HYBRID COMPOSITES OF SILICA GLASS FIBRE/NANO-HYDROXYAPATITE/POLYLACTIC ACID FOR MEDICAL APPLICATION

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ABSTRACT

Fibre reinforced composites (FRC) have shown great potential for the application of internal bone fixation due to mechanical properties that are similar to those of human cortical bones. Ternary composites of silica glass fibres, nano-hydroxyapatite (n-HA) and polylactic acid (PLA) were prepared by compression moulding and their mechanical properties were characterized in this study. With the volumetric content of glass fibre remained constantly at 30% and the volume fraction of n-HA increased from 0% to 5%, the flexural strengths of composites decreased from 625.68 MPa to 206.55 MPa, whereas a gradual increment of flexural modulus from 11.01 to 14.08 GPa were observed at the same time. Within a 28-day degradation period, the flexural strengths decreased by 30%, while no obvious trend of modulus variation was found. The flexural properties of all composites prepared in this study were all found to be close to the reported flexural properties. On the other hand, as more n-HA were incorporated, the water absorption percentages increased, whereas negligible mass loss were recorded. SEM images revealed that the impregnation of fibre mats was poor as loose fibres were observed, which shall be solved in future research to further improve the mechanical properties as well as endurance against degradation.

1. INTRODUCTION

Implantation of internal fixation devices, such as bone fixation plates and screws, are common treatment for severe fracture of long bones. Speaking of the materials used for internal fixation devices,

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metals including stainless steel and Co-Cr alloy have proven their effectiveness for the function of bone fixation and commercially available due to excellent feasibility for large-scale fabrication. However, the mechanical properties of metallic implants are much superior to human bones, thus taking most of the mechanical loading applied and led to insufficient mechanical stimulation which is essential for the regeneration of fractured bones. Such situation is termed "stress shielding" and shall be avoided in the practice of internal fixation [1, 2]. It is therefore necessary to develop new materials with excellent biocompatibility and mechanical properties assimilating the bones for safe and effective healing by internal fixation.

It is reported that fibre reinforced composites are potential substitutes for metallic implants, given that the compositions are meticulously selected to ensure fine biocompatibility and appropriate fibre volume fraction were selected for tailorable, bone-mimicking mechanical properties. For instance, the carbon fibre/poly-ether-ether-ketone (PEEK) composites have been successfully applied as bone-fixation devices [3]. It was further expected that with the incorporation of nanoparticles of bioactive components, i.e. hydroxyapatite and beta-tricalcium phosphate (beta-TCP), the biocompatibility as well as the bone-bonding ability of the composites will be even improved [4]. Based on these ideas, hybrid composites containing both fibres and bioactive nano-fillers have been investigated. Shen et al. reported that with the incorporation of nano-hydroxyapatite (n-HA), flexural strengths and modulus of unidirectional carbon fibre/n-HA/polylactic acid composites increased and peaked with n-HA loading of 20%, and the mechanical properties of these composites were similar to those of human cortical bones . However, the degradation behaviour of composites with different n-HA loading were not studied respectively [5]. Su et al. reported good biocompatibility and improved bone-bonding ability of chopped glass fibres/n-HA/polyamide 66 composites against metal counterparts [6]. Currently, limited studies were done focusing on biocomposites reinforced with unidirectional glass fibres and nano-hydroxyapatite particles.

The aim of this study is to investigate the mechanical properties of a ternary composite system consisting unidirectional E-glass fibres, n-HA and polylactic acid (PLA). It is expected that FRC with unidirectional glass fibre reinforcements will be with flexural properties similar to human cortical bones, thus suitable for the applications of load-bearing and bone-fixation without the risk of causing stress-shielding. With the addition of nano-hydroxyapatite, the toughness of the composites will be further enhanced. The variation in mechanical properties of composites immersed in aqueous environment were also studied to learn the degradation behaviour of the composite.

