J Mater Sci: Mater Med (2011) 22:1825–1834
DOI 10.1007/s10856-011-4361-0

Composites for bone repair: phosphate glass fibre reinforced PLA with varying fibre architecture

I. Ahmed · I. A. Jones · A. J. Parsons · J. Bernard · J. Farmer · C. A. Scotchford · G. S. Walker · C. D. Rudd

Received: 13 September 2010 / Accepted: 28 May 2011 / Published online: 14 June 2011

Abstract Internal fixation for bone fractures with rigid metallic plates, screws and pins is a proven operative technique. However, refracture's have been observed after rigid internal fixation with metal plates and plate fixation has been known to cause localised osteopenia under and near the plate. In the present study, resorbable composites comprising a PLA matrix reinforced with iron doped phosphate glass fibres were investigated. Non-woven random mat laminates of approximately 30% and 45% fibre volume fraction (V_f) were produced, along with unidirectional and 0°–90° samples of approximately 20% V_f. The non-woven composite laminates achieved maximum values of 10 GPa modulus and 120 MPa strength. The 0–90° samples showed unexpectedly low strengths close to matrix value (~50 MPa) although with a modulus of 7 GPa. The UD specimens exhibited values of 130 MPa and 11.5 GPa for strength and modulus respectively. All the modulus values observed were close to that expected from the rule of mixtures. Samples immersed in deionised water at 37°C revealed rapid mechanical property loss, more so for the UD and 0–90° samples. It was suggested that continuous fibres wicked the degradation media into the composite plates which sped up the deterioration of the fibre-matrix interface. The effect was less pronounced in the non-woven random mat laminates due to the discontinuous arrangement of fibres within the composite, making it less prone to wicking. Random mat composites revealed a higher mass loss than the UD and 0°–90° specimens, it was suggested this was due to the higher fibre volume fractions of these composites and SEM studies revealed voidage around the fibres by day 3. Studies of pH of the degradation media showed similar profiles for all the composites investigated. An initial decrease in pH was attributed to the release of phosphate ions into solution followed by a gradual return back to neutral.

I. Ahmed (✉) · I. A. Jones · A. J. Parsons · J. Bernard · J. Farmer · C. A. Scotchford · G. S. Walker · C. D. Rudd
Faculty of Engineering, Division of Materials, Mechanics and Structures, University of Nottingham, University Park Campus, Nottingham NG7 2RD, UK
e-mail: ifty.ahmed@nottingham.ac.uk

1 Introduction

A desirable feature for degradable devices implanted within the body is the ability to maintain their mechanical properties until the device is no longer needed, before being degraded, absorbed and excreted by the body [1]. For bone fractures, internal fixation with rigid metal plates, screws and pins is a proven operative technique. Internal fixation hardware provides excellent reduction of the bone fragments and has the necessary strength to stabilise and support the fracture, allowing early mobility of the limb. However, a significant number of refractures have been observed after rigid internal fixation with metallic plates. While external casting leads to general disuse osteopenia throughout the affected bone, plate fixation causes localised osteopenia under and near the plate [2].

The ideal bone plate should possess sufficient initial rigidity to allow primary union followed by a gradual reduction in stiffness corresponding with the healing bone's ability to serve in a load-bearing capacity. In order to achieve this without the need for additional surgery, the device must biodegrade into components which are neither harmful nor toxic. Additional advantage could also be conferred if the degraded components could be eliminated through normal physiological pathways or actually be incorporated into the bone itself [2, 3].

Stress shielding occurs when two or more components with different moduli form one mechanical system. The component with the higher modulus bears more of the load and protects the other component from stress. Such is the case with rigid metallic fixation, which at first may favour primary bone healing but stress shielding during the latter stages of healing and weight bearing may lead to osteoporosis with decreased bone strength [2]. In addition, the site may also have a tendency to refracture upon removal of the metallic implant, as the bone does not carry sufficient load during the healing process due to the load being carried by the rigid metallic plate [1]. However, an implant prepared using a biodegradable polymer (PLA) may be engineered to degrade at a rate that would slowly transfer load to the healing bone, whilst also negating the need for removal. In addition, delivery of biological components such as bone morphogenetic proteins or antibiotics may be used to speed up the healing process [1].

The mechanical properties of cortical bone vary quite considerably depending on the type of bone in question. Properties for the Femur, tibia and fibula have been reported to range from 10 to 22 GPa for modulus of elasticity and from 67 to 140 MPa for ultimate tensile strength [4, 5]. Properties for the mid-shaft human radius have been reported to range from between 10.4 and 18.7 GPa for modulus and 142–235 MPa for stress [6].

Polymers such as PLA, PGA and PCL alone have insufficient mechanical properties to match cortical bone. However, composites comprising of a biodegradable polymeric matrix and bioactive fillers are regarded as a promising approach in the field of regenerative medicine and have huge potential applications in orthopaedic surgery for hard tissue repair and reconstruction. These degradable composites have the potential to replace some commonly used metal plates.

Recent studies investigating PCL reinforced with binary calcium phosphate glass fibres revealed that these fibres had a strength of 474 MPa and a modulus of 44 GPa. Composites made using these fibres as reinforcement showed that the flexural strength and modulus values obtained were 25–30 MPa and 2.5 GPa respectively for an approximately 18% fibre volume fraction sample. It was stated that these values were in line with human trabecular bone properties and not suitable for cortical bone [7].

