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# Effects of aqueous aging on the mechanical properties of $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres

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**Abstract** Melt-spun phosphate glass fibres (40 mol% $P_2O_5$-20 mol% $Na_2O$-16 mol% CaO-24 mol% MgO) were aged for up to 7 days in doubly distilled water at 37 °C prior to single-fibre tensile testing. The effects of aqueous aging on the evolution of strength and modulus are discussed along with the possibilities for mitigating property loss via surface treatment and annealing. Whilst as-drawn fibres exhibited a strength loss over time, annealing produced a significant increase in strength over the same period. Silane pre-treatment of as-drawn fibres yielded no significant benefit to strength.

## Introduction

The key mechanisms for strength reduction of phosphate glasses in aqueous environments include hydration and pitting corrosion [1]. Reductions in fibre strength are anticipated due to the polymeric phosphate chains being weakened. Slivka et al. [2] monitored property evolution in 66 mol% $P_2O_5$-23 mol% CaO-8 mol% ZnO-3 mol% $Fe_2O_3$ phosphate glass fibres. Their results indicate early mechanical property loss, after 12 h tensile strength decreased by 17% and tensile modulus by 39%.

Our earlier work [3] attributes no particular benefits to fibre properties from silane surface treatment and it was anticipated that the mechanical properties during aging would be likewise unaffected by silane. However, annealing has been shown to decrease initial tensile strength whilst moderating the dissolution rate [4, 5]. Thermal agitation during heat treatment relaxes the polymer chains, promoting a more stable configuration. This also consolidates the glass, especially in the radial direction, where the weaker bonds (non-bridging oxygen) tend to become oriented during drawing or spinning [1, 6–8]. Bonds broken during processing may even reform [1, 7, 8]. The induced anisotropy and loss of ductility are likely to be associated with a decrease in strength. However, annealed fibres although initially weaker [5] exhibit great environmental durability. An increase in the number and severity of flaws also occurs when annealing in a humid environment. Hayden et al. [9] linked this effect to a tensile layer at the glass surface where OH groups may cleave the P–O–P chains and generate cracks. Thus, the fibre skin and core may exhibit different properties and surface cracking of this type may contribute to premature fragmentation of annealed fibres during environmental aging. This article deals with the study of the effect of dissolution on the mechanical properties of phosphate glass fibres. The fibres were studied as-prepared, after treatment with a silane sizing agent and after being annealed. They were mechanically tested using single-fibre tensile testing.

## Materials and methods

$P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres, i.e. 40 mol% $P_2O_5$-20 mol% $Na_2O$-16 mol% CaO-24 mol% MgO, were produced via melt-spinning in a 10% rhodium/90% platinum alloy crucible at 1100–1150 °C. The continuous fibre ranging from 10 to 40 μm diameter was wound onto a 1-m circumference drum at up to 2000 rev/min. Surface

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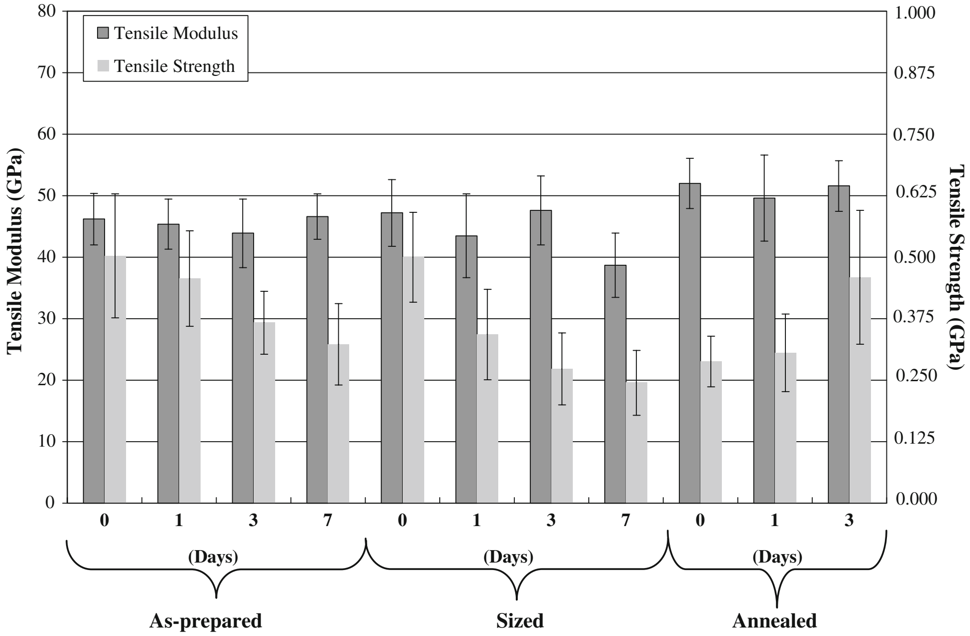

