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Confirmation of thin surface residual compressive stress in silica glass fiber by FTIR reflection spectroscopy

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ABSTRACT

Recently, a new method of glass strengthening for silica glass fibers was proposed and demonstrated. The method involves the process of surface stress relaxation while the glass fiber is subjected to a tensile stress. Upon release of the applied tensile stress, the glass fiber acquires a residual surface compressive stress which can make the glass fiber stronger. The presence and magnitude of residual surface stress in the fibers were evaluated by observing the permanent bending of 1) fibers that were bent, heat-treated, and released, as well as 2) fibers that were heated while held under a uniaxial tensile stress, released, and then sliced. Direct observation of birefringence due to surface residual stress in the treated fibers was not possible due to the extremely thin surface layer of the residual stress. In this work, the previously evaluated magnitude of residual surface stress formed in silica fibers was confirmed by observing a shift of an IR reflection silica structural band after both bending and uniaxial tensile treatments at a temperature far below the glass transition temperature.

1. Introduction

Glasses can be made mechanically stronger by forming a compressive residual stress on the surface by processes such as thermal tempering [1] or ion-exchange [2]. Recently, a new strengthening mechanism, which, in principle, is applicable to any glass composition with any dimension, was proposed and demonstrated for silica glass fibers, and the depth and magnitude of residual compressive stress formed were evaluated, indirectly, using a fiber bending method [3,4]. This compressive stress formation method is based upon a surface stress relaxation process while a sub-critical (i.e. less than the fracture strength) tensile stress is applied at a temperature far below the glass transition temperature, in the presence of water vapor, where upon release of the tensile stress, a surface compressive stress is formed. By using this method, it was possible to build a surface compressive stress nearing a magnitude of 3 GPa immediately at the surface of silica glass fiber [4].

Up to this point, no direct measurement was made of the depth or magnitude of residual compressive stress produced by this method in silica glass fiber. Traditionally, optical birefringence is used to determine the surface residual stress profile of glasses [5]. Unfortunately, due to the very thin layers of surface residual compressive stresses created so far, of estimated thicknesses less than 100 nm on the surface of the pristine silica glass fiber, this method is not applicable to stress/strain profiling of the strengthened silica glass fibers.

Some authors however, have found that applied stresses on the structure of silica glass fibers are proportional to FTIR reflection and Raman peak shifts. Michalske et al. performed Raman on silica glass fibers held under tensile stresses up to 10 GPa [6,7] and found a continuous shift of the 1050 cm^{-1} band to lower wavenumber proportional to increasing the tensile stress. Similarly, Tomozawa et al. [8,9] and Hepburn [10] performed Fourier transform infrared (FTIR) reflection peak wavenumber measurements on silica glass optical fibers in an elastically bent configuration which allowed them access to both the tensile and compressive sides. They found that the 1120 cm^{-1} reflection band shifted to a higher wavenumber proportional to the applied compressive stress and to a lower wavenumber proportional to the applied tensile stress [8–10]. The peak positions of the 1120 cm^{-1} IR reflection and the 1050 cm^{-1} Raman band are related since both are attributed to the asymmetric stretching vibration of Si–O–Si and have been used to determine the fictive temperature of silica glasses [11–15]. However, since the intensity of the IR band is much stronger than the Raman band the peak wavenumber of the IR band can be determined much more accurately than the Raman band.

In the present work, silica glass fibers with a residual surface stress were produced and the 1120 cm^{-1} IR reflection peak position shift, $\Delta\nu$, relative to that of an unstressed fiber with an identical thermal history, was evaluated by FTIR spectroscopy. It was necessary to consider the combined effects of probe depth and residual stress profiles in order to accurately determine the residual stresses being measured. The observed IR reflection peak shifts due to residual stresses were compared with the known peak shifts produced by elastically applied stresses.

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2. Experimental

Two different methods were employed to produce the surface residual stress on the surface of silica glass fibers. In one method, silica glass fibers were subjected to a low bending stress by inserting the fiber into silica glass tubes with various diameters in a two-point bending manner and heat-treated. In the second method, the fibers were subjected to various high tensile stresses and heat-treated [3,4].

2.1. Residual surface stress formation by fiber bending at 500 °C

It was found that when bare silica glass fibers were heat-treated in a two-point bend configuration in the presence of water vapor at various temperatures below the glass transition temperature, there was a retained residual curvature when the bending stress was removed at room temperature [3,4,8,9]. This effect was attributed to surface stress relaxation accelerated by water diffusion, resulting in the formation of surface residual stress, and a simple method was developed to calculate an effective surface stress relaxation diffusion coefficient as a function of temperature and water vapor pressure [3,4].

The plastic coating on the fibers was removed by immersing the fibers in 96% H_2SO_4 at 200 °C for 10 s to obtain bare silica glass fibers (Furukawa) with a diameter of 125 μm. The glass fibers, after removing the plastic coating, were subjected to a bending stress by placing them in silica glass tubes with an inner diameter of 3.0 cm, in a two-point bending arrangement with the two ends of a fiber being parallel and in full contact with the inner wall of the tube. The bent silica glass fibers were under a maximum bending stress of 361 MPa, as estimated using the equation derived by Matthewson et al. [16]. The two-point bent fibers were heat-treated at 500 °C in a wet atmosphere of 355 Torr H_2O, for 7 h. The high water vapor pressure atmosphere of 355 Torr was generated by bubbling air through a hot deionized water bath held at 80 °C.

