

Apparent activation energy of fused silica optical fibers in static fatigue in aqueous environments

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Abstract

Static fatigue of fused silica optical fiber is known to be caused by stress assisted reaction of silica with ambient moisture. Past studies have often been conducted in hot water to accelerate experiments compared with cooler vapor environment. However, changes in the pH of water with temperature has an important influence on the fatigue rate, but has been ignored in the literature. To study the effect of pH, static fatigue of fused silica fibers has been characterized over a range of temperatures in both distilled water and pH 7 buffer solution. The apparent activation energies were then obtained for the different environments. The silica fibers were found to fatigue faster in pH 7 buffer solution than in distilled water, and the apparent activation energy for fatigue was higher in pH 7 buffer. The difference in the results for the two environments can be understood in terms of the difference in their pH and how the pH varies with temperature. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Static fatigue (strength degradation under a constant stress) of fused silica optical fiber is well known to occur when ambient moisture reacts with the fiber surface causing subcritical crack growth.^{1–3} Fatigue of silica optical fiber is therefore controlled by the crack growth rate, \dot{c} , which depends on the reaction rate between water and silica. Wiederhorn and Bolz developed a chemical kinetic model for the crack growth, which was originally proposed by Charles and Hillig, based on simple chemical kinetics in which the stress at the crack tip modifies the effective activation energy for the bond rupture via an activation volume:^{4,5}

$$\dot{c} = \frac{dc}{dt} = \dot{c}_0 \exp \frac{-E^* + bK_I}{RT} \quad (1)$$

where E^* is the apparent activation energy under zero stress, K_I is stress intensity factor, and the term bK_I represents the stress effect on the apparent activation energy. E^* and b can be determined experimentally by the method

of least squares. Wiederhorn and Bolz found that Eq. (1) fit their crack velocity data of various glasses.⁵ From Eq. (1), the time to failure of the material, t_f , which inherits the temperature dependence of \dot{c} , is therefore inverse Arrhenius:

$$t_f = t_0 \exp \frac{E_a}{RT} \quad (2)$$

where E_a is the apparent activation energy. From Eqs. (1) and (2),

$$E_a = E^* - bK_I \quad (3)$$

Eq. (3) suggests a linear dependence of the activation energy on stress. However, several kinetics models concerning the crack growth rate in silica fiber have been proposed in the literature, which leads to a different stress dependence of the activation energy.⁶ These models include the empirical power law,^{7,8} the activation volume model,^{4,5} and the chemical potential model.^{9–11} Since there is uncertainty which model gives the correct form for the kinetics, the stress effect on the activation energy is not yet clear.⁶ The work by Inniss et al.¹² summarizes some results for the apparent activation

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energy for static fatigue of silica fiber, and suggested that a linear dependence on applied stress is observed.¹² However, the standard deviations of the measured activation energy are not presented in their paper,¹² but are expected to be large since the experimentally accessible temperature range is small.¹³ It is thus hard to be convinced the stress dependence trend is linear. The apparent activation energy, E_a , in Eq. (3) therefore should contain a functions of stress, $f(K_I)$, instead of a linear dependence for generosity; i.e.

$$E_a = E^* - bf(K_I) \quad (4)$$

In addition to the stress effect, the concentration of the reactants also plays a role in the fatigue rate. The concentration of the reactants can change with temperature and this effect is mostly ignored in the literature. It has been suggested that the dominant reaction leading to strength degradation is hydroxyl ions (OH^-) rather than molecular water,¹⁴ because the fatigue has been found to be sensitive to the pH.^{15–17} Shiue and Matthewson¹⁸ proposed a theory concerning the effect of dissociation energy for water on apparent activation energy for fatigue of silica fiber. According to their theory, the apparent activation energy measured in pH 7 buffer solution should be higher than measured in distilled water, because pH is constant in pH 7 buffer, but varies with temperature in distilled water.¹⁸ However, as indicated in their paper, the E_a difference between the two solutions is not easy to obtain since the pH of water is affected by more than the water dissociation.¹⁸

Fig. 1 shows the temperature dependence of the pH of “pH 7” buffer solution and distilled water. As shown in Fig. 1, the pH of the buffer is ~ 7 at all temperatures, while the pH of distilled water (calculated from the

equilibrium constant) decreases with increasing temperature due to the greater dissociation at higher temperature. The measured pH of distilled water is lower than the calculated value because of the reaction of water and CO_2 from ambient air. However, unlike pH 7 buffer solution, which is insensitive to temperature, the measured pH of distilled water is a function of temperature.

