HEAT-TREATMENT OF PHOSPHATE GLASS FIBRES AND ITS EFFECT ON COMPOSITE PROPERTY RETENTION

Andrew J. Parsons, Ifty Ahmed, Jing Yang, Sophie Cozien-Cazuc, Chris D. Rudd
School of M3, University of Nottingham, UK

Keywords: *Phosphate glass, fibre, composite, resorbable, heat-treatment*

Abstract

Degradable phosphate glass fibres were produced using a melt-drawing process and then subject to heat-treatment in order to assess the change in their properties and in the properties of polycaprolactone composites reinforced with the fibres. It was found that the heat-treatment causes a change in the mode of degradation of the fibres that is attributed to the relaxation of the glass structure. The heat-treatment also increases the fibre stiffness but causes an initial loss in strength that recovers as the fibre degrades. Composites made using the fibres showed a better long-term retention of properties but still suffered an initial loss in properties comparable to composites produced using non heat-treated fibres. Early stage losses in composite properties would appear to be the result of another process that is not related to the fibre degradation.

1 Introduction

Current degradable medical implant devices are based on polymers such as polylactic acid (PLA), polyglycolic acid (PGA) and polycaprolactone (PCL), sometimes self-reinforced, that can only provide low modulus materials of a few GPa [1]. Compounding this, these polymers degrade through bulk hydrolysis, resulting in a rapid loss of mechanical properties before any significant loss of volume [2]. As a result, current resorbable composites do not provide load-bearing support in the body. Structural implants rely on durable materials such as metal alloys and ceramics that exceed the stiffness of parent bone tissue approximately tenfold [3]. Because the bone structure constantly adjusts to local conditions, this tends to weaken surrounding tissues and can result in recurring damage after removal of the device [4].

Several resorbable polymer composites have been produced with Bioglass® reinforcement [5,6] a phosphate doped silica glass which has good bone bonding properties but that is essentially non-resorbable. However, silica-free phosphate glasses can be produced that possess appropriate stiffness values and are entirely resorbable.

Phosphate glasses fibres are of interest to the field of biomedical materials as they represent one of very few types of totally resorbable yet high stiffness, synthetic fibre. Additionally, the phosphate and often calcium components of phosphate glass fibre make them particularly attractive in hard tissue applications. Phosphate glasses have seen successful use in dental cement [7] and in glass-ceramic components for bone repair [8]. Less success has been apparent in the production of phosphate glass fibre composites, due to a rapid loss in properties [9].

To date relatively few resorbable composites have been produced using phosphate glass and only two papers report composites that have been produced using long fibres of phosphate glass [9,10]. A phosphate glass fibre composite would represent a very attractive possibility for hard tissue repair. The combination of glass and fibre properties would allow the production of easily formable but mechanically robust implant materials, capable of complete resorption in the body. Research into these materials has been ongoing for over a decade and while initial composite properties have been very encouraging, it is the rapid loss of properties in an aqueous environment that has caused concern.

Work is presented that has been undertaken in order to attempt to extend the lifetime of the mechanical properties of phosphate glass fibres and composites produced using these fibres when subjected to a aqueous environment. Fibres were treated thermally in order to affect their degradation.

2 Materials and Methods

2.1 Glass Fibre Production

ANDREW J. PARSONS, Ifty Ahmed, Jing Yang, Sophie Cozien-Cazuc, Chris D. Rudd

A 5%Au/95%Pt alloy crucible is charged with the required mixture of phosphate salts. They are dehydrated for 1 hour at 350°C before being transferred to a 1200°C furnace for 2 hours. The glass is then cast onto a cold plate. The resulting glass cullet is transferred to the furnace in our glass fibre drawing equipment (cut-through in Fig.1). Normally the furnace is pre-heated to above the drawing temperature and then charged with around 50-75g of glass. The glass is allowed time to melt after which the temperature is reduced and the glass is drawn off as a single filament at up to 2000 rpm (providing diameters of around 10-40 μm) using a specially built winding apparatus. The fibres are then stored in a desiccator pending further treatment and use in composite fabrication.
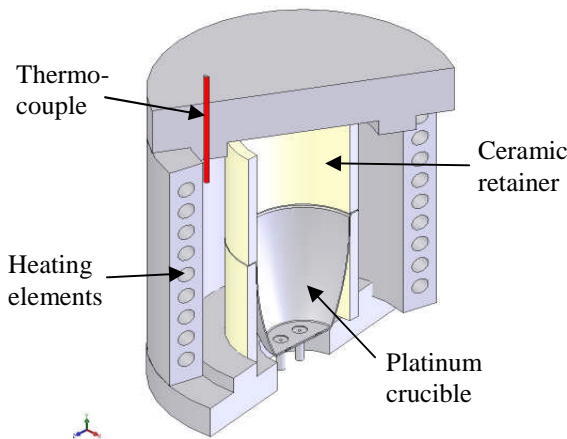

