

# SUITABILITY OF PHOSPHATE GLASS FIBRES FOR RESORBABLE BIO-MEDICAL COMPOSITES

S. Cozien-Cazuc<sup>1</sup>, A.P. Parsons<sup>1</sup>, L.K. Burling<sup>1</sup>, G.S. Walker<sup>1</sup>, I.A. Jones<sup>1</sup>, F. Robitaille<sup>2</sup> and C.D. Rudd<sup>1</sup>

<sup>1</sup> *School of Mechanical, Materials and Manufacturing Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD*

<sup>2</sup> *Department of Mechanical Engineering, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5*

**SUMMARY:** Bio-medical composite materials made from a degradable poly( $\epsilon$ -caprolactone) (PCL) matrix and degradable phosphate glass fibres are being developed for skull bone repair. Unique fibre tensile properties were obtained by testing single filaments to BS 11566. The phosphate glass fibres offer tensile moduli between 23 and 57 GPa and tensile strengths between 0.1 and 0.9 GPa. A detailed study of  $P_{40}Na_{20}Ca_{16}Mg_{24}$  quaternary phosphate glass fibres was carried out (immersion in distilled water at 37 °C, annealing treatment and sizing). The degradation of  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres was carried out in distilled water at 37°C giving novel results on fibre degradation rate. Tensile testing of  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres was performed at several gauge lengths (10, 25 and 40 mm) to determine the fibre strength at the critical length  $l_c$  by applying Weibull distribution.

**KEYWORDS:** degradable phosphate glass fibres, single-fibre tensile testing, degradation test, Weibull distribution

## INTRODUCTION

Between April 2001 and March 2002, there were just over 39,000 fractures of skull bones recorded in NHS Hospitals in England. About 20,000 of them required an operation [1]. For a human being, Young's modulus of compact bone ranges from 3 to 30 GPa [2]. Human bones are composite materials with anisotropic properties made of collagen fibres and apatite mineral crystals. Bone repair can be carried out by tissue transplant or by using synthetic implants made from metals, bio-ceramics, polymers or composites. The problem with tissue transplant is the risk of infection. Current biomaterials are metals, ceramics, polymers and composites. Disadvantages of metal implants include low biocompatibility and high stiffness compared to bone. Disadvantages of ceramics include high modulus, brittleness, low fracture strength and difficulty of manufacture. More specifically, the elastic moduli of metals and ceramics are at least 10-20 times higher than that of bone. The mismatch of stiffness between bone and implant is a major problem. In the load-sharing between bone and implant the amount of stress carried by each of them is directly related to their stiffness. The load is not sufficiently transferred to the surrounding bone and stress shielding occurs. It affects the bone remodelling and healing process leading to increased bone porosity. Therefore, ceramics and metals cause stress shielding around the fracture due to their high modulus. Polymers are too flexible and weak to meet the mechanical demands of orthopaedic surgery. Implants made of

polymer composite materials offer a good compromise since they exhibit appropriate moduli and high strengths and they offer similar structural properties to human tissues.

The aim of this project is to create a composite material for bone repair, such as in craniofacial and maxillofacial treatments, made of degradable constituents. For such repair, the mechanical properties of the implant are required to be retained for about six weeks after which the implant should begin to degrade and be absorbed in the body at the same time as bone is remodelling itself. A potential benefit of using degradable biomaterials is that there is no need for follow-up surgery.

Poly( $\epsilon$ -caprolactone) PCL, an aliphatic polyester, is chosen as matrix in this project. It degrades via hydrolysis. However, it has a low stiffness of 0.5 GPa [3]. To improve the mechanical properties of the polymer, fibre reinforcement is necessary. Several types of fibres are used nowadays as thermoplastic polymer reinforcement (see Figure 1).

