Original Article

Preparation and characterization of cornhusk/sugar palm fiber reinforced Cornstarch-based hybrid composites

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A B S T R A C T

In the current study, a series of hybrid composite films were prepared from cornhusk fiber (CHF) and sugar palm fiber (SPF) through a solution casting technique, using cornstarch (CS) as matrix and fructose as a plasticizer. SPF at 2%, 4%, 6%, and 8% (w/w dry starch) concentrations was loaded into CS/CH composites with 8% CHF and 25% fructose. The physical, morphological, thermal, tensile, and barrier characteristics of the final product were evaluated. From the findings, there was a marked decrease in density, moisture content, solubility, and water absorption of the hybrid films. SEM images exhibited a strong interfacial interaction and good biocompatibility between polymer matrix and reinforcement fiber, which reflected on the enhanced tensile strength and Young’s modulus as well as the relative crystallinity. The thermostability of hybrid films has also been enhanced, as indicated by the increased onset degradation temperature. Fourier transform infrared analysis revealed an increase in intermolecular hydrogen bonding following fiber loading. As well as the water barrier assessment showed greater resistance to vapor transmission, evidenced by the lower water vapor permeability rate following SPF loading. To sum up, the hybridization of CS/CH composites with SPF, in general, has improved the performance of the biocomposites for biomaterials applications, especially for 6% of SPF loading.

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1. Introduction

Current environmental concerns, such as non-biodegradable disposal materials and the growing mountain of garbage, are increasingly recognized as ecological threats. The area allocated for landfills is limited, and additional incineration
capacities require high capital investment and cause further environmental problems, all these issues have inspired researchers and scientists to move toward the manufacturing and development of environmental engineering materials from renewable sources to replace conventional non-biodegradable materials in several applications, that could preserve the green environment [1,2].

Thermoplastic starch-based polymers are recognized as one of the most promising materials for the large-scale production of biodegradable and recyclable materials. Nevertheless, starch-based polymers are known to have poor mechanical performance and high-water propensity [3]. Therefore, the incorporation of strengthening materials such as plasticizers becomes a persistent need to improve the mechanical characteristics of starch-based biomasses. The main function of plasticizers is to facilitate the mobility of starch molecules by reducing the intermolecular attraction of hydrogen bonds within the starch structure [4,5]. Several studies have been reported about the incorporation of plasticizers to enhance the performance of starch-based biopolymers. The results showed partial improvement in the materials produced [1,6–9].

Reinforcing starch-based materials with natural fibers showed remarkable improvement, especially in terms of thermal stability and mechanical performance, as well as water barrier properties; this improvement was mainly due to the high correlation and structural similarity between starch and cellulose [10]. Agriculture residues such as sugar palm, corn, cassava, and pineapple are the most abundant source of natural fibers, it is produced annually in large quantities and low cost. In addition to their availability, the cellulosic plant fibers characterized by durability, flexibility, low density, and high elongation, that made them interesting research area [11].

Corn (maize) consider one of the most abundant agricultural grains in the world. Large agricultural areas dedicated to maize cultivation, in 2002, the production of corn reached 602,026,822 Mt [12]. The value of harvested corn plants can be improved by processing corn stover to produce natural cellulosic fibers. The stover of corn plants typically composed of 15% husk, 35% leaves and cobs, 50% stalk [13]. Cornhusk is indicated to the outer layer that covers the ear of corn; it is a natural lignocellulosic fiber characterized by flexibility, low density, and high elongation with a high cellulose content and low concentration of ash and lignin [14,15]. In a previous study, biocomposite films have been produced from cornstarch/cornhusk fiber by solution casting method, using fructose as a plasticizer by 25% (w/w dry starch). The findings showed that the addition of 8% husk fiber established the most efficient reinforcing agent, resulting in remarkable mechanical and physical characteristics of the final product. Despite its acceptable properties, the bio-composite produced has revealed some flaws, especially in terms of water resistance characteristics [16]. In an attempt to resolve such defects, hybridization of corn husk composite with fiber that characterized by high-water resistance such as palm fiber sugar is expected to provide better results.