Prabhaker et al. [8] investigated PCL composites reinforced with phosphate-based glass (PBG) particulates and showed that it was possible to bestow control over the composites properties via incorporation of particulates with differing degradation profiles.

Andriano and Daniels [9] investigated a poly orthoester (POE) polymer reinforced with calcium sodium metaphosphate micro-fibres. Fibre composites comprising 0–50% volume of fibres were investigated and the highest flexural yield strength obtained was for the 40% (by volume) composite with a value of 115 MPa and modulus of 8.2 GPa, the highest flexural modulus obtained was for the 50% volume composite with a value of 9.4 GPa and yield strength of 103 MPa.

More recently Ahmed et al. [10] produced composites with randomly distributed iron doped PBG fibres within a PLA polymer matrix were fabricated and tested. The mean fibre strength obtained for these glass fibres was 456 MPa with a modulus value of 51.5 GPa (slightly higher than the binary Ca/P fibres quoted above). The flexural strength of the composites was nearly 90 MPa with a flexural modulus of almost 5 GPa for both non-treated and heat-treated fibre reinforced composites. Both of these composite types had a fibre volume fraction (V_f) of approximately 13.5%. The strength values obtained were in the range required for cortical bone, though the modulus values were much lower than required for cortical bone. However, given that the V_f was only 13.5% there was significant scope to improve the modulus. In addition, degradation studies of these composites revealed that the strength values were comparable to the polymer alone, however the rate at which these properties decreased was not recorded.

Bone has anisotropic properties to allow it to support load where needed. Composites can be produced in a similar way, biasing the reinforcement to provide improved properties in certain directions. The composites investigated in this study are similar to those in [10] in that they also comprise a PLA matrix reinforced with iron doped phosphate glass fibres. However, the volume fractions have been increased significantly for the random fibre composites and additional fibre geometry (i.e. 0–90° and unidirectional fibres) within the composites have also been investigated. In addition, composite mass loss and loss of mechanical properties has been evaluated over time for up to 40 days.

2 Materials and methodology

2.1 Phosphate glass and fibre production

The starting materials used in this study to produce the glass were NaH_2PO_4, $CaHPO_4$, $FePO_4{\cdot}2H_2O$ and P_2O_5. The precursors were mixed, placed into a 100 ml volume Pt/5% Au crucible type BC 18 (Birmingham Metal Company, UK), heated in air at 350°C for half an hour and then melted at 1100°C for 2 h. The resulting glass was poured onto a steel plate and left to cool to room temperature. The mol% of the glass formulation used in this study was $50P_2O_5$–$40CaO$–$5Na_2O$–$5Fe_2O_3$.

Continuous fibres were produced by melt-draw spinning using a dedicated in-house facility (see Table 1 for the

composite codes used in this study). Fibres were used as drawn, without further treatment.

2.2 Assembly of non-woven random and UD fibre mats

Randomly orientated non-woven mats (RM) were produced from fibres cut to 10 mm in length. The fibres were separated into 3 g bundles and dispersed within a water/Cellosize solution. 10 g of Cellosize (hydroxyethyl cellulose based material obtained from Univar Ltd, UK, used as a fibre binding agent) granules were blended into 4 litres of deionised water and continuously agitated at 500–600 rpm for 10 min. Fibres were added to the solution during stirring, left to disperse for 10 min before extraction using a fine mesh strainer and rinsed with deionised water (using a spray bottle and repeated several times) to remove any residual binder.

For the UD and 0°–90° composites, small fibre bundles were peeled/separated away from the main fibre tow produced (see Fig. 1) and aligned parallel to each other. Cellosize solution was then poured onto the fibres and rinsed (excess moisture was removed via suction), after which they were placed into an oven (at 60°C) to dry for 10 min. Approximately 100 × 100 mm fibre sheets were obtained. These sheets were stacked within polymer sheets to produce the UD composites and stacked alternately in 0° and 90° orientations to produce the composites. NB: The fibre bundles produced reasonably satisfactory composites by this method; however the fibres were not completely straight due to slight curvature incurred during fibre sheet manufacture.

2.3 Composite production

5 g of PLA pellets (Resin 3051-D, Natureworks®, average Mw ~90,000–120,000) were heated to 210°C before pressing at 3–4 bar for 30 s (in a J.R. Dare Ltd, heated press) in order to produce films of approximate 0.2 mm thickness. These films were then cooled to room temperature (also under pressure) within a cold press (Daniels, UK). The films were stacked alternately with non-woven mats placed into a 170 mm diameter, 1.6 mm high circular mould cavity. For the 0°–90° and UD composites produced a 100 × 100 mm square, 1.6 mm high mould was used.

Fig. 1 Fibre tow obtained using a specially made in-house fibre production facility

The individual stacks (RM, 0°–90° or UD) were compressed at 38 bar for 15 min at 210°C and then cooled under pressure (38 bar) at room temperature for a further 15 min (Daniels, UK). Temperatures ~40°C above the melting temperature for PLA were used for composite production, in order to reduce the viscosity of the polymer sufficiently to allow for complete fibre wet out. The resulting laminated composites were sectioned into 32 mm length, 15 mm width with 1.6 mm height specimens, for physical testing. The volume fractions of the composites produced were calculated using the matrix burn off method, via the standard test method ASTM D2584-94 [11]. See Table 1 for the composite fibre volume fractions obtained from this study.