**Fig. 1** Tensile properties of $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres with varying pre-treatments as a function of immersion time in doubly distilled water at 37 °C

treatments were applied in a subsequent batch process. 1 wt.% 3-Aminopropyltrioxyethyl silane was stirred for 15 min with a solution of 90 vol.% ethanol and 10 vol.% deionised water. The fibre bundle was immersed in solution for 15 min, then rinsed with ethanol. The sizing curing took place in air at 120 °C for 24 h. Annealing took place in an air recirculation furnace at 444 °C (i.e. 5 °C below the glass transition temperature $T_g$ to prevent deformation) for 90 min. The heating cycle involved a 20 °C $min^{-1}$ ramp to 200 °C, followed by 1 °C $min^{-1}$ to 444 °C, 90 min dwell, cooling to 300 °C at 0.25 °C $min^{-1}$ and finally to 20 °C at 1 °C $min^{-1}$.

A 30 mg sample of fibres was immersed in 30 mL doubly distilled water at 37 °C for up to 7 days and then dried under vacuum at room temperature for at least 12 h. Extracted fibres were taken from the bundle after immersion and drying. The gauge length was 25 mm for all tests. Weibull analysis was used for each fibre batch and Student's *t*-tests were applied to compare the sample means. A high-speed camera (Photron Ultima APX) was used to capture the fracture processes for a subset of the tensile tests.

## Results and discussion

Figure 1 summarises the evolving mechanical properties of $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres for up to 7 days in 30 mL doubly distilled water at 37 °C. The tensile modulus of the fibres remained substantially unaltered at 40–50 GPa and was not subject to significant decay over the test period, save for the 7-day silane treated samples. The tensile strength of as-prepared and sized fibres reduced with immersion time. However, for annealed fibres the strength appeared to increase and recover to values similar to that of the as-prepared fibres over the same period. More detailed analysis of these effects follows for each fibre batch.

### As-prepared $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres

Table 1 lists mechanical properties of as-prepared fibres over the test period. After 1 day, the strength did not significantly decrease at the 5% significance level[1] although the reduction had become statistically significant after 3 days at the 0.1% level.[2] At 7 days, the fibre strength was lower than that of immersed for 3 days at 5% significance.[3] Therefore, the tensile strength decrease became statistically significant between 1 and 3 days and continued thereafter.

No significant change in fibre modulus was anticipated during aging since there was no change in the intrinsic glass structure caused by the dissolution as its surface erodes. The decrease in fibre strength was attributed to formation of a hydrated outer layer and its subsequent hydrolysis and pitting corrosion. These dissolution mechanisms imparted significant damage to the fibre surface as revealed by scanning electron microscopy (SEM) examination (Fig. 2). Spalling of the hydrated layer was non-homogeneous and provoked cracking at the fibre surface.

These surface defects were responsible for the significant decrease in fibre strength. Note that no sensible

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[1] $t = 0.74$, 68 degrees of freedom.

[2] $t = 3.54$, 38 degrees of freedom.

[3] $t = 1.89$, 38 degrees of freedom.

**Table 1** Tensile properties for as-prepared $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres in 30 mL doubly distilled water at 37 °C

| Immersion time (days) | Sample number, N | Diameter (μm) | Nominal strain at break (%) | Tensile strength (GPa) | Tensile modulus (GPa) | Normalising strength $\sigma_0$ (GPa) | Weibull modulus, $m$ |
|---|---|---|---|---|---|---|---|
| 0 | 50 | 15.4 (2.8) | 1.15 (0.39) | 0.484 (0.153) | 44.0 (4.8) | 0.538 | 3.6 |
| 1 | 20 | 15.4 (1.4) | 1.07 (0.23) | 0.457 (0.097) | 45.4 (4.1) | 0.496 | 5.5 |
| 3 | 20 | 15.2 (1.8) | 0.86 (0.13) | 0.367 (0.064) | 43.9 (5.6) | 0.394 | 6.1 |
| 7 | 20 | 25.8 (4.6) | 0.77 (0.19) | 0.323 (0.083) | 46.6 (3.7) | 0.353 | 5.2 |

