THE PROPERTIES OF POLY(LATIC ACID) (PLA)/HYDROXYAPATITE (FsHAp) COMPOSITE PREPARED THROUGH SOLVENT CASTING TECHNIQUES

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Abstract. In this study, the properties of composites produced using solvent casting technique from poly(lactic acid) (PLA) and fish scale hydroxyapatite (FsHA) were investigated. Some amount of FsHAp powders (from 10 to 70 wt%) were added to the PLA solution and stirred for eight hours after the PLA was dissolved in the dichloromethane (DCM) solvent. The homogeneous mixture of PLA and FsHA was poured into the metal mould and dried in the oven for 4 hours to produce a dried PLA/FsHA composite sheet. The PLA/FsHA composite sheet with different FsHA filler contents was successfully prepared. These composites were characterised by Fourier transform infared spectroscopy (FTIR), differential scanning calorimetry (DSC), tensile tester and scanning electron microscope (SEM). It can be seen that by addition of 50 wt% FsHA filler contents gave the highest Young's Modulus and tensile strength values of 2114.8 MPa and 23.3 MPa, respectively due to effective interaction between fillers and matrix. The melting point of pure PLA, which was 147 °C increased to 149 °C when it was loading with 30 wt% FsHA and this enhancement may attributed to the capacity of natural FsHA to encourage surface contact between PLA matrix. The DSC result was consistent with the FTIR result which demonstrated that the peaks' shifting implied some degree of chemical interaction between the matrix and FsHA. From SEM analysis, it proved good distributions of FsHA fillers in the matrix of PLA/FsHA composites and this indicated that the composite has potential to be used in biomedical applications.

Keywords: Poly(lactic acid), fish scale hydroxyapatite (FsHA), solvent casting, dichloromethane (DCM), PLA/FsHA composite

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Introduction

Conventional synthetic polymers have had a significant impact on the environment since this kind of polymers are manufactured using non-renewable fuels and release greenhouse gases throughout productions, mainly carbon dioxide (CO_2) [1-2]. In order to minimize the reliance on non-renewable polymers, the scientists of this field have boosted their efforts in developing a variety of sustainable polymer-based materials.

PLA is made from plants such as corn, sugar beets, sugar cane, wheat and etc and it is not from the petroleum resources. Fermentation in the plant converts starch into lactic acid, which is polymerized to produce PLA [3]. Recently, the most promising biodegradable polymer is PLA. PLA is biocompatible materials, non-toxic and eco-friendly polymer which is currently used in bone replacement materials [4]. However, the brittleness of PLA polymer has limit in its applications [5-6]. For many applications, PLA needs to be modified with fillers and some other additives to improve their thermal and mechanical properties [7]. Currently, PLA is widely used as polymer in biomedical applications such as tissue engineering scaffolds and implant due to their biocompatibility and biodegradability properties in the human body [8].

There are a few bioceramic fillers that are widely used in polymer matrix to improve mechanical properties for biomedical applications. Some examples of them are alumina, zirconia, bioactive glass, glass ceramics, hydroxyapatite (HA), and resorbable calcium phosphates [9]. According to the previous study [10-11], synthetic HA is the most common filler used in biomaterials composite due to its biocompatibility, bioactivity and osteoconductivity properties. Currently, most of commercial HA is produced from chemical reactions but this technique is relatively very expensive [12]. Alternatively, HA from natural resources from minerals or biological have been widely studied [13]. The best alternative material to replace synthetic HA is natural HA which comes from aquatic such as fish scales and bones [13]. FsHA was produced by thermal or chemical extraction from fish scales and proved to have biological properties similar to synthetic HA [14-15]. Mixing of HA filler and PLA successfully improved the mechanical and biological properties of the composite [16]. Recently, PLA/HA composite has been used in various biomedical products such as scapula prosthesis, knee prosthesis, dental implants, interbody fusion cage, acetabular cup and hip prosthesis [16]. However, there is very little information on the application of FsHA as filler in polymer matrix composite for biomedical applications [14].

The solvent casting method is a common procedure in making polymer film. This technique is simple, economical and easy to control. However, the polymer needs to be dissolved in a suitable solvent before casting into a suitable mould and dry it to evaporate the solvent completely [12]. In this study, the potential of FsHA as a filler in PLA polymer matrix was investigated. This research investigated the effects of FsHA filler on the thermal, tensile properties and morphology of the PLA/FsHA composites.

Materials and Methods

Materials

Poly(lactic acid) resin (Ingeo 2003D) was purchased from NatureWorks LLC, USA and dichloromethane from Sigma-Aldrich. FsHA powders were extracted from fish scales as

reported previously [15], ball milled and spray dried into powders and sieved. Table 1 shows the formulation of PLA/FsHA composite.

