Chapter 11

Micro Porous Silica: The All New Silica Optical Fibers

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A new type of optical fiber has been developed. It is made with all pure silica in both the core and cladding. This is possible because the cladding is a micro porous silica produced by a modified sol-gel technology. The formation and characteristics of this new optical fiber type are described. In particular the optical and mechanical properties are illustrated and described. The strength and fatigue of these optical fibers are very good, even without additional protective jackets. Unjacketed fibers have mean Weibull strengths in bending of 6.5 to 7.6 GPa with Weibull slopes in the 40 to 60 range. Fatigue results for fibers tested in ambient air, ambient water and boiling water are presented. The dynamic and static fatigue parameters are around 20. The micro porous structure of the sol-gel cladding provides sites for attaching different moities which could activate biochemical reactions or be useful as sensing sites. Based on preliminary experiments, some possibilities are presented. In general this new structure can provide opportunities for as yet unidentified applications where chemicals and or light must be brought in close contact with body tissue to effect beneficial reactions there.

In 1993 a new approach to "sol-gel" material processing was discovered[1]. Micro porous silica could be produced on a pure silica core, such that a truly functional optical fiber was fabricated[2]. These experiments were an outgrowth of work begun in the 1980s[3-5]. Objectives of this research are to complete feasibility studies on the development of lower cost, ultra-long (>50 km) single mode optical fibers and to develop radiation resistant multi mode optical fibers for extra-terrestrial applications, such as space satellites. A secondary objective is to establish the advantages of a micro porous clad pure silica core optical fiber as a specialty optical fiber for new applications.

The micro porous clad fibers behave like hard plastic clad silica (HPCS) optical fibers[6] in that they do not require a buffer or jacket over the cladding. As with HPCS fibers, however, a jacket is beneficial for most practical environments[7,8].

The optical and the mechanical properties of the micro porous silica clad optical fibers, including the strength and fatigue properties are presented. Potential new applications within medical and biochemical fields are suggested.

Experimental

The material used as a precursor is a hydroxy, ethoxy terminated ladder oligomer with significant Si-C linkages as methyl groups attached to silicon[9]. Details of the materials and application scheme appear below.

Chemical Details

The material used as a precursor is a hydroxy, ethoxy terminated ladder oligomer with significant Si-C linkages as methyl groups attached to silicon as shown in Figure 1. This spin glass resin, GR650, is manufactured by Techneglas of Toledo, Ohio. It was applied from a solution in ethyl acetate, generally at a 50/50 solute/solvent weight percent ratio. A polymeric jacket, when applied, consisted of a single coat of a polyimide, typically a HD Microsystems product, applied in line but on a coating wall after the optical fiber came off the draw tower. A material similar

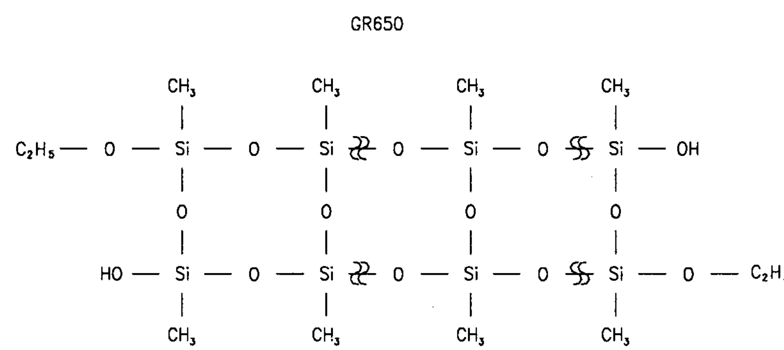

Figure 1: Idealized chemical structure of the glass resin used as the sol-gel precursor for the cladding. This oligomer is end capped with hydroxy and ethoxy groups and has one methyl group per silicon atom.

to GR650, hydrogen silsesquioxane, whose molecular structure was similar but which had to be applied as a dispersion, was used early in the work[2]. It had several problems, in general including having to apply dispersions with less than 10% solids, and gave more scattered results.

Processing Details.

The micro porous silica clad optical fibers were drawn on conventional fiber draw towers[10] using thermal ovens to cure/convert the precursor materials to the micro porous silica cladding. The majority of the fibers were drawn on a standard 8 meter tall fiber draw tower with up to four ovens available in line. Typically temperatures in the range of 450 to 700 ^{0}C were employed. Some of the fibers were drawn on a 12 meter tall fiber draw tower which was equipped with six ovens in line.

