INVESTIGATION ON MECHANICAL AND THERMAL PROPERTIES OF POLY (LATIC ACID) (PLA)/FISH SCALES HYDROXYAPATITE (FsHA) COMPOSITES

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Abstract. This study investigates biomaterial composites made from a poly(lactic acid) (PLA) polymer matrix and hydroxyapatite (HA) extracted from fish scales (FsHA) for biomedical applications, especially in 3D printing. Fish scale HA is considered a halal alternative to synthetic or bone-derived HA. The research aims to explore the chemical, mechanical, and thermal properties of PLA/FsHA composites. Samples were prepared by melt-blending PLA with varying FsHA weights (10-50 wt%) at 190 °C, followed by hot pressing. Mechanical properties were analyzed using tensile tests, while scanning electron microscopy (FESEM) characterized the morphology of fractured specimens. Fourier transform infrared spectroscopy (FTIR) studied the functional groups between PLA and FsHA. Thermal properties, including glass transition temperature (T_g) and melting temperature (T_m), were investigated using differential scanning calorimetry (DSC). Mechanical analysis revealed that optimal properties were achieved at 20 wt% FsHA filler loading, with tensile strength, yield strength, and elongation at break measured at 80 MPa, 56 MPa, and 35.4%, respectively. FESEM analysis showed that FsHA improved stress distribution, enhancing mechanical properties. FTIR results confirmed surface interactions between the PLA matrix and FsHA filler. Additionally, the incorporation of FsHA improved the thermal stability of the composites. In conclusion, the study indicates that PLA/FsHA composites exhibit improved mechanical properties with the addition of FsHA, although the impact on thermal properties is minimal. These findings suggest that PLA/FsHA composites hold promise for future biomedical applications, particularly in 3D printing, due to their enhanced mechanical performance and the suitability of fish scale HA as a halal material.

Keywords: Poly (lactic acid) (PLA), fish scales hydroxyapatite (FsHA), composites, mechanical properties, thermal properties

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1. INTRODUCTION

Over the past few decades, the annual global production of plastic has shown a steady increase, surpassing three million tons at present. Notably, the predominant share of this production consists of petroleum-based plastics [1-3]. Various methods are employed for plastic processing after its used. While some are segregated for recycling or utilized in diverse energy recovery procedures, a substantial volume ends up in landfills or oceans. The persistent non-biodegradability of most plastics which does not decompose naturally stands as a pivotal contributor to environmental pollution.

Increased awareness of environmental issues and sustainability concerns associated with conventional petroleum-based polymers has led to a shift in research focus towards the development of bio-based and biodegradable polymer alternatives that hold promise in replacing the petroleum counterparts [4]. Among the diverse range of biodegradable polymers, poly (lactic acid) (PLA) stands out due to its origin as biodegradable aliphatic polyester derived from renewable sources such as corn and starch. PLA exhibits desirable physical properties; however, its inherent brittleness requires refinement to further broaden its applications [4-6]. PLA is brittle because it's a biodegradable thermoplastic which made from renewable resources like sugarcane or cornstarch.

Natural hydroxyapatite (HAp) materials have been found to replace synthetic HAp in various application due to their low production cost [7]. HAp can be produced through chemical interactions with calcium and phosphate ions from manufactured or natural calcium sources, including hen's eggshells, shells, and corals. Moreover, hydroxapatite can be obtained from biogenic materials like fish, cow, and pig bones as well as scales. Because they are readily available and plentiful, hen's eggshells, fish bones, and scales offer intriguing sources of calcium [8]. Recently, natural HAp is extracted from fish scale and reported to be biocompatible as its chemical structure is similar with synthetic HAp and also due to the halal issue to use this filament for 3D printing purpose in future. Besides that, several million tons of fish scale are being generated daily as biowaste around the world. This scenario will end up with abundant of biowaste and become a liability to government to dispose them [8]. Therefore, through the research of utilizing biowaste from fish scale will certainly transform them to becomes an asset particularly in biomaterials field. Among the best alternative materials has been found to replace synthetic HAp is natural HAp from aquaculture waste such as fish scales (FsHA) [9].

