The Strength characteristics of Chitosan- and Titanium- Poly (L-lactic) Acid Based Composites

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Abstract

The problem of bone fracture and the need to avoid revision surgery in osteosynthesis are the critical reasons for the gradual shift from the use of metallic fixations to the polymeric scaffold in the orthopaedic applications. However, the mechanical properties of polymers that have become a substitute for metals need to be improved upon. An attempt was made to improve the mechanical properties of poly(L-lactic) acid (PLLA), a biopolymer, by loading it with 1.04, 2.08, 4.17, 8.33 and 16.67 wt.% of chitosan (an organic filler) and Ti-6Al-2Sn-2Mo-2Cr-0.25Si (an inorganic particle). Melt blend technique was the processing technique. Hardness, compressive modulus and fracture toughness of virgin PLLA improved significantly while the resulting composites were found to be less ductile than unreinforced PLLA. Titanium reinforced PLLA displayed superior mechanical properties over the neat and chitin reinforced PLLA. Compressive modulus values of the developed composites were much lower than the modulus of cortical bone, they were, however, mechanically compatible with the properties of cancellous bone. Optical microscopy images also show the formation of pores which are a catalyst for cell proliferation and cell differentiation.

1.0 Introduction

Poly(L-lactic) acid (PLLA) is a biodegradable polymer that has been copiously processed for tissue engineering application [1], [2], although its versatility has endeared it to many other applications beside [3], [4]. The bid to find viable substitutes for metallic fixations stems from the clinical issues with the use of metals in osteosynthesis [1], [5]–[7]. Some metals that are still retained till date in orthopaedics have been reported to cause the loss of bone mineral density, majorly, because of their high mechanical strength [8]. The mechanical properties of an ideal bone fixation are neither expected to be excessively higher than the mechanical properties of bone nor overly lower [9]. The former has always been the case with metals and the later with polymers. This has made the search for better internal fixation an unending exercise.

PLLA becomes a much sort material because of its biodegradability, bio-resorbability, biocompatibility, non-carcinogenicity of its degradation products, among others [1], [3], [10]–[12]. However, some of its limitations in medical applications have been noticed to include slow degradation profile, hydrophobicity and brittleness [10]. Attempts to improve on these drawbacks of PLLA have resulted in the use of reinforcement like natural polymers and ceramics [4], [5], [13] and significant success has been recorded, especially with respect to its degradation profile [13]. Its application in orthopaedics, however, requires
improvement on its mechanical properties and biodegradability. Besides, the processing of PLLA for such application requires pores formation necessary for cell proliferation [14], [15]. It would be necessary to achieve this with less complicated processing techniques to save cost and time without compromising quality. In the present work, an attempt has been made to develop and study the mechanical properties of Poly(L-lactic) acid composites using chitosan (Ch) (an organic) and titanium (Ti) (an inorganic) powders as reinforcements.

Unlike the use of titanium as a filler in PLLA, reinforcing PLLA with chitosan has been well researched [4], [16]. The main reason for the addition of chitosan to PLLA is majorly to help its biocompatibility and degradation profile. Reinforcing PLLA with chitosan to enhance its mechanical properties is usually a secondary consideration. This is because Chitosan is itself structurally weaker than PLLA [16].

2.0 Materials and Methods for Sample Preparation

PLLA (3,6-dimethyl-1,4-dioxane-2,5-dione) with the molecular weight 144 g/mol was purchased from NatureWorks, China. Chitosan (chemically extracted from shrimp shells purchased from Ijora Olopa market, Oyigbo, Lagos in Nigeria) and Titanium (Ti-6Al-2Sn-2Mo-2Cr-0.25Si) powders were the fillers. A 6mm thick titanium plate has cylindrical through-holes diameter 12.7 mm [17] machined into it. Using a CNC milling machine located at Resolution Centre, University of Johannesburg, South Africa.

Melt blend technique was used as the processing method for making the composites as this method allows for a wider range of reinforcement weight percentage (wt.%) addition than methods like electrospinning, Fused Deposition Modelling (FDM) and some other methods for making polymeric composites. Degassing was not done after mechanical stirring to give room for the creation of pores which is necessary for cell proliferation and differentiation [14], [18].

Each sample was a cylinder of 12.5 ± 0.05 mm diameter and 7 ± 1 mm long. Individual Chitosan reinforced PLLA (PLLA/Ch) and Titanium reinforced PLLA (PLLA/Ti) contained 1.04, 2.08, 4.16, 8.33 and 16.7 wt.% of Ch and Ti fillers respectively. Variational relationships between different weight percentages and structural strength differences between the two reinforcements were observed.