The different variation of pH with temperature in different aqueous environments leads to a variation in apparent activation energy for the same material. It has not been generally appreciated in the literature that the apparent activation energy is not one single number. Indeed it has been observed that pH 7 buffer solution degrades the strength of silica more severely than water,¹⁹ though the cause of the differences in fatigue rate was not identified.

This paper aims to elucidate the effect of the temperature variation of water pH on the static fatigue of silica optical fiber and its impact on the apparent activation energy. In the current study, static fatigue of fused silica optical fiber was measured over a range of temperatures in both pH 7 buffer and distilled water. The apparent activation energies were then calculated from the static fatigue data obtained using Eq. (2). The determination of the crack velocity in high strength silica fiber is not the concern of this paper. Both polymer coated and bare optical fibers were investigated to understand any influence of the coating. The results are used to verify the prediction that the two environments give different times to failure and apparent activation energies. The dependence of the apparent activation energy on stress is also discussed.

2. Experimental procedure

Static fatigue experiments have been performed on two UV-curable polyurethane acrylate coated fused silica optical fibers. Fiber I is single coated with the coating diameter of 215 μm , and fiber II has dual coatings with an overall diameter of 250 μm . The glass fiber diameter of both fibers is 125 μm . A two-point bending technique was used to conduct the static fatigue experiments.^{20,21} The fibers are bent inside a precision internal diameter borosilicate glass tube, from which the constant applied stress is determined.²¹ Many specimens can be loaded into the same tube. After loading the fibers, the tubes are immersed in the liquid test environment. The break of each fiber is detected acoustically and recorded by a computer. The time to failure of coated fiber was measured under applied stress with range of 2.5 to 4.5 GPa in both pH 7 buffer solution and distilled water. The testing temperature ranges from 30 to 90 $^\circ\text{C}$. Fifteen specimens were measured in each testing condition. All specimens were pre-equilibrated overnight in the testing solution under zero stress at room temperature

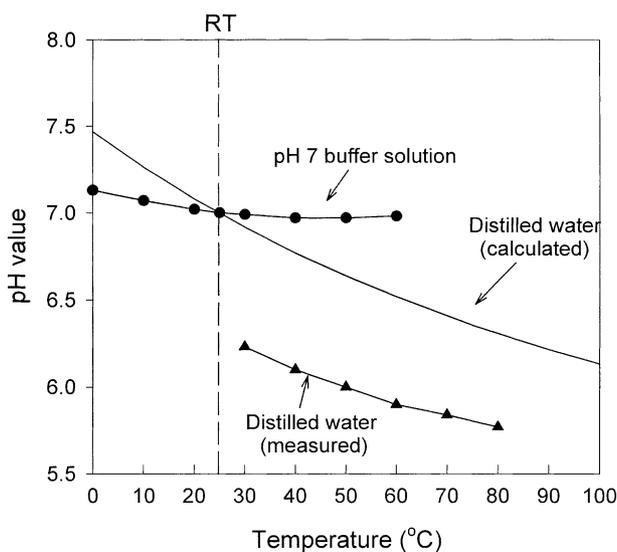


Fig. 1. pH of distilled water and pH 7 buffer solution at various temperatures.

to ensure that the specimens were in equilibrium with the test environment during the experiment.

The experimental procedure for the static fatigue of bare fiber is as follows. The bare fiber specimens were prepared by stripping the coating in concentrated sulfuric acid at $\sim 190^\circ\text{C}$ for ~ 20 s, which does not degrade the strength of the fiber.²² The bare fibers were also tested in both pH 7 buffer solution and distilled water. The time to failure of bare fiber was measured in the applied stress range of 3.5 to 4 GPa at temperatures ranging from 30 to 80°C by using a dynamic 2-point bending apparatus run in static mode due to the difficulty of loading bare fiber specimens into the glass tubes. Fifteen specimens were used for each measurement.