2.4 Flexural mechanical properties

The mechanical properties (Flexural modulus and strength) were evaluated via 3 point bending tests on a Hounsfield Series S testing machine. These studies were conducted in accordance with BS EN ISO 14125:1998 [12]. A crosshead speed of 1 mm/min was used, with a 1 kN load cell. Flexural studies were performed using 3–5 repeat specimens. Flexural tests were also conducted on specimens degraded over time.

Table 1 Composite codes, fibre orientation and volume fraction of the composites investigated in this study

Composite codes	Fibre orientation	% Volume fraction (V_f) (theoretical)	% Volume fraction (V_f) (actual)	References
RM 20	Random mat	20	14	[8]
RM 30	Random mat	30	30.32	This paper
RM 40	Random mat	40	45.96	This paper
0°–90°	0°–90°	20	19.88	This paper
UD	Unidirectional	20	23.51	This paper

2.5 Mass loss and pH studies

The sectioned test specimens ($32 \times 15 \times 1.6$ mm^3) were placed into glass vials containing deionised water (30 ml) and incubated at 37°C (the samples here were open-ended and hence the fibres and interface were in direct contact with the media). At various time points (every 24 h up to 72 h, followed by 3–4 day intervals for up to a 4.5 week period) the specimens were extracted and blot dried before weighing and replaced into fresh solution. The specimen measurements were conducted in triplicate and the solution was pH adjusted to 7.4 ± 0.2 prior to use. The data were plotted as percentage weight loss against time.

Change in pH was also recorded alongside the mass loss studies and measurements were taken at every time point. The pH meter (Hanna Instruments, UK) was calibrated using pH calibration standards (Colourkey Buffer Solutions, Sigma–Aldrich, UK).

Statistical analysis (using *t*-test to compare two means) was performed on the results obtained (GraphPad Software Inc).

2.6 SEM analysis

SEM analyses were conducted on all the composites. The specimens were sputter-coated (SC500, Emscope) with gold and examined using an XL 30 scanning electron microscope (Philips, UK) at an accelerating voltage of 20 kV using both secondary electron (SE) and back scattered electron (BSE) modes.

3 Results

3.1 Mechanical studies

Figure 2 shows the initial flexural (3 point bend test) results obtained for the composites studied. The data used for specimen RM 20 was obtained from a previous study [10]. An increase in both flexural strength and modulus was seen with an increase in fibre volume fraction from 20 to 40%, for the random mat composites produced (as expected). Values of 80, 105 and 121 MPa were obtained for the flexural strength properties for these composites, respectively. For the flexural modulus values of 5, 8.4 and 9.4 GPa were obtained for the RM 20, 30 and 40 specimens tested, respectively.

The lowest initial flexural strength properties were obtained for the 0°–90° composite produced with a value of 52 MPa. The initial flexural modulus obtained was 7 GPa. The highest flexural strength and modulus was obtained for the UD composite produced. Values of 129 MPa and 11.5 GPa (for strength and modulus) were obtained respectively.

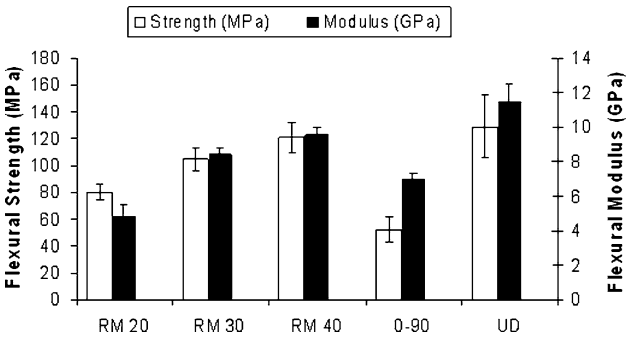

Fig. 2 Initial mechanical properties (3 point flexural bend test) collated for the random mat, 0°–90° and unidirectional fibre composites produced

Statistical analysis showed that there were significant differences between the modulus results for the RM20, 30 and 40 specimens. Specifically, $P < 0.01$ for the comparison of modulus for RM20 vs RM30, while $P < 0.05$ for the comparison of moduli for RM30 and RM40. For the strength values, the difference for RM20 and RM 30 was found to be statistically significant ($P < 0.01$), but the strengths of RM30 and RM40 showed no significant difference ($P > 0.05$).

The 0°–90° composite data in comparison with all other specimens produced was found to be statistically significant ($P < 0.001$). Comparing flexural strength values for the RM 30 and 40 specimens with the UD composite, the data was found not to be statistically significant ($P > 0.05$). However, for the modulus values RM 30 vs the UD specimens was found to be statistically significant ($P \leq 0.01$) whereas RM 40 vs the UD composite was found not to be statistically significant ($P > 0.05$).

The composites were immersed in deionised water at 37°C and their mechanical properties tested over time. The flexural strength profiles obtained are presented in Fig. 3a. For specimens RM 30 and RM 40 a gradual decrease of the properties to polymer matrix values (of 40–50 MPa and 2.5 GPa for strength and modulus respectively [10]) were seen at day 14 and remained at this level up to day 42. The flexural strength profiles for the 0°–90° composite specimens started at near matrix properties, after which a rapid decline in strength (to 6–8 MPa) was observed by day 7. This value is significantly below the matrix only properties stated above. A decrease in strength for the UD composite to almost half its initial value was seen by day 3. After this a further steady decrease was seen to matrix property levels by day 7. Further decrease to approximately 30 MPa was seen by day 28.

