NOVEL BIORESORBABLE TEXTILE COMPOSITES FOR MEDICAL APPLICATIONS

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ABSTRACT

Currently, phosphate glass fibre (PGF) reinforced composites are a potential solution for bone repairing due to sufficient mechanical properties and full bioresorbability. In this study, a small inkle-type loom for hand weaving facilitated the production of PGF in textile form. These PGF textiles, along with unidirectional (UD) fibre mats made from the same batch of yarns, were utilised to manufacture fully resorbable textile composites (T-C) and 0 ⁄90 ° lay-up UD fibre reinforced composites (0/90-C). Retention of flexural properties and weight loss of the composites were evaluated during degradation in phosphate buffered saline (PBS) at 37 ℃ for 28 days. The initial flexural strength values that were observed for the T-C and 0/90-C composites were ~176 MPa and ~137 MPa, whilst the modulus values were 8.6 GPa and 6.9 GPa, respectively. The higher flexural strength and modulus values for the T-C when compared to those of 0/90-C were attributed to the textile weaving manually, resulting in a biased fabric with a higher density of fibres in the warp direction. ~20% flexural strength and ~25% flexural modulus were maintained for all composites at the 28 day interval. For this study, this textile achievement will be the significant milestone on the research of bioresorbable PGFs reinforced composite in medical application, and important step on the industrial direction of bioresorbable medical device.

1 INTRODUCTION

Traditional implants used for bone fracture repair in load-bearing situations have usually been made using metal materials. This is to ensure sufficient mechanical support and includes stainless-steel, Cr-Co and Ti alloys [1]. The high stiffness of metallic bone plates is known to result in "stress shielding" effects [2], whereby the majority of the load is carried by the plate rather than by the underlying bone. This causes resorption of the unloaded bone tissue, with the possibility of a resulting fracture at the same site after removal of the plate [3]. Biodegradable polymers such as polylactic acid (PLA) exhibit good cytocompatiblity and their degradation behaviour has been heavily explored for biomedical applications [4-6]. However, the relatively low stiffness properties of PLA render it incapable for use in load-bearing conditions [7, 8]. To achieve sufficient modulus for load-bearing bone repair applications, composites have been investigated that are based on biodegradable polymers with a bioactive reinforcement phase [9].

Phosphate based glasses (PBG) are a potential inorganic reinforcement phase that have been investigated to produce fully bio-resorbable composites. They offer variable degradation rates as their solubility can be tailored via altering their chemical composition [10]. In addition, their polymeric structure allows them to be drawn into continuous fibres to provide improvements in strength [11]. The ionic components of the glass released during degradation could provide trace elements support for bone growth and promote fracture site healing [12].

Ahmed et al [13] developed PLA composites (18%V_f) reinforced with random and unidirectional (UD) iron doped PGF and reported that the flexural strength values of random and UD composites were 106 MPa and 115 MPa whilst the modulus values were 6.7 GPa and 9 GPa respectively. More recently, phosphate based glass fibres with addition of 5-10% B_2O_3 presented significant improvement of mechanical properties (~1000 MPa of tensile strength and ~12 GPa of Young's Modulus) [14]. As such, it was reported that borophosphate glass fibre reinforced UD PLA composites (with 20% V_f) could achieve values of ~156 MPa and ~12 GPa for flexural strength and flexural modulus [15], providing mechanical properties similar to those of cortical bone [16].

However, current phosphate glass fibres (PGF) are produced only in single filament form in lab-scale quantities, composites produced using hand layup of UD fibres have limitations in terms of fibre alignment, are time consuming to make and are not easily scalable. However, as the textile fabric is a well-utilised form of reinforcement in the composites industry, developing phosphate glass fibres into textile forms is the prerequisite condition, significant facilitating eventual industrial production [17]. Due to success of developing PBG formulations that were both suitable for scaled-up fibre production and also cytocompatible [18, 19].

In this study, the yarns of PBG formulation $48P_2O_5$-$12B_2O_3$-14CaO-20MgO-$1Na_2O$-$5Fe_2O_3$ [20] was produced and used to weave pure PBG textile fabrics using an Inkle loom. The effectiveness of these textiles was then assessed by incorporating them into fully resorbable PGF/PLA composites. In order to compare mechanical properties with a textile reinforced composite, a 0°/90° unidirectional lay-up composite was also fabricated as a pseudo-zero crimp textile composite. The retention of flexural properties and weight loss of the composites was evaluated during immersion in PBS at 37 ℃ for up to 28 days.

2 MATERIALS AND METHODS

2.1 Preparation of fibre products for textile manufacture

In this study, phosphate based glass fibre products used for UD mats and textile weaving utilising yarns of phosphate glass fibre were made at pilot scale in Sinoma Co. Ltd (China). The glass formulation was $48P_2O_5$-$12B_2O_3$-14CaO-20MgO-$1Na_2O$-$5Fe_2O_3$ and the fibres were coated with water-soluble epoxy size. This formulation has been characterized in the previous studies and the fibre drawing

performance was confirmed [20]. As the application of a twist on yarns can provide additional integrity before it is subjected to the weaving process [21, 22], yarns production in this study was accomplished by twisting together two 50-filament strands (with S twist type) to be one pre-twist yarn, then re-twisting four pre-twist yarns (with Z twist type) to be balance twisted yarn (eight strands). This process was finished using a twisting machine (TKV216 Type, Tianchen, China) with inserted twist of 55 tpm (twist per meter).