3. Results and discussion

3.1. Static fatigue: distilled water vs. pH 7 buffer solution

3.1.1. Coated fiber I: single coating

The failure time for coated fiber I measured in pH 7 buffer solution and distilled water is shown in Fig. 2 as a function of applied stress, where the error bars represent a 95% confidence interval. The time to failure are

approximately the same in both solutions for the fiber under high applied stress (> 3 GPa). This is because of the buffering species in the pH 7 buffer do not have enough time to diffuse through the polymer coating on the order of 10^2 – 10^3 s, thus the strength of the fiber is only affected by water molecules which penetrate the polymer coating.²³ As the applied stress below 3 GPa, the failure times in distilled water are substantially longer than in pH 7 buffer. As shown in Fig. 1, pH 7 buffer is more basic than distilled water at temperatures above 25°C . The buffer solution is therefore expected to be more aggressive than water, and indeed, the experiment verifies this.

3.1.2. Coated fiber II: dual coating

Another fiber (fiber II), which was obtained from a different source and has dual polymer coatings, was tested and the results are shown in Fig. 3. The failure times for fiber II measured in both solutions are very close for stresses higher than 2.7 GPa. The behaviors at 90°C diverge for stress below 2.7 GPa. Similar behavior might be observed at lower temperatures but at very much longer time to failure. Compared to fiber I, fiber II shows qualitatively similar behavior, except that the divergence in behavior at longer time (lower applied stress). At 90°C , an abrupt fatigue “knee”¹⁵ is observed in distilled water, resulting in a reversal cross-over at

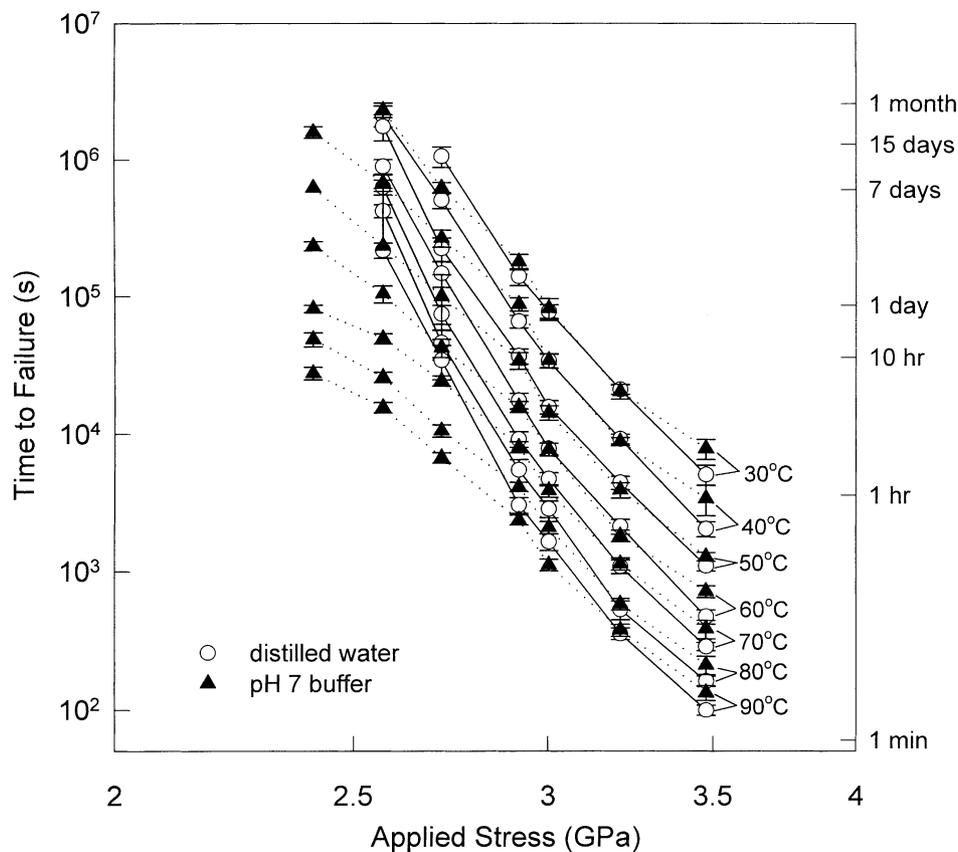


Fig. 2. Static fatigue data for single coated fiber (fiber I) measured in distilled water and pH 7 buffer solution at various temperatures as a function of applied stress.