Sugar palm fiber (SPF) is a natural lignocellulosic fiber characterized by high resistance to seawater, high tensile strength, low degradation rate, and durability [17]. According to Edhirej et al. (2017) [18], the preparation of SPF does not require any efforts, because it does not involve any secondary processing or treatment such as mechanical decorticating or water rating. In the field of composite materials, many types of research have been reported about the utilization of sugar palm fiber as a reinforcing agent with the polymer matrix. The results indicated that sugar palm fibers have the potential to be used in many applications of composite materials, especially those requiring high water resistance.

In modern material studies, a mussel-inspired chemistry strategy has been widely used to modify the surface of both organic and inorganic materials. It was initially reported in the 1980s by Herbert Waite’s who studied the adhesion of marine mussels [19,20]. The idea of this strategy was inspired by the strong attachment of proteins in mussels; unlike conventional surface modification techniques, the strategy mechanism inspired by mussels is to create a multifunctional layer of the polymer through the self-polymerization of materials in an aqueous solution. Where, the existence of functional groups such as –OH hydroxyl, –CH, –OC, and –NH on the surface structure of the modified materials promotes the immobilization of initiator and allows adequate interactions with the molecules of mussel-adhesion materials in the aqueous solution [21–23]. This method characterized by simplicity in the experimental and operational procedures and fairy Free from defects and hazardous. Besides, mussel-inspired chemistry has been widely discovered for various applications ranging from enzyme inhibition, fluorescent sensors and imaging, cancer remediation, and antibacterial treatment of the environment, energy conversion, and production of biomaterials with efficient adsorption properties [19,24–29].

Hybrid composite is referred to the product that resulted from incorporating two different fibers into a single matrix with the aim of obtaining better properties than the usage of individual fiber [18]. The characteristics of the hybrid composite depend mainly on the concentration and orientation of the individual fiber, matrix to fiber interaction, and the extent of intermingling between both fibers. The mechanical performance of the hybrid composite is also relayed on the failure strain of each fiber; the optimum hybrid performance is achieved when the strain of both fibers is highly compatible [30]. Nevertheless, several studies have been reported about the hybridization of composite materials, especially with sugar palm fiber. For instance, Edhirej et al. (2017) [31] studied the tensile and water barrier properties of cassava/sugar palm fiber reinforced cassava starch hybrid composites. Also, Jumaidin et al. (2017) [32] investigated the thermal, mechanical, and physical properties of seaweed/sugar palm fiber reinforced thermoplastic sugar palm starch/Agar hybrid composite. The authors reported significant results, particularly concerning mechanical performance and water barrier characteristics. The proper combination of the selected reinforcing fibers ensures a considerable enhancement in mechanical and physical properties.

The main objective of the current contribution is to investigate the effect of multi-scales of sugar palm fiber contents on the physical, tensile, thermal, structural, and water barrier properties of the cornstarch/cornhusk hybrid composite. It is worth mentioning that the natural fibers used in the present research were not chemically processed or thermally modified, which will lead to the development of more envi-
environmentally and cost-effective materials. Also, this study was planned to assess the use of agricultural residues, which are inexpensive and highly available, that might be contributed to reducing waste disposal and enhancing economic growth through the transition from waste to health.

2. Materials and methodology

2.1. Materials

Cornstarch (CS) was isolated from fresh corn granules purchased from a night market in Selangor, Malaysia, following the procedure of Ibrahim et al. (2019) [33]. Its composition was 24.64% amylose, amylopectin 74.36%, 10.45% moisture, 7.13% lipids, and 0.62 ash. Cornhusk fiber (CHF), which is the layers covering the corn ear, was cleaned, dehydrated, ground, and examined through 300 µm mesh sieve. Sugar palm fiber (SPF) was gathered from a local farm in Negri Sembilan, Malaysia; it was thoroughly cleaned and converted to powder form. Table 1 shows the composition of CHF and SPF, while Fructose plasticizer was provided by evergreen Sdn. Bhd, Malaysia.

