Effect of Lauric Acid on the Thermal and Mechanical Properties of Polyhydroxybutyrate (PHB)/Starch Composite Biofilms

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Received 23 March 2020; Revised 14 May 2020; Accepted 23 May 2020; Published 19 June 2020

Academic Editor: Christopher Batich

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Polyhydroxybutyrate (PHB) is a biopolymer of natural origin, one of the suitable alternatives for synthetic plastics. However, pure PHB has a high production cost, is relatively brittle, and has poor processability, hence its limited application. Combining PHB with biomass fillers and plasticizers can significantly improve the properties of the polymer, leading to its commercial usage. In this study, PHB was incorporated with starch (S) as a cheap biomass filler and lauric acid (LA) as a potential plasticizer. The PHB/S/LA composites were prepared using a modified solvent casting method with the incremental addition of LA. The PHB/S ratio was maintained at a ratio of 80/20 (w/w). Physicochemical characterization via EDS, XRD, and FTIR proved that the composite components have blended through nucleation and plasticization processes. The morphology of the PHB/S blends was found to be a heterogeneous matrix, with decreased inhomogeneity upon the addition of LA in the composite. Thermal characterization done by TGA and DSC showed that the thermal properties of PHB/S films improved with the addition of LA. Mechanical tests (UTM) proved that the elastic strain of the films also increased with the addition of LA, although the tensile strength decreased slightly compared to pure PHB/S. Overall, the results of this study provide baseline information on the improvement of PHB-based bioplastics.

1. Introduction

The management of plastic wastes is a prevailing concern worldwide. Commercially used synthetic plastics degrade very slowly when disposed and have a relatively unknown decomposition rate [1]. Recent research efforts have focused on biobased polymers and composites as a sustainable alternative to synthetic/petroleum-based polymers, especially single-use plastics [2]. The biodegradability and biocompatibility of these polymers are essential for advanced applications that are critical to the biopolymer’s purity. These include medical applications such as sustained drug release carriers, scaffolding for tissue engineering, and durable and biocompatible medical aids [3, 4]. Industrial applications
of biobased polymers are also sought after in textile manufacturing, construction fillers, composites, foams, etc. [5, 6]. Likewise, these polymers found significance in agriculture in the form of horticultural crop components, soil-retention sheeting and containers, and agricultural films, among others [7].

Biobased polymers can be produced from a wide variety of natural materials, such as plant (cellulose, starch, lignin, etc.) and animal matter (chitin, chitosan, collagen, etc.). Selected microorganisms can synthesize biopolymers through the metabolism of these source components. Typical examples of these polymers are polyactic acid (PLA), polyhydroxyalkanoates (PHA), and their copolymers [8, 9]. Polyhydroxybutyrate (PHB) gained the highest interest among PHA types [10–17]. PHB is produced through carbon assimilation by certain microorganisms that are under physiological stress [18]. It is a biodegradable polyester, characterized as highly crystalline aliphatic thermoplastic [19] that exhibits physical properties comparable to that of petroleum-based synthetics, such as polyethylene terephthalate (PET) and polypropylene (PP) [20]. However, PHB is still in the developmental stage due to its relatively high production cost [21], poor mechanical properties due to brittleness [22], and poor formability during processing [23]. Addressing these problems can be carried chemically by blending with compounds that can improve PHB properties, thus forming a composite. A common route is by incorporating cheap biomass fillers that are locally available in order to significantly reduce the overall production cost. However, previous studies showed that the addition of biomass fillers could negatively affect the mechanical properties of the resulting composite [24–26]. Interestingly, the addition of plasticizers along with biomass fillers can offset property change by increasing the flexibility and processability of bioplastic composites through lowering the glass transition temperature ($T_g$) [27].

