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Mechanical properties of resorbable calcium-phosphate glass optical fibers and capillaries

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Abstract

Calcium-phosphate glass optical fiber and capillaries (with composition identical to the core and the cladding of the fiber) were fabricated and subjected to mechanical characterization. Tensile tests were carried out to determine the strength distribution, the fatigue behavior and the elastic modulus of fibers and capillaries. The tests were performed without the application of any coating, in order to assess the behavior in bare conditions, just like in the provisional application as bio-resorbable elements. Strength ranging from 200 to 350 MPa was measured for both fibers and capillaries, the Weibull's modulus being around 3 to 6, thus revealing quite scattered distributions associated to the presence of variable surface flaws. The elastic modulus of the two glasses was shown to depend on the specific composition, the presence of MgO being responsible for a stiffer material. An evident sub-critical crack growth was also pointed out in the presence of water.

Keywords

Phosphate glass fibers, strength, fatigue, elastic modulus.

1. Introduction

Phosphate glasses, initially used for niche applications [1], have recently attracted increasing interest thanks to the possibility to customize their properties by opportune choice of the glass modifiers and intermediates. Optical quality rare-earth (RE) doped phosphate glass compositions have proven their ability to combine high emission cross-sections and solubility of REs without clustering, thus enabling the fabrication of high performance optical lasers and amplifiers [2–4]. Another interesting feature of phosphate glasses is the possibility to tune their composition to resemble that of the inorganic component of the human bone, making them interesting as base material for the fabrication of scaffolds in biomedicine [5].

Glasses in the $Na_2O - CaO - P_2O_5$ system loaded with metallic ions have been widely studied as promising biomaterials in virtue of their solubility in physiological environment and they have been employed for multiple functionalities in biomedical engineering [6]. An important feature of calcium-phosphate glasses (CPGs) is their ability to dissolve in aqueous media at physiological pH, being therefore resorbable in the human body once their functionality has expired [7]. Another interesting feature of CPGs is the possibility to draw them into fibers [8]. Such feature paved the way towards the development of fiber reinforced resorbable composite materials, used in hard and soft tissue engineering [9,10].

Cu- and Ti-doped CPG fibers have also been proposed for a variety of applications, ranging from wound healing to anti-bacterial action and neural axon growth [11–13].

Some studies also explored the use of hollow phosphate glass fibers as potential drug carriers. In those works, hollow fibers were drawn starting from a tube-shaped preform and loaded with different drugs. Drug release tests have been performed *in-vitro* using different methods [14–16].

More recently, biomedical and optical properties of phosphate glasses were combined to develop bioresorbable optical fibers suitable for biomedical applications [17]. In a recent work, these fibers were used for time-domain diffuse optical spectroscopy, showing the same behavior of standard silica fibers [18].

A fundamental task that is needed to assess the reliability of resorbable CPG fibers in clinical environment relies on their mechanical performance. Mechanical characterization of some CPG fibers has been performed in recent years by Sharmin *et al.* [19], proving their employability in many standard biomedical applications. Nevertheless, it is not straightforward to assume that such results can be extended to hollow geometries and to optical fibers made by coupling different materials.

In the present work, CPG step-index optical fiber and capillaries (with composition identical to the core and the cladding of the fiber) were fabricated by preform drawing technique and subjected to

detailed physical and mechanical characterization. The produced fiber and capillaries were tested without the application of any coating, in order to assess their behavior in bare conditions, this allowing to study their behavior like in typical potential biomedical applications.

2. Materials and methods

Two glasses with slightly different chemical composition, as reported in Table 1, were designed for the core and cladding of the optical fiber. The difference in the composition aims at providing the difference in refractive index to allow for efficient light guiding within the fiber core. Matching of the thermo-mechanical properties of the two materials is also desired to minimize the residual stresses generated upon the fiber drawing. A multimode step-index optical fiber was then designed with core and cladding diameters of 40 and 125 µm, respectively. Furthermore, capillaries were fabricated out of the core and cladding glasses with inner and outer diameters of 110 and 220 µm, respectively.

2.1 Glass and fiber fabrication

The CPGs were produced by melt-quenching method. The chemicals were weighed and mixed under controlled atmosphere to prevent water contamination and then melted in a vertical furnace at 1200 °C for 1 h under dry air flux.

The two capillaries were fabricated by the preform drawing technique, with the tube-shaped preform being obtained by rotational casting, using an in-house-developed set up [20].