2.2. Samples preparation

The CS-based hybrid films were prepared by the conventional solution casting technique. Five grams of pure CS was added to an aqueous solution of 100 ml distilled water. The solution was heated by a thermal-magnetic mixture to 85 ± 3 °C for 25 min with continuous stirring to allow the starch to gelatinize. Following that, fructose plasticizer with 25% (w/w powder starch) concentration along with CHF with 8% (w/w powder starch) concentration was added to the solution. The concentrations of both plasticizer and CHF were selected based on our previous work [1]. The SPF at various loadings (0, 2, 4, 6, 8%) of dry starch-based was used as a hybridized agent. The heating process with continuous stirring was kept for an additional 25 min. After that, the gelatinized solution was discharged evenly in a thermal petri dish with a 140 mm diameter. The dish with a casted solution was desiccated in an air circulation oven for 24 h at 45 °C. The formed films were removed gently from the dishes and kept at ambient conditions for ten days prior to characterization. The obtained films were labeled according to their compositions and concentration of SPF, as shown in Table 2.

2.3. Density (ρ)

The density of film samples was computed directly from their weights (m) and volumes (v). The proposed size was 20 × 15 mm, and thickness was measured by an electronic caliper (Mitutoyo-Co, Japan) with ± 0.001-inch accuracy. Thus, film density (ρ) was obtained via the following equation:

\[
\rho \text{ (kg/mm}^3\text{)} = \frac{m}{v} \tag{1}
\]

2.4. Moisture content (MC)

A sample of 20 × 15 mm film was initially weighed (\(w_1\)) before it being placed in the dehydration oven for 24 h at 105 °C. After that drying period, the sample was again weighed (\(w_2\)). The difference in weights before and after dehydration was used to calculate the amount of water removed from the sample using the following equation:

\[
MC \text{ (％)} = ((w_1 – w_2)/w_1) \times 100 \tag{2}
\]

2.5. Water solubility (WS)

This test was conducted following the method of Shojaee-Alibadi et al. (2013) [34]. A strip of the sample (20 × 15 mm) was dehydrated at 105 °C for 24 h and then directly weighted (\(W_f\)). Following that, the sample was immersed in a lab beaker containing condensed water under constant stirring for 12 h at room temperature. The insoluble remaining of the sample was dried at 105 °C until a constant weight (\(W_i\)) was achieved. WS (%) of the sample was measured by the equation:

\[
WS \text{ (％)} = ((W_i – W_f)/W_i) \times 100 \tag{3}
\]

2.6. Water absorption (WA)

Water absorption is defined by the ability of the dehydrated material to retain water after a certain time of immersion. A film sample (20 × 15 mm) was kept on an air circulation oven at 105 °C for 3 h and then was immediately weighted (\(M_i\)). The sample was then steeped in distilled water at ambient tem-

<table>
<thead>
<tr>
<th>Table 1 – Chemical composition and physical properties of corn husk and sugar palm fibers.</th>
</tr>
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<tbody>
<tr>
<td>No.</td>
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<td>1</td>
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<td>7</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2 – Composition of the films at different stages of SPF loading.</th>
</tr>
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<tbody>
<tr>
<td>Film</td>
</tr>
<tr>
<td>CS-film</td>
</tr>
<tr>
<td>CS-CH</td>
</tr>
<tr>
<td>CS-CH/SP2%</td>
</tr>
<tr>
<td>CS-CH/SP4%</td>
</tr>
<tr>
<td>CS-CH/SP6%</td>
</tr>
<tr>
<td>CS-CH/SP8%</td>
</tr>
</tbody>
</table>
perature. After a specific period of steeping, the sample was removed from the water, dried superficially with a soft cloth, and weighed (M_j). The assessment of WA was obtained after 30 min and 3 h of immersion time, as suggested by previous studies [35,36]. The test was conducted in triplicate and was calculated using the following equation:

\[ WA(\%) = \left(\frac{M_f - M_i}{M_i}\right) \times 100 \]  

(4)

2.7. **Scanning electron microscope (SEM)**

The surface morphological properties of the samples were examined by SEM instrument type (Hitachi S-3400N, Nara, Japan). Before the scanning, the sample was coated with a thin golden layer to conduct electricity. A 20 kV voltage was then applied in a high vacuum to generate a bundle of electrons. The generated electrons send signals to visualize the surface topography of the sample and produce images with high resolution.

2.8. **Fourier transform infrared spectroscopy (FTIR)**

A spectrometer type (Bruker vector 22, Lancashire, UK) was used to track the FT-IR spectrum of samples and determine the existence of functional groups. The test was performed using 16 scans per sample, over a frequency range of 4000–400 cm\(^{-1}\), with a spectral resolution of 4 cm\(^{-1}\).