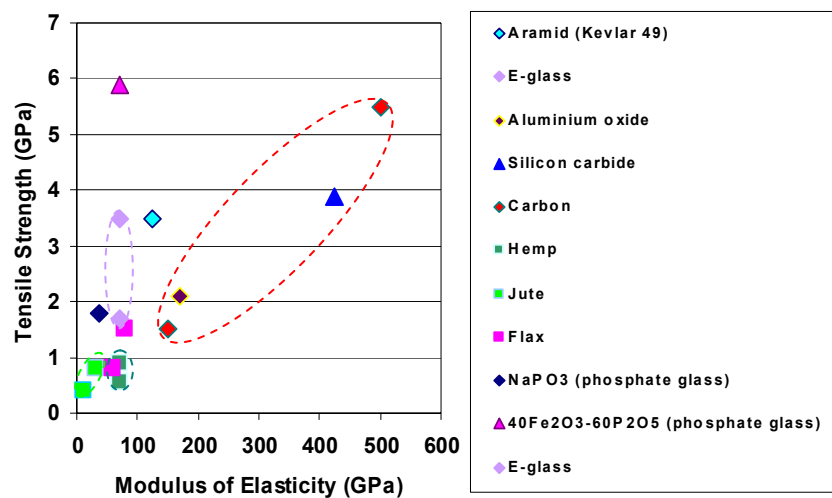


Fig. 1: Mechanical properties of several types of fibres [4-6]

Aramid, carbon and E-glass fibres are commonly used. But none of these fibres are degradable. Cellulosic natural fibres such as flax, jute and hemp encounter more and more interest as composite reinforcement. However, these fibres have dimensional instability. There is still research going on to find out if they are biocompatible and degradable in vivo [7]. Another family of fibres has been identified: phosphate glass fibres. Figure 2 shows the structure, the phosphate polymeric chains lie next to each other in planes, with cations in the spaces in between and ionically bonded to the polymer chains. The cations in the phosphate glass for biomedical applications include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ . Phosphate glasses are free of silica. They are degradable since they hydrolyse and break down into smaller water-soluble phosphate units. They are compatible with the mineral part of bone, named hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ .

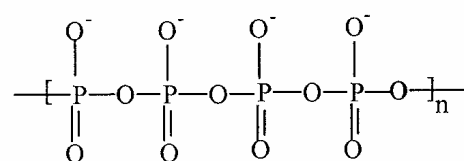


Fig. 2: The chemical structure of the phosphate inorganic polymeric backbone chain [8]

Therefore, the composite group at the University of Nottingham wants to tailor the properties of a degradable composite made of PCL and phosphate glass fibres to that of bone properties.

In this paper, the mechanical performance of phosphate glass fibres, their degradation behaviour and a Weibull analysis are presented.

## MATERIALS AND METHODS

### Materials

Several types of fibres were tested in this project: E-glass, Bioglass® 45S5 and phosphate glasses of different formulations. E-glass and Bioglass® 45S5 fibres were used to provide a comparison. The mechanical properties of these fibres are needed in their original state, sized, annealed and after immersion in water, in order to determine residual properties. Some of the phosphate glass fibres were drawn by hand. Appropriate quantities of phosphate salts were combined together and melted in 5 % Au / 95 % Pt crucibles at 1200 °C for several hours. The fibres were drawn by winding them on a drum rotating at a speed of 7.75 m/s.

Table 1 shows the formulation of several types of quaternary phosphate glass fibres. One type of quaternary phosphate glass fibres ( $P_{40}Na_{20}Ca_{16}Mg_{24}$ ) were drawn on a rig at the University of Nottingham (diameter between 10 and 25  $\mu m$ ). The rig had a large ceramic heating element which can go up to 1250 °C. The crucible is made of a 10 % Rh / 90 % Pt alloy with a single bushing hole from which to draw a fibre. The draw off device is capable of 2000 rpm and is 1 m in circumference.

*Table 1: Quaternary phosphate glass codes and metal oxide nominal composition in mol %*

Glass code	P <sub>2</sub> O <sub>5</sub> content	Na <sub>2</sub> O content	CaO content	MgO content
P <sub>40</sub> Na <sub>20</sub> Ca <sub>8</sub> Mg <sub>32</sub>	40	20	8	32
P <sub>40</sub> Na <sub>20</sub> Ca <sub>16</sub> Mg <sub>24</sub>	40	20	16	24
P <sub>40</sub> Na <sub>20</sub> Ca <sub>20</sub> Mg <sub>20</sub>	40	20	20	20
P <sub>40</sub> Na <sub>20</sub> Ca <sub>24</sub> Mg <sub>16</sub>	40	20	24	16

### Methods

#### *Fibre Mechanical Performance*

Fibre tensile properties were obtained by tensile testing single filaments using the British standard ISO 11566. When performing a test, a single fibre was mounted on a paper frame. Most of samples have a gauge length of  $25 \pm 0.5$  mm. The fibre was glued to the frame with epoxy adhesive. Once prepared the sample was gripped in the tensile machine (Lloyd Instruments M30K, 5 N load cell). Before starting the test, the paper sections were cut using a pair of scissors. A crosshead speed of 1 mm/min was used. Displacement of the crosshead was monitored using a LVDT (Linear Variable Differential Transducer). Each result reported in this paper represents the average of 20 values of the modulus and strength. For each fibre tested the diameter was determined using an optical microscope (Nikon Optiphot).

