Effect of cellulose fiber from sago waste on properties of starch-based films

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Abstract. An increasing interest in developing biodegradable film using natural biopolymers such as polysaccharides is due to concerns on environmental problems caused by non-biodegradable petroleum-based materials. Though the film exhibits low mechanical properties, it can be improved by adding reinforcing agent, for instance, cellulose fiber. The objective of this study is to investigate the effect of adding cellulose fibers extracted from sago waste on the mechanical and thermal properties of sago starch-based films. Cellulose fibers extracted from sago waste showed reaction in size with cleaner surface as shown in FESEM micrographs. Thermal stability also improved indicated that the hemicelluloses and lignin were eliminated. Films were prepared by solution casting with 4 % sago starch and 3 % cellulose (from starch). These films were characterized using several techniques ie. tensile, x-ray diffractometry, TGA analysis, FESEM analysis and hazemeter. The films produced were highly transparent while film reinforced with cellulose fiber was more crystalline. The addition of fibers increased the tensile strength from 38.66 MPa to 40.70 MPa and Young’s Modulus from 1710 MPa to 1713 MPa. The elongation at break also increased from 3.85 % to 4.62 %. On the other hand, the incorporation of cellulose fibers increased the thermal stability of the film. FE-SEM micrographs of the films showed homogenous distribution of the cellulose fibers. The inclusion of cellulose fiber has successfully increased the properties of the sago starch-based film.

1. Introduction

Malaysia has lavish natural resources contributed by it being a tropical country. Other than being recognized as the main world supplier of palm oil and rubber, Malaysia is also producing sago starch. Sago starch is derived from the stem of palm (sago palm). Most of the sago palms in Malaysia are found in Sarawak and it grows well in swampy area. It is reported that sago plantation in Sarawak can produce up to 25 tons per hectare of starch in a year [1]. Sago palm becomes one of the most favourable plants because it is economically acceptable, relatively sustainable, environmentally friendly, and promotes socially stable agro-forestry system. It contains a large amount of starch in its trunk. Sago starch contains 27 % amylose and 73 % amyllopectin. The molecular weight for amylose is in the range of 1.41 × 10⁶ to 2.23 × 10⁶, while for amyllopectin is in the range of 6.70 × 10⁶ to 9.23 × 10⁶ [2]. Typically sago starches are processed for food, cosmetics, biodegradable plastics, adhesive and much more [3]. The
residue left behind in the sago starch industry is called sago waste or hampas sago. Generally, sago waste is used for animal feed, compost for mushroom culture, waste adsorbent and fire retarding panel [4-5]. It is reported that 7 tons of sago waste are produced daily from a single sago starch processing mill. Currently, these residues which are mixed together with wastewater are either washed off into nearby streams or deposited in the factory's compound and may potentially lead to serious environmental problems [6]. Further, this sago waste also processed as a soil improver and natural fertilizer due to the small content of nutrient left in it [7]. Apart from that, this residue also contains fibers which can be extracted to cellulose. Cellulose from agricultural residues such as banana peel [8], sugarcane bagasse [9], potato peel waste [10] and soy hulls [11] have already been reported. The utilization of these residues can help in solving disposal problems. Therefore, development of other value added products such as cellulose as a reinforcing agent from these residues is a potential way to increase the value of agricultural wastes.

The use of cellulose fiber as a reinforcing agent in preparing starch film can improve the properties of the film. Starch can be considered as an alternative to synthetic films because it is cheap, renewable, biodegradable and widely available. However, films from starch have poor mechanical properties. Nevertheless, these limitations can be overcome by several approaches. The addition of plasticizers [12], blending the starch with synthetic polymers [13] and chemically modified the starch [14] are among the approaches to improve the properties of the starch film. The addition of fibers either synthetic or natural fibers as a reinforcing agent for a starch film also can overcome the problems.

In the present work, the effect of cellulose fibers on properties of starch films was examined. The fibers called treated sago waste (TSW) were extracted from sago waste through chemical treatment. Then, these TSW fibers were dispersed into sago starch films (SF) by using casting method. Characterization of the obtained films was made in order to study the effect of TSW on physical, mechanical and thermal properties of SF.