2.9. **X-ray diffraction (XRD)**

The XRD diffraction analysis of the hybrid films was performed using a 2500 X-ray diffractometer (Rigaku, Tokyo, Japan). The angular scattering (2θ) was ranged from 5° to 60°, with a speed rate of 0.02° per angle. The operating current and voltage during the test were set at 35 mA and 40 kV, respectively. The crystallinity index (CI) of samples was calculated based on the calculus of the amorphous area (AA) and the crystalline area (Ac) by the equation:

\[ CI = \left(\frac{Ac}{Ac + AA}\right) \times 100 \]  

(5)

2.10. **Thermogravimetric analysis (TGA)**

The thermal properties of the specimens were obtained by a thermogravimeter analyzer (Q500 V20.13 Build 39, Bellingham, USA). The film sample was placed in a platinum vessel under Nitrogen vacuum and subjected to a temperature ranging from ambient to 500 °C at a rate of 10 °C/min. TGA measures the percentage of weight loss as affected by temperature increase.

2.11. **Tensile testing**

The tensile characteristics of the hybridized films were measured according to D882 (ASTM, 2002) standard in the ambient conditions using 5KN INSTRON tensile machine. The film strip (10 × 70 mm) was firmly mounted between tensile clamps. The initial gauge length was set to 30 mm, and the crosshead speed was maintained at 2 mm/min. Measurements were conducted for five replicates of each specimen to find out tensile strength and elastic modulus as well as elongation at break.

2.12. **Water vapor permeability (WVP)**

The WVP is a physical test for measuring the vapor transmission rate through the thickness of flat material within a specific area. The test was performed based on ASTM E96 (1995) standard, with a slight alteration, according to Edhiring et al. (2017) [31]. A circular cup with a 70 mm diameter and 75 mm height was filled with 5 g of silica gel. A film sample with a known thickness was tightly fixed in the mouth of the cup, and the initial weight was recorded. Thereafter, the test cup was placed in a humidity chamber at 25 °C temperature and 75 % relative humidity. The weight gained of the cup was measured periodically until the steady-state of weight was reached. Finally, WVP (10\(^{-1}\) mm.g. s\(^{-1}\). m\(^{-2}\). Pa\(^{-1}\)) of the sample is calculated by the equation:

\[ WVP = \frac{w \times d}{A \times t \times P} \]  

(6)

Where: w (g) is the weight increment of the test cup, t (mm) is the thickness of the film, A (m\(^2\)) is the area of the sample, t (s) is the time of permeability, and P (Pa) is the surrounded pressure.

3. **Results and discussion**

3.1. **Density**

A part of Table 3 shows the thickness and density values of the hybrid composites. As anticipated, the incorporation of SPF and its various concentrations increased the thickness and reduced the density. The obtained findings might be ascribed to the intermolecular interaction of the reinforcing fibers and the starch matrix. The higher concentration of SPF increases porosity formation and generates a heterogeneous surface less dense than the starch matrix, leading to thicker and more coarse films [37]. The reduction in density of hybrid composites following the fiber addition was also observed in previous researches in the same field [18]. Nevertheless, the low-density of biomaterials makes them attractive materials for the manufacturing of biomasses in comparison with synthetic composite materials, such as fiberglass (2.500 g/m\(^3\)) [38].

3.2. **Moisture content**

Moisture content is a key factor to be considered in the selection of natural fibers as reinforced materials to produce new composite materials. The low water content is required, since the high water content may adversely affect the dimensional stability of the composite material, particularly, in terms of mechanical performance, formation of porosity, as well as water holding capacity [39]. However, the incorporation of SPF resulted in a slight reduction in the moisture content of the hybrid composites, as shown in Table 3. Ilyas et al. (2018) [40] explained this phenomenon through the role of cellulose within the hybrid composite; this means the incorporation of another fiber increases the cellulose content within the composite and thus decreased the rate of moisture content. Because the structural composition of cellulose contains a hydroxyl group that makes it insoluble in water. This explana-
tion is in agreement with that obtained by Soykeabkaew et al. (2004) [41] who prepared tapioca starch-based hybrid composite reinforced with flax and jute fibers. Similarly, to that reported by Edhirej et al. (2017) [18] who hybridized cassava starch composite with cassava bagasse and SPF.