#### *Fibre Degradation*

The degradation of phosphate glass fibres was monitored as a function of time, measuring the mass loss of fibres using an analytical balance. The experimental set-up was modified from that used by Rinehart *et al.* [9]. A bundle of phosphate glass fibres was held in an aluminium frame and hung from the under-hook of a CP 225D Sartorius analytical balance. The frame with the bundle of fibres was immersed in a beaker filled with 400 ml of distilled water,

which was degassed for at least half an hour. 20 ml of oil was added on top of water to prevent evaporation once the fibres were immersed in the water. The beaker was placed in a water bath at 37 °C. The weight loss of the bundle of fibres was recorded by a laptop via an RS-232C interface using SartoConnect software which permits recording of the weight in function of time. Two bundles of unsized  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres were studied. These bundles had a mass of 88 mg and 89 mg.

### *Weibull Distribution*

In this project, it is important to understand the behaviour at the interface between the PCL and the phosphate glass fibres. The method selected to study this interface was the single-fibre fragmentation testing, which allows determination of the shear strength at the interface. Eqn. 1 shows that the strength of the fibre at the critical length  $\sigma(l_c)$  needs to be determined.

$$\tau = \frac{\sigma(l_c)}{2} \left( \frac{d}{l_c} \right) \quad (1)$$

Weibull distribution was used to determine this value. For a constant diameter, the failure probability of a fibre is:

$$P(\sigma_l) = 1 - \exp \left[ - \frac{l}{l_0} \left( \frac{\sigma_l}{\sigma_0} \right)^m \right] \quad (2)$$

where  $\sigma_l$  is the strength,  $m$  is the Weibull modulus (shape parameter) and  $\sigma_0$  is the normalising strength (scale parameter),  $l$  is the fibre length and  $l_0$  is the reference length.

Therefore, the average value of the strength  $\sigma_l$  at gauge length  $l$  can be calculated from the strength  $\sigma$  at gauge length  $l_0$ :

$$\langle \sigma_l \rangle = \langle \sigma \rangle \left( \frac{l}{l_0} \right)^{-1/m} \quad (3)$$

In this weakest-link model, it is assumed that the Weibull shape parameter is constant for all gauge lengths. It was found that, like the average strength, the Weibull modulus  $m$  also changes with gauge length (for aramid, carbon and glass fibres) [10-12]. To correct for this size effect a parameter  $\alpha$  between 0 and 1 (difficult to determine) could be used to calculate  $\sigma_l$ . Thus the modified Weibull model, also referred as to the three-parameter Weibull distribution, is

$$P(\sigma_l) = 1 - \exp \left[ - \left( \frac{l}{l_0} \right)^\alpha \left( \frac{\sigma_l}{\sigma_0} \right)^m \right] \quad (4)$$

or,

$$\langle \sigma_l \rangle = \langle \sigma \rangle \left( \frac{l}{l_0} \right)^{-\alpha/m} \quad (5)$$

Tensile testing of unsized  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres was carried out at different gauge lengths (10, 25 and 40 mm) to calculate the strength of the fibre at the critical length  $\sigma(l_c)$ . To determine the Weibull parameters for each gauge length, 30 samples were tested for each set of results. The statistical software used in this project was Minitab. The Maximum Likelihood (ML) estimation was chosen as method to analyse the data.