The modulus retention profiles obtained (Fig. 3b) were very similar to the strength profiles observed above. The

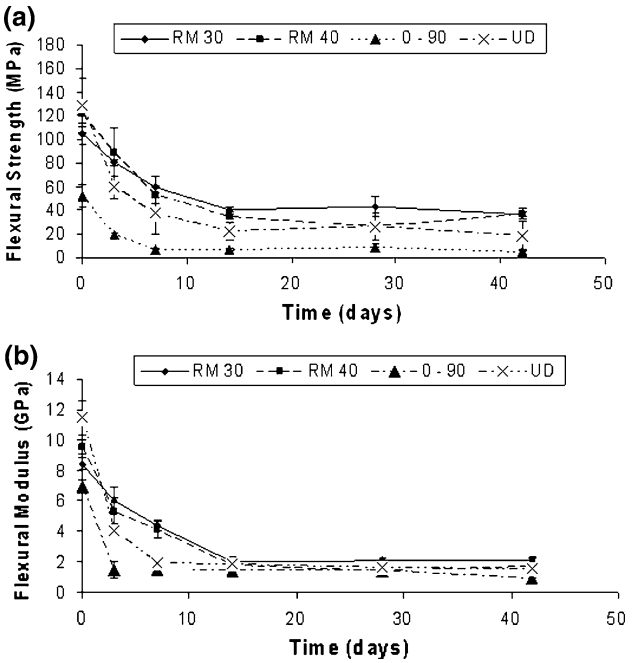

Fig. 3 **a** Flexural strength profiles tested over time. The random mat, 0°–90° and unidirectional fibre composites produced were degraded in deionised H_2O at 37°C. **b** Flexural modulus profiles tested over time. The random mat, 0°–90° and unidirectional fibre composites produced were degraded in deionised H_2O at 37°C

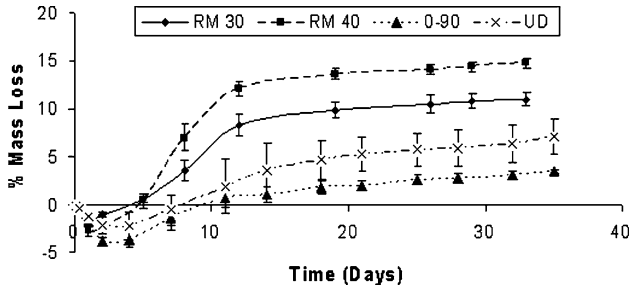

Fig. 4 Degradation studies conducted over time. The random mat, 0°–90° and unidirectional fibre composites produced were degraded in deionised H_2O at 37°C. The media was changed at each time point

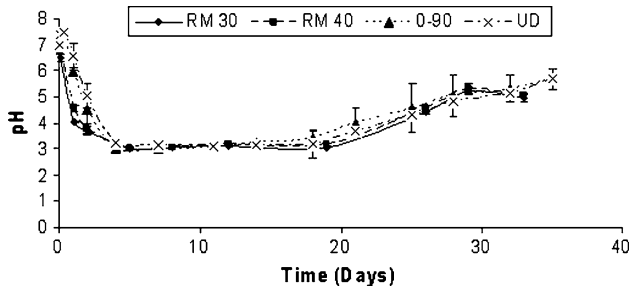

Fig. 5 pH studies conducted over time. Random mat, 0°–90° and unidirectional fibre composites were degraded in deionised H_2O at 37°C and measurements were taken at each time point

modulus for the RM 30 specimens reduced to almost matrix properties by day 14. However, a further decrease than matrix only properties was seen for RM 40 by day 14. Again, the most significant decrease in modulus was seen for the 0°–90° specimens, which occurred by day 3. A huge decrease in modulus was also seen for the UD composite by day 3 (from 11.5 GPa to approx 4 GPa). Further decrease down to approximately 2 GPa was seen by day 7, after which this value remained steady for the duration of the study.

3.2 Degradation and pH studies

From the degradation studies conducted (Fig. 4) it was seen that the random mat composites had greater mass loss than the 0°–90° and UD composites tested. For sample RM30 and RM40 an 8.5% and a 12.5% mass loss was seen respectively at day 12, after which a plateau was observed. The 0°–90° and UD samples saw a higher initial mass gain, suggesting greater water absorption as compared to the random mat composites. Mass change below initial for these samples occurred at approximately day 10 and a plateau was observed by day 18. Overall mass changes of approximately 2 and 5% were observed for the 0°–90° and UD specimens respectively.

From the pH studies conducted it was seen that all four composites experienced exactly the same pH profiles (see Fig. 5). An initial drop in pH from 7.4 to 3.0 occurred by day 5. This pH level remained steady for up to day 18–19, after which a gradual increase in pH to above 5 is observed by the end of the study.

3.3 SEM analyses

Figure 6a and b represents the random mat specimens (RM 30 + RM 40) degraded for 3 days in deionised water at 37°C. The randomly distributed and densely packed fibres can clearly be seen. Fig. 6c shows the 0°–90° composite, also degraded for 3 days in deionised water. Fibre stacks alternating at 0° and 90° are clearly seen. The UD specimen is given in Fig. 6d. The fibre volume fraction for the UD sample was lower than the random mat composites, hence does not appear as densely packed. The fibres are still present at day 3 in all samples investigated, however gaps and voids around the fibres (between fibre and polymer matrix) can be seen. Pull-out lengths remain quite short.