3.3. Water solubility

Table 3 also included the water solubility values of the hybrid composites; this parameter examines the influence of water immersion rate with continuous stirring on the material integrity. Low water solubility is important for the applications that need protection from moisture and water loss [42]. Despite its insoluble nature, the introduction of SPF showed an insignificant decrement in hybrid composite solubility compared to CS-film and CS/CH composite. The solubility decreased as the SPF concentration increased that due to the ability of SPF to resist water diffusion and enhancing composite's integrity by inhibiting water penetration, this, in turn, reduces film solubility [32].

3.4. Water absorption

Water sensitivity, one of the major drawbacks of bio-based materials. Therefore, the effect of the water absorption rate on the CS–CH/SPF hybrid composites was studied. The obtained results were placed in Table 3. Jawaid and Khalil (2011) [39] stated that the physical properties of hybrid biocomposites, in particular, water uptake character has a noticeable impact on the tensile strength, porosity formation, dimensional stability, as well as the swelling index of the final product. However, in the present study, the initial assay of the water absorption rate was examined after 30 min of immersion, and also after 180 min when the samples reached the maximum degree of saturation. After 30 min it was clear that all samples retained the largest amount of water. CS/CH composite film showed the highest propensity to absorb water by 90.46%, while hybridization with SPF resulted in an apparent reduction in the absorption rate reached 80.46% with 6% loading. The variation on water absorption rate was more evident after 180 min of immersion, as the hybridized composites revealed the highest resistance to water uptake. The decline in the absorption rate in the presence of SPF might be attributed to the role of fibers in the formation of strong interfacial bonding in the structure, which hinders the penetration of water through the matrix [35]. Also, the presence of lignin as a major component combined with wax and fatty substances in the formation of fiber stimulates the ability of composites to resist water [43]. Edhirej et al. (2017) [18] and Jumaidin et al. (2017) [32] also reported a significant reduction in the water absorption rate of TPS-based hybrid composites with progressive loading of SPF.

3.5. Morphological properties

The SEM images of the surface fracture of CS–CH/SPF hybrid composites along with neat CS-plasticized film and CS/CH biocomposite are shown in Fig. 1. The CS-plasticized film showed a compact and relatively smooth structure without porosity; also, a presence of undissolved starch particles was observed. The incorporation of CHF to form a biocomposite (CS/CH) resulted in less homogenous surfaces, and the structure turned to be rigid and nonuniform with a coarse texture. Meanwhile, the introduction of SPF to form hybrid composite has created a more rigid structure, as the starch matrix entirely covered the fiber particles, and there were no visible clusters or aggregation of SPF within CS matrix, suggesting that the interfacial interaction between the reinforcing fibers and polymer matrix was perfect. A strong interfacial interaction indicates an effective stress transfer, leading to an increase in strength [44,45]. The surfaces fracture of CS-H/SPF hybrid composite (2%, 4%, and 6%) were coarser than the CS-film, due to the incorporation of SPF as hybrid filler; however, they seemed smoother than CS–CH/SPF8% counterpart, which means that the low concentration of SPF was more compatible with CS-matrix than the high concentration. Because in the case of the highest addition of SPF (CS–CH/SPF8%), the hybrid structure appeared to be less consistent, as evidenced by the occurrence of microcracks and agglomeration of SPF on surface fracture; this was due to the excessive use of fiber, which adversely affects structural integrity [46]. These observations are in good agreement with the tensile test results of the current study and broadly support the work of other researchers in this area, linking cassava bagasse with SPF as a reinforcing agent for cassava starch hybrid composites [18].