The cure and conversion of the silica precursor to micro porous silica is done in line. The general process is that solvent is driven off as the hydroxy and ethoxy groups react to create the cured polymer. The water and ethanol residues flash off. Continued exposure to greater than 400 ^{0}C causes oxidation of many of the remaining Si-C bonds (methyl groups). The conversion is not complete under current conditions. Draw speeds of 7 to 70 meters/min have been employed to date. Typical residence times in a given oven is thus 0.5 to 5 seconds with a total time of exposure to elevated temperatures of approximately 5 to 30 seconds. In line processing refers to processing before the optical fiber is diverted from vertical travel, i.e. before the fiber comes in contact with the pinch wheel at the bottom of the draw tower.

For the results described below, a double application was used with a final sol-gel cladding thickness of ~12 μm. The size of the solid silica core varied among the runs from diameters of about 100 μm to about 200 μm. In a few cases, a preform made from pure silica core and a fluorosilica cladding was used as the starting point. Clad/core ratios varied from 1.1 - 1.4. The core silica material in all cases was a low OH undoped silica, with the OH level typically less than 5 ppm. When applied, the jacket material was a single coat of a polyimide, cured by a series of ovens ranging in temperature from 300 to 500 ^{0}C. Polyimide thickness was ~7 μm.

The actual dimensions of specific fibers are given with the figures displaying results. The core silica material in all cases is a low-OH undoped silica, typically less than 5 ppm of OH. When applied, the jacket material was a single coat of a polyimide, cured by a series of ovens. Polyimide thickness was ~7 μm.

Optical Testing Details

The primary tool in making the optical measurements is an Optical Time Domain Reflectometer (OTDR) having a source emitting at 850 nm. The signal is transmitted to the fiber under test usually through a pigtailed optical fiber, having similar core dimensions and numerical aperture (NA) to the test fiber, which is approximately 0.25 for the sol-gel clad fibers in the current study. A portion of the signal is reflected back as it travels down the test fiber. The OTDR measures the loss in this reflected signal in comparison to the launched signal.

Strength Testing Details

Two point bend strength testing has been described in the literature[11-13]. The two point bend tests were performed on a 2-point bend tester with grooved stainless steel faceplates holding up to 10 fibers at a time. Strain rates and other specifics are given with the figures.

Note that the gage length for this type of test is small, on the order of several millimeters. Samples, however, were normally not taken in a row. Rather, 10m to 100m sections of fiber were produced between sets of ten [10] samples. Additionally many fibers tested were produced under essentially equivalent conditions so that fiber strength measured under ambient test conditions has used total lengths of fiber tested of a meter or more. This sample total is still small but spans a large amount of fiber produced (>20 km) from which the smaller sections of samples have been taken for actual testing.

Fatigue Testing

Static fatigue measurements were performed by the mandrel wrap method[14-16]. The length of fiber under test was about 500 mm. The fibers were wound in ambient conditions and tested in ambient water or boiling water. Stresses lay between 1.4 and 4.6 GPa [200 to 667 kpsi]. A minimum of five samples were used for each mandrel size.

Dynamic fatigue measurements are made in conjunction with the strength testing. By varying the speed of the strength testing, the effects of dynamic fatigue are observed. Typically, if the strength data has a plot without breaks, the mean strength is tracked versus the rate of stress or versus the rate of strain. If there are breaks in the strength plot at a given test rate, then a specific ordered sample strength, one with a specific failure probability, can be tracked versus the change in test rate.

Results

Two-Point Bend Strength Tests.

Figure 2 presents data from several fiber draws where over 220 samples were tested out of >20 km of fiber produced under equivalent conditions over a twelve month period. Except for the very strongest values the curve is rather steep. There appears to be no real breaks in the slope, indicating a single flaw distribution.

Figures 3, and 4 present the change in Weibull strength as the constant strain rate is changed for tests run in ambient air, and in ambient water, respectively.

In each figure the unjacketed fiber results are denoted by Xs, while the polyimide jacketed fiber results are denoted by open circles, Os. As can be seen the jacketed fiber results are generally steeper in slope than the unjacketed fiber results. Curves for the jacketed and unjacketed fibers are very close to one another in ambient water testing (Figure 4).

Static Fatigue Tests.