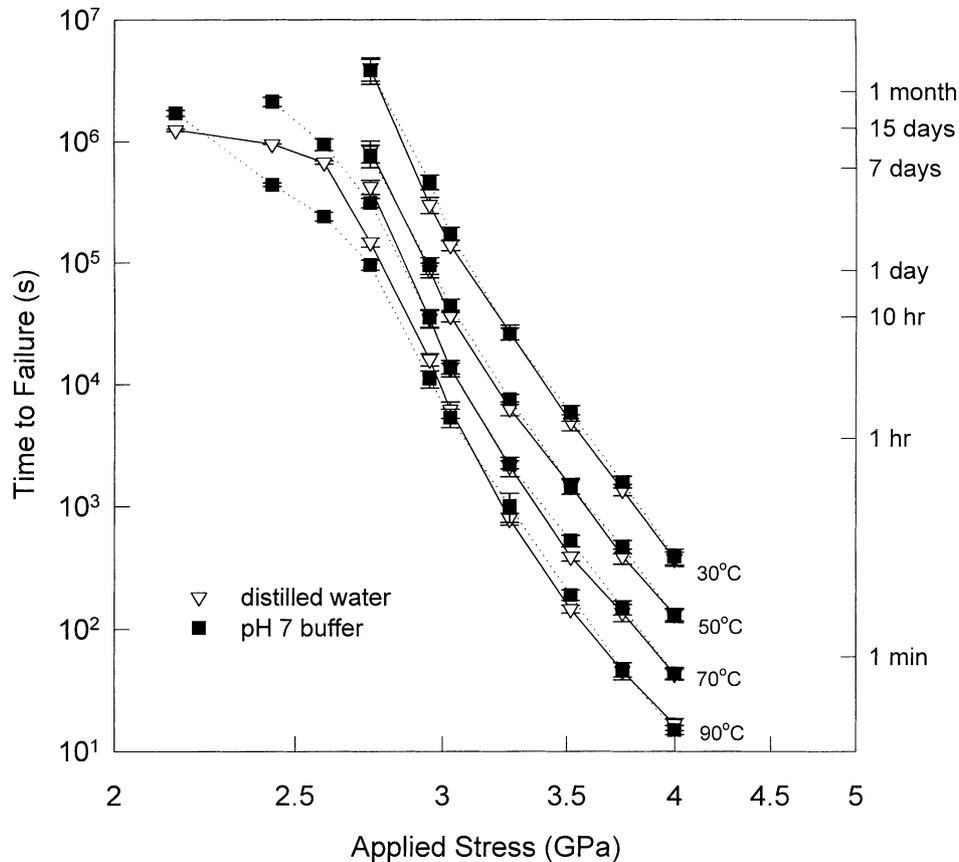


Fig. 3. Static fatigue data for dual coated fiber (fiber II) measured in distilled water and pH 7 buffer solution at various temperatures as a function of applied stress.

very low stress. This phenomenon has been observed before,¹⁹ while the cause of the strength switch in the after knee region is not yet understood. Interestingly, while the times to failure are generally longer for fiber II, the fatigue knee occurs earlier than for fiber I, for which no knee is observed within 1 month. This illustrates the well known result that the coating has a significant impact on fiber reliability and there is considerably variability from coating to coating.²⁴

The fatigue knee behavior, commonly observed for high strength silica optical fiber, should not be confused with the different crack growth stages found on bulk silica. The data for bulk silica are often explained by the three stage crack velocity mechanisms: region I—thermally activated process; region II—transport process; region III—vacuum.²⁵ However, the fatigue of silica fiber in this study was not controlled by the insufficient environmental species (region II), because water can quickly reach the fiber surface with or without the polymer coating, i.e. the data presented here are within region I.

3.1.3. Bare fiber

The fatigue results for coated fiber include the effect of the polymer coating. The coating impedes the species in pH 7 buffer solution from reaching the fiber surface.