3.6. FT-IR analysis

The FTIR spectrum curves of the neat CS-film, CS/CH composite, and CS–CH/SPF hybrid composites with various loading of SPF are shown in Fig. 2. It was clear that the FT-IR spectra of all film samples exhibited characteristic absorption peaks associated with fiber and polymer components. Since the materials used were extracted from biological sources, their chemical composition contains certain constituents, which are lignin, cellulose, and hemicellulose for the fibers and amylose and amyllopectin for the starch. The transmittance bands at the peaks 930–1030 cm⁻¹ are ascribed to O–C stretching

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**Table 3 – Physical properties of the films.**

<table>
<thead>
<tr>
<th>Composite</th>
<th>Thickness (μm)</th>
<th>Density (g/cm³)</th>
<th>Moisture content (%)</th>
<th>Water solubility (%)</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-film</td>
<td>0.195 ± 0.25</td>
<td>1.55 ± 0.09</td>
<td>11.64 ± 0.11</td>
<td>22.05 ± 0.43</td>
<td>82.56 ± 0.18</td>
</tr>
<tr>
<td>CS/CH</td>
<td>0.265 ± 0.25</td>
<td>1.30 ± 0.07</td>
<td>10.95 ± 0.19</td>
<td>20.51 ± 0.17</td>
<td>90.46 ± 0.59</td>
</tr>
<tr>
<td>CS/CH/SP2%</td>
<td>0.320 ± 0.25</td>
<td>1.30 ± 0.04</td>
<td>8.93 ± 0.20</td>
<td>20.07 ± 0.09</td>
<td>83.80 ± 0.08</td>
</tr>
<tr>
<td>CS/CH/SP4%</td>
<td>0.335 ± 0.25</td>
<td>1.29 ± 0.06</td>
<td>9.31 ± 0.23</td>
<td>19.75 ± 0.15</td>
<td>82.39 ± 0.13</td>
</tr>
<tr>
<td>CS/CH/SP6%</td>
<td>0.372 ± 0.25</td>
<td>1.23 ± 0.09</td>
<td>9.21 ± 0.19</td>
<td>19.24 ± 0.17</td>
<td>80.46 ± 0.15</td>
</tr>
<tr>
<td>CS/CH/SP8%</td>
<td>0.397 ± 0.25</td>
<td>1.16 ± 0.07</td>
<td>9.26 ± 0.11</td>
<td>19.48 ± 0.12</td>
<td>82.40 ± 0.19</td>
</tr>
</tbody>
</table>

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**Note:** Errors are ± 95% confidence interval.
within the anhydroglucose ring [47]. The bending of water fragments in starch generated the double bands at around 1500–1600 cm$^{-1}$ [48]. The stretching of C–H groups showed up the sharp bands at 2850–3000 cm$^{-1}$ [49]. The broad adsorption bands with high intensity at 3200–3500 cm$^{-1}$ are attributed to the vibrational stretching of O–H hydroxyl groups within the fiber and starch structure [50,51]. However, no evidence of chemical reactions, as no new peaks appeared. Thus, the interactions between the reinforcing fibers and the starch matrix molecules were determined by detecting the shift of the band position, following the fiber loading. For example, it can be seen from Fig. 2 that the O–H stretching peaks at approximately 3200–3500 cm$^{-1}$ for CS-film were shifted to lower intensity bands after the hybridization. The shifting of band position is an indicator of increasing intermolecular hydrogen bonding in the hybrid structure, which provided stronger interaction and more compatibility [50]. A similar interpretation was reported by Jumaidin et al. (2017) [32] when they hybridized sugar palm starch-based composites with seaweed and SPF.

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**Fig. 1** – Scanning electron micrograph of CS–CH/SPS hybrid composite.
the hybrid composites. According to Bledzki et al. (1999) [54], the observed correlation between fiber loading and increased crystallinity might be explained through the function of cellulose in improving crystallinity by creating a crosslinked network and hindering disintegration of the composite by forming covalent bonding between fiber and matrix. The crystallinity values of cornstarch films as affected by different fiber loadings were displayed in Table 4. Natural fibers are oriented materials; therefore, improvement in the crystallinity of starch-based composites is expected with the increase of fiber content [55].