The results for ambient water immersion include moderately long term failures with all the initial samples of the unjacketed fiber having been broken. In Figure 5 the time to failure for all samples are presented. The data points (diamonds) of an unjacketed fiber clearly show a break in the curve. The short term data in Figure 5

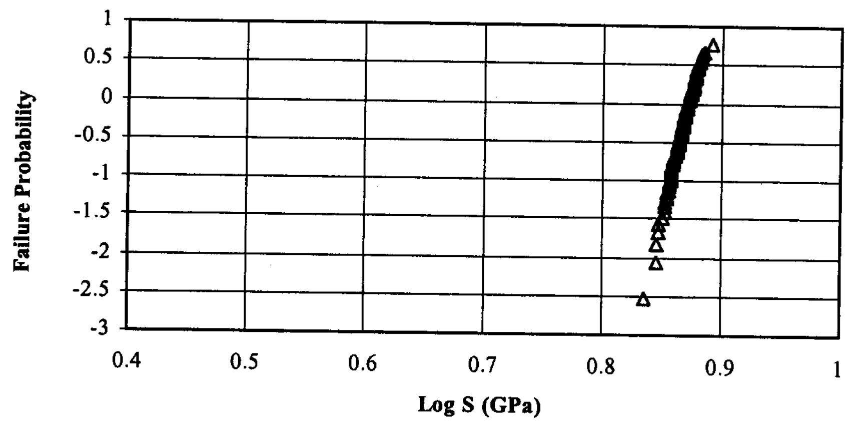

Figure 2: Weibull plot of the dynamic strength for unjacketed sol-gel clad optical fibers, having a pure silica core with diameter of 165 μm and a clad diameter of 195 μm; constant strain rate of 10%/min; 2-point bend test carried out in ambient air, ~23°C 50% RH

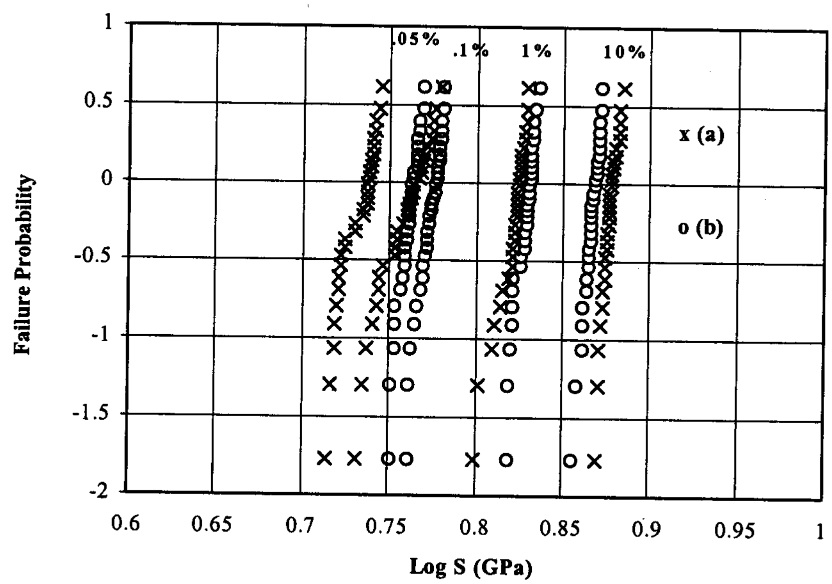

Figure 3: Weibull plots of dynamic strength measurements taken at strain rates varying from 10%/min down to 0.05%/min (a) unjacketed sol-gel clad optical fibers nominally 165/190 μm core/clad diameters, "x" points; (b) polyimide jacketed sol-gel clad optical fibers nominally 204/232/244 μm core/clad/polyimide diameters, "o" points; 2-point bend test; ambient air = 23 °C, 35-60% RH.