## RESULTS AND DISCUSSION

### Fibre Mechanical Performance

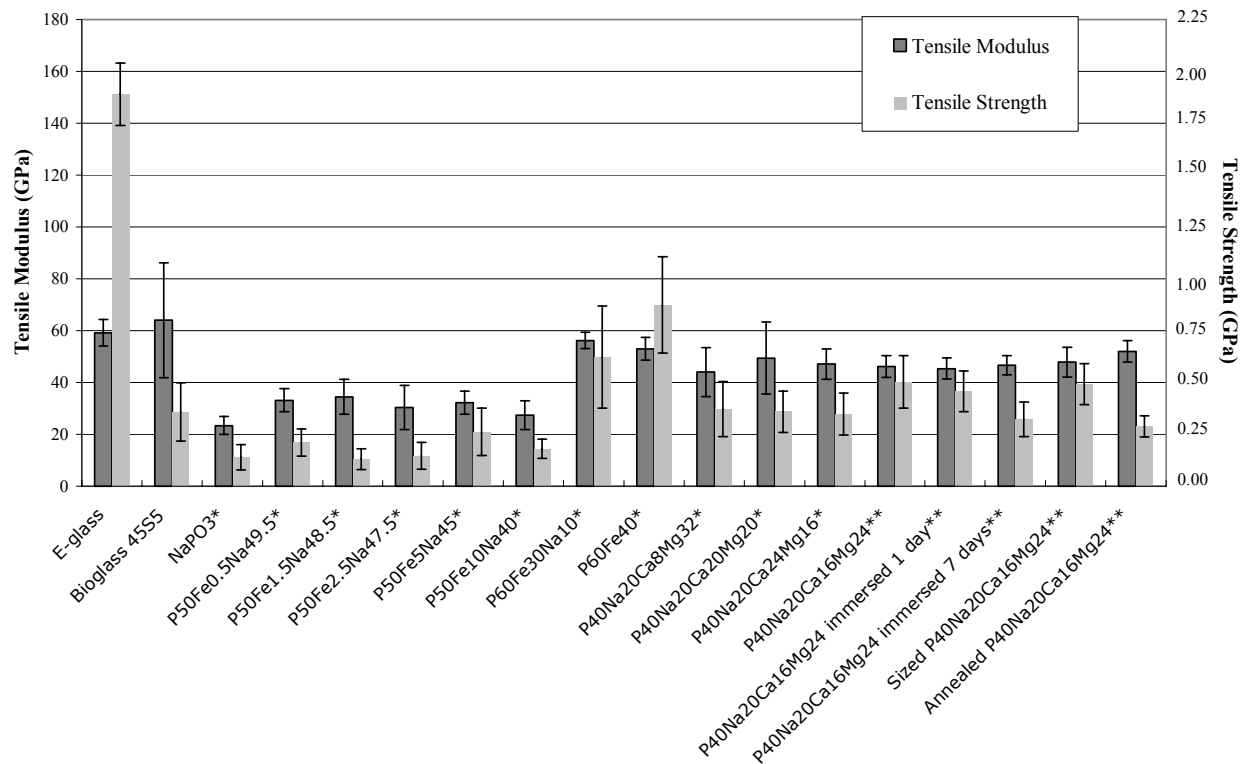
Figure 3 shows the mechanical properties of several types of fibres. The error bars represent the standard deviation. E-glass fibres are used as a reference for comparison with other types of fibres. In the literature [4, 6], moduli around 70 GPa and tensile strengths of at least 1.7 GPa are reported for E-glass fibres. In this work, a tensile modulus  $E$  of  $59.2 \pm 5.2$  GPa and a tensile strength  $\sigma$  of  $1.9 \pm 0.2$  GPa are obtained. Thus, it seems that the single-fibre testing gives values lower than the literature. Cabral-Fronseca *et al.* [13] explain that there is a difference between the mechanical properties given by the manufacturer and those obtained experimentally due to for example the use of different methods of testing.

There is only limited literature giving the mechanical properties of Bioglass® 45S5 fibres. However, Park *et al.* [14] give the following mechanical properties for bioactive glass fibres with a formulation comparable with Bioglass® 45S5 fibres:  $E = 67$  GPa and  $\sigma = 0.7$  GPa. The values obtained in this project ( $E = 64.1 \pm 22.2$  GPa and  $\sigma = 0.36 \pm 0.14$  GPa) correspond to those of literature. Therefore, it can be said that the tensile testing performed to obtain the mechanical properties of fibres is reliable.

Several mechanical tests have been carried out on different types of phosphate glass fibres. Sodium phosphate glass fibres offer a modulus of  $23.4 \pm 3.5$  GPa and a strength of  $0.15 \pm 0.06$  GPa. The mechanical properties of the NaPO<sub>3</sub> fibres are lower than those of E-glass and Bioglass® 45S5 fibres. From the literature, sodium phosphate glass fibres (NaPO<sub>3</sub>) have a modulus of 35.7 GPa and strength of 1.8 GPa [6]. The mechanical properties found in this project are lower than those reported in the literature. This difference in values could come from the fact that the fibres are not manufactured in the same conditions.