In this study, PHB is incorporated with starch (S) as a biomass filler and lauric acid (LA) as a plasticizer to form a PHB/S/LA composite. The resulting blend is investigated for its thermal, physicochemical, and mechanical properties. Zhang and Thomas [28] reported that starch acts both as a filler and as a nucleating agent in PHB/starch blends, significantly reducing the size of PHB spherulites. However, Innocentini-Mei et al. [29] still observed poor mechanical properties after incorporating PHB with starch due to the immiscibility between hydrophilic starch and hydrophobic PHB. Hence, LA is used as a potential plasticizer to address this problem. LA, or dodecanoic acid, is a saturated fatty acid ester with hydroxyl moieties from its carboxylic acid groups that can form bonds with other polymers. In this bioplastic composite, LA promotes hydrogen bond formation to reduce the intramolecular forces between PHB and starch molecules, effectively decreasing the glass temperature of the material [27]. Strong interactions caused by rigid bonds within the polymer groups can be disrupted and can increase the miscibility of the bioplastic composite. As an effect, the polymer molecules will have increased mobility and improved interfacial adhesion [30]. The results would be helpful in the development involving PHA-based bioplastics, especially since the use of LA as a plasticizer in PHB/S has not been explored by existing literature.

### 2. Materials and Methods

#### 2.1. Materials

The polymer blends in this study were prepared using the following reagents: polyhydroxybutyrate powder (98.8% PHB, Biomer®, Germany, $M_w = \sim 350,000$ g·mol$^{-1}$), chloroform (99.8% CHCl$_3$, RCI Labscan Ltd., Thailand), cornstarch (~27% amylose FG cornstarch, Food Industries, Inc., Philippines), and lauric acid (>98.0% C$_{12}$H$_{25}$O$_2$, Tokyo Chemicals Industries Co., Tokyo, Japan). All reagents were used as received without further purification.

#### 2.2. Preparation of Bioplastic Composite Films

Composite films made from PHB/starch (S)/lauric acid (LA) were prepared using a heat-assisted solvent casting method derived from Barud et al.’s study [24]. Chemicals have been predried in a forced air circulation oven (Biobase, China) at a temperature of 60°C at least overnight to remove as much moisture as possible. In an airtight 50 mL Teflon tube, 600 mg of the polymer blend was mixed with 15 mL chloroform to form a 4% (w/v) suspension. PHB/S/LA films were prepared using the amounts shown in Table 1.

The PHB-starch ratio has been maintained at 80:20 (w/w). This ratio was found to be the optimum ratio to avoid film breakage (data not shown). The suspension was subjected to a high-speed vortex mixer (Biobase, China) at a maximum speed for 3 minutes. The suspension was then subjected in a water bath maintained at a temperature of 60 ± 5°C for 30 minutes. The water bath was dispersed evenly using moderate speed magnetic stirring. Depressurization of the Teflon tubes was done every 10 minutes to prevent excessive pressure buildup. The solution was cast in a 100 mm × 15 mm borosilicate petri dish inside a well-ventilated fume hood. The composite films were obtained after a 4-6 h evaporation of chloroform.

#### 2.3. Characterization of the Bioplastic Composites

##### 2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was done to determine the different functional groups present in the bioplastic composites. The analysis was carried out using a Shimadzu IR Prestige-21 spectrometer (Tokyo, Japan) with attenuated total reflectance spectroscopy. The final spectrum was processed using ATR correction. The FTIR spectra were acquired in the range of 600–4000 cm$^{-1}$ and a resolution at 4 cm$^{-1}$.

### Table 1: PHB/S/LA composite film preparation amounts.

| Sample | PHB/S/LA amount (mg) |
|--------|----------------------|
| PHB    | 600/0/0              |
| LA0    | 480/120/0            |
| LA1    | 480/120/10           |
| LA2    | 480/120/20           |
2.3.2. Scanning Electron Microscopy- (SEM) Energy Dispersive X-Ray (EDS). The morphology of the films was observed through SEM using Hitachi S4700 (Tokyo, Japan). Energy-dispersive X-ray spectroscopy was done in conjunction with SEM. The spatial resolution range is 2×2 –10 × 10 μm. The following elements were detected: carbon (C), nitrogen (N), oxygen (O), and chlorine (Cl). The surface roughness of the films was measured from the SEM images through ImageJ software (http://www.imagej.nih.gov/) with SurfCharJ plug-in. The local roughness analysis (ISO 4287/2000) feature was used [31].