Since diffusion through the coating is temperature dependent, this makes it hard to interpret the temperature dependence of the apparent fatigue rate for coated fiber. Bare fiber must be examined in order to eliminate the effect of the coating and to understand the fundamental kinetics of the fatigue process. However, static fatigue data for bare fiber are rarely found in the literature because it is not easy to perform the same experiments on bare fiber using the techniques which are used for coated fiber. In this work, we used a two-point bend dynamic fatigue apparatus run in static mode to perform the static fatigue test on bare fiber. However, because it is inconvenient to use this apparatus for performing long term experiments, the static fatigue studies on bare fiber are not as extensive as the data for coated fiber. Fig. 4 shows the static fatigue results for bare fiber as a function of temperature.

The difference in behavior between the fiber in pH 7 buffer solution and distilled water is significant, as shown in Fig. 4. The fiber lasts ~ 10 times longer in distilled water than in pH 7 buffer solution under the same applied stress. This dissimilarity in behavior in the two environments confirms that the similarity in behavior for the coated fiber in the two environments at high stress is indeed caused by the coating.

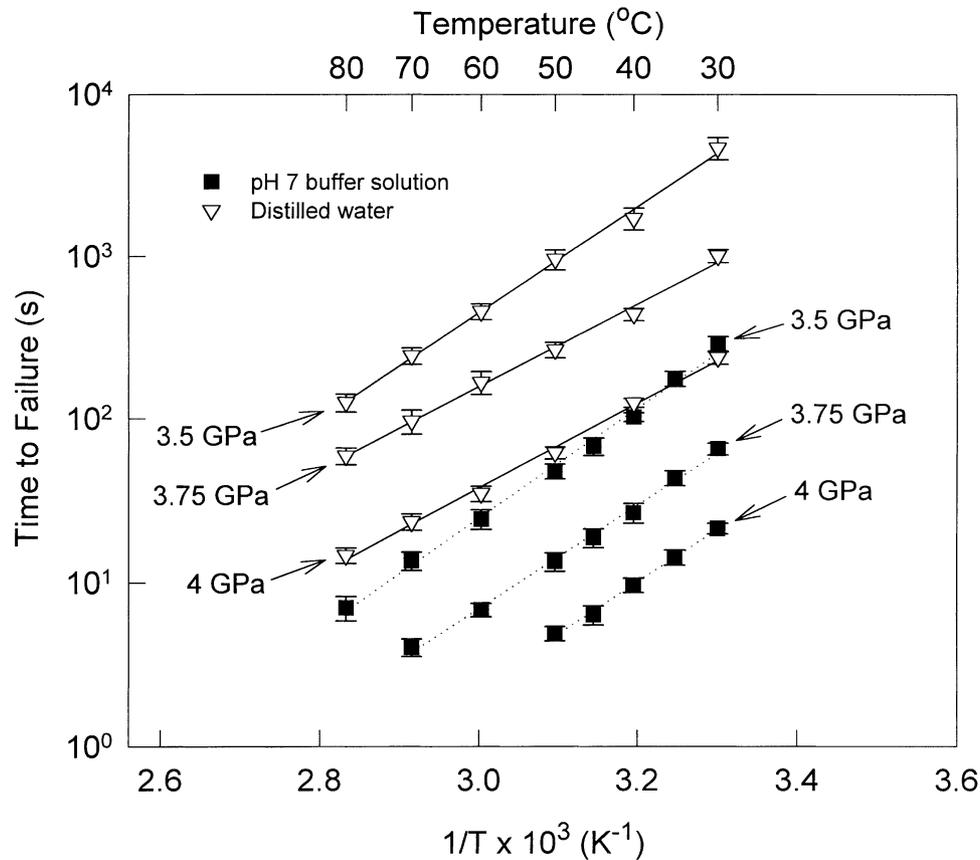


Fig. 4. Static fatigue data for bare fiber measured in pH 7 buffer solution and distilled water under different applied stresses as a function of temperature.

3.2. Apparent activation energies

Fig. 5 shows the same static fatigue data for fiber I from Fig. 2 while plotted as a function of $1/T$. This figure shows that under relatively low stresses, not only does the fiber fatigue more slowly in distilled water than in pH 7 buffer, but also that the temperature dependence of the fatigue in the two testing solutions under the same stress are different. The apparent activation energies calculated from data in Fig. 5 using Eq. (2) are shown in Fig. 6, where the error bars again represent a 95% confidence interval. The apparent activation energies for bare fiber calculated from the static fatigue data (Fig. 4) are shown for comparison. The apparent activation energies for dual coated fiber II are shown in Fig. 7.