Sodium iron phosphate glass fibres were also tested. No significant differences are observed between the five different sodium iron phosphate glass formulations with low Fe content (between 0.5 % and 10 %). For the tensile modulus, the range is 27.4 - 34.5 GPa, with the highest standard deviation being 8.6 GPa. The range for the tensile strength obtained is 0.13 - 0.26 GPa, with the highest standard deviation is 0.11 GPa. For the sodium iron phosphate glass fibres with high Fe content (30 %), the mechanical properties are higher compared to those with low Fe content. The mechanical properties of P<sub>60</sub>Fe<sub>30</sub>Na<sub>10</sub> are  $E = 56.2 \pm 3.1$  GPa and  $\sigma = 0.622 \pm 0.246$  GPa. The tensile modulus of these fibres is close to that of E-glass fibres tested as reference in this project. One type of binary iron phosphate glass fibres with high iron content has been tested. P<sub>60</sub>Fe<sub>40</sub> offers a tensile modulus of  $53.0 \pm 4.4$  GPa and a tensile strength of  $0.873 \pm 0.232$  GPa. These binary phosphate glass fibres have a tensile modulus close to that of E-glass fibres. From the literature, iron phosphate glass fibres drawn by hand (40Fe<sub>2</sub>O<sub>3</sub>-60P<sub>2</sub>O<sub>5</sub>) have a modulus of 69.5 GPa and a strength of 5.9 GPa [6]. The difference in the testing method and the glass fibre processing might explain the difference in mechanical properties. The standard deviation of the strength is high for the high Fe content glass fibres. These fibres were drawn by hand and might have a lot of flaws. P<sub>60</sub>Fe<sub>40</sub> phosphate glass fibres offer the highest strength value compared to all the iron containing phosphate glass fibres, but it is also composed of the highest content of Fe. Therefore, the higher the iron content, the better the mechanical properties. However, these high iron content phosphate glass fibres are durable and therefore cannot be used for degradable bio-medical composite applications.

Sodium calcium magnesium phosphate glass fibres were tested. The four different quaternary glass formulations did not exhibit significant differences. The range for the tensile modulus is 43.0 - 49.4 GPa, with the highest standard deviation being 13.9 GPa. For the tensile strength, the range obtained is 0.35 - 0.50 GPa, with the highest standard deviation being 0.17 GPa. Comparison of the tensile moduli with that of E-glass fibres shows that quaternary glass fibres exhibit good stiffness.



**Notes:** The error bars represent the standard deviation.

\* Fibres drawn by hand.

\*\* Fibres drawn on the fibre drawing rig.

*Fig. 3: Mechanical properties of different types of fibres*

The quaternary phosphate glass fibres offer the best mechanical properties among all the different types of degradable phosphate glass fibres which were tested. To tailor a composite to skull bone having a modulus of 15 GPa and a strength of 0.130 GPa, using an unidirectional composite with 40 % fibre volume fraction, the fibre mechanical properties required are a modulus of 37 GPa and a strength of 0.330 GPa. Therefore, the quaternary phosphate glass fibres offer the needed mechanical properties to manufacture such a composite.

One of the formulations of the quaternary glass fibres was chosen to undertake a closer study:  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres. Mechanical tests were performed on these fibres after immersion in distilled water at 37°C. The tensile strength of the fibres decreases with the period of time of immersion. After 1 day in distilled water,  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres offer a modulus of  $45.4 \pm 4.1$  GPa and a strength of  $0.457 \pm 0.097$  GPa. After 7 days in water, they have a modulus of  $46.6 \pm 3.7$  GPa and a strength of  $0.323 \pm 0.083$  GPa.  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres were sized after drawing using a silane agent (3-aminopropyltriethoxysilane, 99 %). It seems that the sizing did not improve the mechanical

properties of the fibres. The sized fibres have a tensile modulus of  $47.9 \pm 5.7$  GPa and a tensile strength of  $0.493 \pm 0.098$  GPa. An annealing treatment was applied to phosphate glass fibres. The fibres were placed in an oven at  $444^\circ\text{C}$  ( $5^\circ\text{C}$  below the glass transition temperature  $T_g$  of  $\text{P}_{40}\text{Na}_{20}\text{Ca}_{16}\text{Mg}_{24}$  phosphate glass fibres) for 90 minutes. The mechanical properties obtained for these fibres are  $E = 52.0 \pm 4.1$  GPa and  $\sigma = 0.288 \pm 0.051$  GPa. The tensile strength is nearly halved due to the heat treatment, which damages fibre surface. Murgatroyd [15] studied the effect of heat treatment on E-glass fibres. He showed that heat-treatment causes an increase in the number of flaws and therefore a decrease of the fibre strength. He also found that heat-treatment of E-glass fibres at  $520^\circ\text{C}$  leads to an increase in elastic modulus. It can be noticed that the average of the modulus of the annealed  $\text{P}_{40}\text{Na}_{20}\text{Ca}_{16}\text{Mg}_{24}$  phosphate glass fibres also increased compared to the non-annealed fibres.

