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Mechanical Properties of Poly (L-Lactide)-Based Composites for Hard Tissue Repairs

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Abstract: ***The struggle in osteosynthesis continues with the search for more biocompatible materials to replace metallic scaffolds. Poly(L-lactic) acid (PLLA), a biopolymer, was processed via melt-blending technique by blending chitosan and Ti-6Al-2Sn-2Mo-2Cr-0.25Si powders with it in varying compositions at 290 ºC. The microhardness values, compressive moduli and fracture toughness of the reinforced PLLA improved significantly while the resulting composites were found to be less tough than the unreinforced PLLA. Compressive moduli obtained were much lower than the modulus of cortical bone. They were, however, mechanically compatible with the properties of cancellous bone.***

Keywords: Cancellous Bone, Osteologic Repairs, Mechanical Properties, Chitosan, Titanium Powder.

I. INTRODUCTION

The use of poly(L-lactic) (PLLA) acid in osteologic repairs is gradually becoming an overriding phenomenon over the use of the metallic scaffold. The major reasons why metal is becoming an abandoned material in osteosynthesis include a propensity to release toxins, corrosion, bio-incompatibility, stress shielding or 'off-loading', peel-off particulates and many other clinical issues [1]. In contrast to the drawbacks associated with metals, PLLA is a biodegradable, biocompatible, bioresorbable and non-carcinogenic polymer [2], [3] that has been processed for tissue engineering [4]–[6] and some other applications. Although PLLA has been described as an excellent material in regenerative hard and soft tissue engineering, especially in term of its bio-characteristics [4], [7], its relatively weak mechanical properties are the major drawbacks in the field of orthopaedic. For proper osteologic repair, it is necessary to fix this problem so as to enhance the performance of PLLA in the human physiological environment.

In an attempt to improve on the suitability of PLLA for tissue engineering, several processing techniques have been used [5]. Some of these processing techniques are usually cumbersome and complicated. The use of melt-blending techniques is, however, environmentally benign, cost-effective, best for mass production and toxin-free since it does not require the use of a solvent unlike in the electrospinning process.

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Besides, processing PLLA via melt-blending helps in pores formation necessary for cell differentiation and proliferation [8] in any biological system. The melt-blending method was used to produce polymer composites with both organic and inorganic reinforcements with enhanced mechanical properties. Huang, *et al*. for instance, prepared PLLA/n-HA composites by heating the matrix to a viscous flow state at 160 ºC and press moulding it to form a cylinder after melt blending the filler with the matrix [9]. Characterisation shows improved strength characteristics and enhanced *in vitro* degradation. In this work, Poly(L-lactic) acid composites were developed using chitosan (an organic) and titanium (an inorganic) powders as reinforcements. Unlike the use of titanium as a filler in PLLA, reinforcing PLLA with chitosan has been well researched [10]. The main reason for the addition of chitosan to PLLA is majorly to help its biocompatibility and degradation profile. Reinforcing PLLA with chitosan with a view to enhancing its mechanical properties is usually a secondary consideration. This is because chitosan is itself structurally weaker than PLLA [10].

II. MATERIALS AND METHODS FOR SAMPLE PREPARATION

The poly(L-lactic) acid (M_w = *144 g/mol*) used in this work was purchased from NatureWorks, China. Chitosan (chemically extracted from shrimp shells purchased from Ijora Olopa market, Oyigbo, Lagos in Nigeria) was the organic reinforcement and Titanium (Ti-6Al-2Sn-2Mo-2Cr-0.25Si) powder, purchased from TLS Technik GmbH & Co., Germany, was the inorganic filler. Table 1 gives the various compositions of the matrix and the reinforcements.

A. Methods of Melt Compounding

Heat-melt technique, at 290 ºC, was used as the filler-matrix compounding method. The molten composites were mould pressed to form cylinders of 12.5 ± 0.05 mm diameter and 7 ± 1 mm long. Variational relationships between different weight percentages as well as structural strength differences between the two reinforcements were observed.

Table 1: Blend Compositions of the Developed Composites

PLA (wt. %)	Ch (wt. %)	Ti (wt. %)
100	0.00	0.00
98.96	1.04	1.04
97.92	2.08	2.08
95.83	4.17	4.17
91.67	8.33	8.33

a) Composites Characterisation

The compression test was done using a double column Instron Universal testing machine with model number 3369 (equipped with

Bluehill software for data acquisition) located at CERD, OAU, Ile-Ife in Nigeria. The elastic modulus, mechanical strength, etc., were obtained from the compression test. Additionally, Vickers hardness test was done to investigate the hardness property of the composites and to examine the ability of the developed composites to resist crack growth in the presence of microcracks.

The dwell time for the Vickers microhardness test was 10s for all the samples. The indentation load was 100 kg.