The optical fiber was fabricated by the rod-in-tube method. The cladding tube was obtained by rotational casting, while the core rod was obtained by casting the glass into a cylindrical brass mold, featuring a diameter of 12 mm. The rod was annealed at the glass transition temperature for 5 h to relieve internal stresses and then manually polished to optical quality. Finally, the rod was stretched by cane drawing down to 4 mm to fit the internal cavity of the cladding tube.

The obtained preforms were heated in the drawing tower under controlled nitrogen atmosphere with an RF induction heating system (SAET, Torino, Italy) up to 550 °C to draw fibers and capillaries through a cylindrical ring graphite susceptor.

A portion of the glass was cut from the preforms for its physical characterization. Density was measured by the Archimedes' principle using distilled water as immersion fluid. The glass transition temperature (T_g) was determined by Differential Scanning Calorimeter (DSC) analysis (DSC2010, TA Instruments, New Castle, DE, USA) according to ASTM standard C 1356-91 [21].

Thermal expansion coefficient (TEC) measurements were carried out using a Netzsch DIL404PC dilatometer with a constant heating speed of 5 °C/min.

2.2. Mechanical characterization

The produced fibers and capillaries were subjected to mechanical tensile tests following the ASTM C 1557-03 standard [22]. Fibers and capillaries were cut into about 15, 70 and 160 mm-long samples while trying to avoid contact between the samples and any possible damage with other tools. Each single specimen was glued (with acrylic adhesive) to mounting tabs cut from thin cardboard to ease positioning and fastening to the fully articulated clamps of the mechanical testing machine (4502, Instron, USA); gage lengths (L_0) equal to 10, 60 and 150 mm were employed. At least thirty samples were considered for each gage length.

A load cell with maximum capacity of 100 N was used for the measurement of the tensile force, while the cross-head displacement was recorded by the Linear Variable Differential Transformer (LVDT) of the machine. The tensile tests were carried out in lab air (relative humidity = 40 ± 10%, temperature = 25 ± 2 °C) using a cross-head speed of 2 mm/min.

Tensile tests with gage length of 60 mm were also performed using different cross-head speeds (0.2 to 60 mm/min): in this case, a 100% humidity environment was generated by continuously dropping deionized water on the fiber during the test. At least ten specimens were used for each gage length and stressing rate. The diameter of the fibers was measured near the fracture point with an optical microscope after the test.

Some of the broken fibers were carefully collected and, after being placed on a specific sample holder and sputtered with a thin layer of Au-Pd, their fracture surface was analyzed by Scanning Electron Microscope (SEM) (JSM 5500, Jeol, Japan).

3. Materials and methods

The physical properties of the glasses considered in the present work are collected in Table 2. Interestingly, while core and cladding glasses display very similar density, thermal expansion coefficient and glass transition temperature are quite different: one can observe that a larger MgO/CaO content ratio is responsible for slightly lower TEC and higher T_g.

Morphological investigation by optical microscopy revealed perfectly circular geometry and the following dimensions were measured: 127 ± 5 μm for the optical fiber diameter; 109 ± 2 and 220 ± 4 μm for the inner and outer diameter, respectively, in the glass capillaries.

During the tensile tests, both the optical fibers and capillaries always failed from defects within the gage length. The strength was determined as the ratio between failure load and cross-section area; the average failure stress (σ_f) and corresponding standard deviation are collected in Table 3. As expected for typical brittle materials, the average mechanical resistance increased while decreasing the gage length, the scatter being always particularly wide.

For a clearer understanding of the failure stress data, these were analyzed using the Weibull's statistics. The strength data for each sample typology (optical fiber, core and cladding glass capillaries) and gage length were ranked in ascending order and a ranked failure probability was assigned to each measurement as reported in Ref. [23]:

$$F = \frac{j - 0.5}{N}, \tag{1}$$

where N is the number of specimens and j the rank in the ordered distribution. Under the assumption of a two-parameter Weibull's distribution, the probability that a sample fails under an applied uniaxial tensile stress σ is given by the cumulative distribution function:

$$F = 1 - exp\left[-\left(\frac{\sigma}{\sigma_\theta}\right)^m\right], \tag{2}$$

σ_θ being the characteristic strength and m the Weibull's modulus. Every measured strength value $s_{F,i}$ is then related to a specific failure probability, F_i; therefore, Eq. (2) can be linearized as:

$$ln\left[ln\left(\frac{1}{1 - F_i}\right)\right] = m\left(ln\, s_{F,i} - ln\, \sigma_\theta\right) \tag{3}$$

and the graphs reported in Fig. 1 can be accordingly obtained.