## Fibre Degradation

Figure 4 (a) represents the percentage mass of two bundles (88 mg and 89 mg) of unsized  $\text{P}_{40}\text{Na}_{20}\text{Ca}_{16}\text{Mg}_{24}$  phosphate glass fibres, with an average diameter of  $19.2\ \mu\text{m}$ , immersed in distilled water at  $37^\circ\text{C}$  as a function of time. For the first 50 hours, the percentage of mass decreases linearly. After 50 hours, the percentage of mass decreases slower and slower. In 57 hours, the mass of the fibres has reduced by 50 %. Figure 4 (a) shows that after 350 hours about 10 % of the fibre mass is left. Actually, all the fibres degraded. If the curves illustrate that 10 % of the fibre mass is left it could be due to an error in the measurement of the original fibre bundle mass.

The total fibre surface area reduces since the fibre diameter gets smaller during the degradation process. Figure 4 (b) represents the degradation rate of the fibres normalised to their surface area as a function of time. The fibre degradation decreases with time and follows the same trend as the percentage of mass. For the first 50 hours, the average fibre degradation rate is of  $1.4 \times 10^{-5}\ \text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ . Figure 4 (b) is obtained from the data illustrated in Figure 4 (a).

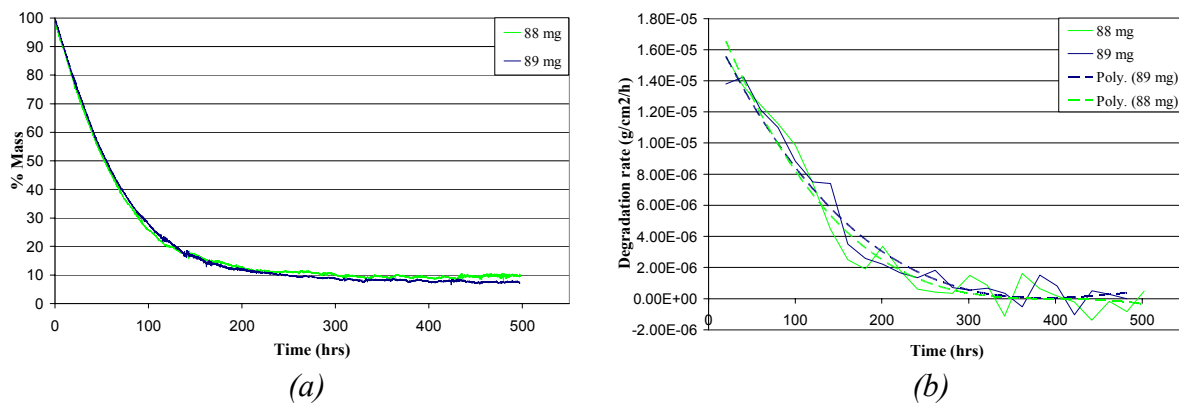


Fig. 4: (a) Unsized non-annealed  $\text{P}_{40}\text{Na}_{20}\text{Ca}_{16}\text{Mg}_{24}$  phosphate glass fibres in distilled water at  $37^\circ\text{C}$ , (b) Fibre degradation rate as a function of time

## Weibull Distribution

Table 2 gives the Weibull parameters (Weibull modulus  $m$ , also referred to as shape and normalising strength  $\sigma_0$ , also referred to as scale) from the Weibull probability plots for unsized  $\text{P}_{40}\text{Na}_{20}\text{Ca}_{16}\text{Mg}_{24}$  phosphate glass fibres (drawn on the drawing rig) at gauge lengths of 10, 25 and 40 mm.