Polymer blending is a popular technique to enhance the properties of polymers by combining them with other materials or additives [10]. Utilizing PLA polymers and HAp fillers in composite form or as mixtures yields superior properties compared to using them individually. However, mixing all these polymers together poses a challenge. PLA is typically processed by melting and therefore preparing composites with these polymers requires methods such, as casting, nonaqueous solvent dispersion, polymer grafting, freeze drying and hot pressing [11-13] When using these techniques, it is crucial to ensure that the polymers are uniformly distributed to maintain the desired properties of the material. Enhancements in the biological and mechanical properties of PLA/HAp composites can be achieved through melt-blending techniques using an internal mixer [9,11]. Remarkably, the aim of this study is to investigate the chemical, mechanical and thermal properties of PLA/ FsHA composites.

2. MATERIALS AND METHODS

2.1 Materials

Poly (lactic acid) resin (Ingeo 2003D) was purchased from NatureWorks LLC, USA. FsHA powders were extracted from fish scales as reported previously [12], ball-milled, spray dried into powders and sieved. Table 1 shows the formulation of PLA/FsHA composite.

Table 1: PLA/FsHA composite formulation

Sample	100 PLA	PLA/ 10FsHA	PLA/ 30FsHA	PLA/ 50FsHA
PLA (wt %)	100	90	70	50
FsHA (wt %)	0	10	30	50

The Brabender (internal mixer) was used to mix the PLA and the FsHA. The internal mixer was run for 10 minutes for each sample at a temperature of 190 ^{0}C. The sample was compression moulded at 190 ^{0}C for 15 minutes (for heating and cooling process). Then, the samples were cut into dumbbell shapes according to the ASTM D638. Figure 1 shows the production of PLA/FsHA composite.

Figure 1: Process of producing PLA/FsHA by using internal mixer (Brabender), (a) Internal mixer (Brabender), (b) top view from the internal mixer on blending the sample, (c) sample produced from internal mixer, (d) hot and cold press (Technovation) (e) tensile specimen of the composites from the mould

2.2 Fourier Transforms Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to identify the changes of the functional group in the polymer, chemical properties of pure PLA and PLA/FsHA composites. A spectrometer (Perkin-Elmer Model Series 2) was employed to obtain the infrared spectra. The equipment was operated with a resolution of 4 cm^{-1} and a scanning range from 4000 cm^{-1} to 650 cm^{-1}. After every usage, ethanol is used the clean up the sample area to avoid contaminate of the previous sample.

2.3 Differential Scanning Calorimetry (DSC)

DSC is used to complement the information obtained from tensile test and was conducted on pure PLA and PLA/FsHA composites samples. The thermal stability was measured by using Perkin-Elmer DSC 7 instrument with a heating temperature of 10 ºC min^{-1}. 4 mg of the samples was encapsulated in aluminum pans and subjected to thermal cycles. The sample was first heated up from room temperature to 200 ºC at 10 ºC min^{-1} and held at this temperature for 5 min to remove its thermal history.

Consequently, the sample was cooled to room temperature at 10 ^{0}C min^{-1} and then reheated to 200 ^{0}C at 10^{0}C min^{-1}. The analysis was done in a nitrogen-filled environment. The maximum peak was used to determine the melting temperature (T_m) and crystallisation temperature (T_c).

2.4 Tensile Test

A Mitutoyo thickness gauge and vernier calliper 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. The thin sheet (approximately 2 mm) composite were cut into dumbbell shape according to ASTM D638. Tensile tests were performed with an Instron Universal Testing Machine (UTM) INSTRON machine (model: 3366) with bluehill software. This machine is used to determine important mechanical parameters such as tensile strength, yield strength and elongation at break. Five samples of each mixture ratio composition were strained at a rate of 50 mm/min at room temperature, and average values of tensile strength, elongation at break (Eb), and yield strength were determined according to ASTM D638.