Linear regression fitting of the data shown in Fig. 1 allows estimating the Weibull's modulus for each strength distribution [23]. The parameter estimate of the Weibull's modulus (m) is generally characterized by statistical bias, which depends on the number of test specimens in the considered sample. An unbiased estimate of m, denoted as m^U, can be obtained by multiplying m by an unbiasing factor, which is given as a function of the number of considered specimens in Ref. [23]. The confidence interval for m^U, corresponding to the 5 and 95 percentile distributions, can also be calculated according to Ref. [23]. Finally, the parameter estimate of the Weibull's characteristic strength σ_θ and its confidence interval is determined according to the same reference norm.

The results are summarized in Table 3. A quite similar Weibull's modulus is obtained for the various samples sets, this being associated to analogous (relatively wide) scatter in the strength distribution and, correspondingly, in the flaws population. Conversely, despite the non-negligible confidence interval, the characteristic strength changes significantly with the specimens typology and the gage length. According to the fractographic analysis reported below, which shows that failure origins are always located on the surface of the fiber, σ_θ (which is not a material property but depends on the test specimen [23]) clearly decreases as the fiber surface (i.e., the gage length)

increases as one expects on the basis of the Weibull's theory for brittle fracture [23,37]; this is also evident from the shift of the distributions reported in Fig. 1 towards smaller strength values. The variation of σ_θ moving from the optical fibers to core and cladding glass capillaries can instead be very likely associated to the different flaws size. Although great care was always used to handle, cut and test the available optical and hollow fibers, it is very probable that the absence of any protective coating determined the creation of dissimilar surface defects, "larger" in the core glass capillaries and "smaller" in the optical fiber.

It is important to point out that the strength values measured in the present work are lower than those determined on other phosphate glass fibers and especially on freshly drawn ones, whose resistance measured by 2-point bending can easily reach 3-4 GPa [24,25]. The difference can be partially accounted for the more extended surface of the samples tested here by uniaxial tensile test with respect to the very limited surface placed under tension during 2-point bending. More importantly, as specified before, the optical fiber and capillaries considered in the present work were tested some weeks after fabrication and without any protection system (like polymer cladding produced just after the drawing process), thus being subjected to some (although carefully limited during cutting and handling) surface contacts, responsible for the creation of more severe flaws. As a matter of fact, the tensile strength values in Table 3 well compare with data previously reported on different phosphate glass fibers subjected to tensile tests without preliminary surface protection [19,20,26,27]. In any case, the strength values reported here correspond to the "real" resistance of the optical fiber and capillaries when these are used in bare conditions for exploiting their resorbability properties, like in biomedical applications. The values are also lower than those measured on other calcium-phosphate glass fibers developed for composite reinforcement [28], although in this case the large diameter difference (10 to 25 μm diameter in [28]) shall be considered.

The load-displacement diagrams recorded during the mechanical tests were always perfectly linear up to the fracture point, apart from the very initial portion where the slope increased from zero to a constant value before all the components (fiber, fixtures, cardboard tab etc.) had reached the same tensile load. According to the ASTM norm C1557 [22], the slope of the force (P) *vs.* cross-head displacement (ΔL) diagram recorded for various gage lengths can be used for the calculation of the elastic modulus of the fibers. Fig. 2 shows $\Delta L/P$ plotted as a function of the ratio between the gage length (L_0) and the cross-section (A) of each fiber. The displacement recorded by the testing machine (ΔL) is the sum of the real elongation of the fiber ($\Delta\lambda$) and the deformation of the machine and gripping system, defined by the product $k\,P$, where k is the compliance of the whole system. Therefore:

$$\frac{\Delta L}{P} = \frac{\Delta \lambda}{P} + k = \frac{L_0}{E\,A} + k, \quad (4)$$

where E is the Young's modulus of the fiber. At this point, if the $\Delta L/P$ *vs.* L_0/A data are fitted by linear regression, the slope and the intercept of the fitting line allow to estimate $1/E$ and k, respectively. The procedure applied to the data shown in Fig. 2 allows the calculation of the elastic modulus values reported in Table 4.