3.8. Thermal properties

The thermostability of CS–CH/SPF hybrid composites at a multi SPF loading is displayed in Fig. 4. TGA and DTG curves were employed to determine the thermal properties of materials in terms of the decomposition temperatures, and the percentage of material residues after the highest degradation rate. Based on the data obtained, the thermal degradation and weight loss of CS–CH/SPF hybrid composites occurred in four heating events, as shown in Table 5. Each event is associated with a prominent peak in the DTG curve and corresponds to a specific weight loss in the TGA graph. The initial weight loss occurred at less than 100 °C due to the elimination of water molecules by evaporation and de-hydroxylation process [56–58]. Samples with higher moisture content experienced higher heating rates and thus more weight loss, this consistent with moisture content results (Table 3). Further heating caused the second loss in weight at 150–200 °C, the weight loss in this stage was mainly due to the volatilization of fructose particles together with residual water fragments. The majority of plasticizers begin volatilization at 150 °C [59]. In the third thermal action, the mass loss started with the degradation of the water-soluble amylopectin in starch structure [33]. While the highest rate of degradation was due to the decomposition of the major components of reinforcing fibers, namely hemicellulose, cellulose, and lignin. According to Lombeli-Ramírez et al. (2014) [60] for all lignocellulosic plant fiber, the thermal decomposition initiates with the decaying of hemicellulose at range (200 °C–260 °C), cellulose at (240 °C–350 °C), and lignin at (280 °C–500 °C), that depends on the plant type and the percentages of fabric components. Finally, once the lignin is completely decayed, the remaining component is inorganics such as silica (silicon dioxide, SiO2), which can be considered as a char (mass residues).

In general, the hybrid SPF-films revealed close onset degradation temperatures ranged in 298–300 °C, less than the degradation temperature of the CS/CH composite film, which
Table 5 – Degradation temperatures of CS–CH/SPF hybrid composites.

<table>
<thead>
<tr>
<th>Film sample</th>
<th>Onset degradation temperature (°C)</th>
<th>Mass residue (%)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase 1 (Moisture)</td>
<td>Phase 2 (Plasticizer)</td>
<td>Phase 3 (Starch)</td>
</tr>
<tr>
<td>CS-FILM</td>
<td>82.92</td>
<td>184</td>
<td>277</td>
</tr>
<tr>
<td>CS/CH</td>
<td>70.14</td>
<td>197.93</td>
<td>282.95</td>
</tr>
<tr>
<td>CS-CH/SPF2%</td>
<td>73.63</td>
<td>197.25</td>
<td>279.88</td>
</tr>
<tr>
<td>CS-CH/SPF4%</td>
<td>70.35</td>
<td>192.24</td>
<td>280.58</td>
</tr>
<tr>
<td>CS-CH/SPF6%</td>
<td>67.14</td>
<td>189.93</td>
<td>280.53</td>
</tr>
<tr>
<td>CS-CH/SPF8%</td>
<td>69.31</td>
<td>189.11</td>
<td>278.63</td>
</tr>
</tbody>
</table>

![TGA and DTG graphs](image)

Fig. 4 – Thermal analysis of CSCH/SPF hybrid composite. (a) TGA, and (b) DTG.

started its maximum decaying at 302°C. Similarly, the mass residues following the final decomposition of the hybrid composite declined slightly (weight loss increased), showing small variations compared to the neat CS-film; such observations indicate that the incorporation of SPF as a hybridizing agent to some extent reduced the thermal stability of CS-based hybrid composites. This finding is consistent with that of Edhirej et al. (2017) [18] who reinforced cassava starch hybrid composites with cassava bagasse and SPF, and stated that the SPF loading has slightly decreased the thermal stability of the hybrid composite.

3.9. Tensile properties

The effect of SPF with different concentrations on the tensile performance of CS-based hybrid films is illustrated in Fig. 5. The tensile testing was carried out to measure tensile strength (TS), tensile modulus (E), and extension at the break (EB). From the findings, the incorporation of SPF and the gradual increase in its concentration resulted in a significant increase in TS and E and an apparent reduction in EB, suggesting that the hybridized composites have turned to be more rigid and stiffness with less flexibility, and have become more resistant materials [61,62].