2. MATERIALS AND METHODS

2.1 Preparation of n-HA/PLA composites

The n-HA/PLA composites were prepared via solvent casting methods. For each batch of composites, 40 g of PLA (Natureworks® 6201-D, USA) were consumed, whereas the consumption of n-HA was determined following calculation. The weighted n-HA were casted into 300 ml of dichloromethane (DCM, 99.8% for HPLC, Sigma–Aldrich ®) and mechanically homogenized (JB90-S Mechanical stirrer, Shanghai Meiyingpu®). Then, 40 g of PLA pellets were casted all-at-once into the n-HA/DCM suspension and stirred until all PLA were dissolved. The resultant n-HA/PLA/DCM slurries were casted into steel dishes, left in fume hood overnight for solvent evaporation before sent into oven for 48 hours of vacuum drying under 45 °C to further evaporate the DCM.

The dried n-HA/PLA were then trimmed into small pieces (~5g per piece), and sandwiched by two pieces of PTFE cloth. Such assemblies were heated under 200 °C for 10 minutes in a hot-presser (ZG-50T, Zhenggong ®) before pressed under the static force of ~150 kN for 30 seconds. The hot-pressed n-HA/PLA were transferred into the lower pressing chamber of the same rig, and pressed with same

forces at room temperature. The obtained n-HA/PLA films were finally trimmed into 140 mm × 128 mm rectangle pieces for further processing.

2.2 Preparation of hybrid composites

A stainless steel mould with a 140 mm × 128 mm × 2 mm cavity was used for compression moulding. 3 pieces of E-glass fibre fabrics and 8 pieces of n-HA/PLA films were symmetrically stacked (2-1-2-1-2-1-2, where 2 stands for 2 pieces of n-HA/PLA films and 1 stands for 1 piece of fibre fabric) inside the mould cavity. Such assemblies were sent into the hot-presser, heated under 200 °C for 15 minutes before hot-pressed under static loads of ~330 kN for 10 minutes. The hot-pressed assemblies were finally cold-pressed under room temperature for 10 minutes to obtain hybrid composite plates.

In this study, hybrid composites with 5 different composition were prepared. The volume fraction of E-glass fibres were constantly set at 30%, while volume fraction of n-HA varied: 0%, 0.5%, 1.5%, 3% and 5%.

2.3 Mechanical testing

Composites plates were cut into 40 mm × 15 mm × 2 mm specimens using band saw, and polished with sand papers to clean the edges of specimens. Then, the specimens were subjected to 3-point bending tests in accordance with BS EN ISO 14125:1998 [7]. A universal testing machine (E45.105, MTS®, U.S.A.) with 50 kN load cell was used for these tests, with the rate of cross-head set at 1 mm/min. For each batch of sample, the mechanical testing were carried out in triplicate.

2.4 Degradation studies

A 28-day degradation study was done to track the variations of media uptake, mass loss and flexural properties of composites. The specimens were immersed in glass vials filled with 30 ml phosphate buffered saline (prepared from P4417-100TAB, Sigma-Aldrich®) and stored in 37 °C oven (DHG-9075A, Shanghai Yiheng®). PBS was refreshed every 7 day. At the 7th, 14th and 28th day, specimens were taken out, blot-dried with tissue and weighted for their wet mass. Then, mechanical testing according to 2.4 were done. The tested specimens were stored in 37 °C oven for 5 days and weighted again for dried mass. Water absorption (WA) and mass loss (ML) were calculated as below:

$$WA= \frac{M_w-M_d}{M_d} \times 100\% \qquad (1)$$

$$ML= \frac{M_i-M_d}{M_d} \times 100\% \qquad (2)$$

Where M_w is the mass of specimens containing water, M_d is the dried mass of specimens after 5-day drying, and M_i is the initial mass of specimens. In addition, statistical analysis comparing the mean values by t-tests were performed using GraphPad Prism 7.