4 Discussion

Bone fracture fixation with metal plates represents a traditional method of repairing fractured bones. Plates are generally made from stainless steel, titanium or cobalt

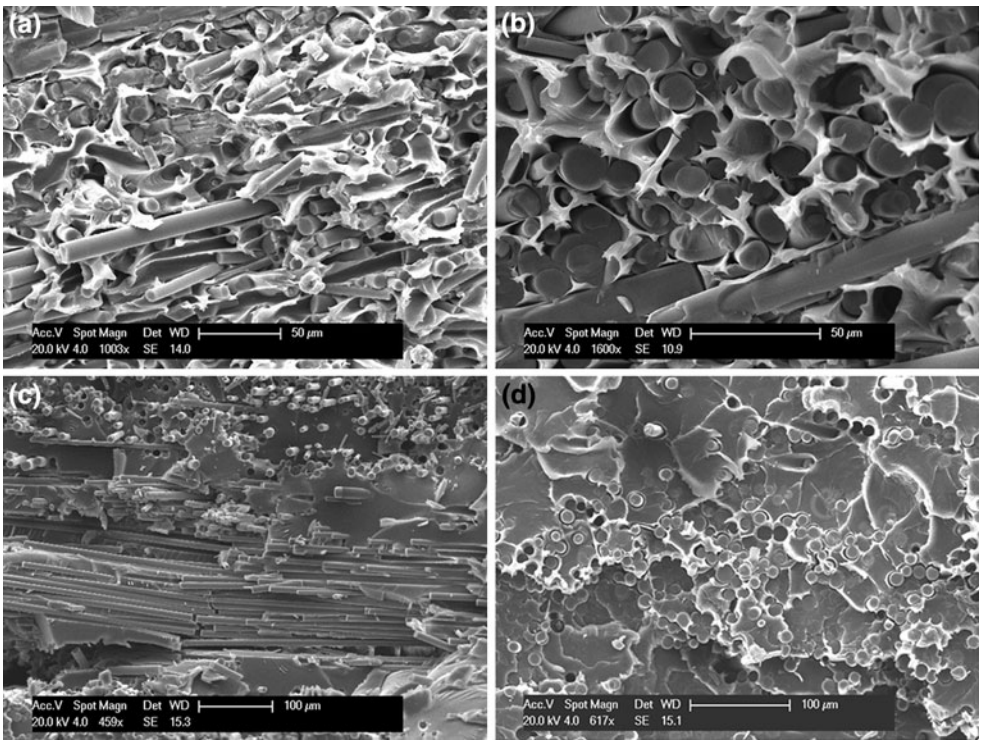

Fig. 6 **a** SEM of RM 30 composite degraded for 3 days in deionised H_2O at 37°C. **b** SEM of RM 40 composite degraded for 3 days in deionised H_2O at 37°C. **c** SEM of 0°–90° composite degraded for 3 days in deionised H_2O at 37°C. **d** SEM of UD composite degraded for 3 days in deionised H_2O at 37°C

chrome alloys and attached to bone with screws that pass into both cortices of the bone [3]. Stress shielding, metal toxicity and allergic sensitisation has also been reported for alloys containing nickel, cobalt and chromium [13].

In an effort to address these problems, composite plates consisting of a PLA and resorbable PBG fibres have been investigated. Medical grade PLA (not all PLA grades) is an FDA approved material and PBG's and their fibres have been heavily investigated for their cyto/biocompatibility properties [10, 14–17]. Four composites consisting of different fibre geometry and fibre volume fractions were tested with the objective of achieving at least a 10 GPa modulus. In a previous study [10] pure PLA as control and random mat composites consisting of 13.5% fibre volume fraction were studied. In comparison, this study investigated random mat composites consisting of approximately 30 and 45% fibre volume fractions, along with approximate 20% fibre volume fraction composites comprising 0°–90° and unidirectional fibre orientations. Both flexural modulus and strength were seen to increase for the random mat composites with increasing fibre fraction. A modulus value close to 10 GPa (along with 120 MPa for flexural strength) was obtained for the 40% random mat composite. The difference in initial strength values obtained for RM30 and RM40 were found not to be statistically significant. However the difference in modulus values for these composites was found to be statistically significant ($P < 0.05$).

Andriano and Daniels [9] reinforced POE with 30 and 40% fibre volume fraction loads. Initial properties obtained for flexural modulus were 7 and 8 GPa respectively and for flexural strength approximately 110 and 115 MPa respectively. These values compare well with the values obtained from this study. This was surprising however, as the phosphate microfibre properties quoted by Andriano were much higher than the properties of the fibres used in this study.

Casper et al. [3] also investigated composite properties of a PLA matrix reinforced with calcium metaphosphate fibres. Converting the units used in their study a modulus value of 14.7 GPa is obtained. However, the fibre volume fraction of the composites tested and the mechanical properties of the fibres used were not stated. Neither was the orientation/layup of the fibres used (i.e. random mat, UD etc.).

Fracture plates fabricated using PLA and CaP fibres were also investigated by Zimmerman et al. [18]. Values for strength and modulus for a 56% (±3%) volume fraction composite were quoted as being approximately 160 MPa and 27 GPa respectively. These values were significantly higher than the values obtained in this study (albeit for a much higher volume fraction composite); however the

values quoted were estimated from theoretical analyses and the fibre (strength) data used was 654 MPa, which was again much higher than the strength of the fibres used here [10]. In addition, the calcium phosphate glass formulation contained aluminium oxide (Al_2O_3), which is known to significantly enhance the properties of these glasses, even with minute additions [19].