2.5 Morphology

The morphology of the pure and PLA/ FsHA composites were characteristised by using scanning electron microscope (FESEM), (model: JEOL JSM-6490LV). For better images and to minimize electrostatic charge, the fracture surfaces of specimens were platinum coated with Quorum Q150R S. The objective of the morphology analysis is to investigate the distribution of filler in the composites. In this study, the 20 kV acceleration voltage of the scanning electron microscope was used.

3. RESULTS AND DISCUSSION

3.1 Fourier Transforms Infrared Spectroscopy (FTIR) Analysis

FTIR was used to analyse 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 cm^{-1} 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].

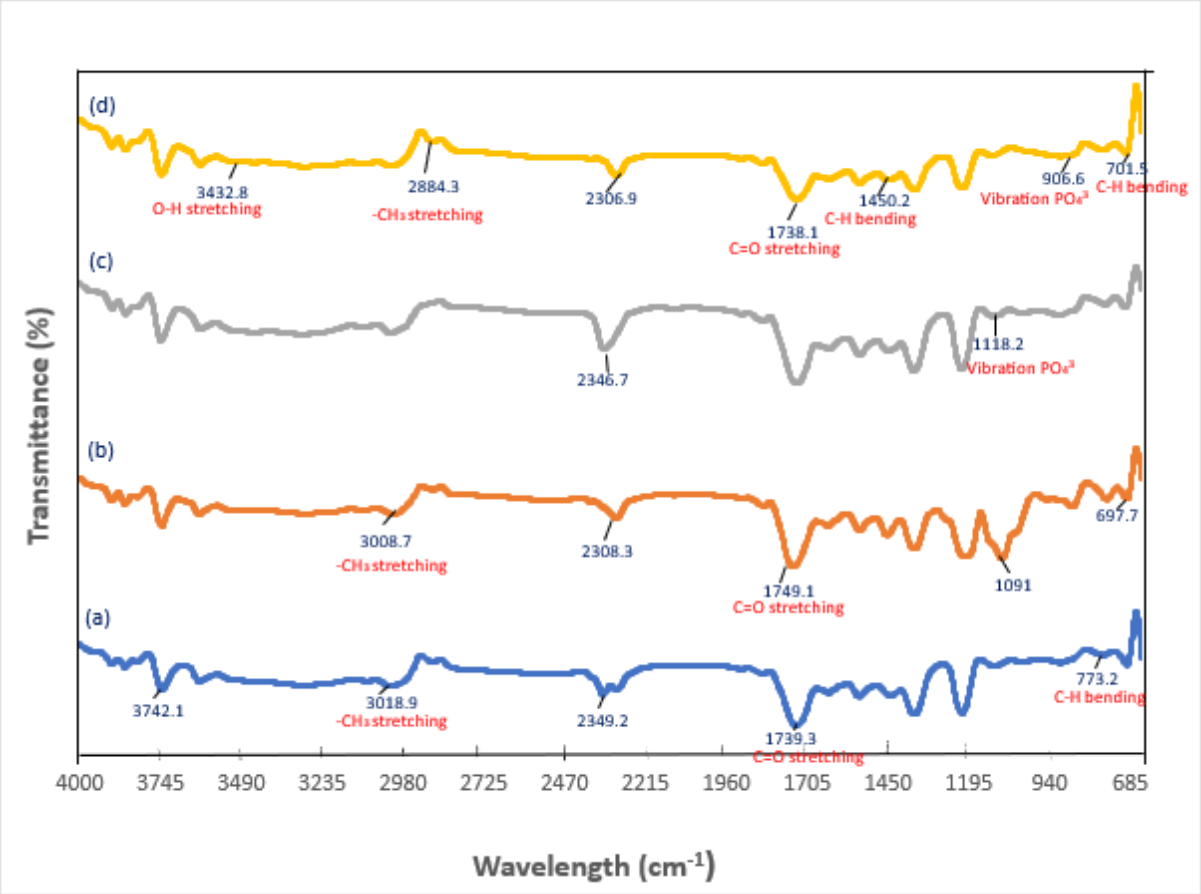

Figure 2: FTIR spectra of (a) pure PLA, (b) PLA/10FsHA, (c) PLA/30FsHA and (d) PLA/50FsHA