3. RESULTS AND DISCUSSION

3.1 Initial mechanical properties

The mechanical properties of non-degraded composites were shown in Figure 1. As the volume fraction of n-HA increased from 0% to 5%, flexural strengths of composites reduced from 625.68 ± 7.86 MPa to 206.55 ± 12.54 MPa. Comparing to composites containing no n-HA, the change of flexural strengths were statistically significant (p<0.05) in all samples except for those with 0.5 vol.% n-HA. On the contrary, the flexural modulus of composites increased gradually from 11.01 ± 0.63 GPa to 14.08 ±

0.63GPa as n-HA contents increased up to 3%, however, unexpectedly dropped to 11.96 ± 0.42 GPa when n-HA volume fraction reached 5%. No statistical significance (p>0.1 in each case) in variation of modulus were observed.
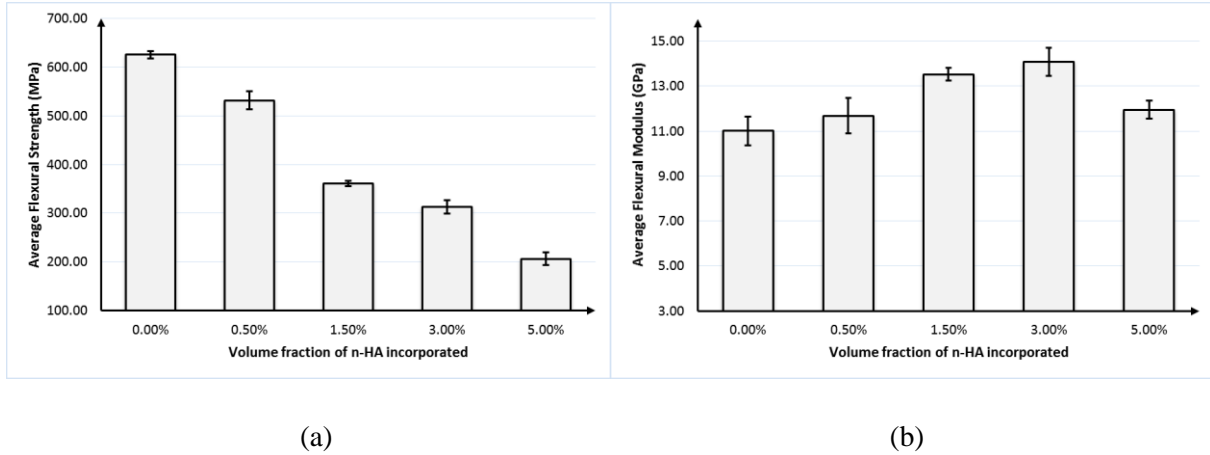

(a) (b)

Figure 1. Flexural strengths (a) / flexural modulus (b) of GF/n-HA/PLA hybrid composites with different n-HA loading. Error bars in both figures represent standard errors (n=3).

With higher percentage of n-HA loading, a general trend of increasing stiffness was observed in this study. This was due to the reinforcing effect of rigid n-HA particles that carry the load effectively [8]. An unexpected reduction of flexural modulus was observed when n-HA loading increased to 5 vol.%, and following calculation, the mass fraction of n-HA dispersed in the PLA in this case was ~16%. This was a relatively low value comparing to reviewed studies where 40 wt.% n-HA was dispersed in PLA phase and the incorporation of n-HA below this amount were generally reported to improve the flexural modulus of HA/PLA composites [9-12]. Hypothesis was made that if the fibre volume fraction and impregnation condition were very close to each other, the composites with higher n-HA loading were expected to be stiffer as the matrix itself possess higher flexural modulus. Given that the fibre volume fraction were controlled to be 30%, it was possible that in composites with 5 vol.% n-HA, the impregnation of fibres were unexpectedly poor, which led to reduction of modulus. The decrement of flexural modulus at high n-HA loading were also found in studies by Shen et al., who reported that when n-HA loading exceeded 20 wt.% in PLA, the modulus of carbon fibre/n-HA/PLA composites were lower and finally become saturated [5]. It was possible that with more n-HA loading, less PLA adhered to the surface of fibre and consequently the fibre bonded to the polymer matrix poorly. Also, the flowing ability of polymer might be lowered as the n-HA particles hindered the mobility of polymer chains [13].

On the other hand, the flexural strengths decreased significantly along with n-HA addition. There are several possible reason for this phenomenon. Agglomeration of n-HA were facilitated as n-HA loading increased, which may cause stress concentration and lead to early failure of composites under flexural tests. Also, the continuous phase of polymer is broken down with the existence of these agglomerations [8]. Generally speaking, the flexural properties of these GF/n-HA/PLA composites were close to those of human cortical bones, which possess flexural strengths of 50-150 MPa and modulus of 5-20 GPa, thus considered eligible for load-bearing applications without the complications of causing stress-shielding [14, 15].