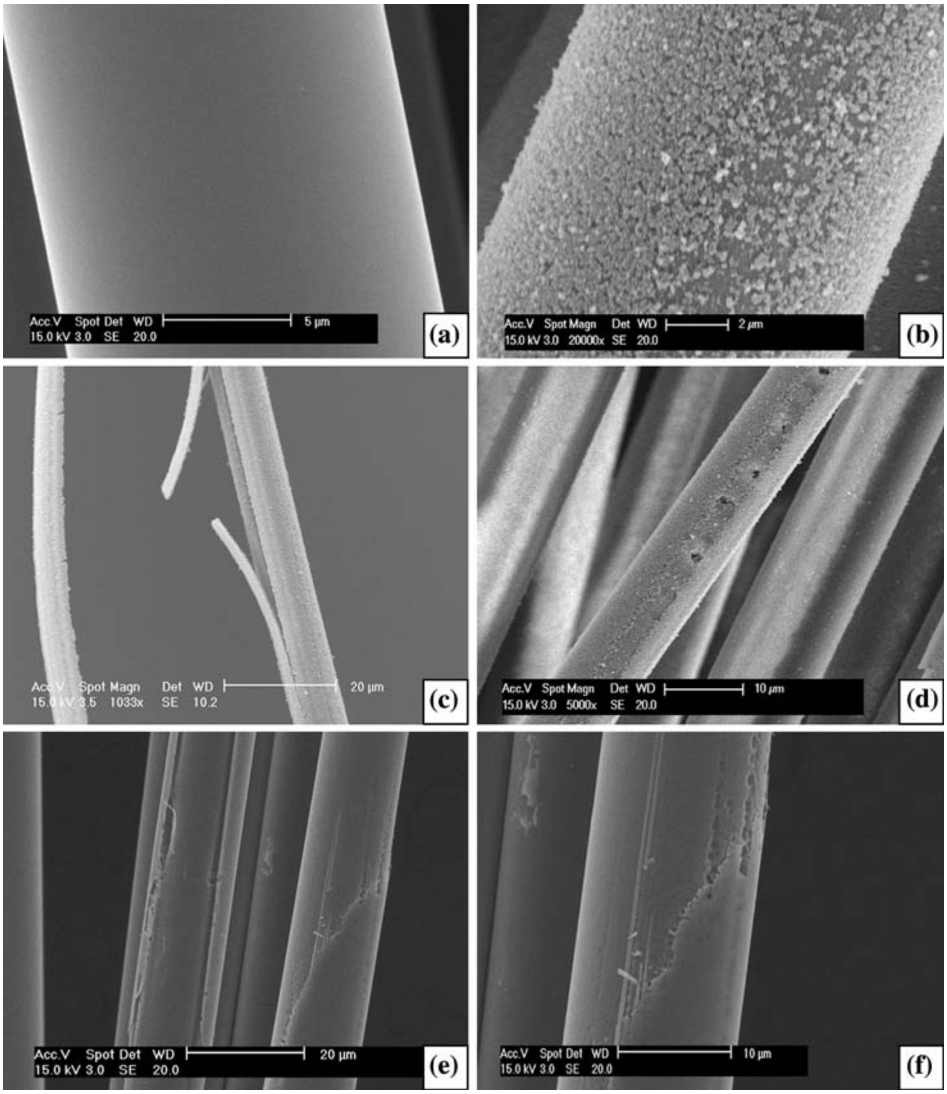

**Fig. 2** $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres: (**a**) in their original state, (**b**–**d**) as-prepared fibres aging in 30 mL doubly distilled water at 37 °C for 7 days, (**e**) and (**f**) annealed fibres aging in 30 mL doubly distilled water at 37 °C for 6 weeks

reduction in fibre diameter was recorded during the test period. The fibres persisted after 6 weeks in 30 mL of water[4] whereas they disappeared after 30 days in 400 mL water[5] as discussed in another study [4]. The solution is likely to have saturated with the release of hydrated metaphosphates due to the high surface area to solution volume ratio. Therefore, the dissolution rate in 30 mL of water was slowed down given that the solution was static [10]. As a consequence, this might result in an overestimation of the fibre strength.