However, the introduction of SPF exhibited a considerable increase in the mechanical performance of the hybrid composites. For example, the 6% concentration demonstrated the highest tensile strength and elasticity modulus of 19.09 MPa and 170.19 MPa, respectively, higher than 6.8 MPa obtained by neat CS-film and 12.84 MPa obtained by CS/CH composite. This enhancement may be explained by the fact that the cellulotic fibers have the ability to dominate the mobility of TPS molecules and promote the interfacial bonding by establishing a network that firmly holds the composites together and hence facilitates the stress transfer [63,64]. Another possible explanation for this enhancement is attributed to the relative crystallinity as described by Salaberria et al. (2014) [65], the researchers stated that the increment in crystallinity promote the rigidity and stiffness, and thus, the system performance. Furthermore, the chemical bonding between the hydroxyl group and glucose anhydride (as in the FTIR analysis) resulted in a better transfer of stress from the matrix to the fiber, resulting in higher tensile strength [54].

Despite this enhancement, the addition of SPF beyond 6% percentage led to a clear trend of decreasing in tensile strength and elasticity modulus. As labeled, SEM images showed cracks appearing due to excess of SPF content. The excessive use of fiber caused poor particle dispersion and large agglomeration, which resulted in weak tensile properties [66].

Regarding the elongation of CS–CH/SPF hybrid composites, the fiber loading showed an opposite impact compared with elasticity modulus and tensile stress. As the loading increased, the elongation of the composite decreased. This factor determines the material extendibility from the initial length to the point of the break [67]. The reduction in film elongation as fiber loading increased is because cellulose content rebuilds...
the composite’s structure by enhancing the intermolecular bonding in the TPS matrix. Such rebuilding in the starch network improves the stiffness and rigidity and thus, decreases the flexibility by eliminating chain mobility [68].

3.10. Water barrier properties

The water vapor permeability (WVP) test measures the rate of a water passage across the unit area of materials. The materials with a low amount of WVP are more suitable for the applications that required prevention or reduction of moisture transmission from the surrounding atmosphere. Therefore, reducing the WVP of CS-based films is a persistent need for their potential applications. Fig. 6 displays the WVP values of the neat CS-film, CS/CH-composite as well as CS–CH/SPF hybrid composite at various concentrations. Based on data obtained, the highest rate of WVP was observed in the neat CS-film, which reached $2.28 \times 10^{-10}$ mm.g.s$^{-1}$.m$^{-2}$.Pa$^{-1}$; this was mainly due to the high hydrophilic character of starches in general [69,70]. To address such a drawback, the incorporation of reinforcement agents like natural fibers is a vital solution. However, the introduction of SPF enhanced the barrier properties of CS-based films, evidenced by the decrement trend of WVP. The addition of 2% SPF reduced the WVP rate by 66.42% compared to the neat CS-film. The noticeable decrease could be attributed to the formation of rigid crystalline structure and rich dispersion of SPF in the polymer matrix, which hinders the permeability path of the vapor molecules [71]. Another possible description of the observed behavior is the increased intermolecular bonding between CS-matrix and SPF-reinforcement, which reduces or eliminates the mobilization of the matrix chain [72]. Further increasing in SPF concentration from 2% to 8% caused an insignificant reduction in the WVP of the hybrid films from $1.37 \times 10^{-10}$ mm.g.s$^{-1}$.m$^{-2}$.Pa$^{-1}$ to $1.16 \times 10^{-10}$ mm.g.s$^{-1}$.m$^{-2}$.Pa$^{-1}$. Hence, CS–CH/SPF8% film exhibited a 96.55% enhancement in WVP compared to native CS-film.
4. Conclusions

Novel hybrid bio-composite films obtained from cornstarch (CS) and fibrous residues of both cornhusk (CHF) and sugar palm (SPF) through solution casting and dehydoration method. The experimental and characterization results showed significant improvement in the performance of the composite film following the hybridization process. The tensile strength and Young's modulus of the hybrid films were increased from 6.8 MPa to 19.05 MPa and from 61.15 MPa to 1133.47 MPa respectively for the film contains 6% SPF, making it the most efficient reinforcing loading. While the water vapor permeability of the hybrid composites decreased by 96.55% compared to the neat CS-film, which means better water barrier properties. The diffraction analysis revealed a noticeable improvement in the crystallinity index following the fiber loading from 15% to 27%. The incorporation of SPF enhanced physical properties and caused an insignificant decrease in the thermal stability of the produced composites. Based on the results obtained, hybridization expanded the use of biomass in various applications, particularly for those requiring certain tensile properties and low water barrier properties.

Conflicts of interest

The authors declare no conflicts of interest.

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