3.2 Failure mode of specimens

No brittle fracture was observed from the tested specimens, as no sudden reduction of load was detected from the bending tests, and the strain continued increasing after the peak loads were achieved. Whitening of polymer phase were observed from the location where loads were applied. Regarding the failure mode, all specimens displayed compressive fractures with interlaminar shear according to BS EN ISO 14125:1998 [7]. Loose fibre bundles can be seen from delaminated specimens as shown in Figure 2. In addition voids between fibres are clearly visible in the cross sections of composites, see Figure 3.

(a)	(b)
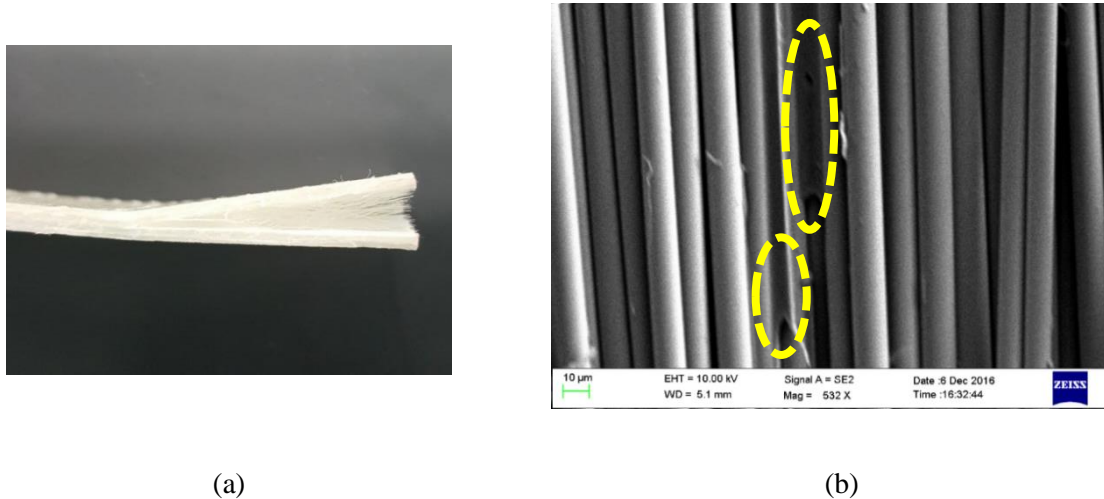
Figure 2: A typical tested specimen with obvious interlaminar shearing and loose fibres exposed (a) and a SEM image (b) of delaminated location (sample with 1.5 vol% n-HA loading). HA/PLA impregnation is marked out by dashed oval.