## Sized $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres

Table 2 summarises the mechanical properties for sized $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres in 30 mL doubly distilled water at 37 °C up to 7 days. The 7 days data were augmented by high-speed fractography. The strength decay

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[4] Initial mass of approximately 30 mg.

[5] Initial mass of approximately 90 mg.

**Table 2** Tensile properties for sized $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres in 30 mL doubly distilled water at 37 °C

| Immersion time (days) | Sample number, N | Diameter (μm) | Nominal strain at break (%) | Tensile strength (GPa) | Tensile modulus (GPa) | Normalising strength $\sigma_0$ (GPa) | Weibull modulus, *m* |
|---|---|---|---|---|---|---|---|
| 0 | 36 | 16.5 (3.8) | 1.15 (0.26) | 0.496 (0.101) | 46.9 (5.1) | 0.537 | 5.6 |
| 1 | 20 | 13.7 (3.1) | 0.82 (0.22) | 0.342 (0.091) | 43.4 (6.8) | 0.377 | 4.0 |
| 3 | 20 | 18.3 (2.9) | 0.63 (0.17) | 0.282 (0.073) | 47.6 (6.2) | 0.310 | 4.5 |
| 7[a] | 37 | 18.4 (1.6) | 0.66 (0.18) | 0.245 (0.066) | 38.7 (5.2) | 0.270 | 4.4 |

[a] High-speed camera was used during the tensile testing of these fibres

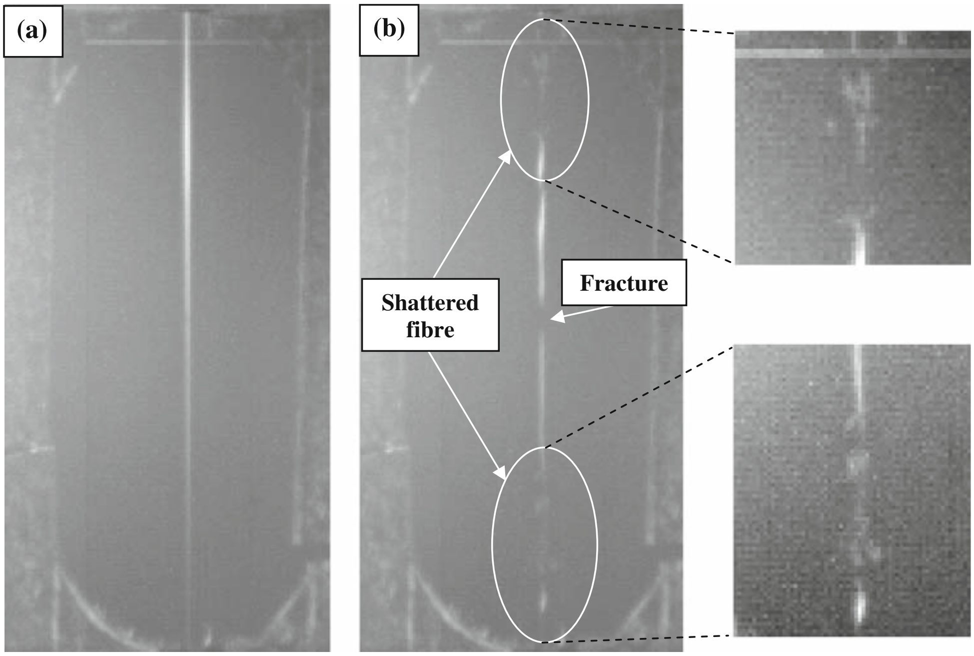

**Fig. 3** Tensile testing: (**a**) before, (**b**) after fracture. Consecutive images taken at 20,000 frames per second ($5 \times 10^{-5}$ s interval) of a silane-treated $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibre after 7 days aqueous aging

for these sized fibres was more immediate than their unsized counterparts,[6] becoming statistically significant at the 0.05% level[7] after only 1 day in solution. Between 1 and 3 days, the strength loss was significant at the 2.5% level.[8] After 3 days in water, the tensile strength was significantly lower than that for the as-prepared fibres at the same stage at 0.05% significance level[9] and this trend was also repeated at 7 days at 0.05%.[10] Between 3 and 7 days the strength loss in the sized fibres was marginally significant at the 5% level. It should be noted that the 7-day specimens were filmed using a high-speed camera and tested under spot lamps which increased the specimen temperature to 40 °C. Taking this uncertainty into account, it seems reasonable that the strength reduction was progressive throughout the 7-day aging period.