2. Methodology

2.1 Materials
Sago starch and sago waste were obtained from Ng Kia Heng Sago Industry Sdn. Bhd. (Batu Pahat, Johor). Sodium chlorite (80 %) and acetic acid (glacial, 99.85 %) were obtained from Sigma–Aldrich Inc. (St. Louis, MO, USA) and sodium hydroxide (98.9 %, ACS grade) were purchased from Fisher Scientific Inc. All reagents and solvents were used as received. Distilled water was used in the preparation of all solutions.

2.2 Extraction of cellulose
The extraction of cellulose fibers required the removal of other components such as lignin, hemicellulose and impurities from sago waste (SW). This step was achieved by chemical treatment. Sago waste which has not been treated (USW) was first soaked in hot water at 40 °C for 2 hours and oven dried at 40 °C for 48 hours to remove starch and impurities. The SW was then treated with 2 % NaOH aqueous solution at 60 °C for 1 h. The samples were then filtered and washed repeatedly with distilled water until a neutral pH was reached. The samples were dried at 40 °C for 48 hours to determine the cellulose yield and sample composition. Alkaline treated SW was then exposed to bleaching treatment. This was done by treating the alkaline treated SW with NaClO2/glacial CH3COOH mixture at 80 °C for 4 hours under mechanical stirring. The TSW was washed thoroughly with distilled water and dried at 60 °C. Each treatment was repeated three times in order to remove other constituents present in the waste.

2.3 Film preparation
The sago starch (SF) and sago starch with 3 wt% TSW cellulose fiber (SFSW) films were prepared by using casting method. Firstly, SFSW solution (3 wt%, starch basis) was prepared by dissolving the TSW in 10 ml of distilled water. The solution was then stirred for 1 hour at ambient temperature followed by ultrasonic treatment (Branson sonifier model 450) for 30 min. Meanwhile, sago starch 4 % (w/w) solution was prepared separately by mixing the starch with 15 ml of distilled water followed by heating to 70 °C while stirring for 30 min. During the heating process, the TSW solution was added to the starch solution. The mixture was poured into a 10 cm × 10 cm plastic mould. Then the films were dried in the oven at 40 ºC for 48 hours, peeled off after drying and kept at 23 ± 2 ºC and 50 ± 5 % relative humidity (RH) prior to testing. The same procedure was applied for SF films without the addition of TSW.

2.4 Morphological examination
Field Emission Scanning Electron Microscope (FESEM), Carl Zeiss model Gemini SEM 500 was used to investigate the morphology of the surface and cross-section for all samples. Images were acquired at 500× magnification for surface and 1000× for cross-section examination.

2.5 Light Transmittance
The light transmittance of films was measured using hazemeter spectrophotometer model BYK Gardner following standard method ASTM D1003. Films with the dimension of 10 cm × 10 cm were used and five replicates measurements were recorded.

2.6 X-ray diffraction (XRD) analysis
X-ray diffraction (XRD) measurement was carried out on a RÖntgen diffractometer system (PANalytical, Netherlands). The diffracted intensity of Cu-Ka radiation was measured at 40 kV, 30 mA at 25 °C. The diffraction patterns were determined over a range of diffraction angle 2θ from 5 ° to 40 ° at a scanning rate of 2 °C/min.

2.7 Thermogravimetric Analysis (TGA)
Thermogravimetric analysis was carried out using Perkin Elmer model Pyris 1 thermogravimetric analyzer to determine the thermal stability of sago waste at different stages of extraction. Thermal stability of SF and SFSW films was examined too. For analysis, the samples were heated from room temperature to 600 °C under nitrogen atmosphere at 10 °C/min.

2.8 Tensile properties
Tensile properties were measured according to ASTM D 882-97. The testing was conducted using 20 N load cell (Model UUK 5, Korea) equipped with Ezi Step micro stopper motor system (Fastec, Korea). The samples were run at crosshead speed of 0.5 mm/min.