III. RESULTS AND DISCUSSIONS

A. The resistance of the Composites to Plastic Deformation by Indentation

Figure 1 shows the result of the Vickers microhardness test, which explains the extent to which the composites resisted deformation by micro indentation. These values are similar to that obtained in some work where the micro indentation responses of polylactic acid were investigated [11]. In this work, it can be seen that the microhardness values increase with an increase in the addition of both fillers. PLLA/Ch, for instance, 10.93, 31.49, 56.27 and 116.33 % increase were obtained with the respective addition of 1.04, 2.08, 4.17 and 8.33 wt.% chitosan. Similarly, with the addition of titanium powder, 121.28, 135.86, 163.12 and 290.82 % increase was recorded as shown in Table 2.

The analysis of microhardness values showed that PLLA/Ti produced composites that were stronger in term of mechanical response to deformation by indentation (Table 1). When compared with PLLA/Ch, PLLA/Ti gave the greater value of hardness. This trend reflects the difference in the structural strength of titanium powder (inorganic reinforcement) and chitosan (organic filler). Expectedly, inorganic fillers (metallic powders in particular) have been reported to produce higher mechanical properties than the organic ones [12].

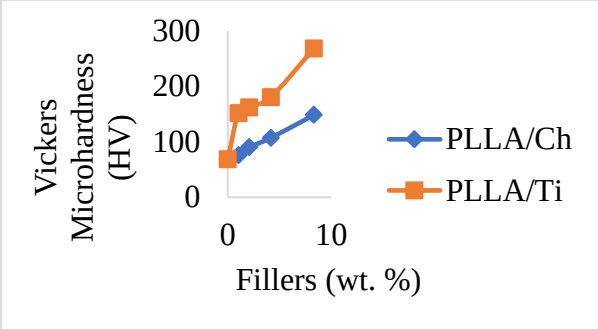

Figure 1: Vickers Microhardness Values

Table 2: Percentage increase in the microhardness values of PLLA composites due to filler loading

Filler (wt. %)	PLLA/Ch % increase over PLLA (%)	PLLA/Ch % increase over PLLA (%)	PLLA/Ti % increase over PLLA/Ch (%)
1.04	10.93	121.28	99.47
2.08	31.49	135.86	79.38
4.17	56.27	163.12	68.38
8.33	116.33	290.82	80.66

B. Ultimate Compressive Strength (UCS) of the Developed Composites

The maximum compressive strengths of the developed composites are shown in Figure 2. The addition of the fillers initially reduced the strength of the matrix. Further addition of the reinforcement, however, gradually increased the strength of the base material. The initial decrease in strength can possibly be as a result of pores, which were filled to some extent as the percentage of the reinforcements increases. The reduction in strength can also be seen in the light of load transfer mechanism. It could be that stress was not sufficiently transferred across the filler-matrix interface [13].

The strengths obtained by adding 1.04, 2.08 and 4.17 wt. % of chitosan match the strength of human cancellous bone [14]. The compressive strengths obtained with increased loading with both titanium powder and chitosan are lower than the strength of the human cortical bone [14]. The composites developed at such increased filler loading can, however, be used as bone internal fixations to avoid stress shielding, which is often the result of using materials with outrageously high strength.

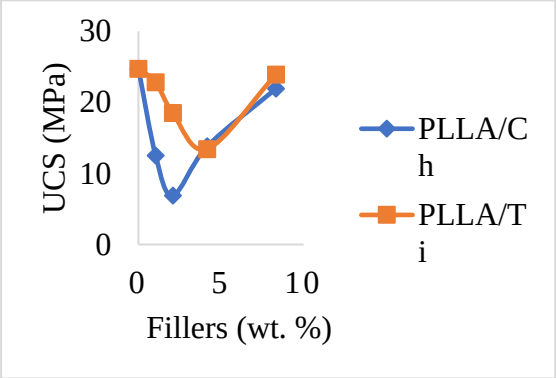

Figure 2: Maximum Compressive strength of PLLA composites

C. Compressive Stress-Strain Behaviour of the Composites

Elastic Modulus, the slope of the stress-strain graph within the elastic region (i.e. to the yield point), is a property that is commonly used to summarise the stress-strain behaviour of a material. The compression test was done within the ambient temperature to avoid temperature interference on the test results. The magnitude of modulus of elasticity (Figure 3) obtained here is quite low. This is becoming of polymer and polymer composites with pores [15], [16].

The initial reduction in the compressive elastic modulus of the composites (compared with unreinforced PLLA) was majorly because of the formation of randomised pores leading to a non-uniform transfer of stress across the boundary of reinforcement-matrix interface. Materials with pores have been generally found to have low elastic moduli [15], [16]. The eventual increase in the compressive modulus when 8.33 wt. % of fillers was added indicates that some pores have been filled with increasing filler loading. Ch, for instance, improved the matrix elastic modulus by 2.7 % while Ti raised its elastic modulus by 22.1 %. Ti being a metallic powder is structurally stronger than Ch, a polymeric organic powder.

Ti increases the compressive elastic modulus by 18.9 % more than Ch loading. Compressive modulus obtained for both composites are though lower than the elastic modulus of human cortical bone; they are a little above that of human cancellous bone [14]. Increasing the wt. % of the reinforcements beyond 8.33 wt. % would likely increase the compressive elastic modulus. The present values of modulus obtained here can help in cancellous bone repairs.