Table 2: Weibull parameters for each gauge length

	10 mm	25 mm	40 mm
$m$	3.80	4.76	5.49
$\sigma_0$ (GPa)	0.634	0.551	0.513

The Weibull analysis assumes that the fibre diameter is constant. Griffith [16] explains that the bigger the fibre diameter, the lower the fibre strength. In this project, the fibre diameter varies between 10 and 25  $\mu\text{m}$ . Thus, in this study the fibre diameter cannot be assumed to be constant. Therefore, it has to be shown what effect the fibre diameter has on the fibre strength. Otto [17] explains that when fibres with different diameters are drawn under nearly identical conditions, the fibre failure strengths are identical and there is no significant effect of diameter. In this project, the phosphate glass fibres drawn on the drawing rig are processed under the same forming conditions. Figure 5 (a) illustrates that in this project the fibre tensile strength does not vary significantly with fibre diameter. The Weibull distribution can be applied in this case.

Tensile strength varies as a function of gauge length. The smaller the gauge length, the higher the tensile strength. Indeed, the longer the fibre, more flaws are probable to exist in the fibre. Therefore, there is a higher fibre failure probability [16]. Hence, the normalising strength varies with the fibre length. As a consequence, Table 2 and Figure 5 (b) show that the scale parameter value decreases when the fibre gauge length increases.

Figure 5 (b) illustrates that the data forms a linear plot which agrees with Eqn. 3 and 5. The Weibull modulus for a determined fibre type should be constant. Considering Eqn. 3, the slope of the plot on Figure 5 (b) should be  $-\frac{1}{m}$ , which gives a Weibull modulus  $m$  of 6.38.

The Weibull modulus derived from Eqn. 3 is higher than the values in Table 2. It is also noticed that the shape parameters values in Table 2 are different. Therefore, the modified Weibull distribution can be applied (see Eqn. 5). The slope of the plot on Figure 5 (b) is actually  $-\frac{\alpha}{m}$ . To determine the strength of the fibre at the critical length  $l_c$  for single-fibre

fragmentation experiments, Eqn. 5 should be used (the value  $-\frac{\alpha}{m}$  being equal to -0.1389).

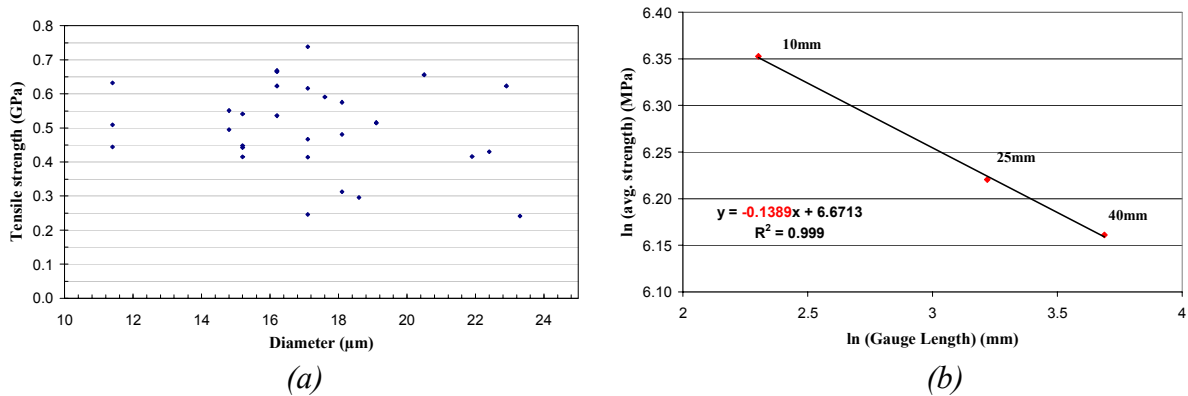


Fig. 5: (a) Tensile strength as a function of diameter (gauge length 25 mm), (b) Graph of  $\ln\langle\sigma_t\rangle$  vs  $\ln(\text{gauge length})$ , for unsized  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres



Quaternary phosphate glass fibres offer good scope to be used as reinforcement in PCL matrix since they offer good mechanical properties. Nevertheless, in the future it is needed to understand their mechanical and physical degradation mechanism in PCL. It will be necessary to decrease the fibre degradation rate in order to maintain the initial composite mechanical properties for the first six weeks of implantation. The fibre degradation rate can be decreased by incorporating some iron into the phosphate glass.

## CONCLUSIONS

The quaternary phosphate glass fibres offer good mechanical properties which are promising for the manufacturing of bio-medical implants for skull bone repair. The fibre strength decreases with time when immersed in distilled water at 37°C. Annealing the fibres also decreases their strength, probably due to surface flaws created by the heat-treatment. Sizing the fibres with silane agent does not improve the mechanical properties of the fibres. Increasing the iron content improves the mechanical properties of the phosphate glass fibres. Unfortunately, however, it decreases their degradability, which is a problem for resorbable bio-medical composite applications.