Besides that, 10 wt% FsHA has an FTIR spectrum that is almost exactly the same as that of pure PLA, with the exception of two extra peaks for the FsHA component at 1091 cm^{-1} and 1749.1 cm^{-1}, which are associated with the PO_4^{-3} and O-H groups. Peaks at 1738.1 cm^{-1} (C=O) and 1450.2 cm^{-1} (O-H) most likely indicate a chemical interaction between the FsHA and PLA matrix. With the exception of extra peaks for PO4-3 at 906.6 cm^{-1}, the FTIR spectra of 30 and 10 wt% of FsHA filler content are nearly identical [13-14]. In addition, The FTIR spectrum of 50 wt% FsHA filler is almost similar to the 30 wt% FsHA filler FTIR spectrum; additional peaks are seen at 701.5 cm^{-1} for the C-H bending of the amorphous region in PLA.

According to Muhamad et al. [15], the peaks around 3570 cm^{-1} and 1367 cm^{-1}, respectively, correlated with the hydroxyl group (OH) in the HAp being stretching and bending. A similar observation was obtained by Sharma et al. [16], who reported that the stretching of the OH groups was indicated by a short, abrupt peak at around 3572 cm^{-1}. The FTIR analysis revealed that the prominent peaks at 3457 cm^{-1} are representative of the HA of sample PLA/50FsHA's functional groups of OH group.

3.2 Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry (DSC) analyses were carried out to study the influence of FsHA filler loading on the thermal transition temperature of PLA and its composite. DSC thermogram of pure PLA in Figure 3(a) exhibited a classic features of a semi crystalline polymer which shows the glass transition temperature (T_g) at (55-60 ^oC), crystallization

temperature (T_c) at (125 ºC) and melting point (T_m) at (151 ºC). Similar observation was also shown for PLA/FsHA composite samples. It was observed that the addition of 10 and 30 wt% of FsHA filler content into PLA polymer matrix gives a slight decreased of T_c and T_m however the T_g does not change much as compared with pure PLA.

The changes of T_m indicated some degree of interaction between FsHA filler interfere with the arrangements of PLA matrix [17]. The second melting point of PLA/50FsHA composite was slightly higher than pure PLA which could be attributed to the ability of natural FsHA in providing surface interaction and increasing the interfacial bonding with the PLA polymer matrix [14,18,19]. Clearly, it was seen that these results supported the FTIR results which shown spectrum peaks changes indicated some degree of chemical interaction between FsHA filler loading and the PLA polymer matrix.