Table 1: The formulation of PLA/FsHA composite

Composite	100 PLA	PLA/10 FsHA	PLA/20 FsHA	PLA/30 FsHA	PLA/40 FsHA	PLA/50 FsHA	PLA/70 FsHA
PLA (wt%)	100	90	80	70	60	50	30
FsHA (wt%)	0	10	20	30	40	50	70

The PLA was dissolved in dichloromethane (DCM) solvent thoroughly by stirring for 1 hour. The FsHA powders were added into the PLA solution and stirrer for 8 hours. The homogeneous mixture of PLA/FsHA was poured into the metal mold (size 254 x 254 mm) and dried in oven for four hours to produce dried PLA/FsHA composite sheet. The steps of sample preparation are shown in Figure 1. The PLA/FsHA composite tensile specimens were prepared according to the ASTM D 638-03 before subjected to tensile test.

Figure 1: Steps in producing of PLA/FsHA composite. (a) stirring PLA/FsHA in DCM at room temparature, (b) casting in metal plate mould, (c) PLA/FsHA composite sheet and (d) tensile specimen of the composite

Differential Scanning Calorimetry (DSC)

Thermal analysis was carried out using DSC (model: DSC1, Mettler Toledo) in order to determine the melting point of the composite. Each sample, with a 10 mg average was sealed in an aluminium pan and heated from room temperature to 200 ˚C at a rate of 10 ˚C/min in a nitrogen environment. The maximum peak was used to determine the melting temperature (T_m).

Fourier Transforms Infrared Spectroscopy (FTIR)

The chemical properties of pure PLA and PLA/FsHA composites were analyzed to identify the changes in functional groups of polymer by using Fourier transform infrared spectroscopy (FTIR). A spectrometer (model: Nicholet 6700 series) was employed to obtain the IR spectra. The composites samples were scraped out into powders and about 7 mg composite powders were then placed direct scanning using Miracle ATR accessory (miracle base optics assembly). FTIR was used with a resolution of 4 cm and scanning ranges of 4000

to 600 cm^{-1}. After each and every sample usage, ethanol was used the clean up the tester placed.

Tensile Test

The mechanical properties of PLA/FsHA composites was monitored by using a universal testing machine (UTM) (model: INSTRON machine 3366) with bluehill software, USA equipped with a 10 kN load cell, the tensile test was performed in accordance with American Society for Testing Materials ASTM D638. The test was conducted on specimen until the failure took place at a cross-head speed of 50 mm/min. A Mitutoyo thickness gauge and caliper were used to measure the specimen's thickness and width prior to the tensile test. The narrow portion of the specimen had the gauge length of 50 mm. Averages of five tested samples were made from the seven specimens of each composite composition and the tensile test was carried out at room temperature.

Morphology

The morphology of the neat PLA and PLA/ FsHA composites were characterized by using SEM machine (model: JEOL JSM-6490LV) operating at 20 kV in order to observe the distribution of FsHA fillers in the PLA/FsHA composites. For getting better images and also to minimize the electrostatic charge of the samples, the surface samples of the composite were platinum coated with Quorum Q150R S.

Results and Discussion

Fourier Transforms Infrared Spectroscopy (FTIR) Analysis

FTIR was used to analyze the chemical structure and interaction between fillers and matrix in the composites. The FTIR peaks correspond to the functional groups present in the samples. The FTIR spectra of PLA and PLA/FsHA composite are presented in Figure 2. FTIR spectrum of neat PLA exhibit absorption bands within the range from 3004 to 2937 cm^{-1}, 1753 cm^{-1} and 1061 cm^{-1} correspondent to stretching of functional groups of C-H, C=O and C-O respectively. The phosphate groups from FsHA were identified by the bands at 1090 cm^{-1}, 1025 cm^{-1} and 960 cm^{-1} which corresponding to the stretching of P-O bonds as reported by Chakravarty et. al. [12].

The FTIR spectrum of 10 wt% FsHA is virtually identical to that of neat PLA with the exception of two additional peaks for the FsHA component that correspond to the PO_4^{-3} and O-H groups at 1195.14 cm^{-1} and 1367.89 cm^{-1}. The chemical interaction between the FsHA and PLA matrix is most likely involved peaks at 1753.12 cm^{-1} (C=O) and 1367.89 cm^{-1} (O-H). The FTIR spectrum of 30 wt% FsHA is almost identical to that of 10 wt% FsHA, with additional peaks for PO_4^{-3} at 1042.48 cm^{-1} [12]. FTIR spectrum of 50 wt% FsHA is almost similar as 30 wt% FsHA, extra peaks are observed for 767.90 cm^{-1} for C-H bending of amorphous region in PLA.