2.3.3. X-Ray Diffraction (XRD) Analysis. X-ray diffraction (XRD) is a surface characterization technique that allows for checking the disorder or misalignment of crystal formations. XRD was done using Bruker D5005 (Bremen, Germany) in the 2θ range of 10° to 70° at 0.1 s intervals equipped with a copper tube operating at 40 kV and 40 mA producing Cu-Kα radiation at 1.54 Å wavelength.

2.3.4. Thermogravimetric Analysis (TGA). Dynamic thermal degradation analysis was carried out using TA Instruments Q500 (Delaware, USA) using an aluminum oxide (Al₂O₃) crucible. The temperature of the samples was raised from 30 to 600°C at a rate of 10°C/min. Nitrogen atmosphere with a flow rate of 50 mL/min was used to prevent thermooxidative degradation.

2.3.5. Differential Scanning Calorimetry (DSC). DSC experiments were carried out in Perkin Elmer DSC 800 (Massachusetts, USA). The heating and cooling rate for the runs was 10°C/min in nitrogen (N₂) atmosphere (50 mL min⁻¹). Around 5–6 mg of the sample was put into sealed aluminum pans. Calibration was done using an indium (In) sample. The experiment consisted of a heating stage from 0°C to 350°C. The glass transition temperature (T_g) was measured as the onset of the baseline change in the heating run. The melting temperature (T_m) was obtained from the heating stage. The degree of crystallinity (x_c) was determined using the following equation [14]:

\[ x_c(\%) = \frac{100 \Delta H_m}{w_{PHB} \Delta H_{m,PHB}} \]  

where \( \Delta H_m \) is the enthalpy of fusion, \( \Delta H_{m,PHB} \) is assumed to be the enthalpy of fusion of purely crystalline PHB (146 J/g) [24], and \( w_{PHB} \) is the weight fraction of PHB in the blend.

2.4. Universal Testing Machine (UTM). The mechanical properties of the bioplastic composites were determined using UTM. UTM is carried out in Instron 4411 (Massachusetts, USA). The films used in UTM were subjected to standard method ASTM D882-09. The film dimensions were 45 mm × 12.5 mm × 0.15 ± 0.05 mm shaped into dogbones with an average gage length of 35 mm and width of 8 mm. The crosshead speed used is 5 mm/min with the extensometer disabled. 10 sets of stress-strain curves were generated per bioplastic composite to account for repeatability of results. The maximum stress (σ_max), elongation at break (ε), and Young’s modulus (E) were all recorded.

3. Results and Discussion

3.1. Effect of Lauric Acid Addition on the Morphology of the Bioplastic Composite

3.1.1. Opacity Test. The synthesized PHB/S/LA bioplastic composite films are shown in Figure 1. While pure PHB is transparent (Figure 1(a)), the biocomposites appear to be slightly translucent and milky white. LA0 was observed to have visible white spots mainly attributed to the starch particles on the PHB surface (Figure 1(b)). The incorporation of
LA decreased the appearance of white spots and increased the transparency of the composites. LA2 (Figure 1(d)) is found to be more transparent compared to LA1 (Figure 1(c)) which implies that a small amount of LA present in the bioplastic can affect its relative opacity. The texture of the films has also improved, with LA1 and LA2 being smoother upon physical contact compared to LA0.

3.1.2. Scanning Electron Microscopy (SEM). The SEM images of the bioplastic composites are shown in Figure 2. Figures 2(a) and 2(b) show pure PHB, which is smoother compared to LA0 (Figures 2(d) and 2(e)), LA1 (Figures 2(g) and 2(h)), and LA2 (Figures 2(j) and 2(k)). It was observed that starch particles ranging from 5.0 to 15.0 μm in relative size were scattered across the bioplastic unevenly, forming a matrix along the film’s surface. These results were consistent with the report of Thiré et al. [32] where starch granules found are polygonal in shape, with a broad numerical distribution of particles from 2.0 to 27.0 μm in equivalent spherical diameter. At low magnifications (200.0 μm), the inhomogeneity seems to have decreased for the LA1 and LA2, suggesting an increased blending in the presence of LA.