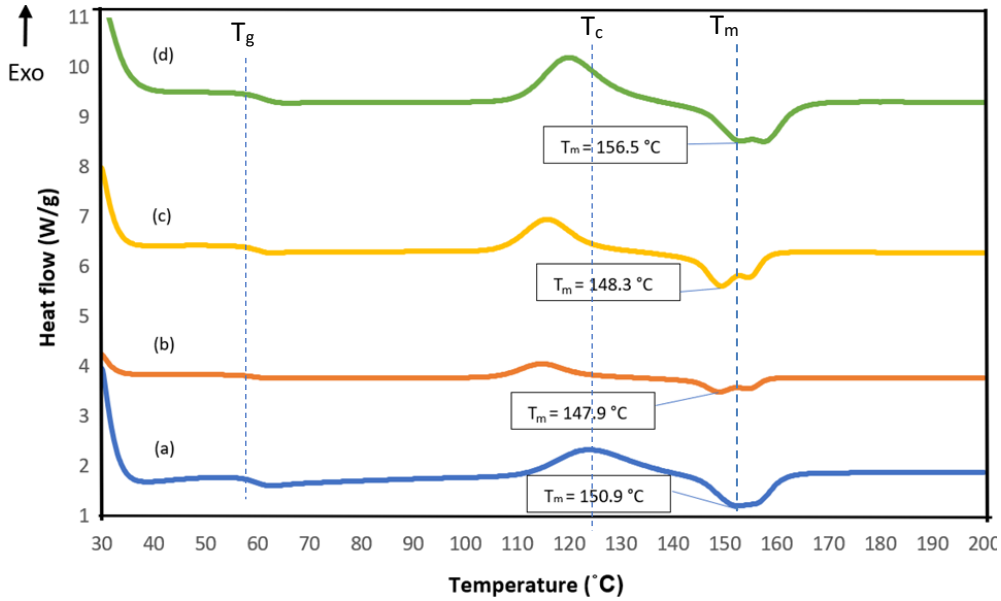

Figure 3: DSC melting thermograms of (a) pure PLA, (b) PLA/10FsHA, (c) PLA/30FsHA and (d) PLA/50FsHA

3.3 Tensile Properties

Figure 4 illustrates the effects of FsHA filler loading on the tensile strength of PLA/FsHA composites. The findings unequivocally demonstrated that the tensile strength value increased with FsHA filler loading up to 20 wt% which is from 1397 MPa to 1926 MPa (increased by 37%). The good interfacial interaction was achieved between the PLA polymer matrix and FsHA fillers and improved the tensile properties of the composites [13] similarly with the previous studies, with solvent dichloromethane (DCM) where tensile strength increased with FsHA fillers loading up to 50%, since the presence of DCM in composite might enhance the relationship between the filler and the matrix, thus it enhanced the stiffness of composites [20]. However, above the 30 wt% of FsHA filler loading the tensile strength of PLA/FsHA composite started to decrease due to poor interfacial bonding between PLA polymer matrix and FsHA filler.

The strength of the interface between the filler particles and the polymer matrix plays a crucial role in determining the overall mechanical properties of the composite. Beyond a certain filler loading, the polymer may not be able to adequately wet and bond with all filler

particles, leading to a weakened interface and reduced tensile strength [15]. According to Siriporn [14], higher filler content on some polymers can caused semicrystalline and have regular repeating units which acts as crosslinks giving the polymer higher tensile strength. The fracture surface study of a FESEM verified these phenomena as well in Figure 7. The FTIR results from this study corroborate the theory that the significant intra- and intermolecular hydrogen bonding in FsHA caused rigidity and stiffness, which improved the tensile strength [18].

In addition, Figure 5 shows a trend in yield strength data of PLA/FsHA composites that is comparable to the tensile strength. It was noticed that the value of yield strength was increased up to 20 wt% of FSHA and decreased when the FsHA fillers was added into PLA and more pronounced with 50 wt% of FsHA filler loading. As demonstrated in earlier research, it is evident that the yield strength increased when the FsHA fillers loading increased [14]. This scenario is expected since the addition of FsHA fillers to the PLA polymer matrix may improve the filler-matrix interaction which enhanced the stiffness of the composite.