The differences between the two glasses (core and cladding) previously observed for T_g and TCE appear amplified here. The presence of a larger amount of Mg with respect to Ca accounts for a much stiffer glass (about 30% more) and this can be related to the different strength of the bonds formed by Mg and Ca with non-bridging oxygens and the corresponding structural modifications. Makishima and Mackenzie [29,30] proposed a model to calculate the Young's modulus of oxide glasses in terms of the packing density (V_t) and dissociation energy of the oxide constituents per unit volume (G_i) according to the relationship:

$$E = 83.6\, V_t\, \sum_i G_i\, x_i, \quad (5)$$

where x_i is the mole fraction of the oxide component i and

$$V_t = \frac{\rho}{W_M} \sum_i V_i\, x_i, \quad (6)$$

ρ and W_M being the density and the effective molecular weight of the glass, respectively, and V_i the packing factor of the i_{th} oxide component. The packing density and dissociation energy for several oxides were calculated by Makishima and Mackenzie using Sun's dissociation energies [31] and Pauling's ionic radii [32], respectively, and values of interest for this study are summarized in Table 5 [29,30]. Young's modulus values equal to 72.7 and 78.1 GPa were calculated for the core and cladding glasses, respectively. These estimates are evidently larger than the experimental values reported in Table 3, although the cladding glass is confirmed to be stiffer than the core one: the larger dissociation energy for MgO compared to CaO appears to have a fundamental impact on the material stiffness, outweighing the packing factor effect.

Similar overestimations were also obtained in a previous work on alkaline earth oxide doped phosphate glasses [33], very likely accounted for the too large packing density (V_t) calculated values, 0.59 and 0.60 for our core and cladding glasses, respectively. As a matter of fact, also using the modified approach by Rocherulle *et al.* [34,35], who proposed the evaluation of the packing factor for the constituent oxides based on their specific "density", very similar Young's moduli are obtained (69.2 and 76.6 GPa for the core and cladding glasses, respectively). In addition, as explained by Varshneya in his famous book [36], any theoretical consideration on the elastic modulus in a glass must include the possibility that not all the force applied externally is expended in pulling the atoms apart; in our systems, a portion of this force attempts to straighten the P-O-P bond angle between two adjacent tetrahedra, the modifiers contributing limitedly to the overall

stiffness of the glass. It seems therefore that a more precise estimate of the Young's modulus of the phosphate glasses considered here shall require the knowledge of a more realistic packing density, definitely lower (especially for the core glass) than that reported in Table 4 for the specific oxides or calculated by Eq. (6) for the glass, which is anyhow outside the aim of the present work.

An additional aspect worth being analyzed is the structure of the two phosphate glasses considered in the present work. Several studies have shown that phosphate glasses are constituted by a three-dimensional (3D) network formed by PO_4^{3-} tetrahedra, which can be attached to a maximum of three neighboring similar units. The cross-linking depends on the number of PO_4 groups attached to three other through bridging oxygens; the addition of modifiers like Na_2O, CaO or MgO results in the creation of non-bridging oxygens [7]. From this point of view, the two glasses considered here are absolutely identical and, therefore, their different elastic modulus must be fundamentally accounted for the different amount of alkaline earth oxides content, MgO being associable to stronger bonds. Moreover, also the thermal expansion coefficient and glass transition temperature difference previously reported can be strictly related to such difference.

At this point it is interesting to compare the elastic modulus measured on the core and cladding capillaries and on the optical fiber. When this latter is subjected to tension, core and cladding experience the same strain and, therefore, its elastic modulus should be:

$$E_f = \Phi_{Co} E_{Co} + \Phi_{Cl} E_{Cl}, \tag{7}$$

E_i and Φ_i being the elastic modulus and the volume fraction of the constituents (Co = core, Cl = cladding). By using the data reported in Table 4 and considering the nominal relative size for core and cladding previously reported, one obtains E_f = 52.6 GPa, which is in extremely good agreement with the Young's modulus measured on the optical fiber.

The results of the tensile tests performed with variable cross-head speeds on the optical fiber and capillaries in humid environment are collected in Fig. 3; the data recorded on the optical fiber tested in lab air at the highest stressing rate are also reported. Failure stress is plotted as a function of the stressing rate ($d\sigma/dt$), as in typical dynamic fatigue diagrams. The strength increases with stressing rates, this being associated with the sub-critical crack growth phenomenon which is typically described by the relationship:

$$v = \frac{dc}{dt} = A\,K^n, \tag{8}$$

where v is the sub-critical crack velocity, c the crack length, t the time, K the stress intensity factor, A and n being two parameters depending on the material and environment; the latter is typically called "fatigue susceptibility" as it identifies, for limited n values (approximately, below 20), the severity of fatigue degradation.

The strength differences previously pointed out among fiber and capillaries (σ_θ in Table 3) are clear also for the dynamic fatigue tests, the optical fiber being always stronger than capillaries. It is also interesting to observe that at the highest stressing rate the effect of the environment is negligible, i.e. the sub-critical crack velocity being lower than the loading rate.