3. Results and discussion

3.1 Morphology of fibers
The structural changes in the fibers were observed via FESEM and are presented in Figure 1. The micrographs displayed in Figure 1(a) and 1(b) showed that the diameter of the fiber decreased from 300 μm to 10-20 μm. The reduction in fiber size after treatment can be ascribed to elimination of extractable elements, other than defibrillation phenomena. The former caused damage to fiber structure resulted in finer and smaller fibers. The later segregated the fibers from bundles to single fibril. Figure 1(c) of USW displays rough surface cemented together with lignin, hemicellulose and wax [15]. Upon chemical treatment, the surface of the fiber became smoother because of the removal of non-cellulosic materials like lignin, hemicelluloses and wax as displayed in Figure 1 (d). This could result in an effective adhesion between the fiber surface and the matrix [16].
Figure 1. FESEM images of (a) USW and (b) TSW at 100× magnification while surfaces of (c) USW and (d) TSW at 500× magnification

3.2 Thermal properties of the fibers
Figure 2 and Figure 3 show the thermogravimetric (TG) and the differential thermogravimetric (DTG) curves obtained from the thermogravimetric analysis data for USW and TSW respectively. Table 1 lists the onset degradation temperature ($T_o, ^\circ C$), maximum thermal degradation temperature ($T_{max}, ^\circ C$) and residue (%) at 600 °C for all samples.

| Sample | $T_{onset}$ ($^\circ C$) | $T_{max}$ ($^\circ C$) | Residue (%) |
|--------|------------------------|-----------------------|-------------|
| USW    | 250                    | 310                   | 9.97        |
| TSW    | 297                    | 343                   | 7.90        |

The curves obtained for both fiber samples show that the initial weight loss started below 100 °C caused by water evaporation from the samples. USW shows an earlier weight loss at around 250 °C with maximum degradation temperature was 310 °C and residue at 9.97 %. For TSW, the degradation temperature was at 297 °C with maximum degradation temperature of 343 °C while the residue at 7.90 %. The increase in degradation temperature indicated that TSW has higher thermal stability than USW due to further removal of non-cellulosic impurities by bleaching process which is beneficial in improving the thermal stability of the cellulose fibers [17]. The percentage of residue for TSW fibers was lesser than USW due to the fact that hemicellulose and lignin were mostly removed from cellulose fibers. This finding supports the morphological observaton as discussed above.
The decomposition peak of USW shown in DTG curve in Figure 3 is wider than TSW due to the composition of hemicelluloses and lignin. Meanwhile, TSW shows narrow decomposition peak suggesting the component that degraded at lower temperature had been removed during treatments.

![Figure 2. TG curves of USW and TSW](image1)

### Figure 2. TG curves of USW and TSW

![Figure 3. DTG curves of USW and TSW](image2)

### Figure 3. DTG curves of USW and TSW

#### 3.3 X-ray diffraction analysis of the fibers

XRD analysis was performed in order to determine the crystallinity of USW and TSW as displayed in Figure 4. USW exhibited strong and broad peaks at both $2\theta = 17^\circ$ and $23^\circ$, medium peaks at around both $2\theta = 5.3^\circ$ and $15.0^\circ$ and a couple of weak peaks scattered around $10.2^\circ$ and $11.7^\circ$ representing the C-Type crystalline structure. This observation was consistent with previous studies by other researchers [18-19]. It is believed that these diffraction patterns belong to sago starch granule that occurred in sago waste. As can be seen, after chemical treatments, TSW displayed sharp diffraction peaks located at $2\theta$ value of around $16^\circ$ and $22.6^\circ$. This diffraction peaks were attributed to the diffraction planes of (110) and (002) representing typical cellulose I crystal form. The other peak observed in the XRD patterns of the TSW was at $2\theta=34.5^\circ$ which was attributed to the diffraction plane of (004), confirming that Cellulose Type I was formed [20]. The treatment of *sago hampas* was aimed to remove hemicellulose and lignin, which exist in the amorphous regions, leading to the realignment of cellulose molecules and
a better packing of cellulose chains. Consequently, the increase in crystallinity of the treated fiber has improved the thermal stability of TSW (Figure 2 and Figure 3).