3.0 Characterisation

The Young’s modulus, toughness and ductility were measured from compression test done using a double column Instron Universal testing machine with model number 3369 (equipped with Bluehill software for data acquisition) located at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. Additionally, Vicker’s hardness test was done to investigate the hardness property of the composites. The dwell time was 10s, except for 16.7 wt.% PLLA/Ti that took 15s for visible indentation to be made. The indentation load was 100 kg. The samples were polished using the gold polishing cloth and the polished surfaces etched with 5% nital solution in preparation for Optical Microscopy. Optical microscopy was done to observe the surface morphology, the reinforcement-matrix dispersion pattern and the presence of pores.
4.0 Results and Discussions

4.1 Hardness

Figure 1 shows the Vicker’s hardness number (HV). It was observed that the hardness values obtained relate well with the hardness value of PLA reported by researchers [19]. HV increases with increase in chitosan for all per cent weight additions. The same trend was observed with the addition of titanium powder. Comparatively, PLLA/Ti composites showed greater values of Vicker’s hardness than PLLA/Ch composites up until 8.33 wt.% addition of reinforcements. For instance, 49.87, 44.25, 40.61 and 44.65% increased hardness were obtained for multiples of weight per cent addition of reinforcements from 1.04 to 8.33 wt.%. The superior HV of PLLA/Ti aligns with the fact that inorganic powders would generally produce polymer composites with higher mechanical properties than would a natural polymer filler [20].

Further addition of titanium beyond 8.33 wt. %, however, shows a drastic reduction in hardness, making PLLA/Ti to be 1.51% less hard than PLLA/Ch. Ceteris Paribus, this is not expected since titanium is far structurally stronger than chitosan as observed in other composites with less concentration. This exception may be due to poor dispersion of the reinforcement in the matrix as Ti grew dense (owing to increase in concentration), making some particles to settle down at the bottom of the crucible during production. This condition is usually somewhat more difficult to avoid in polymer-metal composites than in polymer-polymer composites [21]–[23].
Moreover, this phenomenon imposed a limitation on the comparative analysis of hardness properties of these composites as poor dispersion of Ch was not an observable difficulty in PLLA/Ch composite. Chitosan was also observed to increase the hardness of PLLA by 9.86, 23.95, 36.01, 53.77 and 59.09% with multiples of weight per cent addition of reinforcements from 1.04 to 16.67 wt.% respectively. There was a progressive increase in hardness of PLLA/Ch.

4.2 Compressive Modulus

The compression test was done at ambient temperature to avoid the influence of temperature on the values of obtained. The magnitude of modulus of elasticity obtained here is quite low. This is becoming of polymer and polymer composites with pores [14], [15], [24].

The modulus of elasticity initially decreased (compared to virgin PLLA) with reinforcements loading and thereafter began to increase with 2.63% (at 8.33 wt.%) and 37.98% (at 16.67 wt.%) when Ch was added, while the addition of Ti gave 18.10% (at 8.33 wt.%) and 39.98% (at 16.67 wt.%) increases (Table 1). The initial decrease in the elastic modulus of PLA composites can be attributed to pore formation [14], [15], [25] and poor interfacial adhesion between the matrix and the fillers which consequently led to a non-uniform transfer of stress across the boundary interface [26], [27]. Obviously, PLLA/Ti gave higher moduli of elasticity than PLLA/Ch.

![Figure 2: Plot of (a) Compressive Modulus and (b) Percentage Relative Difference in Compressive Modulus](image-url)
Table 1: Percentage increase in the Young’s Modulus, E, of PLLA due to filler loading

| Mass of PLLA (g) | Mass of fillers (g) | wt.% of fillers | % increase in E (MPa) |
|-----------------|---------------------|-----------------|----------------------|
|                 |                     |                 | PLLA/Ch | PLLA/Ti | PLLA/Ti over PLLA/Ch |
| 84              | 4                   | 8.33            | 2.63     | 18.10   | 15.89                  |
| 80              | 8                   | 16.67           | 37.9     | 39.55   | 5.62                   |

Significant improvement on the modulus of elasticity of PLLA with Ch and Ti as fillers began from the addition of 4g of the reinforcements in 84g of virgin PLLA. Initial decreases observed when reinforcements’ wt.% was below 8.33 could be due to randomise formation of pores (resulting in weakening the composites' strength) which increased filler loading was able to fill to a great extent. Table 1 conveys a message that further addition of Ch and Ti beyond 16.67% could give higher values of Young’s modulus.