Figure 2: SEM images of PHB/S/LA blends at different magnifications. Pure PHB at 10.0 μm (a) and 50.0 μm (b) and cross-section at 50.0 μm (c). LA0 at 10.0 μm (d) and 200.0 μm (e) and cross-section at 50.0 μm (f). LA1 at 10.0 μm (g) and 200.0 μm (h) and cross-section at 50.0 μm (i). LA2 at 10.0 μm (j) and 200.0 μm (k) and cross-section at 50.0 μm (l).
Table 2: Surface roughness ($R_s$) values of the bioplastic composites (at 50.0 μm).

| Sample | $R_s$ |
|--------|-------|
| PHB    | 71.73 |
| LA0 (PHB 80/S 20) | 80.57 |
| LA1 (PHB 80/S 20/LA 10 mg) | 67.23 |
| LA2 (PHB 80/S 20/LA 20 mg) | 64.96 |

To properly check for the compatibility of the composites, a cross-sectional SEM was performed for all bioplastic samples. Several cracks and voids can be observed for all samples (Figures 2(c), 2(f), 2(i), and 2(l)). It was observed that pure PHB reference has no phase separation, as shown in Figure 2(c). Starch particles are observed to be dispersed in the continuous PHB matrix in a typical sea-island structure for LA0, as shown in Figure 2(f). The starch granules are not evenly dispersed and exist in the form of agglomerates that are grouped together in clearly demarcated domains [32]. It is worth noting that even though the starch agglomerated to the PHB matrix, it has still adhered strongly. This suggests that the larger starch particles have become a nucleating agent for the recrystallization/precipitation of PHB bioplastic to form the composite [28]. This is also observed in the cross-sectional SEMs of LA1 and LA2 shown in Figures 2(i) and 2(l). It appears that the LA-incorporated bioplastic shows homogenous interfacial boundaries consistent with plasticized polymers, which suggest good polymer-fatty acid miscibility.

For a more quantitative comparison, the average surface roughness ($R_s$) was calculated from the SEM images through ImageJ software [32]. The $R_s$ values are presented in Table 2. It was observed that LA0 had increased $R_s$ upon the addition of starch, which is attributed to the visible starch granules on the surface of LA0 (Figure 2(b)), significantly contributing to the surface roughness of the bioplastic. This roughness decreased with the addition of LA, with the $R_s$ of LA1 and LA2 decreasing by 16.6% and 19.4% compared to LA0. This implies that surface-level blending occurred for the LA1 and LA2, as evidenced by the micrographs shown in Figures 2(i) and 2(l).

3.2. Effect of Lauric Acid Addition on the Physicochemical Properties of the Bioplastic Composite

3.2.1. X-Ray Diffraction. Biopolymers, much like polymers, can also exist in crystalline or amorphous states, and they can have both amorphous and crystalline regions [1, 32, 33]. X-ray diffraction (XRD) is a surface characterization technique to check the disorder or misalignment of crystal formations or to see if the material is amorphous. The diffraction peaks for the precursors PHB and starch are shown in Figure 3(a). Well-defined peaks at 2θ values of 13.4°, 16.9°, 20.0°, 21.9°, 25.4°, 27.2°, and 44.2° correspond to the orthorhombic crystal planes (020), (110), (021), (111), (121), (040), and (222), respectively, for PHB [24, 33]. Typical A-type crystallinity pattern can be found for starch, with peaks situated at 2θ = 14.9° and 22.7° and a doublet with reflections at 16.9° and 17.8° [32, 34]. Strong peaks centered at 2θ = 20.1°, 21.3°, and 23.7° shown in Figure 3(b) were identified corresponding to the aggregation of lauric acid crystals [34].