2.2 Preparation of textile fabric

Theoretically, textile fabrics are produced by the interlacing of warp (longitudinal) and weft (traverse) fibres in a regular pattern or weave style. The integrity of the fabric is maintained via mechanical interlocking of the fibres [17]. The Inkle-type loom for textile weaving in this study was produced in-house and was presented in Figure 1. During the weaving process, the yarns were wound onto the inkle-type loom to produce a warp. The end of the yarn was fixed onto the tension bar, then taken up from tension bar, over the two top pegs and the warping peg, then returned around the tension bar. The yarn was then wrapped around again, but this time by passing under the top left peg. The warp was built up by alternating wrapping in this way until a warp of sufficient width was produced. During weaving, the shuttle was passed through the shed from left to right as the open warp was lifted up and down. The resulting textile fabric was a plain weave, with each warp and weft yarn passing over and under each other, as shown in Figure 1. Details of the parameters of the textiles are listed in Table 1.

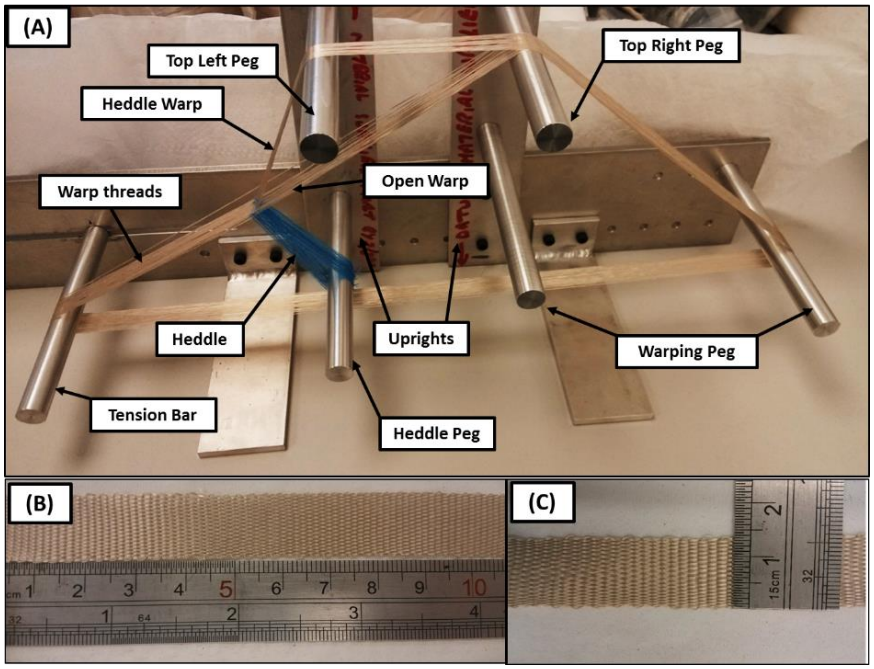

Figure 1: (A) The image of Inkle loom for weaving textile of PGF, (B & C) the image of textile woven by using yarns of phosphate glass fibre.

Pattern	Warp density (yarns/cm)	Weft density (yarns/cm)	Fabric Thickness (mm)
Plain Weave	22.7 ±0.2	6.1 ±0.2	0.362 ±0.013

Table 1: Geometry Parameters of the PGF textiles.

2.3 Preparation of unidirectional fibre mats

Unidirectional (UD) fibre mats were produced from yarns of glass fibre. The yarns were rewound and aligned using a 310 mm diameter drum with a Polytetrafluoroethylene (PTFE) cover sheet. An aerosol method was then used to spray PLA (3251D) /chloroform solution (0.05g/ml) onto the yarn on

the drum. After 2 hours drying. The resulting UD fibre sheets were removed from the drum and cut into sections (140 × 128 mm^2) for composite production, based on the size of the mould.

2.4 Poly-lactic acid film production

PLA films (0.2 mm thickness) were prepared by compression moulding PLA pellets (3251D NatureWorks®, UK), which had been dried in a vacuum oven at 50 ℃ for 24 hours. The PLA pellets (5g) were put between two aluminium plates and placed into a downstroke press (160 TD/S, Daniels, UK) at 210 ℃ for 10 minutes of pre-heating, followed by 1 min pressing at 0.5 MPa. The plates were then moved into an upstroke press (M-B1, Mackey Bowley, UK) for 5 minutes of cooling under pressure 0.5 MPa.