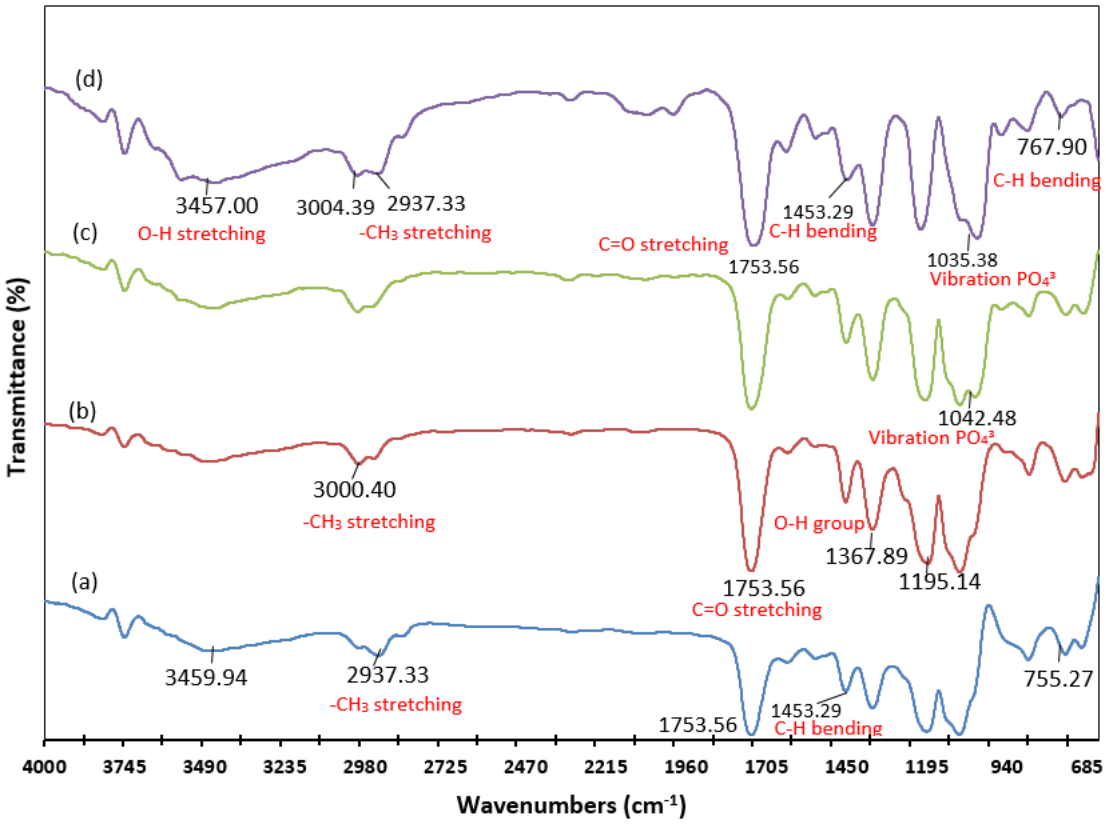

Figure 2: FTIR spectra of (a) neat PLA, (b) PLA/10FsHA, (c) PLA/30FsHA and (d) PLA/50FsHA

Muhamad et al. [17] claimed that the peaks at 3570 cm^{-1} and 1989 cm^{-1} corresponded to the stretching and bending of the hydroxyl group (OH) present in the HA respectively, [17]. Sharma et al. [18] also made a similar observation and noted that a small, sharp peak at about 3572 cm^{1} was indicative of the stretching of the OH groups. The FTIR analysis demonstrated that the noticeable peaks seen at 3457 cm^{-1} are indicative of the functional groups of OH group in hydroxyapatite of sample PLA/50FsHA.

Differential Scanning Calorimetry (DSC) Analysis

The melting peaks of pure PLA and its composites are shown in Figure 3, indicating the significant differences in their positions (Figure 3). The melting point (T_m) of pure PLA is 147 ˚C with 2 peaks and was shifted to a single peak of 145.9 ˚C after the addition of 50 wt% FsHA. This behavior probably due to PLA matrix has lost of its conformational purity and chain alignment throughout the mixing process [10]. It was found that the melting transitions (T_m) of composite with composition of FsHA below than 50 wt% exhibited two melting peaks (T_{m1} and T_{m2}) which is similar to pure PLA.