The PHB/S/LA composites all depict the same peaks of orthorhombic PHB, as shown in Figure 3(c). It was also observed that the peak at 13.4° increases in intensity as the amount of LA increases, which implies that LA might have a direct effect on the crystallinity of the polymer. Despite the strong intensity of LA, these peaks have not reflected for the diffractograms of LA1 and LA2. This can be attributed to the low concentration of LA on the composite. Moreover, the peaks related to A-type crystallinity of starch particles were not observed in LA0, LA1, and LA2. Traces of B-type or Vh-type crystalline patterns have also not been clearly established. These suggest that the presence of starch does not directly affect the PHB crystalline lattice. It may be possible that cocrystallization between the molecules of the blend components has occurred due to starch acting as a nucleating agent. However, due to the similarity of the main peaks of PHB and starch [1, 34], establishing a relationship on the incorporation of starch to PHB will be difficult.

3.2.2. Energy-Dispersive X-Ray Spectroscopy (EDS). EDS was done to check for the relative purity of the bioplastics. The results are summarized in Table 3. It was shown that there are no nitrogen compounds in the composites, suggesting purity. The incorporation of starch decreased the carbon content slightly, as starch has more carboxyl groups than PHB. Residual chloroform in the form of elemental chlorine has been detected in the samples, denoting that chloroform was not completely removed after blending. This could be a possible concern when used in applications concerning biocompatibility. Other blending methods (melt mixing, melt extrusion, etc.) may be implored to avoid dealing with this issue in the future.

3.2.3. Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectroscopy was performed to check for the interactions between the composite components. The FTIR spectra of the bioplastic blends are shown in Figure 4. Figure 4(a) shows the FTIR spectra of PHB, starch, and LA0. It was observed that the absence of broad peaks around 3200 to 3600 cm⁻¹ indicates that hydrogen bonds have formed between the hydroxyl groups of PHB and starch to form LA0 [35]. Reis et al. [1] reported in their FTIR results showed that the PHB/starch composite still possesses broad peaks around 3200-3600 cm⁻¹, in which the intensity is highly dependent on the starch concentration. This absence suggests that PHB interacted with starch as a nucleating agent during the precipitation process. Moreover, the peak around 1645 cm⁻¹ present in pure PHB and starch corresponds to the intermolecular bonding of the carboxyl group [35]. Also, the absence of this peak in all PHB/S/LA films (Figure 4(b)) indicates that esterification took place between the components.

The addition of lauric acid in blending the PHB/S/LA polymer enhanced the esterification of the carboxyl groups, as shown in Figure 4(b) where the flattening of the broad
bands between 980 and 1300 cm\(^{-1}\) that are present in all composite formed after esterification, suggesting C-C stretching (980–1000 cm\(^{-1}\)) can have increased esterification starch gelatinization. This complex suggests that starch to amylose, forming an amylose-lipid inclusion complex during thermal processing. Salleh et al. [37] found that lauric acid is strongly bound caused by destructured starch incorporation on the bioplastic. Lauric acid is strongly bound to amylose, forming an amylose-lipid inclusion complex during thermal processing. This complex suggests that starch can have increased esterification with PHB molecules, denoting the increase of C-O bonds.

3.3. Effect of Lauric Acid Addition on the Thermal Properties of the Bioplastic Composite

3.3.1. Thermogravimetric Analysis (TGA). TGA was performed to study the thermal stability of the composites. The improvement of the thermal processability of plastics desires that the range between its melting point (\(T_m\)) and the onset degradation temperature is sufficiently large. The TGA and DTG curves of the synthesized bioplastic composites are shown in Figure 5.

TGA key parameters such as the initial decomposition temperature (IDT), the maximum rate of decomposition temperature (MRDT), and the maximum degradation temperature (MDT) [38] are summarized in Table 4. The onset degradation temperature (or IDT) is the point wherein the material starts to lose a significant portion of its mass through thermal degradation. The MRDT shows the highest rate of degradation or the highest peak of the DTG curve. The MDT occurs after most of the thermodegradative material is lost. This can be found in the TGA and DTG curves shown in Figures 5(a) and 5(e).