2.5 Manufacture of composites

The 0 ⁄90 ° lay-up fibre mat reinforced composites were produced via a film stacking process (see Figure 2) by using a 140 × 128 × 2 mm^3 steel mould, UD fibre mats were balanced laid alternately in the longitudinal direction (0 °) and traverse direction (90 °). The total mass of fibre mats and PLA film were calculated based on the composite fibre volume fraction (V_f), density of glass fibre, density of PLA and volume of composite. The filled mould was placed into a downstroke press (160 TD/S, Daniels, UK) and pre-heated at 180 ℃ for 10 min, followed by 10 min pressing at 4 MPa. The mould was then moved to an upstroke press (M-B 1, Mackey Bowley, UK) and held under a pressure of 3.5 MPa while cooling to room temperature.

The textile reinforced composites were manufactured via a film stacking process in a similar fashion to the UD composite. Due to the limitations of the textile manufacturing technique, the size of the textile fabric was 140 × 15 mm^2, thus a new steel mould of 140 × 15 × 2 mm^3 was produced for textile reinforced composite manufacture.

A control, neat PLA plate was produced by filling the mould with an appropriate number of PLA films and following the same heating and pressing procedure, so as to ensure a comparable processing history. The fibre/PLA plates were cut to the required dimensions for characterisation by a band saw.

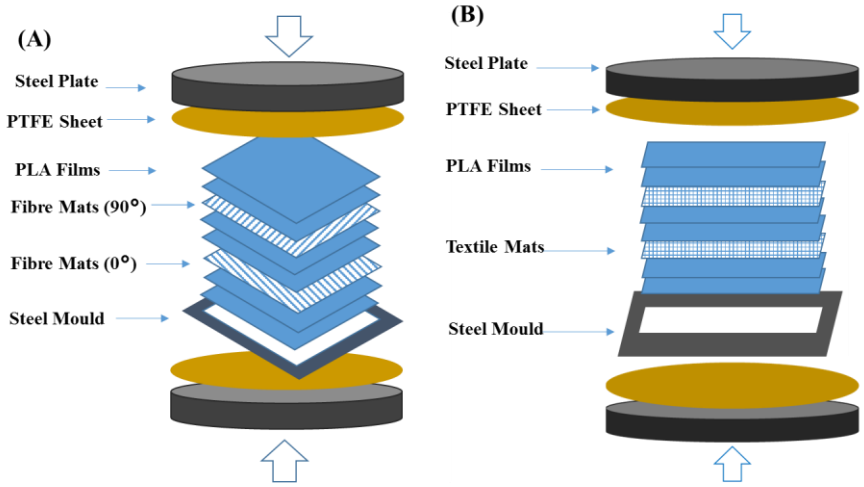

Figure 2: (A) Schematic diagram of 0 ⁄90 ° lay-up composite manufacture, (B) Schematic diagram of textile reinforced composite manufacture.

2.6 Burn off Test

The fibre mass and volume fraction of the composites were obtained using the matrix burn off method, based on the standard test method ASTM D2584-11 [23]. The samples were held at 450 °C for 3 hours in order to allow for the complete combustion of the PLA. The weight of the tray and remaining

fibres was then weighed. The fibre mass fraction (W_f) and fibre volume fraction (V_f) was calculated according to following equations.

$$W_f = \frac{m_{ca} - m_{tr}}{m_{cb} - m_{tr}} \times 100\% \quad (1)$$

$$V_f = \frac{(m_{ca} - m_{tr})/\rho_f}{[(m_{cb} - m_{ca})/\rho_{PLA}] + [(m_{ca} - m_{tr})/\rho_f]} \times 100\% \quad (1)$$

Where m_{tr} is the mass of metal tray, m_{cb} is the mass of metal tray within samples before burn off, m_{ca} is the mass of metal tray within samples after burn off, V_f is fibre volume fraction, ρ_f is the density of glass fibre and ρ_{PLA} is the density of PLA. In this study, the densities of the PLA matrix and phosphate glass fibre reinforcement were: ρ_{PLA} = 1.24g mm^{-3} (PLA 3251D [24]), ρ_f = 2.67 g mm^{-3} respectively [25].

2.7 In vitro degradation study

The specimens of composites and neat PLA plates were immersed in 30 ml phosphate buffered saline (PBS) solution in glass vials, according to the standard BS 10993-13:2010 [26]. Eight time points were considered and the specimens were extracted and weighed after blot drying with tissue. The PBS solution was changed at each time point. Measurement of mass loss, pH value and water uptake were recorded at each time point.

2.8 Flexural properties test

Flexural tests (three point bending) were used to determine initial flexural strength and modulus values. The tests were conducted in accordance with BS 14125:1998 [27] using an ElectroForce® (3330 series, Bose, USA). The sample dimensions were 40 × 15 × 2 (l×b×h) mm with a 32 mm test span. A cross-head speed of 1 mm min^{-1} was used with a 3 kN load cell. The samples were positioned such that the fibre direction was along the span (i.e. a 0 ° orientation). The measurement was carried out in triplicate.

2.9 Scanning Electron Microscopy (SEM)

After flexural testing, the composite samples were cooled in liquid nitrogen for 1 minute and fractured manually. Care was taken to ensure that the fracture was created outside the zone of damage from the flexural testing. After sputter coating with platinum, the cross-section of the freeze-fractured composite was examined by using a Philips XL30 (Oxford, UK) scanning electron microscope operated at 10 KV.