However, as observed in Figure 1, the further addition of Ti beyond 8.33 wt.% impacted the hardness property and the fracture toughness unfavourably. The Elastic moduli of PLLA/Ti at different wt.% showed improved response than with PLLA/Ch. Compressive modulus obtained for both composites are though lower than the elastic modulus of human cortical bone, they are a little above that cancellous bone [28].

4.4 Ductility

Table 2 displays the ductility of the composites. For all wt.% of chitosan, ductility reduced noticeably. There is no defined pattern in the reduction rate due to uncontrolled pores formation. It is, however, at maximum wt.% addition, ductility dropped to the minimum for the two composites, being minimal in Ti filled PLLA than in Ch. Initially, the addition of Ti powder improved the ductility of the composite up to 4.17 wt.% before it began to decline. The reduction in ductility of the matrix with Ch loading appears logical if compared to its hardness property: inverse variation between hardness and ductility being a general phenomenon. The ductility behaviour of PLLA/Ti shows a departure from norms.
4.5 **Toughness**

The toughness values of the developed composites were obtained by evaluating the area under the stress-strain curve [29] using \( \text{trapez} \) in Matlab. The values obtained which implied the amount of energy absorbed per unit volume are presented in Table 3.

In all the cases, virgin PLLA shows the greatest value of toughness. Apparently, the random pores formed, as shown by the results from optical microscopy (Figure 4) hindered a defined variational pattern in the values of toughness obtained. Unlike in ductility where Ti improved the property of PLLA, no reinforcements improved the toughness of the matrix. Drastic reduction in the toughness of PLA composites was also noticed by other researchers [30].

It was noticed that the values of toughness obtained here are higher than the values of fracture toughness. The difference may be explained in the light of the presence of microcracks from which the values of fracture toughness were obtained. Materials with pre-existing cracks are generally expected to those without cracks.

| Filler (wt.%) | PLLA/Ch (%) | PLLA/Ti (%) | Filler (wt.%) | PLLA/Ch (MPa) | PLLA/Ti (MPa) |
|--------------|-------------|-------------|--------------|---------------|---------------|
| 0.00         | 13.71       | 13.71       | 0.00         | 1.82          | 1.82          |
| 1.04         | 11.43       | 15.96       | 1.04         | 0.32          | 1.06          |
| 2.08         | 10.76       | 15.85       | 2.08         | 0.12          | 0.26          |
| 4.17         | 8.89        | 15.52       | 4.17         | 0.59          | 0.50          |
| 8.33         | 12.31       | 12.18       | 8.33         | 0.85          | 0.64          |
| 16.67        | 8.73        | 7.33        | 16.67        | 0.46          | 0.55          |

4.6 **Fracture Toughness**

The resistance of the developed composites to fracture in the presence of a crack was calculated using equations 1 and 2 [31]. Parameters measured from micro radial cracks from Vicker’s hardness were solely used in equation 1 while the combination of these parameters and the values of elastic modulus from the compression test were used in equation 2. Figure 4 is a plot of the results from the two equations.
\[ K_{IC} = 0.0726 \frac{P}{c^2} \]  \hspace{1cm} (1)

\[ K_{IC} = 0.0089 \left( \frac{E}{H_V} \right)^{\frac{2}{3}} \left( \frac{P}{ac^2} \right) \]  \hspace{1cm} (2)

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 average fracture toughness from both equations was 0.22 ± 0.11 MPa.m\(^{1/2}\). Equation 1 predicted a trend that established an approximate inverse relationship between hardness and fracture toughness. This seems to be in consonance with the general knowledge about the mechanical properties of the material. If, however, the fact that composites could exhibit complex unorthodox mechanical properties is considered [32] equation 2 would give the more appropriate values.

![Figure 3: Predicted Values of Fracture Toughness](image-url)

Interestingly, the values predicted using equations 2 are higher than those obtained from the use of equation 1. Equation 2 encompasses more mechanical properties in its consideration for the prediction of fracture toughness than equation 1 as stress and strain in the form of Young’s modulus were also accounted for. Hence, it is logical to assume that the percentage error would be lower with the use of equation 2. Conclusively, the composites developed, therefore, improved the fracture toughness of virgin PLLA by 32.4 and 30.3 % with Ch and Ti loading respectively. However, equation 1 can be used as a quick check to predict the
fracture toughness since it only makes use of parameters measured from Vicker’s indentation micro-hardness test.

5.0 Optical microscopy

Figure 4 is the unprocessed images obtained from Optical microscopy test. It shows the dispersion of the fillers with Ti being more obvious. Chitosan appears to blend well with PLLA except at 2.08 wt.% loading. There are progressive morphological changes with the incremental addition of Ch. The composite with the least Ch wt.% shows light surface morphology while the one with the highest wt.% of Ch has a dense morphological surface. Speckles of whitish materials on the surface morphology, especially at 4.17 and 8.33 wt.% filler addition, are indications of the presence of chitosan [26], [33].