Initial degradation of the films in the range of 50–125°C can be attributed to the evaporation of interstitial water attached to the surface of the bioplastics, specifically on the hydrophilic starch molecules [18]. The small degradation peak around 150°C (Figures 5(a) and 5(b)) corresponds to the volatilization of LA, as only films with LA (LA1 and LA2) exhibited a mass loss accounting for approximately 3% mass loss. Volatilization of pure lauric acid occurs around 150°C–250°C [39]. All of the composites have undergone thermal degradation in the range of 260–270°C and only having less than 10% of their original weight by >305°C. This reflects the observations of the IDT and MDT as shown in Table 4. Studies have found that PHB is degraded through means of nonradical random chain scission (cis-elimination), which involves an aromatic C\(_6\)-derived intermediate/transition state [32]. It was also found that there is no clear trend between the TGA parameters. The mass of residue obtained (Figures 5(a) and 5(d)) after the thermal degradation varied directly with the amount of LA added. The decomposition of the nonvolatile residues of LA is known to occur around 600°C [39]. While the composites retain a small amount of mass, pure PHB has undergone full thermal degradation. The negative value for pure PHB at temperatures >400°C could be caused by residual oxygen trapped in the sample having thermooxidative reactions affecting the inert pan weight.

The temperature at maximum degradation also shifted to higher temperatures with the addition of LA as shown in the DTG curve in Figure 5(e). This reflects the recorded MRDT shown in Table 4. Due to the complete thermal degradation of PHB, its DTG peak is higher than the synthesized composites. The addition of lauric acid indeed improved the thermal stability of PHB/starch films. Also, it was observed that there is a small shoulder in the latter part of the degradation peak at a range of 300–330°C (Figure 5(e)). This can be attributed to the different decomposition rates of the amylose and amyllopectin components of starch. Amylose degrades at a lower temperature compared to amyllopectin, which has a more branched structure [33]. It was also observed that thermal
condensation and dehydration mechanisms begin in the 300°C range, generating ether and ethylene segments. Aromatic and cross-linked structures can also be found at higher temperatures. These reactions lead to the carbon-rich residue, depending on the starch source [32]. Overall, the improvement in thermal stability with the addition of plasticizer to PHB composites is consistent with previous works [13, 40].

3.3.2. Differential Scanning Calorimetry (DSC). To check for the thermal profile of the bioplastic composites ($T_g$, $T_m$, and crystallinity), differential scanning calorimetry (DSC) was done as shown in Figure 6. The miscibility of the bioplastic can be determined through DSC analysis. Blends are considered miscible if only one glass transition temperature ($T_g$) can be detected. As shown in Figure 6(a), there are only four endotherms present with clear distinctions supported by the literature [1, 24, 32]. The first endotherm was identified to be the sole $T_g$ for all composites that were analyzed. Defined endotherms confirm that the PHB/S/LA blends exhibited single, composition-dependent $T_g$ values, indicating that a single homogenous amorphous phase was formed.

Figure 4: FTIR results. (a) FTIR spectra of PHB, starch (powder), and LA0. (b) FTIR spectra of PHB/S/LA composites LA0, LA1, and LA2.

Figure 5: TGA and DTG curves of PHB/S/LA composites. (a) Full TGA curve. (b–d) Selected magnifications of 5A, at regions (a) 0–150°C, (b) 290–320°C, and (c) 450–600°C, respectively. (e) DTG curve.

Table 4: TGA parameters of PHB/S/LA composites.

| Material | IDT (°C) | MRDT (°C) | MDT (°C) |
|----------|----------|-----------|----------|
| PHB      | 270.98   | 295.94    | 303.85   |
| LA0      | 262.03   | 284.39    | 295.61   |
| LA1      | 270.88   | 290.1     | 300.13   |
| LA2      | 270.17   | 291.06    | 296.64   |
present in the two mixtures, which suggests that the mixture is miscible [25, 39].