2.10 Statistical analysis

The average values and standard error of all data involved in this paper were calculated and analysed using the Prism software (version 6.0, GraphPad Software, San Diego, CA, USA). A one-way analysis of variance (ANOVA) was calculated with the Tukey multiple post-test to compare the significance of change in one factor with time. The error bars on all the data represent standard error of mean.

3. RESULTS AND DISCUSSIONS

3.1 Fibre volume fraction and initial flexural properties

The composites in this study were reinforced using 20% V_f of textile fabric (T-C) or unidirectional fibre mats (0/90-C) of the glass system $48P_2O_5$-$12B_2O_3$-14CaO-20MgO-$1Na_2O$-$5Fe_2O_3$. The fibre volume fractions of the composites were ascertained by burn off tests and are listed in Table 2. There was no significant difference ($P>0.05$) between experimental fibre volume fraction of T-C and 0/90-C.

Sample Code	Sample Description	Fibres in warp direction	Target fibre volume fraction (%)	Experimental fibre volume fraction (%)
0/90-C	Non-crimp laminate	50%	20	22 ± 3
T-C	Plain weave	79%	20	21 ± 1

Table 2: The sample description and fibre volume fraction of textiles reinforced composite (T-C) and 0 ⁰/90 ° lay-up composite (0/90-C).

The initial flexural properties of textile reinforced composites, 0 ⁰/90 °lay-up composite and neat PLA plate are presented in Figure 3, where it can be seen that the flexural strength and modulus of neat PLA plate improved as expected due to reinforcement with textile and unidirectional fibre mats. Additionally, with the similar fibre volume fraction (~20%), the flexural strength of neat PLA plate was seen to increase from 92 ± 6 MPa to 176 ±13 MPa for the T-C and to 137 ± 9 MPa for the 0/90-C. Addition of the reinforcement phases improved the flexural modulus of neat PLA from 3.3 ± 0.1 GPa to 8.6 ± 0.3 GPa and 6.9 ± 0.2 GPa for the T-C and 0/90-C, respectively. As such, the textile reinforced composite exhibited statistically significantly higher ($P<0.01$) flexural strength and modulus when compared to those of the 0/90-C and neat PLA plate.

Ordinarily, a plain weave textile would be balanced and have 50% of yarns in the warp direction and 50% in the weft direction. However, due to limitations with the hand weaving process, it was difficult to maintain an equivalent density of the warp and weft yarns. As can be seen from Table 1, for a single laminate of textile fabric there were considerably more yarns (~79%) along the longitudinal (warp) direction than in the in transverse (weft) direction (~21%). Additionally, it was confirmed that the increase in density of yarns parallel to the load direction lead to an increase in textile fabric stiffness due to the increase in yarn quantity and improvement of load capacity [28]. Therefore, the composite with higher density of warp parallel to the load (longitudinal) direction demonstrated greater mechanical properties.

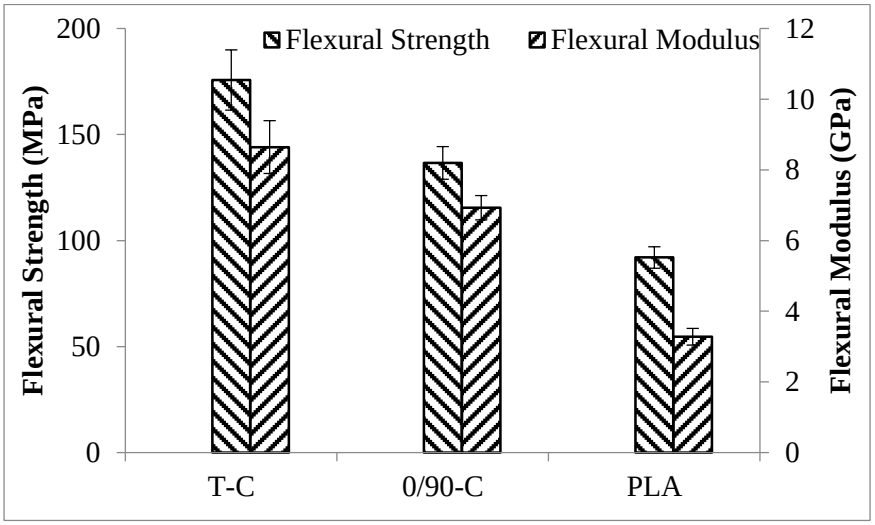

Figure 3: Initial flexural strength and flexural modulus of textile reinforced composite (T-C), 0 ⁰/90 ° lay-up composite (0/90-C) and neat PLA plate.

3.2 Degradation study of composites

The degradation of textile reinforced composites (T-C), 0 ⁰/90 °lay-up composite (0/90-C), and neat PLA plate was investigated in PBS at 37 ℃ for up to 28 days. As can be seen from Figure 4, a significantly higher mass loss was observed for the 0/90-C during the first 11 days. However, all the

composites demonstrated a much higher mass loss when compared to neat PLA and all lost ~20% mass by 28 days, while the neat PLA plate presented a mass loss of only ~0.05%.