The percentage mass of unsized  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres decreases with time. For the first 50 hours, the percentage mass decreases linearly. In 57 hours, 50 % of the fibres are degraded. These first results on the quaternary glass fibre degradation are useful to understand their degradation mechanism which is needed to study the composite degradation.

By carrying out tensile testing on unsized  $P_{40}Na_{20}Ca_{16}Mg_{24}$  phosphate glass fibres at several gauge lengths, the three-parameter Weibull analysis allows the determination of the fibre strength at the critical length  $\sigma(l_c)$  for single-fibre composites fragmentation experiments.

## ACKNOWLEDGEMENTS

The authors would like to thank Dr C.A. Scotchford for his collaboration in this project, Prof. L.L. Hench for supplying Bioglass® 45S5 fibres and to acknowledge the financial support of the EPSRC and IMRC.

## REFERENCES

1. "Hospital Episode Statistics England Financial Year 2001-02", Department of Health.
2. Ravaglioli, A. and Krajewski, A., *Bioceramics: Materials, Properties, Applications*, Chapman & Hall, London, 1992.
3. Jiang, G., Jones, I.A., Rudd, C.D. and Walker, G.S., "Modelling the post treatment process of model implants prepared by in situ polymerized poly(-caprolactone) using a  $BF_3$ -glycerol catalyst system", *Polymer*, Vol. 44, 2003, pp. 1809-1818.
4. Hull, D. and Clyne, T.W., *An Introduction to Composite Materials*, Cambridge University Press, Great Britain, 1996.
5. Wambua, P., Ivens, J. and Verpoest, I., "Natural fibres: can they replace glass in reinforced plastics?" *Composites Science and Technology*, Vol. 63, 2003, pp. 1259-1264.

6. Kurkjian, C.R., "Mechanical properties of phosphate glass", *Journal of Non-Crystalline Solids*, Vol. 263&264, 2000, pp. 207-212.
7. Märtson, M., Viljanto, J., Hurme, T., Laippala, P. and Saukko, P., "Is cellulose sponge degradable or stable as implantation material? An in vivo subcutaneous study in the rat", *Biomaterials*, Vol. 20, 1999, pp. 1989-1995.
8. Andriano, K.P. and Daniels, A.U., "Biocompatibility and Mechanical Properties of a Totally Absorbable Composite Material for Orthopaedic Fixation Devices", *Journal of Applied Biomaterials*, Vol. 3, 1992, pp. 197-206.
9. Rinehart, J.D., Taylor, T.D., Tian, Y. and Latour Jr., R.A., "Real-Time Dissolution Measurement of Sized and Unsized Calcium Phosphate Glass Fibers", *Journal of Biomedical Materials Research*, Vol. 48, 1999, pp. 833-840.
10. Andersons, J., Joffe, R., Hojo, M. and Ochiai, S., "Glass fibre strength distribution determined by common experimental methods", *Composites Science and Technology*, Vol. 62, 2002, pp. 131-145.
11. Zhao, F.M., Okabe, T. and Takeda, N., "The estimation of statistical fiber strength by fragmentation tests of single-fiber composites", *Composites Science and Technology*, Vol. 60, 2000, pp. 1965-1974.
12. Zhang, Y.Z., Wang, X., Pan, N. and Postle, R., "Weibull analysis of the tensile behavior of fibers with geometrical irregularities", *Journal of Materials Science*, Vol. 37, 2002, pp. 1401-1406.
13. Cabral-Fonseca, S., Paiva, M.C., Nunes, J.P. and Bernado, C.A., "A novel technique for the interfacial characterisation of glass fibre-polypropylene systems", *Polymer Testing*, Vol. 22, 2003, pp. 907-913.
14. 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, 2003, pp. 403-419.
15. Murgatroyd, J.B., "The Strength of Glass Fibres. Part II. The Effect of Heat Treatment on Strength", *Journal of the Society of Glass Technology*, Vol. 1944, pp. 388-097.
16. Griffith, A.A., "The Phenomenon of Rupture and Flow in Solids", *Philosophical Transactions of the Royal Society of London, Series A*, Vol. 221, 1920, pp. 163-198.
17. Otto, W.H., "Relationship of Tensile Strength of Glass Fibers to Diameter", *Journal of The American Ceramic Society*, Vol. 38, 1954, pp. 122-124.