Fig. 1. Cut-through diagram of the drawing equipment used to produce phosphate glass fibres

2.2 Fibre Heat-Treatment

Selected fibres are placed into a cold furnace. They are heated up to ~5°C below their glass transition temperature (T_g) and held at this temperature for 90 minutes before gradually being cooled back down to room temperature.

2.3 Fibre Testing

The fibre surface is examined using scanning electron microscopy (SEM) on a Philips XL-30 SEM and stresses in the fibre are observed using cross-polar microscopy with a Leica TCS-4D microscope.

Fibre tensile properties were obtained by tensile testing single filaments using the standard BS ISO 11566. When performing a test, a single fibre was mounted on a paper frame with a gauge length of 25 ± 0.5 mm. The fibre was glued to the frame

with epoxy adhesive (Optum Powerfit®) cured at room temperature, see Fig. 2. Once prepared the sample was gripped in the tensile machine (Lloyd Instruments M30K, 5N load cell - see Fig. 2). The paper sections were cut before starting the test. A crosshead speed of 1 mm/min was used. Displacement of the crosshead was monitored using a Linear Variable Differential Transducer (LVDT). Heat-treated and non heat-treated fibres were tested as drawn and after 1 and 3 days immersion in deionised water at 37ºC. For each specimen, the fibre diameter was determined using an optical microscope (Nikon Optiphot). The measurement was taken through a x1000 magnification lens in reflection mode using a calibration standard (Graticules, Ltd). The diameter variation for all the glass fibres along a 25 mm gauge length did not exceed 0.5 μm. Tensile moduli and strengths were determined as per the directions in the standard (Method B). Weibull analysis was used to provide a statistical base for fibre properties. Bioglass®45S5 and E-glass fibres provided controls and comparisons to literature values have been made [11,12].
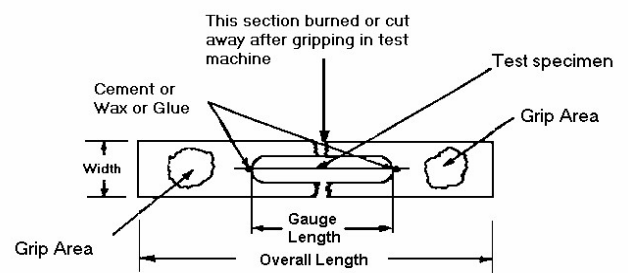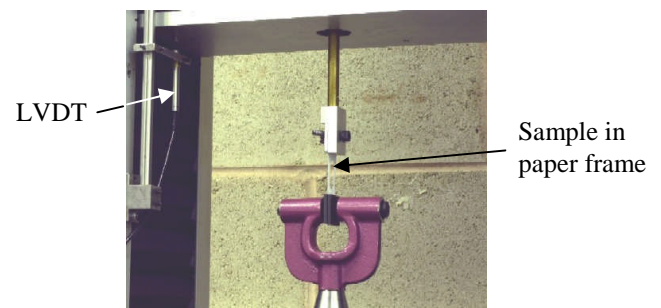

Fig. 2. Photograph (top) of the tensile testing rig and a schematic (bottom) of the paper template used to hold the fibre during testing (schematic taken from the international standard BS ISO 11566)