Single-fibre tensile testing involves a certain probability of failure within the adhesive or at the tabs. These end effects arise from non-uniform stress distribution at discontinuities (stress concentration) where the adhesive secures the fibre. The adhesive surrounding the fibre is a discontinuity. At some region near the discontinuity the stress will be higher than the average stress at distances removed from it. Some failures will inevitably follow this effect, rather that of the flaw population. However, the relative importance of end effects decreases inversely with gauge length. Stoner et al. [11, 12] demonstrated that end effects existed for gauge lengths up to 40 mm for pitch-based carbon fibres. It was not possible to determine the fracture site for most samples with the naked eye since the fibres fractured explosively. Therefore, the high-speed fractography helped to identify where the failure initiated (i.e. at the adhesive or within the gauge length).

Figure 3 shows one test before and after fracture. An explosive fracture is evident at both ends and may be attributed to wave propagation from mid span, following

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[6] Sized fibres after 1 day in water are statistically lower than unsized fibres after 1 day at the 0.05% significance level (calculated $t = 3.87$, 38 degrees of freedom).

[7] Calculated $t = 5.66$, 54 degrees of freedom.

[8] Calculated $t = 2.31$, 38 degrees of freedom.

[9] Calculated $t = 3.92$, 38 degrees of freedom.

[10] Calculated $t = 3.91$, 55 degrees of freedom.

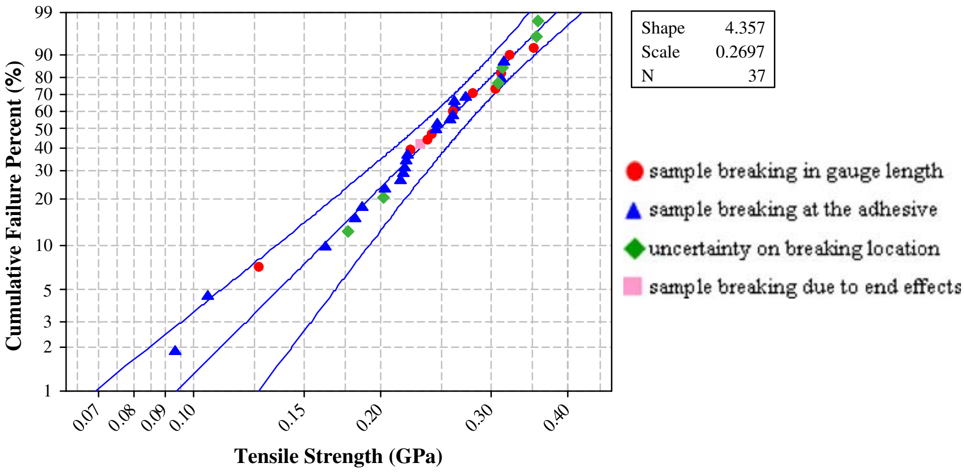

**Fig. 4** Weibull distribution for sized $P_{40}Na_{20}Ca_{16}Mg_{24}$ fibres immersed in 30 mL doubly distilled water at 37 °C for 7 days (25-mm gauge length) using APX high-speed camera to identify location of failure

**Table 3** Tensile properties for annealed $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres in 30 mL doubly distilled water at 37 °C

| Immersion time (days) | Sample number, N | Diameter (µm) | Nominal strain at break (%) | Tensile strength (GPa) | Tensile modulus (GPa) | Normalising strength $\sigma_0$ (GPa) | Weibull modulus, *m* |
|---|---|---|---|---|---|---|---|
| 0 | 20 | 18.1 (2.5) | 0.59 (0.11) | 0.288 (0.051) | 52.0 (4.7) | 0.309 | 6.0 |
| 1 | 20 | 16.6 (1.9) | 0.62 (0.14) | 0.307 (0.073) | 50.4 (7.0) | 0.335 | 4.7 |
| 3 | 20 | 15.1 (2.6) | 0.92 (0.26) | 0.459 (0.136) | 51.6 (4.1) | 0.509 | 3.7 |

similar behaviour to that reported in the classical studies of Griffith [13]. Of the samples tested, 27% failed within the gauge length, 56.8% failed at the adhesive and 2.7% failed due to end effects [11, 12].