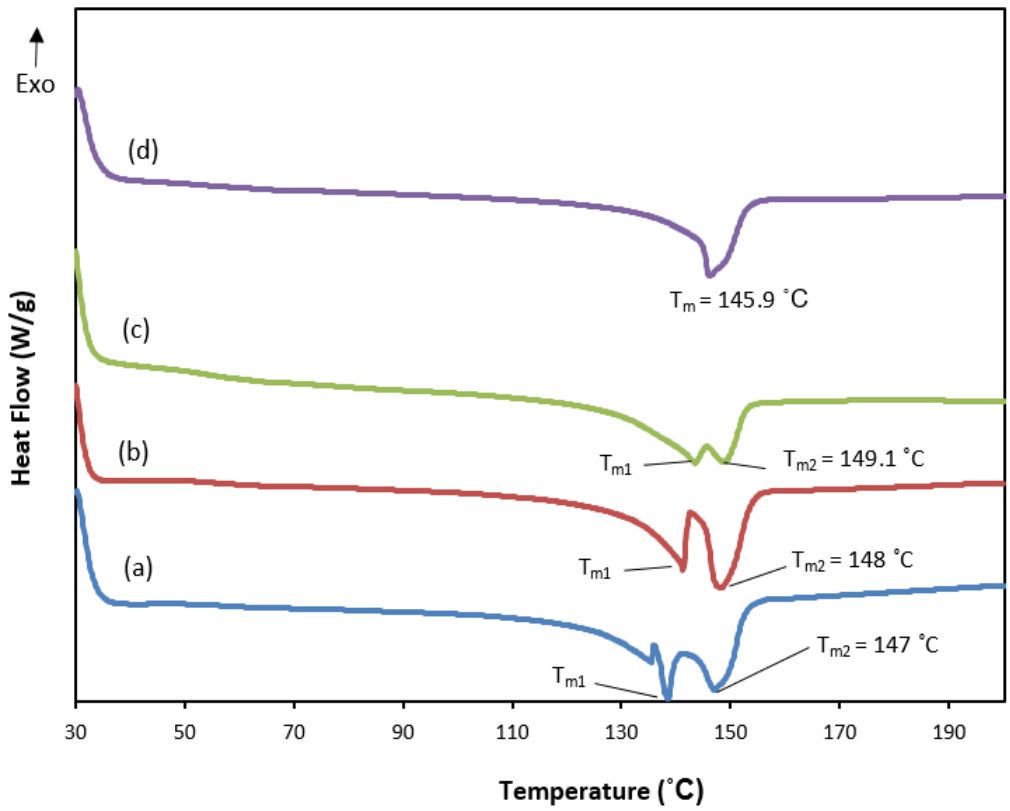

Figure 3: DSC melting thermograms of (a) neat PLA, (b) PLA/10FsHA, (c) PLA/30FsHA and (d) PLA/50FsHA

Increasing of melting temperature of PLA/FsHA composite when the filler (FsHA) content increased up to 30 wt% may attribute to the surface interaction between FsHA and PLA matrix during mixing process. This finding was supported by FTIR results, which demonstrated the peak shifted to that changes in the peak regions of the spectrum indicated some degree of chemical interaction between the matrix and the FsHA.

Tensile Properties

The impact of PLA filler on tensile strength of composite is shown in Figure 4. The results clearly showed that value of the tensile strength increased as the filler loading increased up to 50 wt.% and then it decreased beyond of 50 wt.% of FsHA loading, (17.1 MPa to 23.3 MPa). This situation might be explained by the good interfacial interaction between the FsHA filler and the PLA matrix that was attained using the solvent DCM blending method. [12].

Figure 5 shows the Young's modulus of PLA/FsHA composites with different filler contents. It has been seen that the Young's modulus results has similar trend to the tensile strength results. It was clearly observed that the Young's modulus values increased with the increasing of FsHA filler contents and this trend was similar with the result found in previous studies [13]. This finding was expected since the presence of DCM in composite might enhanced the interaction between the filler and the matrix, thus it increased the stiffness and strength properties of the PLA/FsHA composites [12].