2.4 Glass Fibre Mat Production

To make each chopped fibre mat, 3g of fibres were put into 4 litres of a standard water-based dispersion medium containing 3g/l viscosity

modifier hydroxyethyl cellulose (HEC, from Dow Chemical Company). The mix is then stirred at 600 rpm for 5 minutes and then a wire mesh is drawn through the mix in order to form a 16cm diameter fibre mat. The mat is washed with water for 10 minutes in order to remove residual HEC and then dried in an oven at 120ºC for 20 minutres before being stored in a desiccator until use. The distribution of fibre lengths in the fibre mats is shown in fig.3.
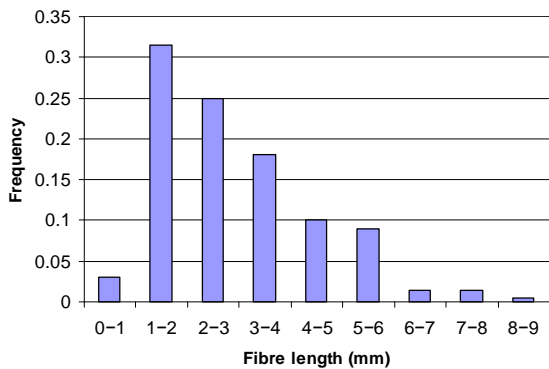

Fig. 3. Distribution of fibre lengths in fibre mats

2.5 Composite Production

Composites are produced by standard film stacking methods. The composites were made using heat-treated and non heat-treated fibres of the type Ca16Mg24Na20P40 prepared as random fibre mats as described in section 2.4. Four fibre mats were interspersed with the required number of sheets of PCL (made using pellets of PCL obtained from Aldrich, Average M_w ~65,000) and pressed at 150ºC and 100 bar for 10 minutes in order to produce composites with a nominal fibre volume fraction of

12%. After the hot press the samples were transferred to a room temperature press at 100 bar and allowed to cool for 10 minutes.

2.6 Composite Testing

Mechanical properties of the composites were assessed in triplicate using a 3-point bend test according to BS EN ISO 14125 on a Hounsfield Series S testing machine. Samples of the composites were then immersed in deionised water at 37°C and tested weekly.

Fracture surfaces of the composites were produced by cooling the composites using liquid nitrogen and then snapping them with by hand.

3 Results

Table 1 shows the fibre testing results for a range of fibres that have been produced, along with E-glass and Bioglass® comparisons and Weibull analysis results (Fig. 4. shows an example Weibull plot). Tensile moduli for the phosphate glass fibres lay between 20 and 50 GPa and tensile strengths lay between 140 and 500 MPa. The tensile modulus results obtained for Bioglass® and E-glass fibre are very close to those provided by literature. The phosphate fibre modulus is of the same order as seen in literature but considerably lower value, though the measurements in the literature were taken by a different means. Tensile strength values observed are all significantly lower than expected. The Weibull modulus, m, gives information about the physics of the fibre failure. The higher the value of m, the smaller the variation in stress to failure [13]. All the fibres show low values of m, which is common to this type of material (for ceramic-type materials, m generally lies in the range 2-15).

Table 1. Mechanical properties of selected fibre compositions (standard deviation in brackets)

| Fibre type (by oxide content)	Flexural Modulus (GPa)	Flexural Strength (GPa)	Weibull parameter m
Bioglass® 45S5	69(16)	0.4(0.1)	3.8
Bioglass® 45S5 (from literature [11])	67(13)	0.7(0.2)	3.6
E-glass (from roving)	59(5)	1.9(0.2)	13.4
E-glass (from literature [12])	70	5.8	-
Na50P50	23(4)	0.14(0.07)	2.5
Na50P50 (from literature [12])	35.7	1.8	-
Ca24Mg16Na20P40	47(6)	0.3(0.1)	3.5
Ca20Mg20Na20P40	49(14)	0.4(0.1)	4.2
Ca16Mg24Na20P40	44(5)	0.5(0.2)	3.6
Ca16Mg24Na20P40 (1 day degraded)	45(4)	0.5(0.1)	5.5
Ca16Mg24Na20P40 (3 days degraded)	44(6)	0.37(0.6)	6.1
Ca16Mg24Na20P40 (heat-treated)	52(5)	0.29(0.05)	6.0
Ca16Mg24Na20P40 (heat-treated, 1 day degraded)	50(7)	0.31(0.08)	4.7
Ca16Mg24Na20P40 (heat-treated, 3 days degraded)	52(4)	0.5(0.1)	3.7
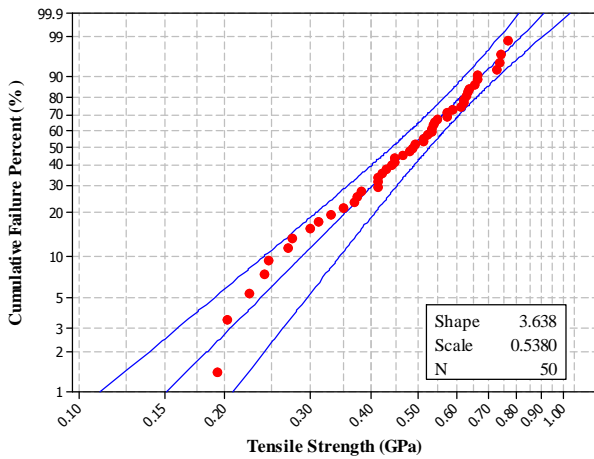
Fig. 4. Example Weibull plot of fibres of the Ca16Mg24Na20P50 glass composition produced using the Maximum Likelihood Estimation method on Minitab 14.2 software