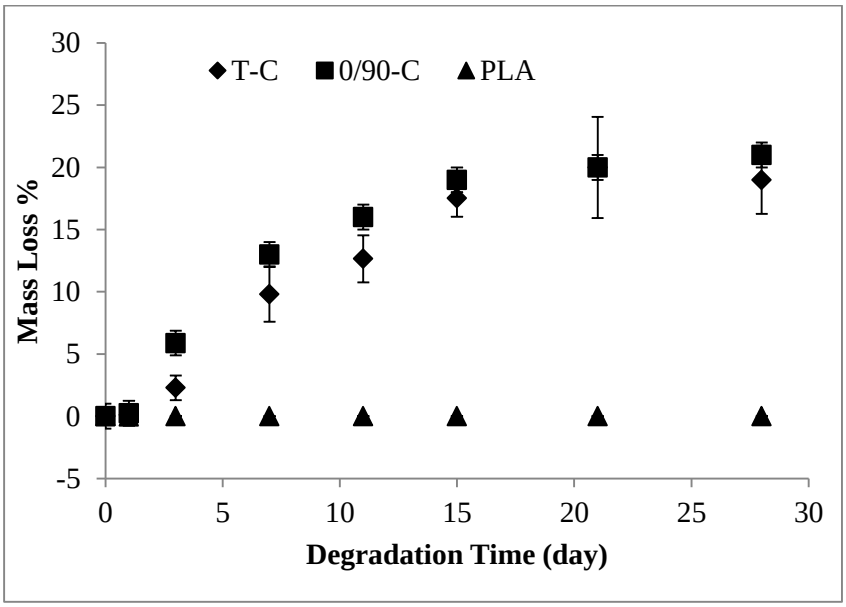

Figure 4: Mass loss of unidirectional yarn reinforced composite (UD-C), textile reinforced composite (T-C), 0 ⁄90 °lay-up composite (0/90-C), and neat PLA plate, over degradation time in PBS at 37 ℃.

The primary factors affecting the degradation were degradation of bonding between fibres and matrix resin due to hydrolysis of coupling agent on the surfaces of fibres, and weakening of the strength of glass fibres due to the fibre dissolution [29]. Since the mass loss of the neat PLA plate appeared to be negligible, the mass loss of the composite was attributed to the dissolution of phosphate glass fibre. Due to the open-ended issue, which meant that the fibre ends were exposed at the edges of the composites, this could allow water to wick along the fibre/matrix, causing the fibres to degrade from the ends to the middle region. As can been seen from Figure 5, the fibres in 0/90-C degraded from the ends to the middle region, along both longitudinal and transverse directions, whilst the fibres in T-C only degraded from the two ends along the longitudinal direction.

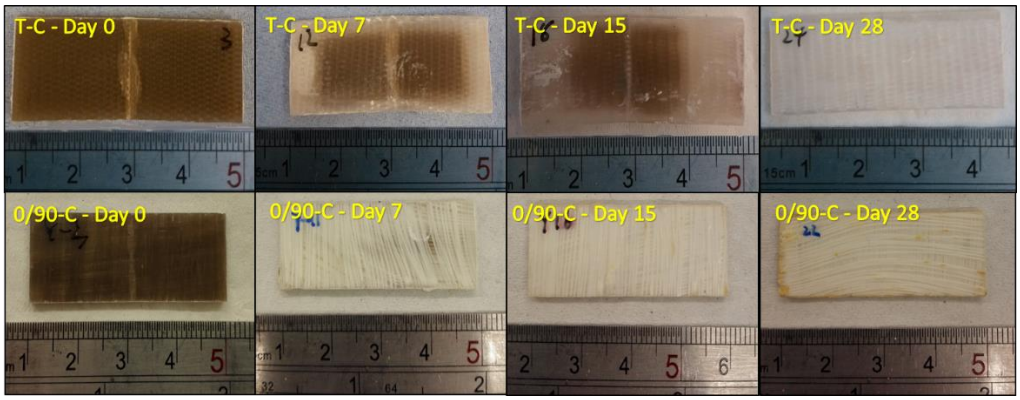

Figure 5: Images of textile reinforced composite (T-C), 0 ⁄90 °lay-up composite (0/90-C) during degradation in PBS at 37 ℃

3.3 Retention of the flexural properties

Figure 6 and Figure 7 show the flexural strength and modulus of the T-C, 0/90-C and neat PLA plate during the degradation period. The T-C and 0/90-C revealed a rapid decrease of flexural strength within

the first 7 days of the degradation period, falling from 176 ± 13 MPa and 137 ± 9 MPa to 108 ± 8 MPa and 74 ± 5 MPa respectively, then reached final values of 32 ± 3 MPa and 28 ± 8 MPa after 28 days. Moreover, a relatively higher flexural strength and modulus was observed for T-Cs when compared to 0/90-C during the initial 15 days degradation period. The flexural modulus for the T-C and the 0/90-C reduced to ~3 GPa after 7 days and plateaued at ~2 GPa after 28 days of immersion in PBS. On the other hand, no significant change in the flexural strength and modulus was observed for neat PLA during the course of the study.