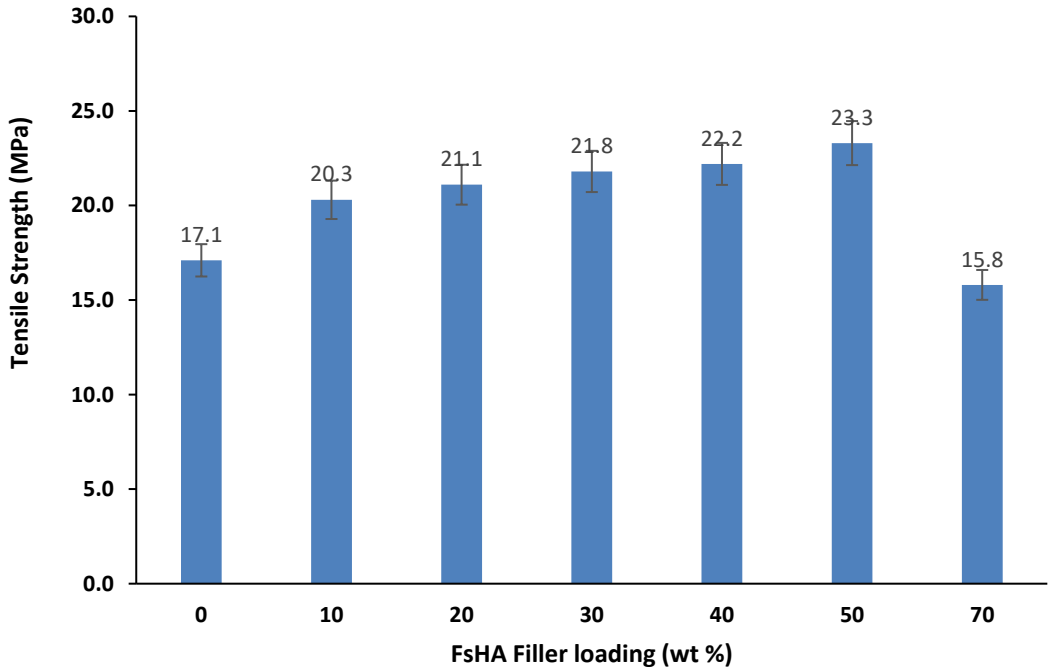

Figure 4: Tensile strength of PLA/FsHA composites with different filler contents

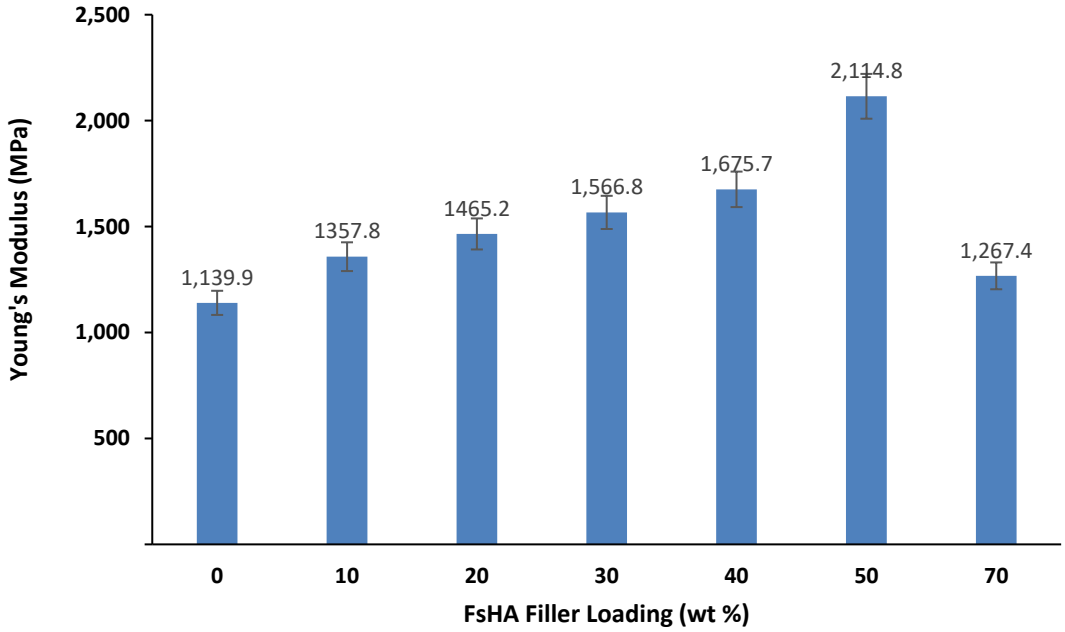

Figure 5: Young's modulus of PLA/FsHA composites with different filler contents

Figure 6 shows the elongation at break (%) of PLA/FsHA composite with different filler contents. It was observed that neat PLA exhibited ductile failure with the elongation at break at about 127.8 %. The addition of 10 wt% FsHA filler into PLA has been drastically reduced the elongation at break to 58.8 %. Generally, by adding rigid fillers such as FsHA into PLA matrix has decreased the elongation at break of composite. The improvement of the tensile strength was due to the rigidity and stiffness in FsHA by the extensive intra and intermolecular hydrogen bond [15] and this is supported with the FTIR results obtained from this study (Figure 2).