The highest flexural mechanical properties were seen for the UD composite. Values of almost 130 MPa and 12 GPa for strength and modulus were obtained. In addition, this composite only had an approximate 23% volume fraction of fibres. However, comparing flexural strength and modulus values for RM 30 and RM 40 with the UD composite no statistical significance was seen (with exception of modulus values for RM30 against the UD sample). It is well known that unidirectional orientated fibres have a greater reinforcing effect in composites due to the stress loads being axially distributed along the fibre lengths. As a result, a composite with long fibres oriented in the direction of maximum stress will have superior properties compared to short-fibre composites with random fibre distributions. NB: Due to the production process of the UD fibre mats, the fibre alignment was not perfectly straight. In fact, the nominally unidirectional composites exhibited significant fibre waviness. Higher composite mechanical properties could potentially have been gained if the fibre alignment had been better. Processing to allow for a more effective UD layup is being developed within the group.

From the mechanical studies of samples degraded in deionised water over time (Fig. 3a, b), mechanical property reduction occurred much more rapidly for the UD and 0°–90° composites than for the random fibre mat composites. The degradable phosphate glass fibres used were not treated with any sizing or coupling agents, thus creating a potentially water sensitive fibre matrix interface. In addition, the rates of failure observed were consistent with those observed in previous studies. The mechanical behaviour and durability of composite materials not only depends on the properties of each component (i.e. matrix and fibre) but also on the structure of the interface/interphase [20].

Delamination and failure of a PLA composite reinforced with calcium phosphate glass fibres via absorption of fluid was also seen by Zimmerman et al. [18]. The high content of continuous fibres were said to wick the fluid into the composite plates which sped up the breakdown process. In addition it was also reported that in comparison to this UD composite a chopped-fibre composite also underwent a decrease in properties although less severely. It was said that the discontinuous arrangement of fibres within the composite made it less susceptible to wicking [18]. This explanation fits well with the decrease in mechanical properties seen for the random and UD fibre composites investigated in this study.

Slivka and Chu [21] investigated the interfacial properties of several different fibre types within a PLLA matrix. One of these fibre types was a calcium phosphate (CaP) glass fibre doped with 3% Fe_2O_3. It was seen that the CaP fibre PLLA interface degraded the fastest and the rate was higher for open-end vs. closed-end composite specimens. It was stated that composite failure can occur as a result of premature fibre and/or matrix degradation, delamination of ply-laminated designs, or de-bonding of the fibre from the matrix. These failure modes could be evidenced by the formation of micro-void spaces within the composite, particularly at the fibre-matrix interface, after being exposed to a degrading medium. They also stated that moderate strain levels (>10%) on bioabsorbable composites could cause deleterious effects on the fibre-matrix interface and should be considered when designing devices for load bearing applications. In addition, they reported that wicking played a significant role in the rate of degradation for these composites.

From the composite degradation (mass loss) studies conducted (Fig. 4) it was seen that the random mat composites (RM40 > RM30) had a higher mass loss than the UD and 0°–90° specimens. It is suggested that this was due to the higher degradable fibre volume fractions of these composites as compared to the UD and 0°–90° samples. Moisture absorption properties of a polycaprolactone (PCL) polymer reinforced with phosphate glass fibres were investigated by Onal et al. [22]. It was seen that maximum moisture content increased with increasing fibre load. Fitting of a 1-D form of Fick's second law permitted the water diffusion to be estimated and the overall diffusion coefficient was seen to increase with an increase in fibre volume fraction, probably due to internal voidage in the specimens tested. This effect could potentially explain the mass loss data observed in this study. From the pH studies conducted similar profiles were observed for all four composites investigated. The initial decrease in pH was attributed to the release of phosphate ions into solution, which may form H_3PO_4 (phosphoric acid). The pH values obtained correlated well with previous studies [7, 10] where similar profiles were observed. Zimmerman et al. [18] also stated that the release of phosphate ions resulting in the formation of phosphoric acid could have enhanced the corrosive effect on the fibres of the lactic acid that is expected to form during polymer degradation. Significant degradation of PLA in terms of mass loss would not normally be expected within the time frame of this study; however the presence of acid would accelerate the breakdown. A return to neutral pH towards the end of the study suggested that most if not all the fibres had degraded. In a recent study [15] conducted by the authors, pH analysis of novel (invert) phosphate glass formulations showed these glasses remained neutral during their degradation studies in

deionised water throughout the duration of the study. Future studies will focus on obtaining fibres from these formulations to be used as reinforcement, as the fibres used in this study degraded far too rapidly for application.

Figure 6a, b shows SEM images of the fracture surfaces of the random mat composites after immersion in deionised water at 37°C for 3 days. The fibres are still clearly present; however gaps and voids around the fibres are visible suggesting loss of interface due to wicking of the degrading medium as mentioned above. The 0°–90° configuration of the fibres embedded can clearly be seen from Fig. 6c. Although short fibre pull out lengths are observed (which suggest good interfacial adhesion) a large break/crack is observed in the centre of the fibre ply in the '*x*' direction. This breakage of the ply (which was in the direction of the load applied during the 3 point bend test) was suggested as the main reason for the much weaker properties observed for the 0°–90° specimens in comparison. Lassila et al. [23] stated that lower than expected properties could be due to variations in fibre positions caused during the hand laminating process. In addition, if the failure included compressive stresses, microbuckling or shear splitting, then the failure stresses would also be lower.

Figure 6d shows the fibre distribution in the UD composites (also after 3 days immersion in water). Voids can clearly be seen around the fibres embedded within the matrix, which again was consistent with the observations made above.