Notably, the heat-treatment process appears to provide an increase in modulus but a decrease in initial strength which recovers during degradation. SEMs of the fibre surfaces for the Ca16Mg24Na20P40 composition are shown in Fig. 5 and cross-polar microscopy images are shown in Fig. 6. It can be seen that the heat-treatment appears to alter the manner in which the fibres degrade, with non heat-treated fibres suffering from surface roughening. The heat-treated fibres present a relatively pristine surface, seeming to undergo an initial slight roughening before becoming smooth again, with gradual degradation almost uniformly across the surface. The cross-polar pictures show that only the non heat-treated, non-degraded fibre exhibits any stress (a thin yellow line at the fibre edge) though there are no stresses apparent across the fibres, just at the surface.

Fig. 7 shows the change in modulus and strength for the composites over a 28 day period. It can be seen that while the properties of the non heat-treated fibre containing composites drop to that of the matrix material within the space of a week, the heat-treated fibre containing composites maintain around 50% of their initial modulus and 75% of initial strength at 28 days. Figs. 8 and 9 show SEM pictures of fracture surfaces of the heat-treated and non heat-treated fibre containing composites at 3, 7, 14 and 28 days. The difference in modes of degradation is quite clear.

4 Discussion

The phosphate fibres demonstrated good moduli, which were in the range that would be expected from literature [12], but the strength offered scope for improvement. Also, Weibull analysis indicated low *m values* which, when coupled with low strength values, suggests that the fibres have significant surface defects. These surface defects are likely a result of the drawing and handling process. The presence of defects is not echoed in the SEM images which show a very smooth surface finish (see Fig. 5).

Only the as-drawn, non heat-treated fibres show any surface stress in cross-polar microscopy
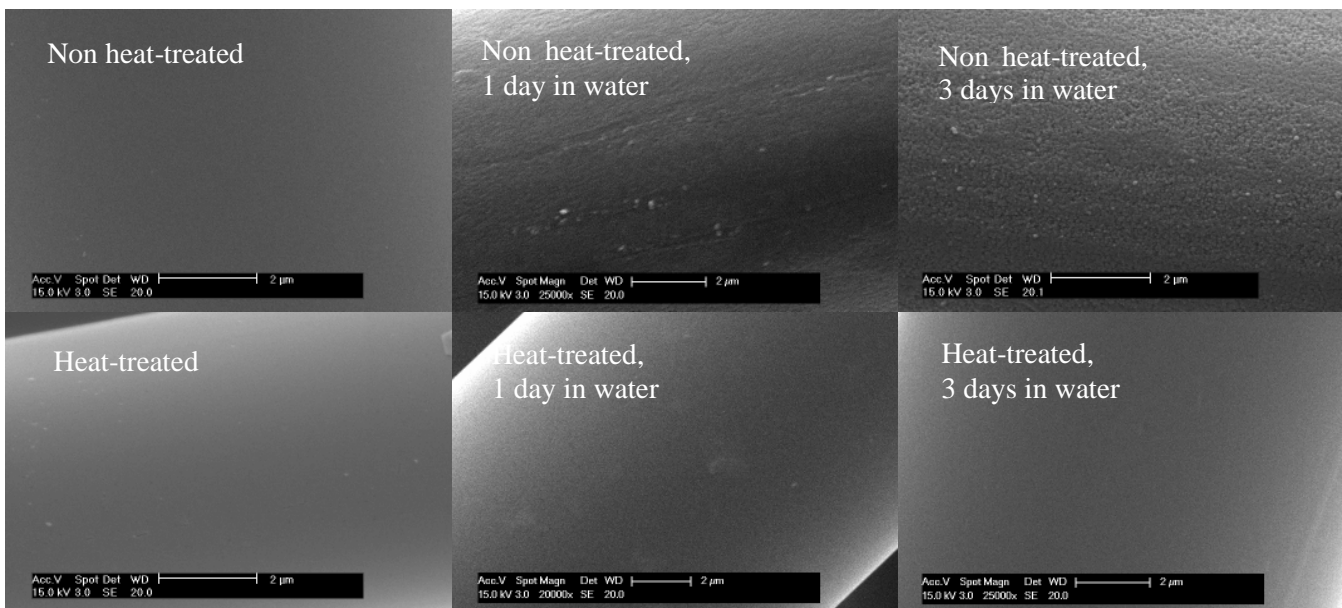