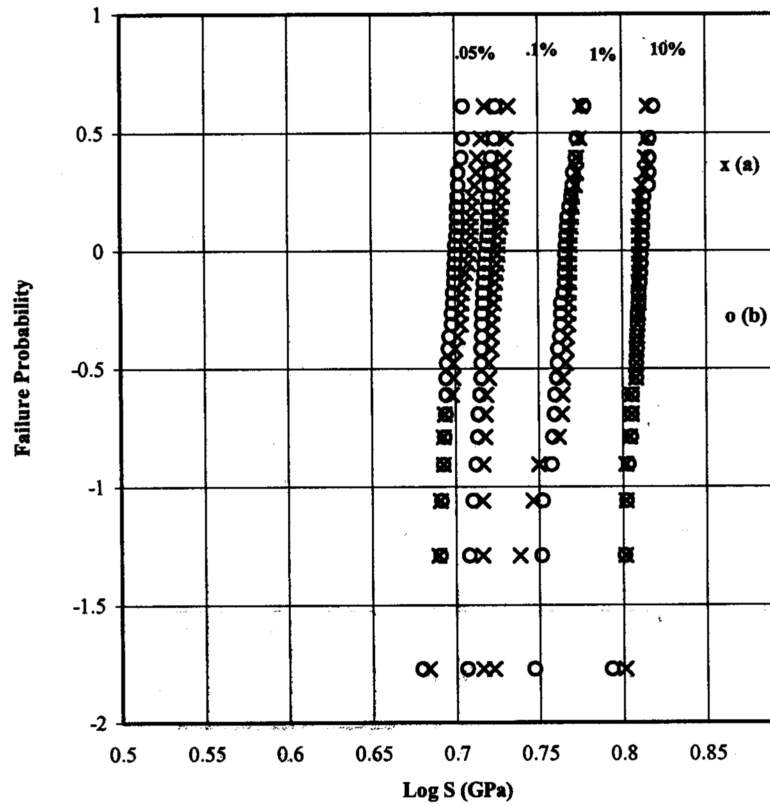

Figure 4: Weibull plots of dynamic strength measurements taken at given strain rates, "x" points for unjacketed fiber of Figure 3(a), "o" points for jacketed fiber of Figure 3(b); 2-point bend test; testing in ambient water, 23 °C.

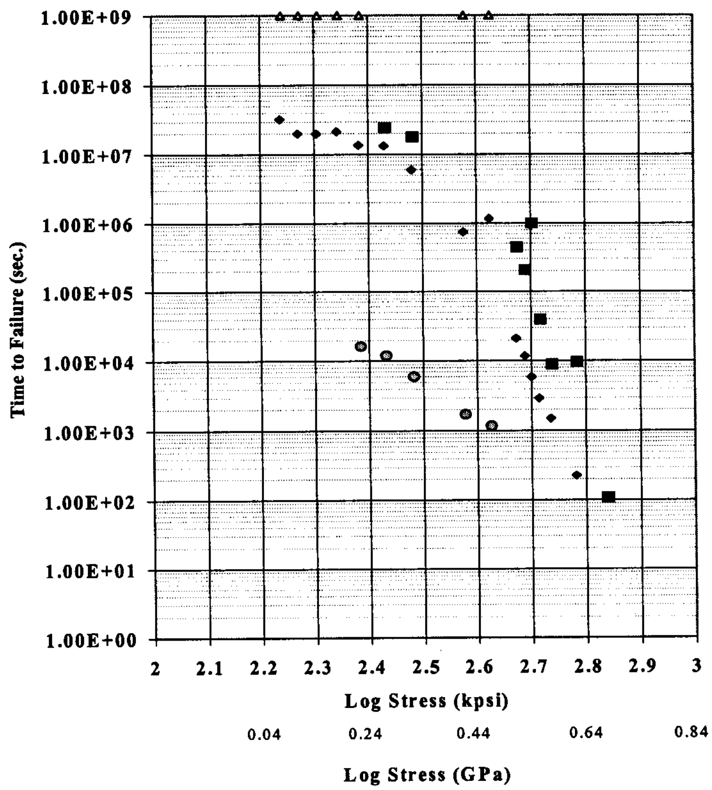

Figure 5: Static fatigue plots of average failure times of 0.5 m length of sample fiber wrapped around mandrels giving the bending tensile stresses plotted, "diamond" points for unjacketed fiber whose dimensions are 164/184 μm core/[sol-gel clad],N_S (hi) = 18, N_S (knee) = 3; "box" points for jacketed fiber whose dimensions are 162/192/208 μm core/[sol-gel clad]/polyimide; testing in ambient water, 23 ^0C; points at top of graph are fiber samples which have not yet failed; N_S (PI, water) = 25, N_S (PI, boiled) = 6.

indicate a static fatigue parameter, N_S, of about 18 for the unjacketed optical fiber. Above the break at longer times, the static fatigue parameter has dropped to a value of about 3. Further in this figure the upper squares represent the time to failure for the polyimide jacketed optical fiber. Triangular points at the top of the figure represents samples which had not broken when this graph was prepared about 690 days, >16,600 hours [~6 x 10^7 sec], into the testing program. The static fatigue parameter is 21. Also note that the highest stress tested is over 4.6 GPa [660 kpsi].