4.1 Theoretical composite properties

The experimental properties of the composites were compared to theoretical values using the well known rule of mixtures (Eq. 1)

$$E_1 = \eta_o \eta_l E_f V_f + E_m(1 - V_f) \quad (1)$$

where η_o is a correction factor depending on fibre orientation (0.375 for random in-plane fibres, 0.5 for a balanced 0°/90° lay-up and 1 for unidirectional) and η_1 is a correction factor dependent on fibre length. E_f and E_m are the fibre and matrix moduli respectively and V_f is the fibre volume fraction. Using this model assumes that the modulus contribution from fibres perpendicular to the testing direction (E_2) is equivalent to the matrix modulus. The value of η_l is 1 where fibres are $\geq 10 l_c$ (l_c being the critical fibre length) and is greater than 0.9 for fibres more than 1 mm in length. Previous studies within the group showed that fibres in the random mats reduce from a starting 10 mm length to an average 3 mm length during processing, due to damage incurred during the mixing and binding phase. Typical l_c for these fibres is around 0.7 mm, signifying that the real value of η_l lies between 0.9 and 1 in this case. Figure 7 shows the experimental results alongside the rule of mixtures estimations. As can be seen the estimations match quite well with experimental results. However the 30% V_f composite gives a value above expectation. Given that the rule of mixtures represents an idealised situation (i.e. perfect interface) this would suggest either that the random fibres are not completely randomly orientated (meaning that η_o is greater than 0.375) or that the contribution from fibres perpendicular to the testing direction is not equivalent to the matrix modulus. It would seem unusual that there would be a noticeable orientation effect in only one of the random composites, given all the random mats were made using the same process. An alternative estimation for modulus from Lavengoode and Goettler [24] that takes into account contributions due to E2 is:

$$E = \eta_o E_2 + (1 - \eta_o) E_2 \quad (2)$$

where E_1 is as above for the unidirectional situation and E_2 is given by

$$E_2 = \frac{E_f E_m}{E_m V_f + E_f(1 - V_f)} \quad (3)$$

The Lavengoode and Goettler estimations have also been plotted in Fig. 7. These are slightly higher in all cases than the experimental results and would suggest that there is a contribution above matrix value for perpendicular fibres in these composites. NB: Any parameter that is related to the initial assumptions made from theoretical analysis may be responsible for the discrepancies observed (for e.g. fibres and matrix are linearly elastic and homogeneous and there are no voids etc.).

The study above highlights that the initial properties obtained were close to expectation as evinced by the 'rule of mixtures'. However, rapid deterioration of the mechanical properties after immersion within a degrading medium (as seen above) will limit the use of these composites for biomedical applications, especially for use as fracture fixation plates. Future investigations will thus focus on improving the fibre-matrix interface/interphase via the use of coupling and/or other sizing agents to increase retention of the mechanical properties in line with the specific application.

5 Conclusions

Four PLA/phosphate glass fibre reinforced composites were produced: random mat composites of approximately 30 and 40% V_f; a 0°–90° composite with approximately 20% V_f and a unidirectional composite of approximately 20% V_f.

Both flexural modulus and strength was seen to increase for the random mat composites with increasing fibre

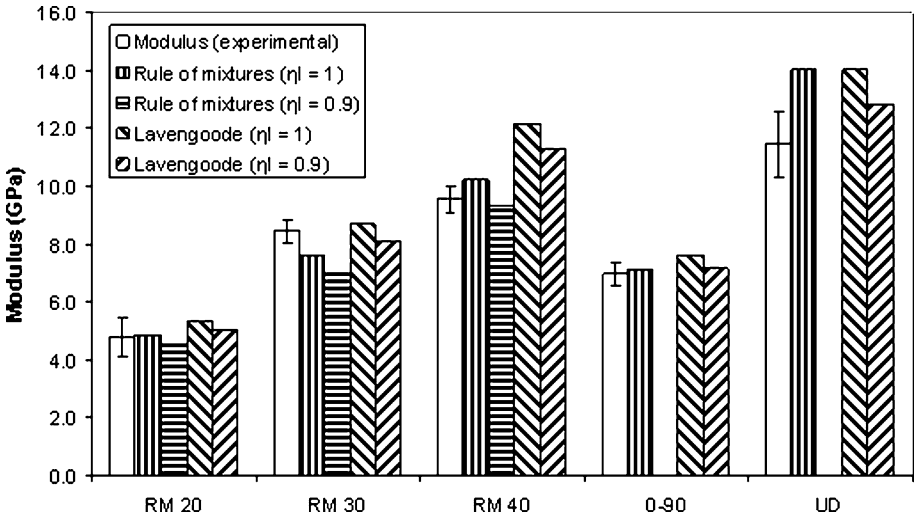

Fig. 7 Graph of experimental results along with estimations derived using the 'rule of mixtures' estimations

volume fraction, as expected. Maximum observed modulus and strength for the random fibre (RM) composites were 10 GPa and 120 MPa respectively. The UD composite exhibited a modulus of 11.5 GPa and a strength of 130 MPa. Both of these composites properties are within the lower range for cortical bone.

All the composites experienced a rapid loss of mechanical properties when exposed to an aqueous environment. This was more pronounced for the 0°–90° and UD specimens. Voids were observed between fibres and matrix by day 3.