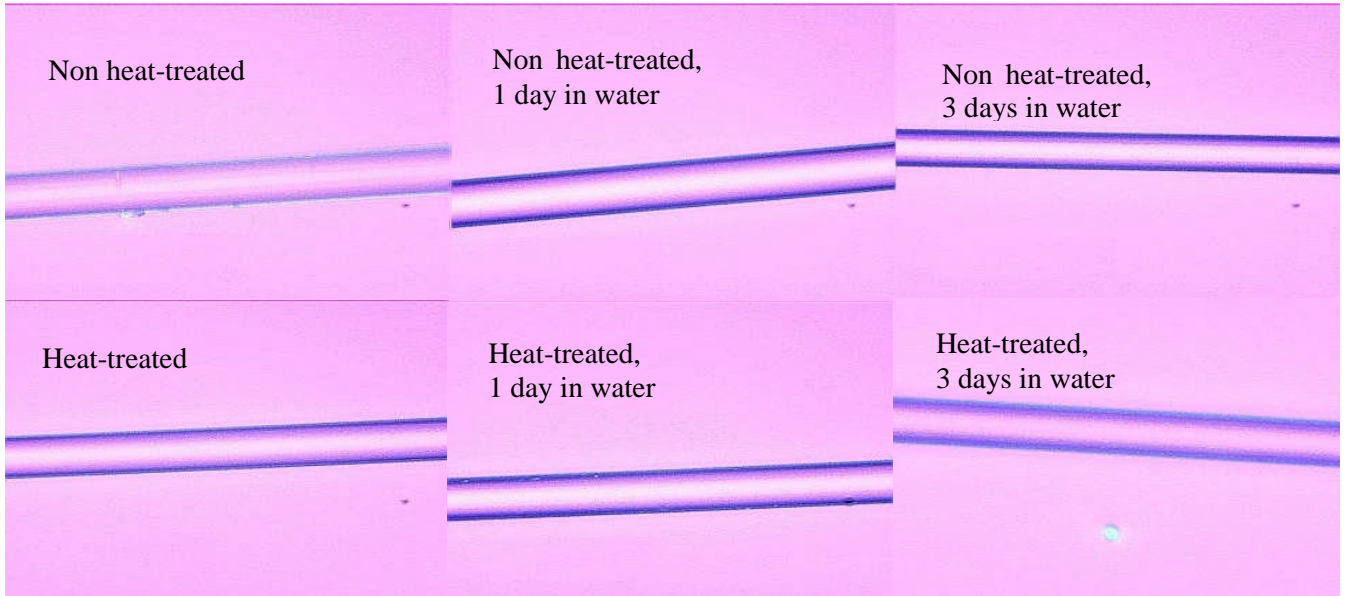Fig. 5. SEMs of the surface of degrading fibres