The lowest set of points in Figure 5, the gray circles, represent the average time to failure for polyimide jacketed optical fibers immersed in boiling water. The plot of these points appears to be linear, though some curvature seems present. The static fatigue parameter, N_S (100 ^0C), has a value of approximately 6.

Modification/use of micro porous clad structure.

Studies are underway to explore the doping or modification of the micro porous structure of the cladding to provide either active sites for chemical or biological activity or for sensing applications. Preliminary results indicate attachment of Rhodamine complexes which were activated by light energy transmitted down the fiber to the sites where the complexes were 'incorporated'. Also gratings have been formed within the micro porous structure through the use of photo activated precursors.

Discussion

Two-point bend strengths vs. strain rates.

The results in Figure 2 demonstrate the consistency of the results obtained from a large number of fiber draw runs, i.e. a large number of silica rods and sol-gel precursor preparations. The samples tested for this figure represent a random sampling of over 20 kilometers of modified sol-gel clad optical fiber. A main feature of Figure 2 is the steepness of the slope, especially in the upper region, which tends to imply that the flaw distribution may actually be unimodal[17].

The results of Figures 3 and 4 demonstrate the relatively equivalent behavior of the unjacketed sol-gel clad fibers and the polyimide jacketed fibers. At the two slowest strain rates the data for the unjacketed fiber clearly shows a discontinuity in the slope.

Dynamic fatigue results

The dynamic fatigue of unjacketed and polyimide jacketed fibers were determined from the results given above for the two conditions presented. Within experimental error it can be stated that the dynamic fatigue parameter is $N_D = 22 \pm 2$ regardless of whether the sol-gel clad optical fiber is jacketed with polyimide or not.

Static fatigue behavior

By their nature static fatigue measurements usually yield much longer times to failure and thus samples experience much longer exposure to the test environment than in dynamic fatigue testing. Small differences in the fatigue behavior of similar samples become more pronounced in static fatigue testing. Furthermore in studies, like the present one, where dynamic measurements are made by the two point method, the gage length of the static fatigue samples are generally longer than for the dynamic fatigue samples. The two features greatly enhance the observation of differences in sample behavior by static fatigue testing over dynamic fatigue testing. The appearance of a 'knee' in the data plotted in Figure 5 for the unjacketed fiber samples is an example of this phenomenon. This 'knee' is a well recognized feature of the standard telecom optical fibers and many other fibers as well. The research groups at Bell Labs and at Rutgers University[11,19,20,21] and others[22] have reported on the occurrence and significance of this feature. The 'knee' feature was found present in bare fiber work and in most acrylate jacketed optical fibers.

It should be noted that neither the ambient water data nor the boiling water data for the polyimide jacketed fibers show a clear break (or knee) in the their plots. The absence of a break in the static fatigue test results has been reported earlier for Hard Plastic Silica Clad optical fibers[6] and some silicone clad/coated fibers[13]. Final judgment on the long term behavior for these jacketed fibers awaits completion of the tests.

Micro porous structure

The basic science and engineering studies are underway which utilize the micro porous structure to incorporate other materials, which in turn permit the modified sections to interact with the surrounding environment and transmit a modified signal. Preliminary tests have established that complexes such as Rhodamine can be activated by signals traveling in the fiber core after incorporation of the complex in a section of the modified sol-gel clad fiber. The guided waves within the fiber core extend a distance into the cladding. Where the complex is incorporated into the cladding, it can interact with the waves travelling within the core and become activated.

The new studies underway look to explore further these effects to design and construct sensors for various chemical and biochemical moieties. We are looking at several different processing conditions and other variables to create micro pores of different sizes for use with materials of differing dimensions.

Conclusions

A new type of optical fiber has been developed. It is made with all pure silica in both the core and cladding. It has been shown to have high strength properties, good fatigue behavior and good optical properties. With its micro porous structure, it appears to provide sites for other molecules which can be activated by light traveling down the core of the optical fibers. Several different properties have been found, some of which present 'problems' compared to standard optical fibers. Among the latter problems are cleaving, and gripping the fibers for testing or other high stress situations. The micro porous structure can be crushed at high grip pressures needed to tensile test long lengths or it can be consolidated when attempting to fusion splice the fiber with itself or any other all silica fiber. Preliminary spectral experiments have also indicated some unique behavior at wavelengths in the near infrared region of the electromagnetic spectrum. All these aspects are part of the continuing study of these fibers and the push for applications of their unique structure.

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