Figure 4: Optical Microscopy images of Neat PLLA, PLLA/Ch and PLLA/Ti

The surface morphology of both composites shows micro-surface pores which are a catalyst for cell proliferation and differentiation [14], [15].

Conclusions

Poly(L-lactic acid) was reinforced with an organic polymer (chitosan) filler and inorganic metallic particles (titanium) by heat-melt technique. Hardness and compressive modulus properties of titanium reinforced PLLA were found to be a little higher than that of PLLA/Ch. PLLA/Ti also simultaneously improved the ductility of PLLA. 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 by simply
not degassing the molten polymer. These formed pores are necessary in any biological structures for cell growth and consequently, enhanced biological performance.

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REFERENCES

[1] O. P. Gbenebor, R. A. Atoba, E. I. Akpan, A. K. Aworinde, S. O. Adeosun, and S. A. Olaleye, “Study on Polylactide-Coconut Fibre for Biomedical Applications,” in TMS 2018 147th Annual Meeting & Exhibition Supplemental Proceedings, M. & Materials Society, The Minerals, Ed. Cham: Springer International Publishing, 2018, pp. 263–273.

[2] C. Li et al., “Severe pathological fractures caused by vertebral hemangiomas with posterior decompression, bone cement augmentation and internal fixation,” Orthop. Traumatol. Surg. Res., vol. 102, no. 4, pp. 489–494, 2016.

[3] M. Murariu and P. Dubois, “PLA composites: From production to properties,” Adv. Drug Deliv. Rev., vol. 107, pp. 17–46, Dec. 2016.

[4] S. Deepthi, M. Nivedhitha Sundaram, J. Deepti Kadavan, and R. Jayakumar, “Layered chitosan-collagen hydrogel/aligned PLLA nanofiber construct for flexor tendon regeneration,” Carbohydr. Polym., 2016.

[5] F. Ya’ish, C. A. Bailey, C. P. Kelly, and M. A. Craigen, “Bioabsorbable Fixation of Scaphoid Fractures and Non-Unions; Analysis of Early Clinical Outcomes,” Hand Surg., vol. 18, no. 03, pp. 343–349, 2013.

[6] A. U. Daniels, M. K. O. Chang, K. P. Andriano, and J. Heller, “Mechanical properties of biodegradable polymers and composites proposed for internal fixation of bone,” J. Appl. Biomater., vol. 1, no. 1, pp. 57–78, 1990.

[7] J. J. Dias, “Definition of Union after Acute Fracture and Surgery for Fracture Nonunion of the Scaphoid.” pp. 321–325, 2001.

[8] A. K. Harrison, T. J. Gioe, C. Simonelli, P. J. Tatman, and M. C. Schoeller, “Do porous tantalum implants help preserve bone?: Evaluation of tibial bone density surrounding tantalum tibial implants in TKA,” Clin. Orthop. Relat. Res., vol. 468, no. 10, pp. 2739–2745, 2010.

[9] A. K. Aworinde, S. O. Adeosun, F. A. Oyawale, E. T. Akinlabi, and E. Emagbetere, “Mechanical Strength and Biocompatibility Properties of Materials for Bone Internal Fixation: A Brief Overview,” in Proceedings of the International Conference on Industrial Engineering and Operations Management, 2018, pp. 1–12.

[10] L. Xiao, B. Wang, G. Yang, and M. Gauthier, “Poly(Lactic Acid)-Based Biomaterials: Synthesis, Modification and Applications.” pp. 247–282, 2012.

[11] Z. Li and C. Wang, “Effects of Working Parameters on Electrospinning,” in One-Dimensional Nanostructures Electrospinning Technique and Unique Nanofibers, 2013, pp. 15–28.
[12] S. O. Adeosun, A. K. Aworinde, I. V. Diwe, and S. A. Olaleye, “Mechanical and Microstructural Characteristics of Rice Husk Reinforced Polylactide Nanocomposite,” *West Indian J. Eng.*, vol. 39, no. 2, pp. 63–71, 2016.

[13] Z. Wang, Y. Wang, Y. Ito, P. Zhang, and X. Chen, “A comparative study on the in vivo degradation of poly(L-lactide) based composite implants for bone fracture fixation,” *Sci. Rep.*, vol. 6, pp. 1–12, 2016.