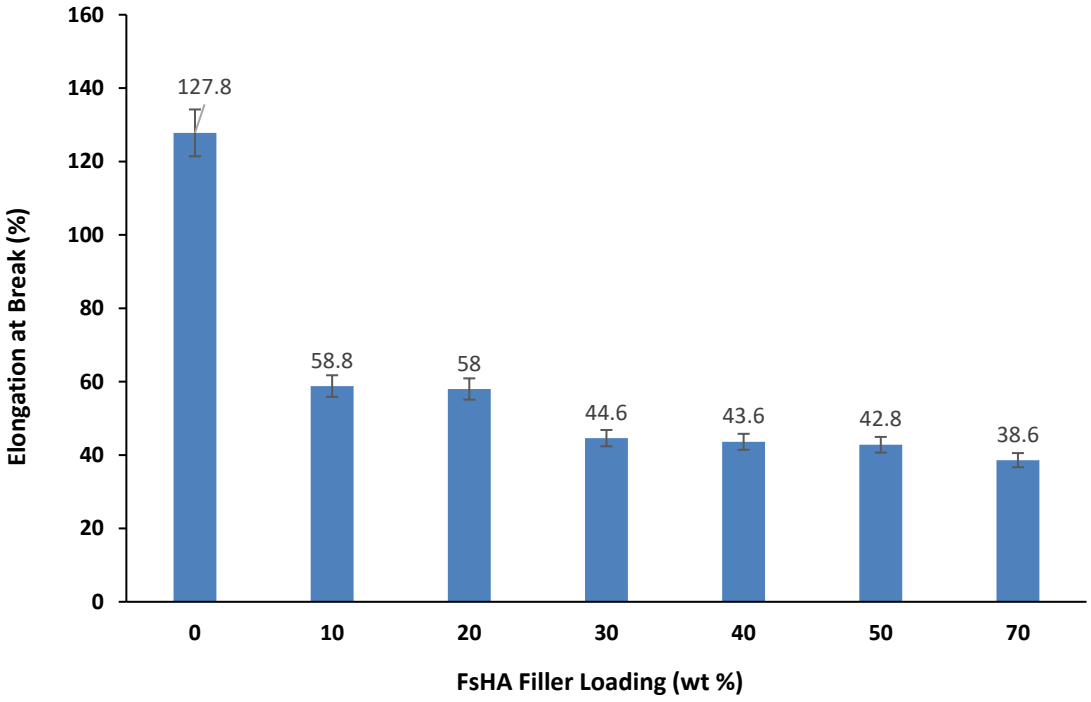

Figure 6: Elongation at break of PLA/FsHA composites with different filler contents

SEM Analysis

SEM analysis was carried out to examine the surface morphology of the PLA and composites (Figure 7). From Figure 7(a), the smooth surface and uneven structure was observed for the PLA polymer. As the amount of FsHA filler contents increased up to 30 wt%, the surface of composite became rougher and porous structure (Figures 7(b) and (c)). However, by addition of 50 wt% of FsHA fillers content in the composite, the bigger pores on composite surface was clearly seen (Figure 7(d)).

Figure 8 shows the SEM micrographs of fracture surface of PLA/FsHA composite with different filler contents (10 and 50 wt% FsHA). According to SEM micrographs, the fracture surface of the solvent cast PLA/FsHA composite exhibited fibril formation and rougher surface. The formation of fibril-like and the rough surface structure of the PLA/FsHA composite may resulted from the slow rate evaporation process of DCM solvent as reported by Chakravarty et al. [12]. It has been found that the higher the filler contents, the rougher the surface of composites. The result obtained from morphology analysis by SEM was agreement with the research study by Chakravarty et al. [12].