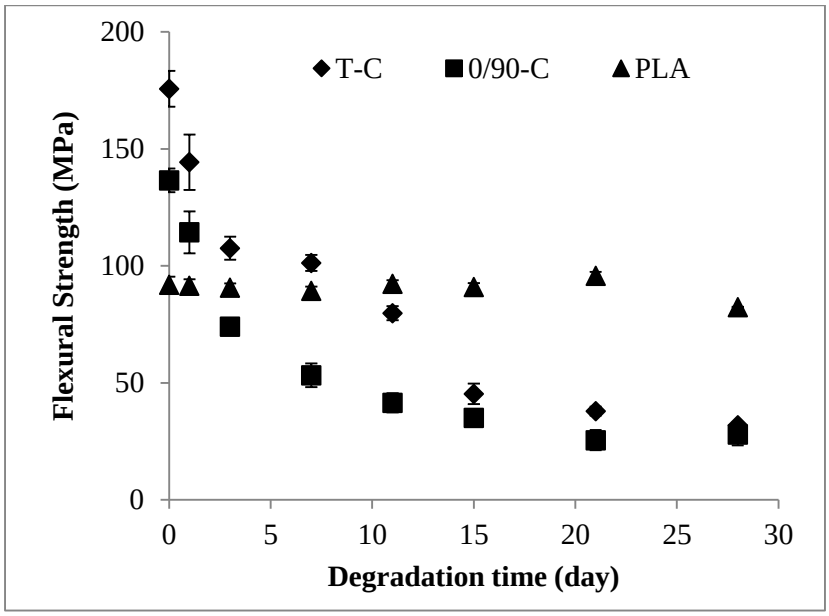

Figure 6: Variation of flexural strength for textile reinforced composite (T-C), 0 ⁄90 ° lay-up composite (0/90-C) and neat PLA plate, over degradation time in PBS at 37 ℃.

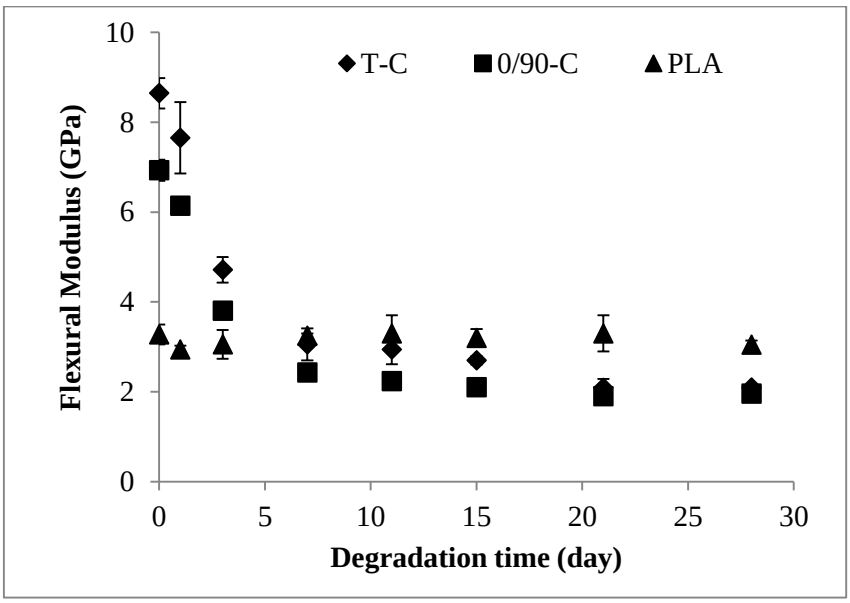

Figure 7: Variation of flexural modulus for textile reinforced composite (T-C), 0 ⁄90 ° lay-up composite (0/90-C) and neat PLA plate, over degradation time in PBS at 37 ℃.

In theory, the mechanical properties of composites were dependent on the fibres and polymer matrix for load bearing and the interfacial bonding between fibre and matrix for load transfer [30]. The decrease of flexural strength and modulus with time was due to the water which diffused into composite samples, acting as a plasticiser and reducing the mechanical properties of the PLA matrix [31]. Additionally,

water that diffused into the composite samples was able to degrade the interface between fibre and matrix, resulting in poor stress transfer efficiency and reduction of flexural properties [32, 33].

This explanation was also supported by microscopy images of composites in Figure 8, debonding between fibre and PLA matrix was seen for all the composites after 7 days of immersion in PBS. Due to the apparent degradation of fibre and fibre pull-out during the three point bending tests, pores and channels were observed in all composites. Furthermore, no fibre was seen in the images of the 0/90-C after 15 days of degradation, and T-C after 28 days degradation.