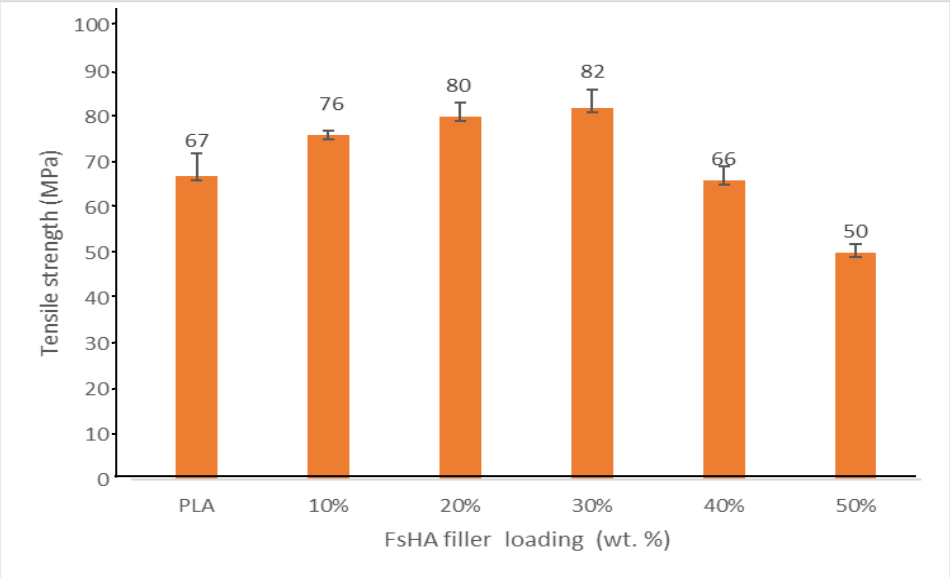

Figure 4: Tensile strength of PLA/FsHA with various amount of filler loading

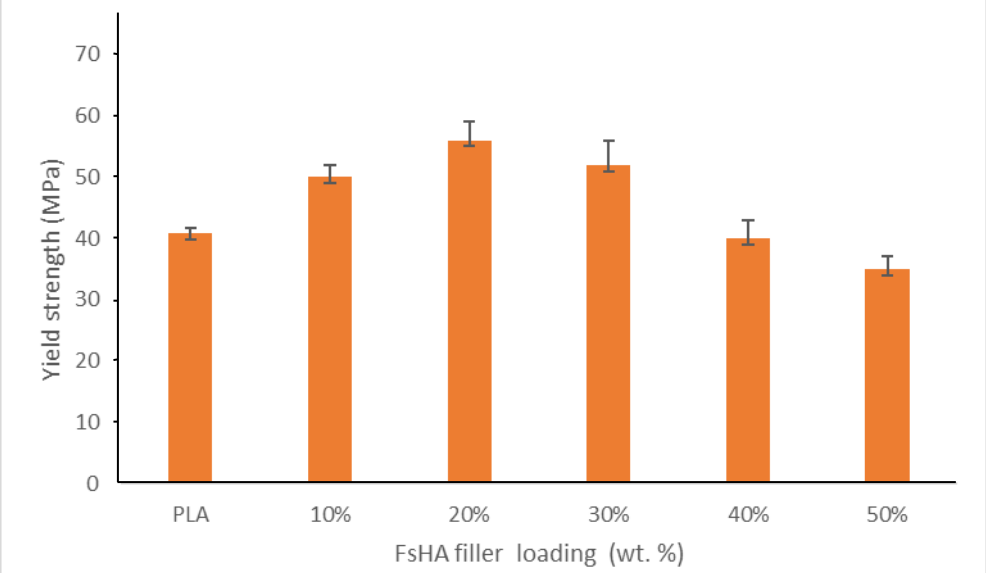

Figure 5: Yield strength of PLA/FsHA with various composites of filler loading

The elongation at break (%) of the PLA/FsHA composites at various FsHA filler contents is shown in Figure 6. Pure PLA has been demonstrated to show ductile failure, with an elongation at break of approximately 18.2%. It was noticed that the elongation at break of PLA/FsHA composite increased gradually up to 30 wt% FsHA filler content. The FsHA fillers enhanced the flexibility of the composite by altering the stress distribution and contributing to energy dissipation mechanisms during deformation and thus increasing the stiffness of materials [21]. However, at higher FsHA filler content the elongation at break has dropped significantly since the agglomeration tend to occur which decreases the contact area and generates structural flaws between PLA polymer matrix and FsHA fillers [22-23].