The phenomena of interlaminar shearing along with loose fibres suggested that the impregnation of polymer phase (n-HA/PLA) were poor. This was also evidenced by the internal voids observed from the cross-section of ternary composites, as the E-glass fabrics used in this study were too thick to be completely impregnated. As can be seen from Figure 3, the outermost region of fibre fabrics were well wet-out by the polymer matrix, whereas the inner fibres remained unimpregnated. There was no doubt that the voids compromised the effect of fibre reinforcement. Therefore, it was assumed that by replacing E-Glass fabrics with prepregs, these defects could be avoided and mechanical properties of composites would be further improved. It shall be pointed out that while filling the gaps between fibre fabrics with more polymer (films) were considered to improve the wet out, the actual finding was that excessive polymer were filled into the mould cavity. As a result, when hot-pressing was applied to the whole assembly, excessive polymer flowed out from the mould, and the alignment of fibres were destructed. It was also assumed that the wet-out ability of n-HA/PLA was lower than those of pure PLA, due to the reason that particle fillers hindered the mobility of polymer chains when molten[13].
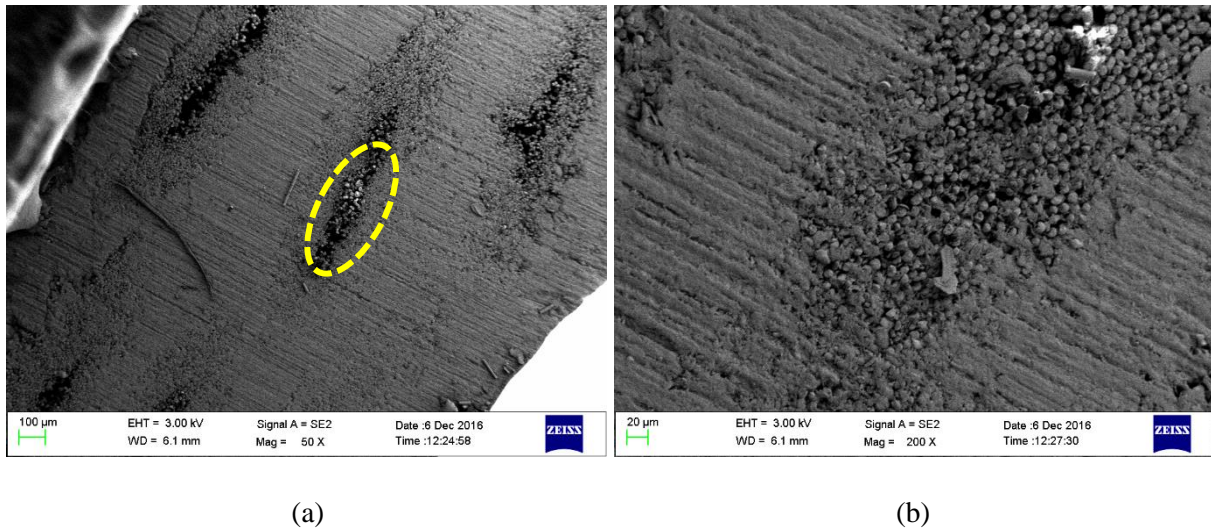
(a)   (b)

Figure 3: SEM images (a) showing the cross-section of untested specimen (1.5 vol.% n-HA loading), and a detailed view of marked area (b).

3.3 Retention of mechanical properties along with degradation

Figure 4 and 5 illustrated the variation of flexural strengths and modulus of each composition during the 4-week degradation period. It can be observed that while fluctuation of flexural modulus were recorded in each sample, no certain trend of either reduction or increment could be concluded from the results. The fluctuation of modulus was due to differences between specimens, most probably the variation in fibre alignments as the fibres were not completely parallel to the longitudinal direction of some of the specimens. These fluctuation might have overshadowed the trend of modulus variation in the 28-day degradation period.

On the contrary, reduction of flexural strengths were rather obvious, especially for composites with 0.5% n-HA loading which lost ~47% of initial strengths after 28 days. Samples with 0%, 1.5% and 3% volume fraction of n-HA all lost ~30% of initial strengths after 4 weeks, however, the strength lost was more smoothly in composites without n-HA, whereas a burst reduction of ~20% followed by minor variations in week 2 were observed in the other 2 composites. The significant reductions of flexural strengths ($p < 0.05$, except for composites with 5% n-HA) were observed after 1 week were believed to be results of hydrolysis of polymer at the fibre-polymer interface As for composites with 5% n-HA reinforcement, the smooth reduction of strengths might be the reason that effect of water attack was less significant, as the polymers adhering to glass fibres were reduced with the existence of n-HA particle, therefore less sensitive to hydrolysis.