The values of apparent activation energies presented in the current work range from ~ 50 to ~ 75 kJ/mol. Table 1 summarizes the activation energies for polymer coated fiber measured in water as obtained from several authors' static fatigue data by Inniss et al.¹² The current results are in general agreement with the results shown in Table 1. It should be noted that the current results are obtained from 2-point bend static fatigue, while the results in Table 1 were obtained from the tensile static fatigue experiments, except for the technique used for Brownlow's work which was not mentioned in the paper.¹²

Several observations are made from the data for apparent activation energy presented in this study and are now described in the following subsections.

3.2.1. Coating effect

It is expected that the apparent activation energies for silica fiber tested in pH 7 buffer solution and distilled water should be different, since the pH and how the pH varies with temperature are different in the two solutions. However, the apparent activation energies for fiber I in coated states are very similar under high stress region (Fig. 6). Such results are not surprising since the two static fatigue results are similar in high stress region as described above. The apparent activation energies measured in the two testing solutions thus only show a difference in the low applied stress region for coated fiber I. However, once the coating is removed or enough time is provided for pH ions to penetrate through the coating, the apparent activation energies measured in pH 7 buffer is higher than measured in distilled water.

The apparent activation energy results for coated fiber II shown in Fig. 7 are similar in the two solutions. It further shows that the coating strongly affect the apparent activation energy measured, since the difference of the apparent activation energy in the two solutions are insignificant for this dual coated fibers.

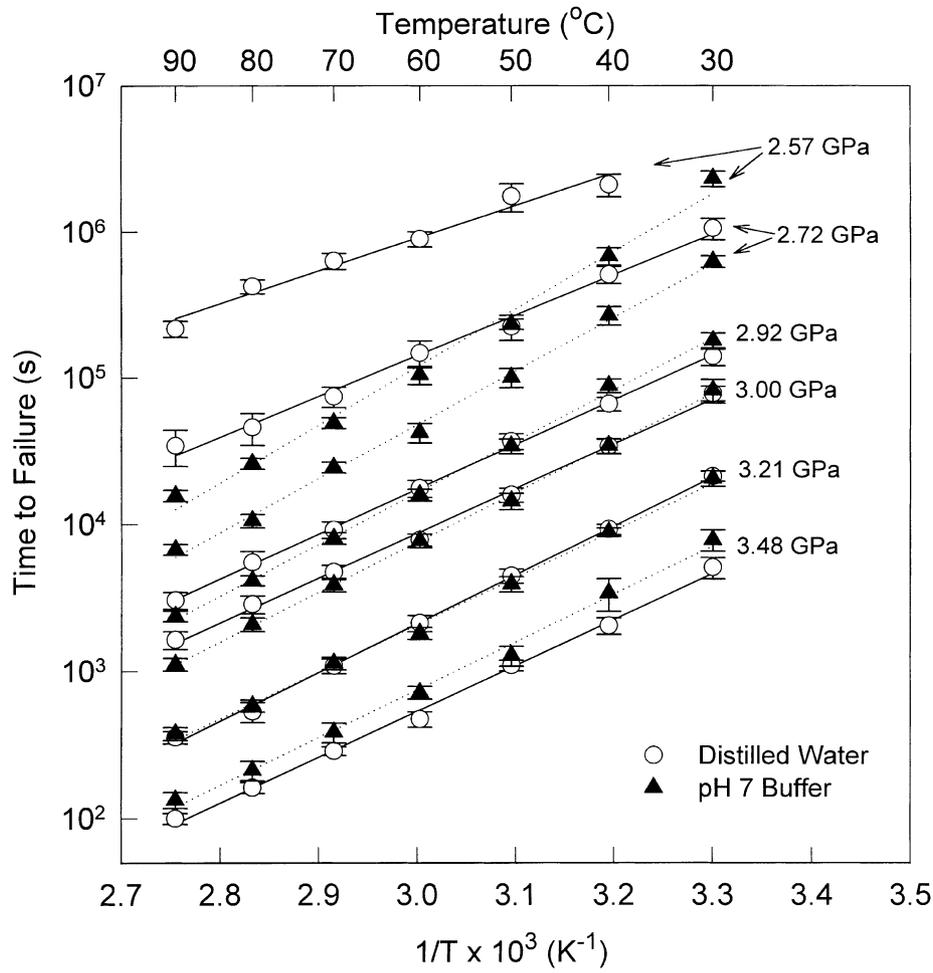


Fig. 5. Static fatigue data for single coated fiber (fiber I) measured in distilled water and pH 7 buffer solution as a function of temperature.