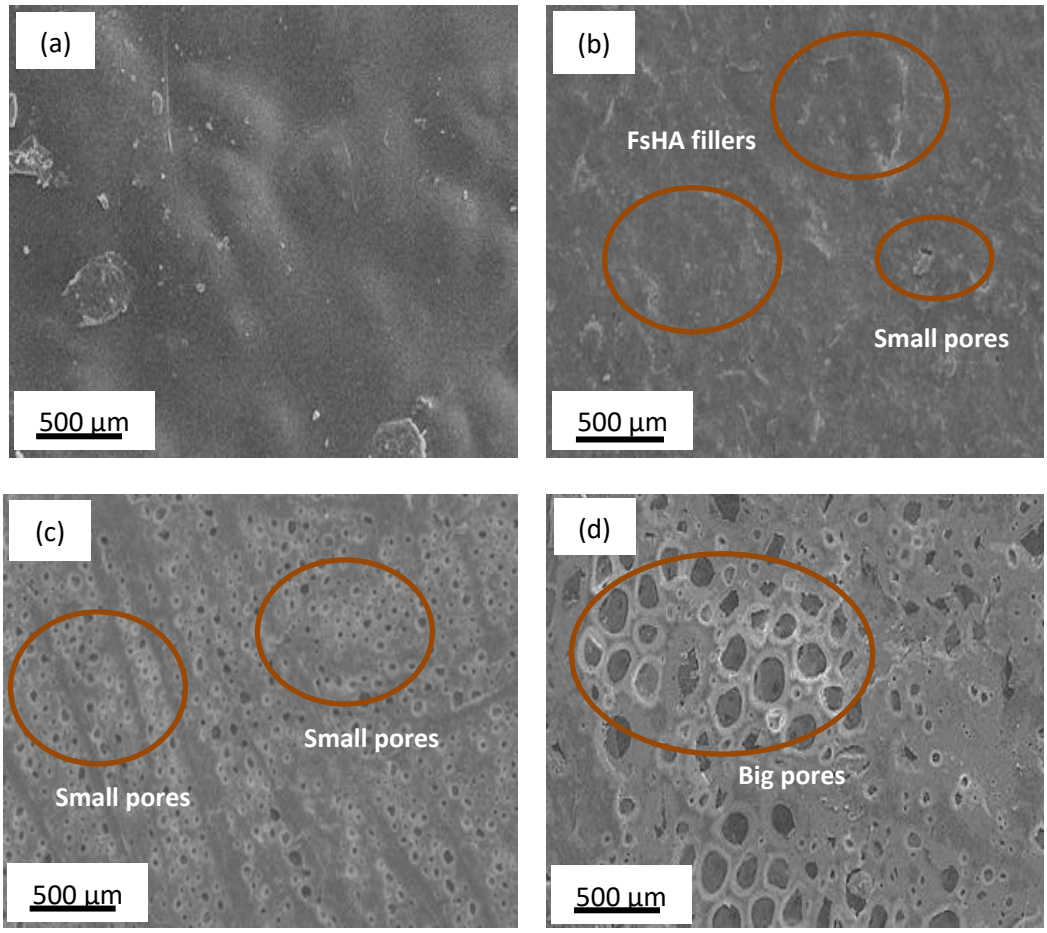

Figure 7: SEM micrographs of surface of PLA and composite (a)100 PLA, (b) PLA/10 FsHA, (c) PLA/30FsHA and (d) PLA/50FsHA

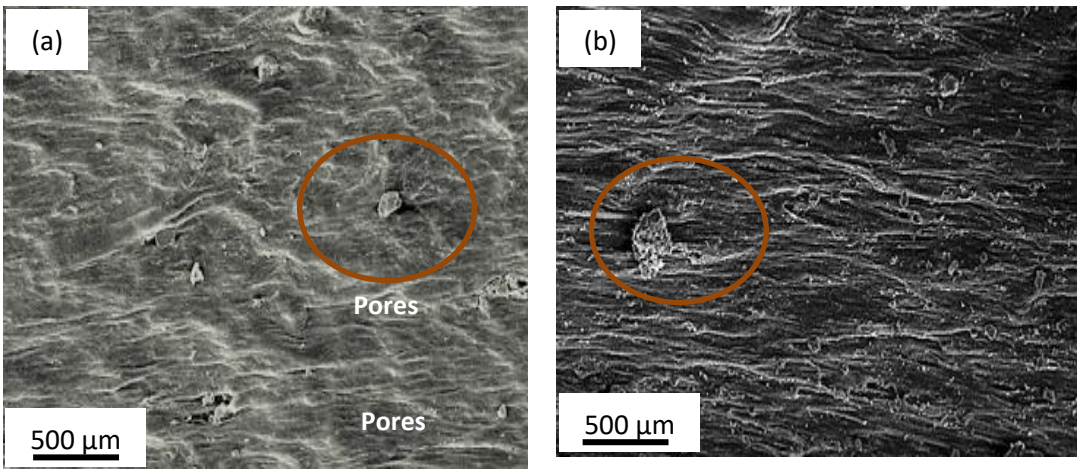

Figure 8: SEM micrographs of facture surface (a) PLA/10FsHA and (b) PLA/50FsHA

Conclusions

Solvent casting technique was successfully used to prepare PLA/FsHA composite sheet with different FsHA fillers contents. The addition of 50 wt% of FsHA filler contents in the composite contributed to higher mechanical properties with the values of Young's Modulus and tensile strength of 2114.8 MPa and 23.3 MPa, respectively. SEM analysis shows good distribution of FsHA fillers in the matrix. The interaction between FsHA fillers and PLA matrix has been shown by FTIR and DSC analyses. Thus, it can be concluded that the composite produced in this research has potential to be used in biomedical application as this composite has good mechanical properties as a results of good interaction between FsHA filler and PLA polymer matrix.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

References

[1] Takkalkar, P., Nizamuddin, S., Griffin, G. & Kao, N. (2019). Thermal properties of sustainable thermoplastics nanocomposites containing nanofillers and its recycling perspective. In *Sustainable polymer composites and nanocomposites.* Ed. Inamuddin, Sabu, T., Raghvendra Kumar, M. & Abdullah, M. A. (Springer International Publishing), pp. 915–933.