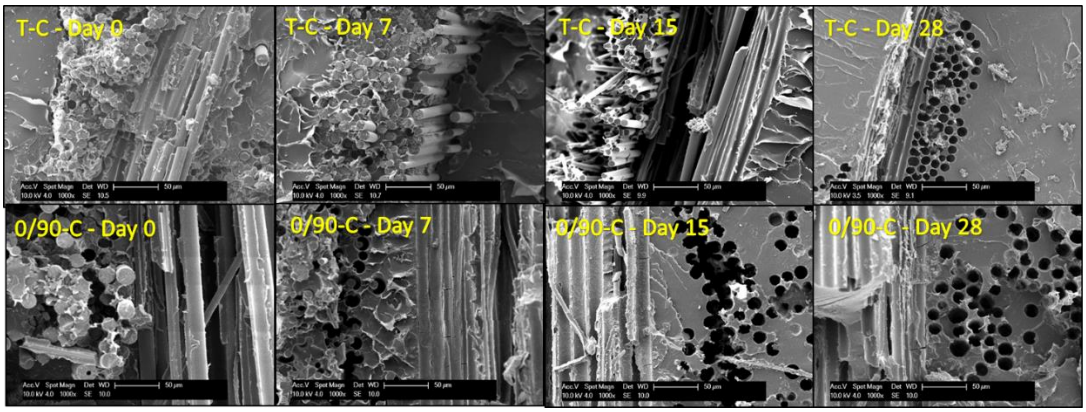

Figure 8: SEM images of fracture surfaces of textile reinforced composite (T-C), 0 ⁰/90 °lay-up composite (0/90-C) and UD composite reinforced with yarn (UD-C), during degradation in PBS at 37 ℃

In summary, the results in this paper indicated some important challenges. Firstly, the degradation study of the composites revealed that the phosphate glass fibre degraded too fast, resulting in a significant reduction of mechanical properties of composite due to dissolution of fibre and fibre-matrix interface. As such, the development of suitable coating agent to protect the fibre surface and improve fibre-matrix interface via forming chemical bonding should be taken into account for follow-on studies. Further, there were limitations in the textile hand weaving process such as low weaving efficiency, different warp and weft density and difficulty in controlling crimps of textile. Automation of the textile manufacturing process via a suitable weaving machine (suitable for PGFs) should be investigated further in order to produce uniform textile fabrics. In a word, this achievement will be the significant milestone on the research of bioresorbable PGFs reinforced composite in medical application, and important step on the industrial direction of bioresorbable medical device.

4 CONCLUSIONS

This research reported on the first PGF textile products developed for composite reinforcement using yarns produced through industrial processes. Multifilament yarns produced from $48P_2O_5$-$12B_2O_3$-14CaO-20MgO-$1Na_2O$-$5Fe_2O_3$ glass were successfully converted into woven textiles using an Inkle loom. The results indicated that the textile reinforced composite performed with comparable efficacy to the composite reinforced by UD fibre mats, when accounting for fabric bias and degree of crimp. However, the degradation rate of all of the composites was faster than desired, with only ~20% flexural strength and ~25% flexural modulus maintained by the 28 day time point. For future study, a suitable coating agent could be taken into account in order to improve the interface and protect fibre surface.

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REFERENCES

1. J. Malekani, B. Schmutz, Y. Gu, M. Schuetz, and P.K. Yarlagadda. Biomaterials in orthopedic bone plates: a review. in *Proceedings of the 2nd Annual International Conference on Materials Science, Metal & Manufacturing (2011)*. Global Science and Technology Forum.
2. Z. Huang, Stiffness and strength design of composite bone plates. *Composites Science and Technology*. **65**, 2005: p. 73-85.
3. J. Wolff, Das Gesetz der Transformation der inneren Architektur der Knochen bei pathologischen Veränderungen der äusseren Knochenform. Gedruckt in der Reichsdruckerei 1884.
4. R.L. Prabhakar, S. Brocchini, and J.C. Knowles, Effect of glass composition on the degradation properties and ion release characteristics of phosphate glass--polycaprolactone composites. *Biomaterials*. **26**, 2005: p. 2209-18.
5. A.J. Parsons, I. Ahmed, N. Han, R. Felfel, and C.D. Rudd, Mimicking bone structure and function with structural composite materials. *Journal of Bionic Engineering*. **7**, 2010: p. S1-S10.
6. R.A. Khan, A.J. Parsons, I.A. Jones, G.S. Walker, and C.D. Rudd, Preparation and characterization of phosphate glass fibers and fabrication of poly(caprolactone) matrix resorbable composites. *Journal of Reinforced Plastics and Composites*. **29**, 2009: p. 1838-1850.
7. J. Tams, F.R. Rozema, R.R.M. Bos, J.L.N. Roodenburg, P.G.J. Nikkels, and A. Vermey, Poly(l-lactide) bone plates and screws for internal fixation of mandibular swing osteotomies. *International Journal of Oral and Maxillofacial Surgery*. **25**, 1996: p. 20-24.
8. S. Ramakrishna, J. Mayer, E. Wintermantel, and K.W. Leong, Biomedical applications of polymer-composite materials a review. *Composites Science and Technology*. **61**, 2001: p. 1189-1224.
9. K. Fujihara, Z.M. Huang, S. Ramakrishna, K. Satknanantham, and H. Hamada, Feasibility of knitted carbon/PEEK composites for orthopedic bone plates. *Biomaterials*. **25**, 2004: p. 3877-85.
10. I. Ahmed, M. Lewis, I. Olsen, and J.C. Knowles, Phosphate glasses for tissue engineering: Part 1. Processing and characterisation of a ternary-based P2O5–CaO–Na2O glass system. *Biomaterials*. **25**, 2004: p. 491-499.
11. J. Choueka, J.L. Charvet, H. Alexander, Y.H. Oh, G. Joseph, N.C. Blumenthal, and W.C. LaCourse, Effect of annealing temperature on the degradation of reinforcing fibers for absorbable implants. *J Biomed Mater Res*. **29**, 1995: p. 1309-1315.
12. I. Ahmed, M. Lewis, I. Olsen, and J.C. Knowles, Phosphate glasses for tissue engineering: Part 2. Processing and characterisation of a ternary-based P2O5–CaO–Na2O glass fibre system. *Biomaterials*. **25**, 2004: p. 501-507.
13. I. Ahmed, P.S. Cronin, E.A. Abou Neel, A.J. Parsons, J.C. Knowles, and C.D. Rudd, Retention of mechanical properties and cytocompatibility of a phosphate-based glass fiber/polylactic acid composite. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. **89**, 2009: p. 18-27.
14. N. Sharmin, M.S. Hasan, A.J. Parsons, D. Furniss, C.A. Scotchford, I. Ahmed, and C.D. Rudd, Effect of boron addition on the thermal, degradation, and cytocompatibility properties of phosphate-based glasses. *Biomed Res Int*. **2013**, 2013: p. 1-12.