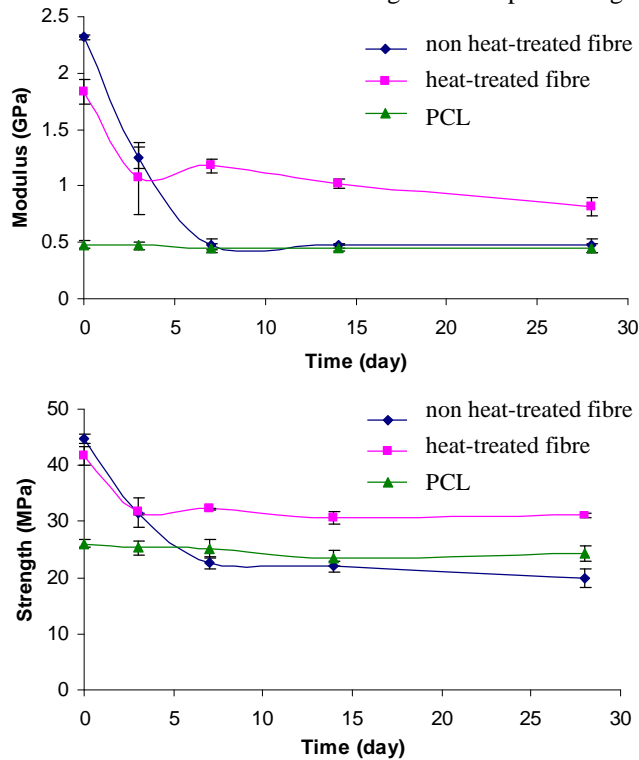Fig. 6. Cross polar images of the surface of degrading fibres

Fig. 7. Property retention of composites after degradation

even though the heat-treated fibres exhibit lower strength. This stress is also likely to be due to the drawing process, since the fibres are drawn under high shear and cool very rapidly. The observation fits well with traditional expectation of stress developed in rapidly cooled glass systems [14] and observations with E-glass [15].

These results would suggest that while heat-treatment does reduce stresses, it also exacerbates existing flaws in the surface. The nature of these surface flaws is less apparent. No cracks or defects

are obvious on the fibre surface in the SEM images. Defects may exist that cannot be seen at the resolution of SEM microscopy or point-stresses may exist that are not detectable in the resolution of the cross-polar microscopy. It is likely that there are very small imperfections on the surface of the fibre that are exacerbated by hydrolytic attack until they reach critical length, at which time they cause the surface to fracture. This extensive surface cracking can be seen in the SEMs of the composites at later stages (see Fig. 8).

However, other studies [16] suggest that heat-treatment of a phosphate glass produces a tensile layer on the surface due to the interaction of water causing a surface re-arrangement. This is not apparent in the cross-polar images but may be below the level of resolution. This would account for the low initial strength values, since the tensile layer would be prone to cracking, and also fits quite well with the SEM observation of an initial slight roughening (which could be the loss of this stressed layer) followed by a uniform degradation. This is also corroborated by an increase in the strength of heat-treated fibre after 3 days in water (see Table 2).