Figure 4 shows the Weibull distribution of the fibre strength, sorted by failure mode. The samples fracturing within the gauge length followed a similar Weibull distribution to those fracturing at the adhesive and, because no single mode dominated one section of the curve, the samples failing at the adhesive were retained in the analysis.

The tensile modulus was unaffected by aging. However, the tensile strength was severely reduced. The as-prepared and sized fibres exhibited similar weakening whilst the increased proportion of failures at the adhesive (56.8% vs. 7.3% for as-prepared fibres[11]) also suggests that aging affects failure mode. This probably reflects a higher incidence of flaws and subsequent embrittlement at the adhesive as handling and mounting may induce further damage.

The tensile strengths of the sized fibres after aging were significantly lower than those for as-drawn equivalents. The aqueous silane sizing procedure (120 °C for 24 h) may have accelerated the loss in tensile strength, causing the flaws to become more severe. However, as the dissolution time increased, the silane goes into solution along with the spalling outer layer. Hence, the surface of sized fibres after 3 day aging might be similar to that of the as-prepared fibres and this would not explain the difference in tensile strengths (assuming dissolution down the fibre length).

## Annealed $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres

Table 3 summarises the mechanical properties of annealed $P_{40}Na_{20}Ca_{16}Mg_{24}$ fibres in the doubly distilled water at 37 °C up to 3 days. The tensile modulus was unaffected by aging and remained statistically higher than that of the as-prepared fibres. Heat treatment increased the tensile modulus of these glass fibres by approximately 15% [5]. This observation correlated with that of Murgatroyd [7, 8] for E-glass fibres i.e. that heat treatment to a high enough temperature (above 520 °C for E-glass fibres) increased the elastic modulus. A suggested explanation was that long chains might break up and displace in the axial direction, leading to a higher stiffness. However, the tensile strength generally increased with immersion time, becoming statistically significant after 3 days at 0.05% level[12] with a strength increase of approximately 62%. Annealing appeared to impart very significant improvements in durability, although the initial dry strength was significantly reduced compared to the as-drawn fibres. The strength loss was attributed to an increase in the number

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[11] See footnote 1.

[12] Calculated $t = 4.60$, 38 degrees of freedom.

and severity of flaws incurred during the annealing process [8]. Hayden et al. [9] showed that phosphate glasses annealed in ambient air had a greater hydroxyl content near the surface than in the interior. Ambient moisture attacks the glass surfaces during annealing, cleaving P–O–P chains and leaving behind shorter chains that terminate in hydroxyl groups. The resulting glass surface assumes different properties from those of the interior, including an increase in thermal expansion and a decrease in $T_g$. The surface layer contracts and this tensile layer promotes a network of shallow surface cracks, which may initiate fibre fracture. Once the annealed fibres were immersed, the tensile surface layer may dissolve. An spalling outer hydrated layer was also noted by Choueka et al. [1] on annealed fibres. Hence, the spalling between 1 and 3 days due to the hydration reaction may yield a new surface (see Fig. 2). It is believed that annealed fibres lost part of the oriented structure imparted by the fibre drawing via relaxation of the polymeric chains, giving fibres a structure close to that of bulk glass [1, 6, 8]. Because of the formation of a more durable structure, annealed fibres dissolved more slowly and would be less susceptible to stress corrosion effects [14–16]. Thus, the apparent increase in tensile strength as the annealed fibres are aged may be explained by the progressive removal of the outer tensile layer with its inherent flaws, over 1–3 days in this particular test. Extension of the test period should yield interesting information concerning the latter stages of this potentially complex mechanism.

## Conclusions

The tensile strength of the as-prepared and sized $P_{40}Na_{20}Ca_{16}Mg_{24}$ phosphate glass fibres in 30 mL doubly distilled water at 37 °C decreased with immersion time and this effect was not moderated by silane pre-treatment. However, annealed fibres exhibited a progressive tensile strength increase under similar conditions. High-speed fractography showed that the percentage of fractures at the adhesive increased for aged fibres compared to those in their original state and this was attributed to a greater frequency of flaws in the aged specimens.

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