The reported values of $T_g$ are summarized in Table 5, along with other thermal properties. It was shown that the $T_g$ was found in the first endotherm (0–10°C). This parameter slightly increased upon the incorporation of starch. LA addition to the biopolymer decreased the $T_g$, with a downward trend [27]. Theoretically, this suggests that lauric acid can still be added to attain a smaller $T_g$. There are three other endotherms for PHB/starch/LA films, as shown in Figures 6(a), 6(c), and 6(d). Figure 6(c) shows endotherm 2 for PHB/S/LA blends. Blending of starch to PHB shifted the amylose gelatinization peak to approximately 80°C for all composites. For comparison, in the thermogram of pure starch (Figure 6(a)), the recognizable peak at 86.59°C denotes amylose gelatinization [18]. The second irregular peak found at 307°C for starch is attributed to the phase transition of the amylose-lipid complex [41]. Endotherm 3 in PHB/S/LA films shown in Figure 6(d) corresponds to the melting of PHB in the blends [42]. As observed, the melting temperature of the films shifted to lower temperatures with an increasing amount of lauric acid. This clearly helps with the thermal processability of the biopolymer composites, as they are much further from the onset degradation temperature, as discussed in the TGA results (Table 4). Only one melting peak was observed for pure PHB, while two peaks were observed for PHB/S/LA composites. The presence of double endothermic melting peaks in the PHB composites was ascribed to the melt recrystallization mechanism. This behavior is common among polymeric materials and has been explained based on two theories: (1) double lamellar thickness population model [43] and (2) melting and recrystallization model [44]. Hong et al. [45] refer to the smaller peak as a melting temperature of small and imperfect crystallites that formed during the evaporation of the solvent (metastable crystals). The high-temperature endotherm was classified to

Table 5: Thermal properties of PHB/S/LA composites.

| Material | $T_g$ (°C) | $\Delta H_m$ (J g$^{-1}$) | $T_m$ (°C) | $\chi_c$ (%) |
|----------|----------------|-----------------|-------------|--------------|
| PHB      | 6.7             | 88.3            | 179.0       | 60.5         |
| PHB 80/S 20 (LA0) | 7.1             | 63.1            | 179.8       | 54.0         |
| PHB 80/S 20/LA 10 mg (LA1) | 6.5             | 68.4            | 176.4       | 60.5         |
| PHB 80/S 20/LA 20 mg (LA2) | 5.4             | 66.2            | 175.4       | 60.6         |

![Figure 6: DSC curves of PHB, starch, and PHB/S/LA blends. (a) Full spectra. Endotherms are denoted by gray areas. (b–d) Enlarged thermogram regions.](image-url)
be the melting of ordered polymer crystals [32]. As a result, even though endotherm 3 consists of a pair of peaks, they are considered one due to this behavior. Lastly, endotherm 4 for pure PHB (296.22°C) and PHB/S/LA films (271-277°C) is due to degradation of the polymer, which occurs at breaking of ester bonds and thus decreasing the molar mass [46].

Lastly, the degree of crystallinity of the samples was determined from Equation (1). $\Delta H_m$ is the apparent enthalpy of fusion observed for PHB and PHB/S/LA blends in endotherm 3 from the DSC thermograms. The computed degree of crystallinity of pure PHB and PHB blends are summarized in Table 5. A decrease in the degree of crystallinity of samples was then observed with the addition of starch. The presence of a plasticizer in the polymer blend interfered with the intermolecular forces between chains such that the folding/arrangement among polymeric chains is altered. The addition of a plasticizer increased the crystallinity of the polymer, making it similar to the crystallinity of pure PHB. However, no certain trend was established between the degree of crystallinity and the amount of lauric acid added. Also, the crystallinity results directly correlate to the XRD results (Figure 3(c)), wherein LA1 and LA2 have an increased peak compared to LA0, which suggests increased crystallinity.