3.4 Water absorption and mass loss

The water absorption profile were diagrammed in Figure 6. For all composites, the water absorption were found to be significant in the first week, followed by minor changes in the second week. It was also observed that as more n-HA were incorporated, higher water absorption was recorded. In contrast, negligible mass loss (Figure 7) were recorded from all composites after 4 weeks of degradation. Additionally, saturation of water absorption was observed from composites without n-HA from week 2, whereas further water uptake were found on all other samples with n-HA incorporated. This was due to the hydrophilicity of n-HA that contributed to increased water uptake. However, further characterization is required to examine the effects of internal spaces brought by either voids within fibres (Figure 3a) or degradation of long-chain PLA on water absorption.
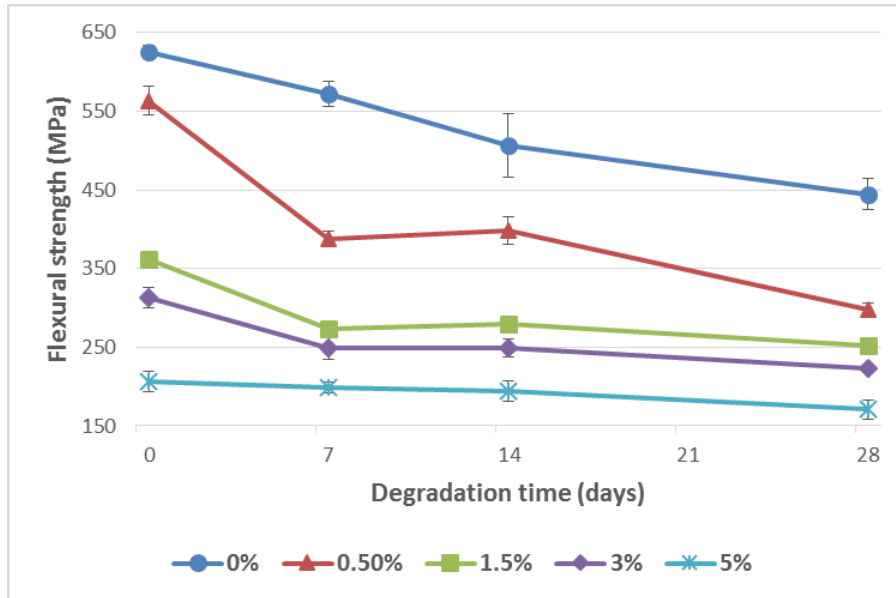
Figure 4: Variation of flexural strengths during the 28-day degradation period. Error bars represent standard errors (n=3)
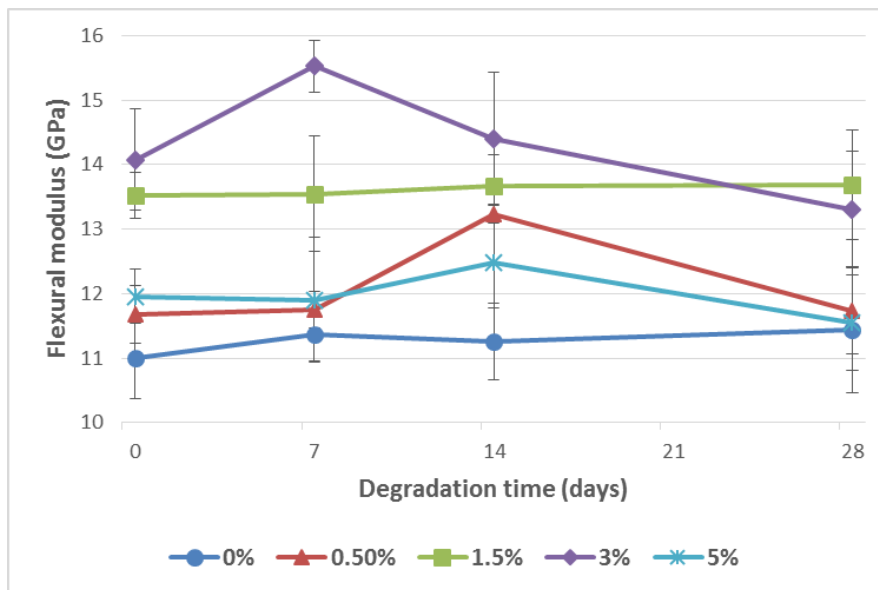

Figure 5: Variation of flexural modulus during the 28-day degradation period. Error bars represent standard errors (n=3)