The affect of heat-treatment extends to the behaviour of composites produced using the fibres. The rapid loss of properties for non heat-treated fibre containing composites is evident and can be ascribed to water attacking weak spots in the fibre surface that are under stress and causing fragmentation of the fibre. However, even though the heat-treated fibre composites maintained their properties for longer, the initial drop in properties follows a very similar profile to that of the non heat-treated composites (see Fig. 7). This suggests that
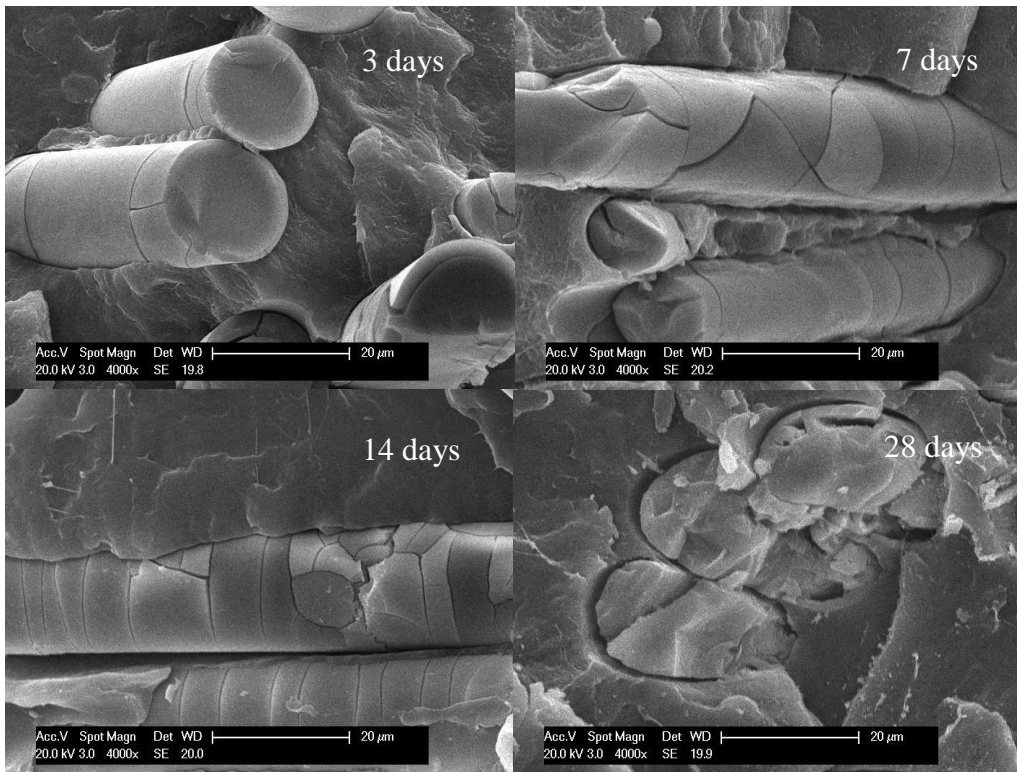
Fig. 8. Fracture surfaces of degraded composites containing non heat-treated fibres
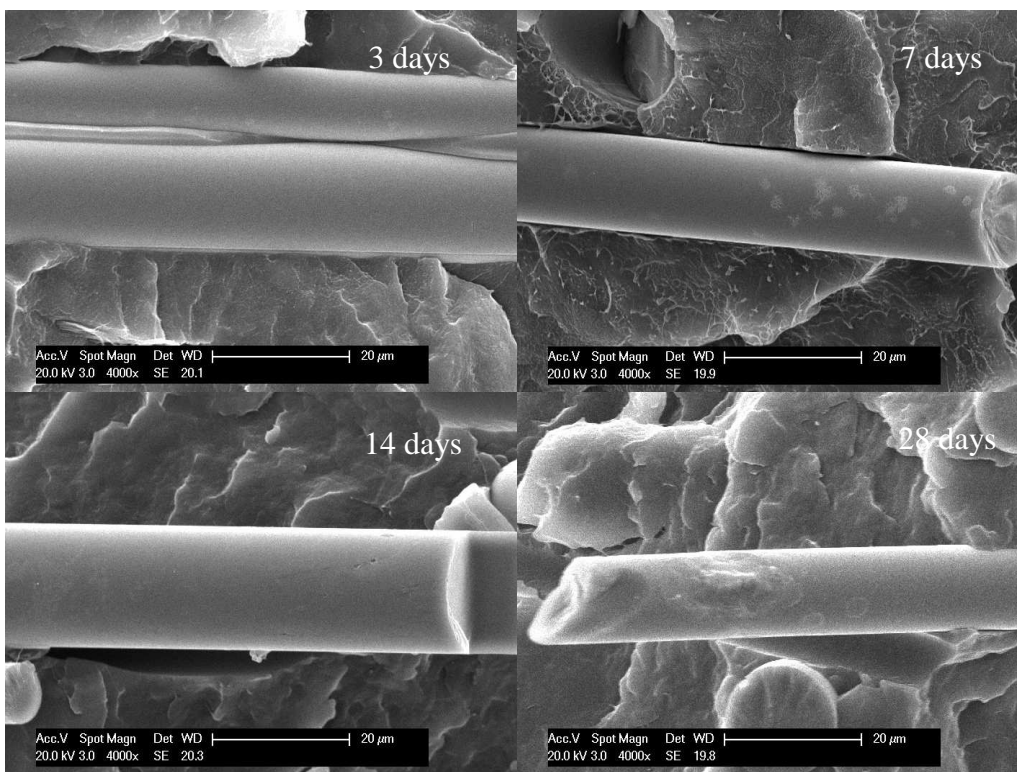

Fig. 9. Fracture surfaces of degraded composites containing heat-treated fibres

there is another mechanism in place to decrease the mechanical properties of phosphate glass composites other than the fibre degradation. It is likely that this is related to the infusion of water into the fibre/matrix interface, lubricating the fibre surface and causing a reduction in the interfacial shear strength and a drop in macroscopic properties. This effect would seem to occur relatively rapidly,

taking a few days. After this stage the composite properties arguably plateau in the case of the still smooth heat-treated fibres or drop to zero with the badly damaged non heat-treated fibres.