15. N. Sharmin, M.S. Hasan, A.J. Parsons, C.D. Rudd, and I. Ahmed, Cytocompatibility, mechanical and dissolution properties of high strength boron and iron oxide phosphate glass fibre reinforced bioresorbable composites. *J Mech Behav Biomed Mater*. **59**, 2016: p. 41-56.
16. Q. Fu, E. Saiz, M.N. Rahaman, and A.P. Tomsia, Bioactive glass scaffolds for bone tissue engineering: state of the art and future perspectives. *Mater Sci Eng C Mater Biol Appl*. **31**, 2011: p. 1245-1256.
17. A.C. Long, Design and manufacture of textile composites. Taylor & Francis 2006.
18. J. Liu, Q. Zu, C. Rudd, S. Huang, and X. Liu, The Textile Products of Cytocompatible Continuous Phosphate Glass Fibre CN 201610188354.
19. Y. Wang, N. Sharmin, A. Parsons, X. Liu, J. Liu, I. Ahmed, and C. Rudd, *Novel bioresorbable textile composite for biomedical applications*,| Publisher|: Place Published|Year|,
20. C. Zhu, I. Ahmed, A. Parsons, K.Z. Hossain, C. Rudd, J. Liu, and X. Liu, Structural, thermal, in vitro degradation and cytocompatibility properties of P2O5-B2O3-CaO-MgO-Na2O-Fe2O3 glasses. *Journal of Non-Crystalline Solids*. **457**, 2017: p. 77-85.
21. K.L. Loewenstein, Manufacturing Technology of Continuous Glass Fibres. Elsevier Science Ltd 1973.
22. F.T. Wallenberger, J.C. Watson, and H. Li, Glass fibers. *Materials Park, OH: ASM International.*,2001: p. 27-34.
23. American Society for Testing and Materials, Standard Test Method for Ignition Loss of Cured Reinforced Resins, American Society for Testing and Materials, ASTM D2584-11: 2011.
24. Ingeo™ Biopolymer 3251D Technical Data Sheet, N. Works.
25. C. Zhu, Scale-up Manufacture and Characterisation of Resorbable Phosphate Based Glass Fibre for Textile Production, University of Nottingham, Doctor of Philosophy, 2016.
26. British Standard Institution, Biological evaluation of medical devices - Part 13: Identification and quantification of degradation products from polymeric medical devices, London: British Standards Institution, BS 10993-13:2010.
27. British Standard Institution, Fibre-reinforced plastic composites - Determination of flexural properties, London: British Standards Institution, 1998, BS 14125:1998.
28. G.A.A. Nassif, Effect of Weave Structure and Weft Density on the Physical and Mechanical Properties of Micro polyester Woven Fabrics. *Life Science Journal*. **8**, 2012.
29. H. Sekine, K. Shimomura, and N. Hamana, Strength deterioration and degradation mechanism of glass chopped reinforced plastics in water environment. *JSME international journal. Ser. 1, Solid mechanics, strength of materials*. **31**, 1988: p. 619-626.
30. R.F. Gibson, Principles of composite material mechanics. Taylor & Francis 2011.
31. R.M. Felfel, I. Ahmed, A.J. Parsons, P. Haque, G.S. Walker, and C.D. Rudd, Investigation of crystallinity, molecular weight change, and mechanical properties of PLA/PBG bioresorbable composites as bone fracture fixation plates. *J Biomater Appl*. **26**, 2012: p. 765-89.
32. H.N. Dhakal, Z.Y. Zhang, and M.O.W. Richardson, Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. *Composites Science and Technology*. **67**, 2007: p. 1674-1683.
33. L.V.J. Lassila, T. Nohrström, and P.K. Vallittu, The influence of short-term water storage on the flexural properties of unidirectional glass fiber-reinforced composites. *Biomaterials*. **23**, 2002: p. 2221-2229.