On the other hand, the mass loss profile of composites in this studies were negligible, as less than 0.2% mass loss were recorded. No relationship between mass loss and n-HA loading was found. Considering that only 28-day degradation were carried out, the degradation of bulk n-HA/PLA were considered to be rather limited. The negligible degradation of polymer in this study also indicated that the weakening of composites after immersion in PBS were basically due to destruction of interface integrity, as neither bulk n-HA/PLA nor E-glass fibres degraded during this period.
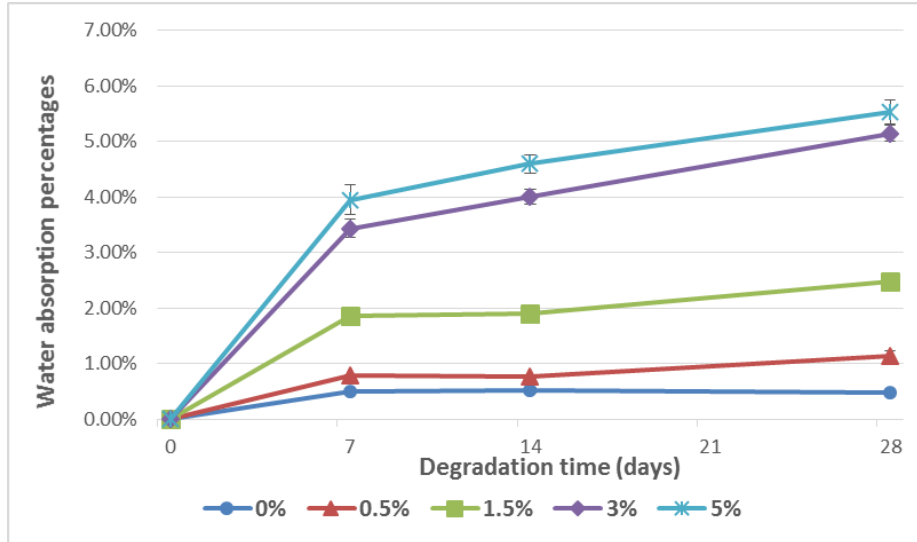
Figure 6: Water absorption profile during the 28-day degradation period. Error bars represent standard errors (n=3)
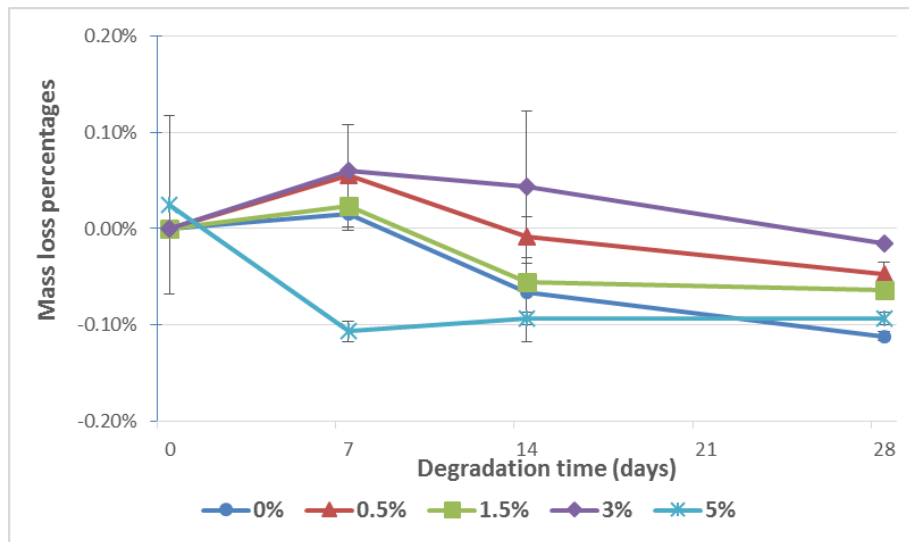

Figure 7: Mass loss profile during the 28-day degradation period. Error bars represent standard errors (n=3)

4. CONCLUSIONS

Hybrid composites of PLA, n-HA and silica glass fibres were produced via solvent casting followed by compression moulding. Flexural properties of these composites can be tailored with the manipulation of n-HA loading. With increasing amount of n-HA incorporated into the composite, the flexural strength decreased whereas the flexural modulus were improved. The flexural properties of composites were very close to those of human cortical bones and showed good retention during a 28-day degradation period. Poor interfacial bondings as evidenced by delamination well as internal voids were considered to be limiting the mechanical properties of composites as well as its endurance against degradation. Further research is required to improve the impregnation of glass fibres inside the composite to enhance the performance of these composites as biomaterials for internal fixation.

ACKNOWLEDGEMENTS

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