[2] Raquez, J-M., Habibi, Y., Murariu, M. & Duboishe, P. (2013). Polylactide (PLA)-based nanocomposites. *Progress in Polymer Science.* 38(10–11), 1504–1542.

[3] Arrieta, M. P., Fortunati, E., Dominici, F., Rayon, E., Lopez, J. & Kenny, J. M. (2014). Multifunctional PLA-PHB/cellulose nanocrystal films: processing, structural and thermal properties. *Carbohydrate Polymers.* 107,16–24.

[4] Spinella, S., Re, G. L., Liu, B., Dorgan, J., Habibi, Y. & Raquez, J. M. (2015). Modification of cellulose nanocrystals with lactic acid for direct melt blending with PLA. *AIP Conference Proceedings.* 1664, 070019.

[5] Sukindar, N. A., Ariffin, M. K., Baharudin, B. T., Jaafar, C. N. A. & Ismail, M. I. (2016). Analyzing The Effect of Nozzle Diameter In Fused Deposition Modeling For Extruding Polylactic Acid Using Open Source 3D Printing. *Jurnal Teknologi,* 78(10), 7-15.

[6] Matta, A., Rao, R. U., Suman, K. & Rambabu, V. (2014). Preparation and Characterization of Biodegradable PLA/PCL Polymeric Blends. *Procedia Materials Science*. 6, 1266-1270.

[7] Li, H. & Huneault, M. A. (2008). Crystallization of PLA/Thermoplastic Starch Blends. *International Polymer Processing*. 23(5), 412-418.

[8] Bijarimi, M., Ahmad, S., Rasid, R., Khushairi, M. A. & Zakir, M. (2016). Poly(lactic acid) / poly(ethylene glycol) blends: Mechanical, thermal and morphological properties. *AIP Conference Proceedings*. 1727(1), 020002

[9] Hussain, C. M. & Thomas, S. (2021). Handbook of polymer and ceramic nanotechnology. Springer International Publishing.

[10] Daood, U. & Fawzy, A. (2023). Development of a bioactive dentin adhesive resin modified with magnesium-doped synthetic hydroxyapatite crystals. *Journal of the Mechanical Behavior of Biomedical Materials*. 140, 105737.

[11] Wang, Z., Huang, C., Wang, J., Zou, B., Abbas, C. A. & Wang, X. (2020). Design and characterization of hydroxyapatite scaffolds fabricated by stereolithography for Bone Tissue Engineering Application. *Procedia CIRP*. 89, 170–175.

[12] Chakravarty, J., Rabbi, M. F., Chalivendra, V., Ferreira, T. & Brigham, C. J. (2020). Mechanical and biological properties of Chitin/polylactide (PLA)/hydroxyapatite (HAP) composites cast using Ionic Liquid Solutions. *International Journal of Biological Macromolecules*. 151, 1213–1223.

[13] Zainol, I., Adenan, N. H., Rahim, N. A. & Jaafar, C. N. A. (2019). Extraction of natural hydroxyapatite from tilapia fish scales using alkaline treatment. *Materials Today: Proceedings.* 16, 1942-1948.

[14] Jaafar, C. N. A., Zainol, I., Khairani, I. M. I. & Dele-Afolabi, T. T. (2022). Physical and mechanical properties of tilapia scale hydroxyapatite-filled high-density polyethylene composites. *Polymers*, 14 (2), 251.

[15] Zainol, I., Zainurin, M. A. N., Bakar, N. H. A., Jaafar, C. N. A. & Mudhafar, M. (2022). Characterisation of porous hydroxyapatite beads prepared from fish scale for potential bone filler applications. *Malaysian Journal of Microscopy*. 18(2), 48-57

[16] Siriporn, T., Somruethai, C. & Pakkanun, K. (2023). Physico-chemical properties and biocompatibility of in situ-hardening polylactide/nano hydroxyapatite composite for bone substitute. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 72(2), 108–118.

[17] Muhammad, N., Gao, Y., Iqbal, F., Ahmad, P., Ge, R., Nishan, U., Rahim, A., Gonfa, G. & Ullah, Z. (2016). *Separation and Purification Technology*, 129-135.

[18] Sharma, C., Dinda, K. A., Potdar, P. D., Chou, C. F. & Mishra, N. C. (2016). *Materials Science & Engineering: C*. 64, 416-427.