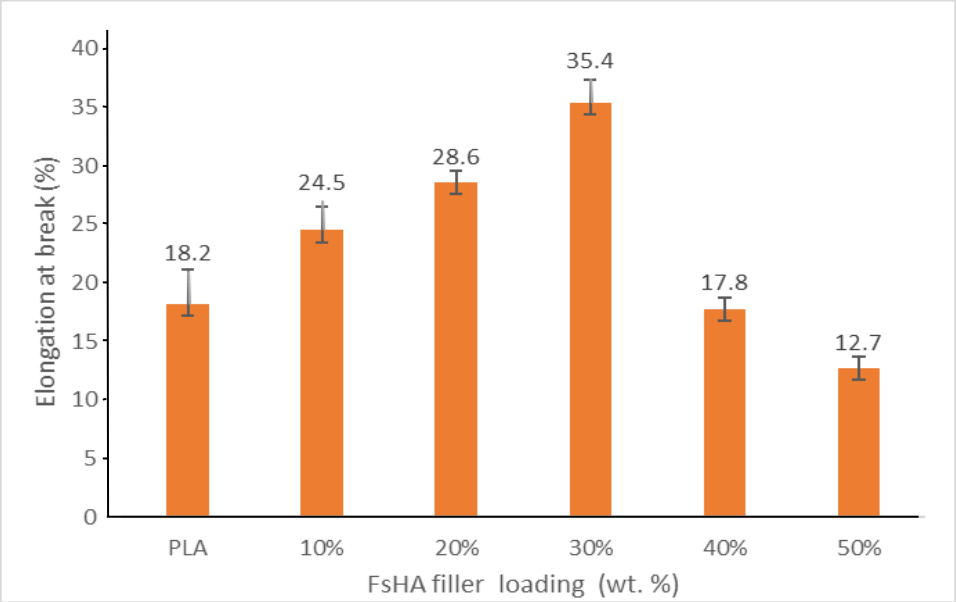

Figure 6: Elongation at break of PLA/FsHA composite with various amount of FsHA filler loading

3.4 Morphology analysis

FESEM analyses on the fractured surface sample is shown in Figure 7. The information of FsHA filler dispersion within the PLA/FsHA composites materials are obtained, and it can be related to the mechanical properties such as tensile strength and ductility. In Figure 7 (a), it can be observed that pure PLA sample present a smooth surface, indicating a brittle failure behaviour with some small cracks. Nevertheless, it was observed in Figure 7 (b) that after mixing PLA with FsHA particle fillers, the morphology of composite surface has become rough indicating less brittle [8]. However, the PLA/FsHA composite at high FsHA filler content (30 wt%) becomes ductile failure which increase the elastic properties of PLA polymer matrix. Based on the SEM images in Figure 7, the fractured surface structure of the solvent cast PLA/FsHA film appeared to be rougher and exhibit symptoms of fibril formation as compared to the neat PLA film. The fibril-like structure and the rough surface of the solvent cast PLA/FsHA film may have resulted from the solvent DCM's slow rate of evaporation as also reported by Chakravarty et.al. [24].

The fibrous structure was observed on the surface of PLA/FsHA composites especially composite with 50 wt% filler loading, due to the necking of the polymer and subsequent fractured. This phenomenon is due to the concentration of stress in a particular region, causing it to undergo more significant elongation. The fracture propagates along the polymer chains, resulting in the separation of chains and the formation of fibrous structures on the surface.

These fibrous features are essentially the exposed cross-sections of the fractured polymer chains or segments [23]. It is also believed that fibrous can be formed in the composite during tensile test due to different surface properties of polymer and filler [14,19].