3.4. Effect of Lauric Acid Addition on the Mechanical Properties of the Bioplastic Composite. Flexibility is an important property for plastics, especially for single-use packaging, where the plastic is subjected to continuous wear and tear that forces the material to be stretched during usage. It is very important for the mechanical properties of the synthesized bioplastics to properly dictate their range of applications.

UTM results for the mechanical properties and their summary are shown in Figure 7.

The stress-strain curves obtained from tensile testing of the bioplastic composites are shown in Figure 7(a). All curves depict a behavior characteristic of a ductile material and not of a polymeric material. Still, it can be observed that there is a reduction in the slope of the initial linear region (corresponding to Young’s modulus) with an increasing amount of LA (Figure 7(d)), in comparison with LA0. This observation verifies the plasticizing effect of LA on PHB/starch films, due to the aforementioned formation of hydrogen bonds between the two matrix molecules (PHB and starch) and the plasticizer (LA) [27]. The effect of LA addition on the tensile strength and extension at break of the films is shown in Figures 7(b) and 7(c). As expected, the tensile strength slightly decreased with the incorporation of starch, amounting to at most 20% loss of tensile strength with no clear trend. The presence of heterogeneity through crystallite formation can vitrify amorphous polymer chains. This leads to the indication that a level of interfacial adhesion lacked between PHB and starch, albeit its nucleation-induced blending states otherwise. This implies that the PHB-starch mixture behaves as a thermoplastic, but small amounts of loose starch granules in the composite matrix provide avenues for tensile fracture.

It has also been observed that the tensile strength has decreased with increasing plasticizer amount, which has been reported elsewhere [14, 30, 37, 39]. This is due to the plasticizer’s effect on the promotion of intermolecular forces, consequently diminishing the strong intramolecular forces within the PHB and starch polymer chains. Moreover, although Young’s modulus has no observable trend.
tensile strength and Young's modulus of PHB-HV are approximately 0.12–4 GPa. From Figures 7(b)–7(d), the reported tensile strength values ranging from 3 to 31.50 MPa, elongation at break of LA1 (15.985 ± 4.236%) and LA2 (17.955 ± 4.76%). Reis et al. [1] have incorporated maize starch to PHB. Their mechanical properties show that a 20% starch incorporation in PHB led to a 67% tensile strength loss and a low elongation at break (1%). However, this resulted in a relatively high reported Young’s modulus (E = 0.75 GPa). Other studies, as summarized by Yeo et al. [17], have reported tensile strength and Young’s modulus are within the average to the high end of current literature results. Interestingly, the elongation at break values was higher than reported from previous studies. Overall, the mechanical properties of the PHB/S/LA composite are competitive with the data reported from other existing studies.

4. Conclusions

PHB/S/LA bioplastic composite films were prepared, and the morphology, physicochemical, thermal, and mechanical properties of the bioplastic films were investigated. The characteristic peaks in the FTIR spectra showed that the addition of LA as a plasticizer promoted the formation of hydrogen bonds between the PHB, starch, and LA components. This can also be observed in the SEM images where a decrease in the inhomogeneity of the samples can be seen, as well as a decrease in the surface roughness as the amount of LA added was increased. The DSC profiles of the films also indicate an improvement in the miscibility of the polymer blends. A decrease in the glass transition temperature (T_g) suggests an improvement in the flexibility of the samples. Moreover, the TGA and DTG profiles also exhibited increased thermal stability. The temperature at the maximum degradation of the PHB/S/LA films was likewise higher with the addition of LA. The plasticizing effect of LA was further verified when Young’s modulus was decreased and the elongation at break (maximum 250% increase) was significantly increased. The addition of LA has therefore exhibited promising results in the thermal and mechanical properties of PHB/starch films. Further studies are still necessary to further improve the utility of the aforementioned blends to make the product suitable for practical packaging applications.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no competing interest.

Acknowledgments

This study was financially supported by the Department of Science and Technology, National Academy of Science and Technology, and Philippine Council for Industry, Energy, and Emerging Technology Research and Development.

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