Overall the heat-treatment of the fibres provides an improved mode of degradation at a cost of a proportion of the initial strength, though this could be mitigated somewhat by a more gentle

drawing process, including the use of sizing. While the heat-treated fibres present a means of extending the effective life of a resorbable composite there is still an initial drop of properties attributable to another process. This is likely to be related to water ingress into the interface region of the composite and reinforces the significant need for further research into coupling agents specific to the phosphate glass/polymer interface. Silane coupling agents are effective at bonding to silica glasses but little long-term success has been achieved when using silanes with phosphate glasses [9].

5 Conclusions

Heat-treatment of phosphate glass fibres relieves the stress created by the fibre drawing process, reducing their susceptibility to stress corrosion and thereby altering their mode of degradation. This process allows the phosphate glass fibres to maintain their integrity and mechanical properties over a longer period of time. Very early stage loss of properties in resorbable phosphate glass fibre composites is not dependent on the degradation of the fibre.

References

[1] Vainionpaa, S., Rokkanen, P. and Tormala, P. "Surgical applications of biodegradable polymers in human tissues". *Progress in Polymer Science,* Vol. 14, No. 5, pp 679-716, 1989.

[2] Pietrzak, W. S., Sarver, D. and Verstynen, M. "Bioresorbable implants – practical considerations". *Bone,* Vol. 19, No. 1 suppl, pp 109S-119S, 1996.

[3] Long, M. and Rack, H. J. "Titanium alloys in total joint replacement. A materials science perspective". *Biomaterials,* Vol. 19, No. 18, pp 1621-1639, 1998.

[4] Bobyn, J. D., Mortimer, E. S. and Brooks, C. E. "Producing and avoiding stress shielding. Laboratory and clinical observations of noncemented total hip arthroplasty". *Clinical orthopaedics and related research, Vol.* 274, pp 79-96, 1992.

[5] Kokubo, T., Kim, H.-M. and Kawashita, M. "Novel bioactive materials with different mechanical properties". *Biomaterials,* Vol. 24, No. 13, pp 2161-2175, 2003.

[6] Leonor, I. B., Sousa, R. A. and Greenspan, D. "Novel starch thermoplastic/Bioglass® composites: Mechanical properties, degradation behaviour and in-vitro bioactivity". *Journal of Materials Science: Materials in Medicine,* Vol. 13, No. 10, pp 939-945, 2002.

[7] Chen, W. S. and Monroe, E. A. "Phosphate glass cement bone graft*". Biomaterials*, Vol 12, No 6, pp 561-564, 1991.

[8] Dias, A. G., et al. "In vivo performance of biodegradable calcium phosphate glass ceramics using the rabbit model: histological and SEM observation". *Journal of Biomaterials Applications*, Vol 20, No 3, pp 253-266, 2006.

[9] Lin, S. et al. "Totally Bioabsorbable Composites". *International SAMPE Symposium and Exhibition*, Vol 39, pp 1981-1985, 1994.

[10] Casper, R. A., et al. "Fiber-reinforced absorbable composite for orthopedic surgery". *Polymeric Materials Science and Engineering*, Vol. 53, pp 497-501, 1985.

[11] Park, J.-M., Kim, D.-S. and Kim, S.-R. "Interfacial properties and microfailure degradation mechanisms of bioabsorbable fibers/poly-L-lactide composites using micromechanical test and nondestructive acoustic emission". *Composites Science and Technology, Vol.* 63, No. 3-4, pp 403-419, 2003.

[12] Kurkjian, C. R. "Mechanical properties of phosphate glasses". *Journal of Non-Crystalline Solids,* Vol. 263&264, pp 207-212, 2000.

[13] Hull, D. and Clyne, T. W. "*An Introduction to Composite Materials*". 2nd edition, Cambridge University Press, 1996.

[14] Varshneya, A. "*Fundamentals of Inorganic Glasses*". Academic Press, London, 1994.

[15] Stockhorst, H and Brückner, R. "Structure sensitive measurements on E-glass fibers". *Journal of Non-Crystalline solids*, Vol. 49, pp 471-484, 1982.

[16] Hayden, J. S., Marker III, A. J. and Campbell, J. H. "Surface tensile layer generation during thermal annealing of phosphate glass". *Journal of Non-Crystalline Solids,* Vol. 263&264, pp 228-239, 2000.