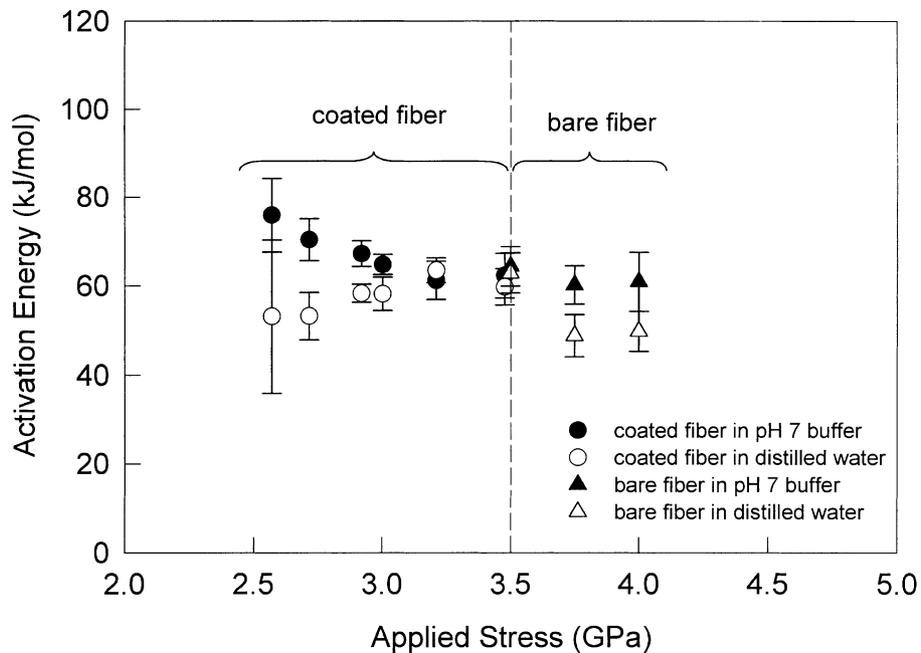


Fig. 6. The apparent activation energies for fiber I and bare fiber measured in pH 7 buffer and distilled water.

