used for fiber sensors used in harsh environments of the chemical industries.

*РЕЗЮМЕ.* Досліджено еволюцію міцності оптичного кварцового волокна під час старіння у розчині хлористого цетилтриметиламонію (ХЦТА) та механічні властивості волокон з кварцовим покритвом і без нього, що контактують з розчином ХЦТА за різних концентрацій. Результати аналізу підтвердили, що занурення трубок у ХЦТА значно погіршують міцність волокна, особливо біля точки критичної концентрації міцел (ККМ). Виявили незначне зростання міцності волокна поза точкою ККМ. На основі аналізу сканівною електронною мікроскопією морфології поверхні зістарених волокон виявлено пошкодження ядра волокна та полімерного покритву.

*РЕЗЮМЕ.* Исследовано эволюцию прочности оптического кварцевого волокна во время старения в растворе хлористого цетилтриметиламония (ХЦТА) и механические свойства волокон с кварцевым покрытием и без него, что контактируют с раствором ХЦТА при разных концентрациях. Результаты анализа подтвердили, что погружения трубок в ХЦТА значительно ухудшают прочность волокна, особенно около точки критической концентрации мицел (ККМ). Обнаружили незначительный рост прочности волокна вне точки ККМ. На основе анализа сканирующей электронной микроскопией морфологии поверхности состаренных волокон выявлены повреждение ядра волокна и полимерного покрытия.

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