[14] X. Wang, T. Lou, W. Zhao, G. Song, C. Li, and G. Cui, “The effect of fiber size and pore size on cell proliferation and infiltration in PLLA scaffolds on bone tissue engineering,” *J. Biomater. Appl.*, vol. 30, no. 10, pp. 1545–1551, 2015.

[15] P. Song et al., “Novel 3D porous biocomposite scaffolds fabricated by fused deposition modeling and gas foaming combined technology,” *Compos. Part B Eng.*, vol. 152, no. June, pp. 151–159, 2018.

[16] A. R. C. Duarte, J. F. Mano, and R. L. Reis, “Novel 3D scaffolds of chitosan-PLLA blends for tissue engineering applications: Preparation and characterization,” *J. Supercrit. Fluids*, vol. 54, no. 3, pp. 282–289, 2010.

[17] ASTM-D695, *D 695 -15 Compressive Properties of Rigid Plastics*. 2015, pp. 1–8.

[18] Y. Chen et al., “Mechanical properties and biocompatibility of porous titanium scaffolds for bone tissue engineering,” *J. Mech. Behav. Biomed. Mater.*, vol. 75, pp. 169–174, Nov. 2017.

[19] S. Farah, D. G. Anderson, and R. Langer, “Physical and mechanical properties of PLA , and their functions in widespread applications — A comprehensive review ☆,” vol. 107, pp. 367–392, 2016.

[20] H. G. B. Premalal, H. Ismail, and A. Baharin, “Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites,” *Polym. Test.*, vol. 21, no. 7, pp. 833–839, Jan. 2002.

[21] M. Pozuelo et al., “Stretching Micro Metal Particles into Uniformly Dispersed and Sized Nanoparticles in Polymer,” *Sci. Rep.*, vol. 7, no. 1, pp. 3–7, 2017.

[22] M. Šupová, G. S. Martynková, and K. Barabaszová, “Effect of Nanofillers Dispersion in Polymer Matrices: A Review,” *Sci. Adv. Mater.*, vol. 3, no. 1, pp. 1–25, 2011.

[23] J. Liu, Y. Gao, D. Cao, L. Zhang, and Z. Guo, “Nanoparticle dispersion and aggregation in polymer nanocomposites: Insights from molecular dynamics simulation,” *Langmuir*, vol. 27, no. 12, pp. 7926–7933, 2011.

[24] C. Esposito Corcione et al., “Highly loaded hydroxyapatite microsphere/ PLA porous scaffolds obtained by fused deposition modelling,” *Ceram. Int.*, no. xxxx, pp. 1–8, 2018.

[25] C. Esposito Corcione et al., “Highly loaded hydroxyapatite microsphere/ PLA porous scaffolds obtained by fused deposition modelling,” *Ceram. Int.*, vol. 45, no. 2, pp. 2803–2810, 2019.

[26] V. M. Correlo, L. F. Boesel, M. Bhattacharya, J. F. Mano, N. M. Neves, and R. L. Reis, “Properties of melt processed chitosan and aliphatic polyester blends,” *Mater. Sci. Eng. A*, vol. 403, pp. 57–68, 2005.
[27] H. Frans, “Impact Testing of Polypropylene Blends and Composites,” Polym. Eng. Sci., vol. 35, no. 24, pp. 1962–1971, 1995.

[28] G. Narayanan, V. N. Vernekar, E. L. Kuyinu, and C. T. Laurencin, “Poly (lactic acid)-based biomaterials for orthopaedic regenerative engineering,” Adv. Drug Deliv. Rev., vol. 107, pp. 247–276, 2016.

[29] D. Taylor, “Measuring Fracture Toughness in Biological Materials,” J. Mech. Behav. Biomed. Mater., 2017.

[30] J. L. Orellana, D. Wichhart, and C. L. Kitchens, “Mechanical and Optical Properties of Polylactic Acid Films Containing Surfactant-Modified Cellulose Nanocrystals,” J. Nanomater., vol. 2018, pp. 1–12, Oct. 2018.

[31] A. Moradkhani, H. Baharvandi, M. Tajdari, H. Latifi, and J. Martikainen, “Determination of fracture toughness using the area of micro-crack tracks left in brittle materials by Vickers indentation test,” J. Adv. Ceram., vol. 2, no. 1, pp. 87–102, 2013.

[32] W.-L. Li and J. C. M. Li, “The effect of grain size on fracture toughness,” Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop., vol. 59, no. 6, pp. 1245–1261, 1989.

[33] Z. Zakaria et al., “Mechanical Properties and Morphological Characterization of PLA/Chitosan/Epoxidized Natural Rubber Composites,” Adv. Mater. Sci. Eng., vol. 2013, pp. 1–7, 2013.