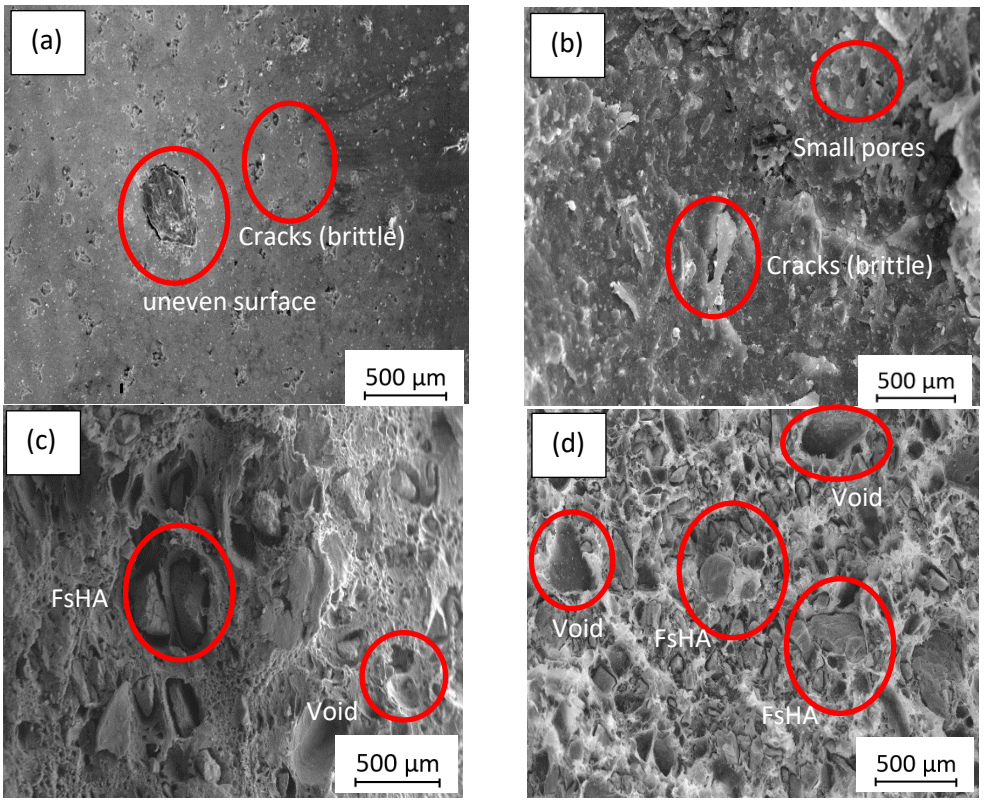

Figure 7: FESEM micrographs of facture surface (a) pure PLA, (b) PLA/10FsHA, (c) PLA/30FsHA, and (d) PLA/50FsHA

The microstructure analysis supported the tensile strength and elongation at break results which showed that the value of tensile strength and elongation at break properties started to decrease at higher FsHA filler content in the PLA/FsHA composite. This is due to FsHA particles impede the motion of PLA matrix under shear stress in turn caused decreased in the tensile properties of the composite [12,23]. As can be seen in Figure 7 (c) and (d), the tensile fracture surface morphology of the PLA/30FsHA and PLA/50FsHA is more brittle compared to other formulations. This is due to higher filler content and void formation which has been observed in the morphology analysis [9,16].

4. CONCLUSIONS

In this study, the PLA/20FsHA composite exhibited the highest tensile strength among all formulations, attributed to favorable interfacial interaction between the PLA matrix and FsHA fillers. However, at higher FsHA content, tensile properties declined due to FsHA particles acting as stress concentrators and hindering PLA matrix mobility. Morphological analysis revealed increased brittleness at higher FsHA content, further diminishing mechanical performance. Additionally, the melting temperature of PLA improved with the 50 wt% FsHA, as FsHA served as a nucleating agent, promoting PLA crystallization. FTIR analysis confirmed surface interaction between FsHA filler and PLA matrix, evidenced by shifts in absorption bands and the presence of functional groups. These results underscore the potential for

enhancing composite properties through optimized filler content and highlight the importance of filler-matrix compatibility in composite design.

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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.

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