2.2. Residual surface stress formation by uniaxial tension at 500 °C

By subjecting silica fibers to a tensile stress at temperatures far below the glass transition temperature, with the help of surface stress relaxation, it is possible to produce a surface compressive residual stress upon release of the tensile stress. By slicing these stress-treated fibers in half and by measuring the radius of curvature of the bending, the effective depth of the residual compressive surface stress was obtained, assuming that the maximum magnitude of the stress was the same as the originally applied stress at the surface of the fiber [4].

Tensile stresses were applied to silica fibers using an Instron machine (Model 4204) with rubber grips. Silica glass fibers (Suprasil II) with a plastic coating and a 15 cm gauge length were used. Thick cardboard was used as a tab material to provide extra cushion and prevent undesired breakage of the fiber in the grips. A 5 cm section in the middle of the gauge length was dipped into 96% H_2SO_4 at 200 °C for 5 s to remove the plastic coating and obtain bare fibers with a diameter of 125 μm without adversely affecting the surface condition.

The samples were loaded into the grips and subjected to tensile stresses of 1 GPa, 2 GPa, or 3 GPa at a loading rate of 100 MPa/s. While held at a constant load, an approximately 1 cm length of the central portion of the bare fiber was heated for 60 s by exposing it to gas passed through a heated coil. The back end of the gun is not sealed, allowing additional air intake, and as a result the gas blown over the glass fiber is a mixture of laboratory air and tank N_2. The humidity of the gas exiting the gun is estimated to be approximately that of lab air, ~6 Torr [4]. The temperature of the exiting gas was controlled to be 500 ± 10 °C using a variable AC transformer. After 60 s, the hot gas flow was stopped and then the fiber was unloaded.

2.3. IR reflection analysis of silica glass fiber with residual stress

In the present work, the IR surface reflection peak wavenumber near 1120 cm^{-1} was measured on silica glass fibers which were heat-treated under stresses. For bending treated fibers, a Nicolet 560 FTIR spectrophotometer with a microscope attachment was used. After the bending stress/thermal treatment, IR specular reflection measurements with a 28° reflection angle were performed at four points around the circumference of the fiber at the bending vertex including: the point of maximum tension during bending, the point of maximum compression during bending, and the two neutral points between them. Infrared reflection spectra of silica glass fiber samples given the tensile stress treatments were measured using a Bruker Vertex 70 FTIR spectrophotometer with a Hyperion Microscope at normal incidence. After the tensile stress/thermal treatment, IR reflection measurements were performed on the glass directly in the middle of the 1 cm heat-treated region.

Reflection measurements were performed to discern how the 1120 cm^{-1} peak position was affected by heat-treatment under stress. In every case, some fibers were also heat-treated in an identical manner, without any applied stress, to separate any effects that thermal history may have from the stress effect. The IR reflection spectrum was collected in the range of 1500 to 600 cm^{-1} because all necessary silica structural bands fell within this region, and 1000 scans were taken at a data spacing of 0.482 cm^{-1} using a knife-edge aperture with approximate dimensions of 20 μm × 200 μm with the longer dimension being in the fiber length direction. The 1120 cm^{-1} peak positions were determined using a smoothening program, Opus. All measurements were repeated five times, and error bars were taken to be one standard deviation from the mean. The peak positions of fibers with a stress were compared to those of fibers that had been heat-treated under similar conditions but under 0 GPa stress to determine the stress-induced peak shift, $\Delta\nu$, as a function of stress, σ, where a positive stress denoted tension.

3. Results

The results of the 1120 cm^{-1} peak position determined by FTIR analysis on silica fibers heat-treated at 500 °C under 355 Torr in bending with a maximum bending stress of 361 MPa for 7 h, and released, are shown in Fig. 1. For IR measurements on the bent fiber it was possible to stay within ±0.5 cm of the bending vertex, such that the maximum

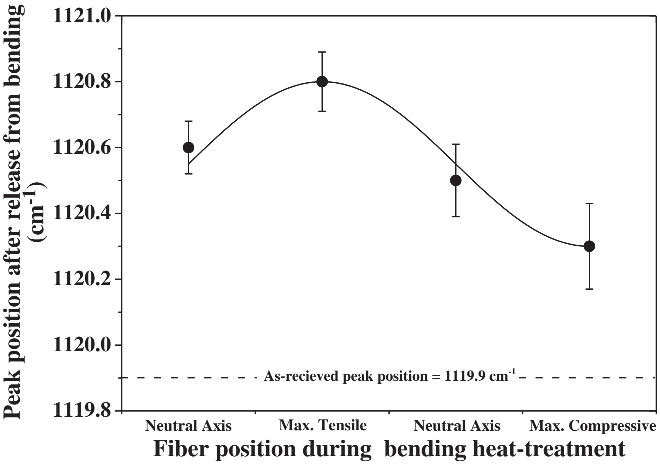

Fig. 1. IR peak positions of a permanently bent silica glass fiber after being heat-treated at 500 °C under a maximum stress of 361 MPa and 355 Torr water vapor pressure for 7 h and released. IR measurements were performed within ±0.5 cm from the vertex of the bend, corresponding to a possible range of probed stresses from 95% of the maximum stress to the maximum residual stress present [3]. The line is shown as a guide to the eye.