The higher fibre volume content composites experienced a greater loss off mass during degradation. Measurement of pH showed similar profiles for all the samples tested, decreasing to near pH 3 before rising back towards neutral.

The composites investigated in this study exhibited initial properties close to expectation; however rapid deterioration of mechanical properties in deionised water was seen. Future investigations will thus focus on manufacture of composites from more durable fibre formulations and also improving the fibre-matrix interface via coupling or sizing agents.

Acknowledgments The authors would like to kindly acknowledge EPSRC support under EP/E001904/1.

References

1. Middleton JC, Tipton AJ. Synthetic biodegradable polymers as orthopaedic devices. Biomaterials. 2000;21:2335–46.
2. Ferguson SJ, Wyss UP, Pichora DR. Finite element stress analysis of a hybrid fracture fixation plate. Med Eng Phys. 1996; 18(3):241–50.
3. Casper RA, Kelley BS, Dunn RL, Potter AG, Ellis DN. Fibre reinforced absorbable composite for orthopaedic surgery. Polym Mater Sci Eng. 1985;53:497–501.
4. Kayacan R. The effect of staining on the monotonic tensile mechanical properties of human cortical bone. J Anat. 2007;211: 654–61.
5. Evans FG. Mechanical properties and histology of cortical bone from younger and older men. Anat Rec. 1976;185(1):1–12.
6. Bosisio MR, Talmant M, Skali W, Laugier P, Mitton D. Apparent Youngs modulus of human radius using inverse finite-element method. J Biomech. 2007;40:2022–8.
7. Ahmed I, Parsons AJ, Palmer G, Knowles JC, Walker GS, Rudd CD. Weight loss, ion release and initial mechanical properties of a binary calcium phosphate glass fibre/PCL composite. Acta Biomater. 2008;4:1307–14.
8. Prabhakar RL, Brocchini S, Knowles JC. Effect of glass composition on the degradation properties and ion release characteristics of phosphate glass—polycaprolactone composites. Biomaterials. 2005;26:2209–18.
9. Andriano KP, Daniels AU. Development of phosphate-microfiber-reinforced poly (orthoester) for absorbable orthopaedic fixation devices. In: Wise DL, editor. Encyclopaedic handbook of biomaterials and bioengineering: part B. Applications. New York: Marcel Dekker; 1995. p. 333–57.
10. Ahmed I, Cronin PS, Abou Neel EA, Parsons AJ, Knowles JC, Rudd CD. Retention of mechanical properties and cytocompatibility of a phosphate-based glass fibre/polylactic acid composite. J Biomed Mater Res B Appl Biomater. 2008;89(1):18–27.
11. ASTM Standard D2584-94. Test method for ignition loss of cured reinforced resins. ASTM International. doi:10.1520/D2584-94. www.astm.org.
12. Carbon fibre—determination of the tensile properties of single filament specimens. International Standard, ISO 11566. BS ISO 11566:1996.
13. Alpert B, Seligson D. Removal of asymptomatic bone plates used for orthognathic surgery and facial fractures. J Oral Maxillofac Surg. 1996;54:618–21.
14. Ahmed I, Collins CA, Lewis MP, Olsen I, Knowles JC. Processing, characterisation and biocompatibility of iron-phosphate glass-fibres for tissue engineering. Biomaterials. 2004;25(16):3223–32.
15. Ahmed I, Parsons AJ, Jones IA, Walker GS, Scotchford CA, Rudd CD. Cytocompatibility and effect of increasing MgO content in a range of quaternary invert phosphate-based glasses. J Biomater Appl. 2010;24(6):555–75. doi:10.1177/088532820910 2761.
16. Burling LD. Novel phosphate glasses for bone regeneration applications. PhD Thesis, University of Nottingham, Nottingham; 2005.

17. Parsons AJ, Evans M, Rudd CD, Scotchford CA. Synthesis and degradation of sodium iron phosphate glasses and their in vitro cell response. J Biomed Mater Res. 2004;71A:283–91.
18. Zimmerman MC, Alexander H, Parsons JR, Bajpai PK. The design and analysis of laminated degradable composite bone plates for fracture fixation. In: Vigo TL, Turbak AF, editors. High tech fibrous materials. Washington: ACS Publications; 1991. p. 132–48.
19. Parsons AJ, Burling LD, Rudd CD, Scotchford CA, Walker GS. The effect of production regime and crucible materials on the thermal properties of sodium phosphate glasses produced from salts. J Biomed Mater Res B Appl Biomater. 2004;71(B):22–9.
20. Zinck P, Wagner HD, Salmon L, Gerard JF. Are microcomposites realistic models of the fibre/matrix interface? I. Micromechanical modelling. Polymer. 2001;42:5401–13.
21. Slivka MA, Chu CC. Fiber-matrix interface studies on bioabsorbable composite materials for internal fixation of bone fractures II. A new method using laser scanning confocal microscopy. J Biomed Mater Res. 1997;37:353–62.
22. Onal L, Cozien-Cazuc S, Jones IA, Rudd CD. Water absorption properties of phosphate glass fibre-reinforced poly-ε-caprolactone composites for craniofacial bone repair. J Appl Polym Sci. 2008;107:3750–5.
23. Lassila LVJ, Nohrstrom T, Vallittu PK. The influence of short-term water storage on the flexural properties of unidirectional glass fibre-reinforced composites. Biomaterials. 2002;23:2221–9.
24. Lavengoode RE, Goettler LA. Stiffness of non-aligned fibre reinforced composites. Springfield: National Technical Information Service; 1971.