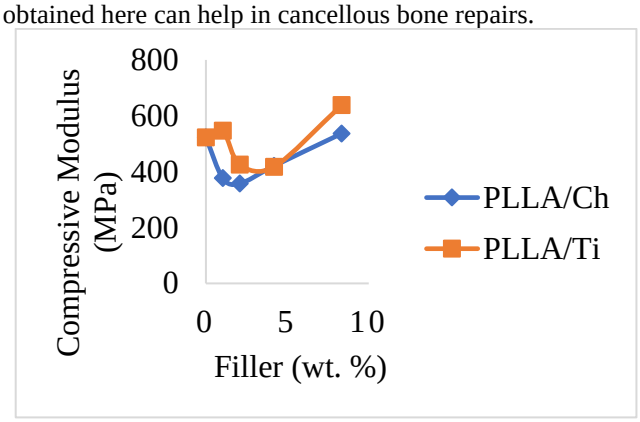

Figure 3: Compressive Stress-Strain Behaviour of the Composites

D. Toughness Characteristics of the Composites

The toughness values of PLLA/Ch and PLLA/Ti presented in Table 3 were obtained by estimating the area under the stress-strain curve using *trapz* in MATLAB R2019a. The results of the estimation implied how much energy was absorbed per unit volume. Pure PLLA has the highest toughness. Randomised pore formation, which is the characteristic of melt-blending technique, affected a proportionate relationship between different wt. % of fillers and the corresponding values of absorbed energy per unit volume. The resistances to crack growth by the composites discussed in section 5 are low compared with the values of toughness because toughness does not generally account for the presence of cracks.

Table 3: Toughness of PLLA/Ch and PLLA/Ti

Filler (wt.%)	PLLA/Ch (Jm^{-3})	PLLA/Ti (Jm^{-3})
0.00	1.82	1.82
1.04	0.32	1.06
2.08	0.12	0.26
4.17	0.59	0.50
8.33	0.85	0.64

E. Predicted Resistance to Crack Growth by the Composites

The resistance of the developed composites to fracture in the presence of a crack was predicted using equation 1 [17]. The combined effects of the parameters from the Vickers microhardness test and mechanical compression test were examined by the equation to predict the fracture toughness values of the developed composites.

$$K_{IC} = 0.0089\left(\frac{E}{H_V}\right)^{\frac{2}{5}}\left(\frac{P}{aC^{\frac{1}{2}}}\right) \quad \text{---------- Eq. 1}$$

where

$K_{IC} = Fracture\ \ toughness\ (MPa.m^{0.5})$

$P = indentation\ loading\ (N)$

$E = Young's\ modulus\ (GPa)$

$H_V = Vickers\ hardness\ (GPa)$

$a = half -$
$diameter\ of\ the\ sample's\ indented\ section\ (mm)$

$c = the\ crack\ length\ (mm)$

The results shown in Figure 4 revealed that the composites developed in this work exhibited some complex, unconventional mechanical properties when compared with the values of Vickers microhardness (Figure 1) and Young's moduli in Figures 3. PLLA/Ti showed improved fracture toughness in all wt. % addition of Ti with the greatest value of fracture toughness at the highest wt. % addition. Improved fracture toughness was noticed from 4.17 wt. % addition of chitosan. The two fillers used improved the fracture toughness of virgin PLLA by 18.47 and 23.02 % with Ch and Ti loading respectively. Generally, the low values of fracture toughness obtained in this work are indicative of low ductility [18].

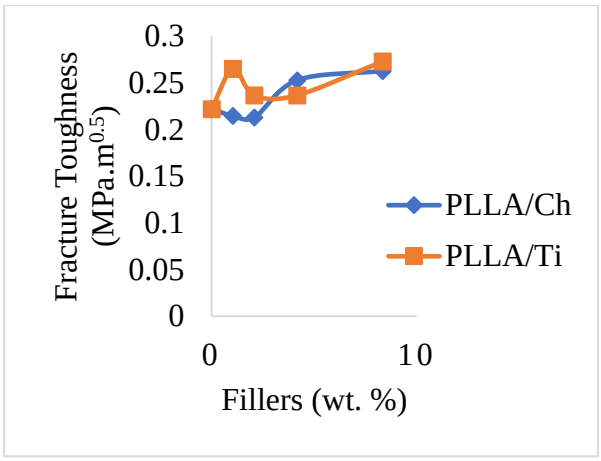

Figure 4: Fracture Toughness

IV. CONCLUSION

Poly(L-lactic acid) was reinforced with an organic polymer (chitosan) filler and inorganic metallic particles (titanium) by melt-blending technique. Hardness and compressive modulus properties of titanium-reinforced PLLA were found to be a little higher than that of PLLA/Ch. The higher values obtained from using titanium particles as filler validates the stronger structural property of Ti over the strength of the structure of Ch. The mechanical properties of the developed composites are in the neighbourhood of the properties of cancellous bone.

The processing technique employed automatically led to the formation of pores in the composites. These formed pores are necessary for any biological structures for cell growth and would enhance biological performance.

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