Under conditions of dynamic fatigue, the failure stress can be expressed as [37,38]:

$$\sigma_f = \left[\frac{d\sigma}{dt} B(n+1)\sigma_{fi}^{n-2}\right]^{\frac{1}{n+1}}, \tag{9}$$

where σ_{fi} is the strength measured in the absence of sub-critical growth ("inert strength") and

$$B = \frac{2}{A\,(n-2)\,\psi^2}, \tag{10}$$

ψ being the crack shape factor. The strength measured in lab air at the highest stressing rate on the optical fiber and capillaries with gage length of 60 mm was chosen for σ_{fi}; such assumption was made according to the results reported in Fig. 3, where the strength seems to be independent of the environment at stressing rates as high as 230-250 MPa/s, thus appearing unaffected by fatigue phenomena. Equation (9) can be linearized as:

$$\ln \sigma_f = \frac{1}{n+1}\ln\left(\frac{\mathrm{d}\sigma}{\mathrm{d}t}\right) + \frac{1}{n+1}\ln\left[B(n+1)\sigma_{fi}^{\mathrm{n}-2}\right]. \tag{11}$$

Linear interpolation of data in Fig. 3 allows calculating the n and B values reported in Table 6. In general, a certain fatigue degradation in water can be pointed out, in agreement with previous findings on phosphate glasses [26,39–42].

The optical fiber and core and cladding capillaries show similar fatigue susceptibility within the scatter of experimental data; this is absolutely expected if one compares the fiber and the cladding capillaries, their "exposed surface" being exactly the same. As for the core capillaries, this finding points out that the different composition in terms of alkaline earth oxides does not influence the reactivity of the glass with water to a significant extent. This agrees with the results obtained by performing an *in-vitro* dissolution test at physiological pH and temperature for 28 days. Phosphate-Buffered Saline (PBS) solution was prepared (concentration = 0.01 M, pH = 7.4, T = 37 °C) and the fibers and capillaries were immersed in the liquid maintaining a (liquid/exposed surface) ratio of 0.1 ml/mm^2. The solution was refreshed every three days [12] and the external diameter of the samples was measured by optical microscopy. It was shown that the dissolution rate is substantially constant with time and values equal to 1.9, 2.8 and 2.0 μm/day were determined for the optical fiber and the core and cladding capillaries, respectively.

A large portion of broken fibers and capillaries were subjected to fractographic analysis under SEM to detect the presence of the fracture mirror and try to identify the critical defect. Some exemplary fracture surfaces are shown in Fig. 4. Only for some specimens tested in water the fracture mirror could not be identified, being larger than the fiber diameter due to the sub-critical crack growth

effect. In such cases, it was also possible to identify core and cladding in the optical fiber and point out their perfect concentric structure. The starting flaw was always localized on the surface of the specimen and associated to small defects generated by the contact between fibers or with an external body or to limited undulations or discontinuities on the glass surface. In some capillaries, the critical defect was interestingly localized on the inner surface.

In several specimens it was possible to measure the mirror radius (R_0) and to correlate it to the failure stress according to ASTM C1678-10 norm [43]; the data are reported in Fig. 5. It is well known that the two measures are interrelated by the Orr's equation [44,45]:

$$\sigma_f \sqrt{R_0} = \mathrm{C}, \tag{12}$$

where C is the mirror constant, usually considered as a property of the material. Fitting of the experimental results reported in Fig. 5 by Eq. (12) allowed calculating the mirror constant for the optical fiber and the capillaries considered in the present work. Values equal to 1.60, 1.50 and 1.47 MPa $m^{0.5}$ (standard error < 0.1 MPa $m^{0.5}$) were assessed for the fiber and the core and cladding capillaries, respectively. These values agree with previous findings on phosphate glasses and, being *C* a parameter which scales with fracture energy [37,45], one can estimate a fracture toughness of about 0.5 MPa $m^{0.5}$ for the glasses studied in this work [26].

Conclusions

Calcium-phosphate glass optical fiber and capillaries (with composition identical to the core and the cladding of the fiber) fabricated by the preform drawing technique were subjected to physical and mechanical characterization. The tensile strength measured on bare samples (without the application of any protective coating) ranges from about 200 to 350 MPa for both fiber and capillaries. The Weibull's modulus was determined to be around 3 to 6, thus revealing quite scattered distributions associated to the presence of surface flaws with variable size. The elastic modulus of the capillaries is shown to depend on the specific composition, the presence of MgO being responsible for a stiffer material; the compliance of the optical fiber strongly depends on the elastic modulus of the constituting glasses. A certain sub-critical crack growth is also pointed out for fiber and capillaries, the fatigue susceptibility parameter (*n*) being around 16-18 with no clear dependence on the composition.

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