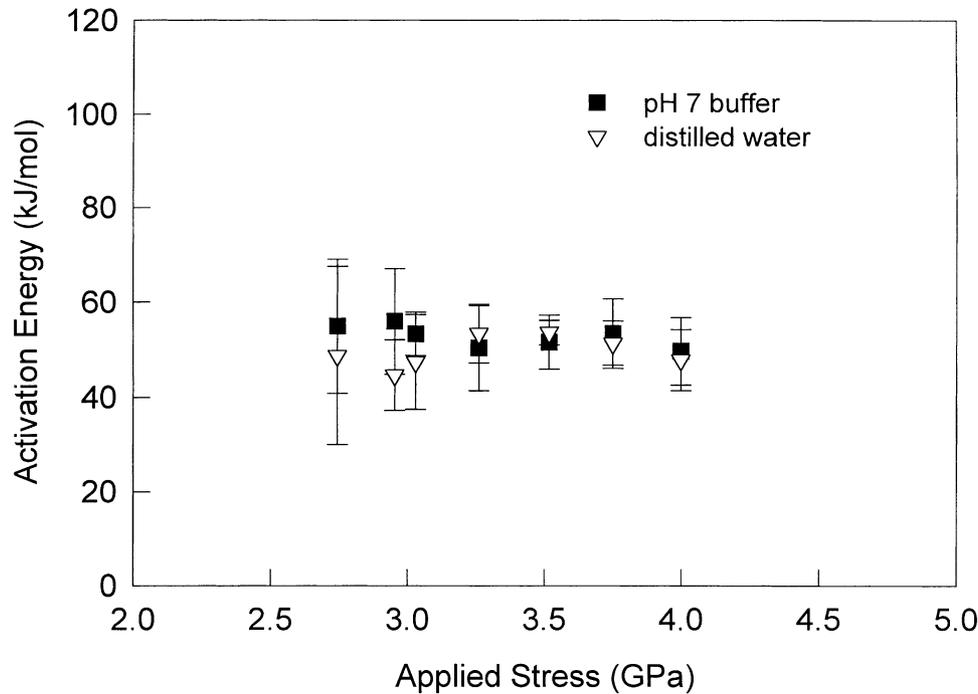


Fig. 7. The apparent activation energies for fiber II measured in pH 7 buffer solution and distilled water.

Table 1
Summary of the activation energy for silica optical fibers in water from several authors

Fiber coating	Polymer	Polyurethane acrylate	Polyurethane acrylate
Testing technique	Tensile test	Tensile test	–
Environment	Water	Water	Water
Activation energy (kJ/mol)	~44–55	~63–89	~46–63
Stress (GPa)	~2.8–3.4	~2.34–3	~2.8–4.2
Authors	Kao ²⁶	Chandan and Kalish ²⁷	Brownlow's data cited in Inniss et al. ¹²

3.2.2. Stress effect

The stress is generally believed to reduce the activation energy for fatigue in silica optical fiber.¹² Fig. 6 shows that the apparent activation energy results for fiber I tested in pH 7 buffer solution meet such expectation. However, the results for the same coated fiber tested in distilled water do not show such a behavior. The data for bare fiber are not sufficient to draw a conclusion on stress effect. As shown in Fig. 7, the apparent activation energies of fiber II in the two solutions are similar due to coating effect; the large error bars are results of few data points rather than the quality of fit. However, the trends for fiber II (Fig. 7) are similar to fiber I (Fig. 6), i.e. the apparent activation energies of silica fiber in static fatigue do not increase with the decreasing stress when measured in distilled water. The unexpected stress dependence on apparent activation energy of static fatigue measured in water has not been observed in the past, but can be understood in terms of pH effect. The apparent activation energy, which is a measurement of temperature effect, takes into account of all the tempera-

ture dependent factors; these factors may be overlooked in the past and the apparent activation energy was thought only as a result of the applied stress. pH effect, as mentioned in the introduction, is one important factor. When the fiber is measured in distilled water, the pH on fiber surface is not a constant due to various reasons, such as coating effect, water/glass reaction, and water dissociation. The change of pH on fiber surface is complex and depends on temperature, therefore the resulting apparent activation energy is different. It is thus suggested the study on fatigue of silica fiber should be conducted in a pH controlled environment (pH buffer solution) instead of commonly used distilled water.

4. Conclusions

The two-point bending static fatigue of fused silica optical fiber has been studied at various temperatures in pH 7 buffer solution and distilled water over the applied stress range of 2.5–4.5 GPa in the coated states and 3.5–

4 GPa in the bare state. The apparent activation energies for the fibers have been determined from the static fatigue data.

Silica optical fibers were found to fatigue faster in pH 7 buffer solution than in distilled water, because pH 7 buffer is more basic than water at the temperature above room temperature. This phenomenon is not significant for the coated fiber under high stress due to the insufficient time for the effective ions in the buffer to diffuse into fiber coatings. The fibers survive longer in distilled water than in pH 7 buffer solution in the “pre-fatigue knee” region. However, in the after-knee region, the fibers fatigue faster in water than in pH 7 buffer. The reason of such a strength switch has not yet been clear.

The apparent activation energies of static fatigue of bare silica fiber measured in distilled water is lower than measured in pH 7 buffer solution. For coated fibers, the apparent activation energies are not significantly different in high stress region because coating preclude pH controlling ions diffusing into fiber surface. However, giving longer testing time (under low stress), the apparent activation energies for coated fiber are found to be higher in pH 7 buffer.

The stress effect on the apparent activation energies for the fibers measured in water and pH 7 buffer were found to be different. The apparent activation energy was found to decrease with the increasing stress for the fiber in pH 7 buffer solution. Such a stress effect was not observed for the fibers measured in distilled water. The pH change in water and the resulting local pH change on fiber surface, which are both temperature dependent, are thought to be responsible for the different apparent activation energies.

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