![XRD patterns of (a) USW and (b) TSW](image)

**Figure 4.** XRD patterns of (a) USW and (b) TSW

3.4 Morphological investigation of films

Figure 5 shows the FESEM observation onto the surface and cross-section of the films. Micrographs of the SF showed homogenous and smooth surface as can be seen in Figure 5(a). The surface of SFSW was rougher than SF with a very minimum presence of crack and more compact as displayed in figure 5(b). It shows that the TSW was well dispersed within the starch matrix. Meanwhile, the cross-section of SF and SFSW are depicted in Figure 5(c) and Figure 5(d) respectively. For SFSW, some holes and cracks were observed indicating the fiber pull out from the matrix. It shows that there is an interaction between the fiber and the matrix. Nevertheless, it can be clearly seen that presence holes indicate the adhesion between fiber-starch matrixes was less bonded. Thus, this can explain the reason of slightly increased in tensile properties. The treatment of the fiber or the addition of plasticizers is among the method that can be introduced in order to improve and enhance the adhesion.

![FESEM observation](image)

(a) (b)

**Figure 5.** FESEM observation onto the surface and cross-section of the films.
Figure 5. FESEM images showing film surfaces of (a) SF and (b) SFSW at 500× magnification, and film cross-section of (c) SF and (d) SFSW at 1,000× magnification

3.5 Thermal properties of the films
The onset degradation temperature ($T_{\text{onset}}$, °C), maximum thermal degradation temperature ($T_{\text{max}}$, °C) and residue (%) of the films were summarized in Table 2.

Table 2. The onset degradation temperature ($T_{\text{onset}}$, °C), maximum thermal degradation temperature ($T_{\text{max}}$, °C) and residue (%) of the films at 600°C.

| Sample                  | $T_{\text{onset}}$ (°C) | $T_{\text{max}}$ (°C) | Residue (%) |
|-------------------------|-------------------------|------------------------|-------------|
| Starch Film (SF)        | 291                     | 323                    | 2.32        |
| Starch with cellulose (SFSW) | 307                     | 330                    | 0.73        |

The thermal stability of the films was characterized using TGA analyzer. The TGA and DTGA curves were shown in Figure 6 and Figure 7. Both SF and SFSW showed two decomposition peaks. The first weight loss was observed from room temperature to 60 °C which was referred to evaporation of water. The second weight loss occurred from 270 °C to 400 °C with maximum degradation around 323 °C and 330 °C for SF and SFSW respectively. SFSW exhibited higher thermal stability than SF. This improvement is connected to the chemical interaction between starch matrix and fiber generated from chemical compatibility resulting in improved interfacial interactions between fiber and matrix. The amount of residue left after final decomposition of SFSW was less than that of SF. This is due to higher ash content of starch.
3.6 X-ray diffraction analysis of the films

Figure 8 depicts the x-ray diffraction pattern of SF and SFSW. The sago film without cellulose displayed diffraction peaks around \(2\theta = 5.9^\circ, 15.2^\circ\) and \(17.3^\circ\) representing the C-type crystalline structure. The addition of cellulose fiber decreased the intensity of peak at \(2\theta = 17.3^\circ\) but increased the intensity peak at \(2\theta = 22.6^\circ\). The increasing value of \(2\theta\) showed that crystalline structure of cellulose I from cellulose fiber presents in the film. It is suggested that the incorporation of highly crystalline fibers enhances the crystallinity of the films.
3.7 Tensile properties of the films

Tensile properties of SF and SFSW are summarized in Table 3. Sago starch films reinforced with TSW presented higher values of tensile strength, Young’s modulus and elongation at break as compared to film without fibers. Generally, the tensile stress and modulus of the starch film increased and the elongation at break decreased with the addition of fibers. The introduction of cellulose fibers into the SF increased the tensile strength from 38.66 MPa to 40.70 MPa and Young’s modulus from 1710 MPa to 1713 MPa. The elongation at break also increased from 3.85% to 4.62% as compared to film without cellulose fiber. The increment in tensile properties could be attributed to homogeneous distribution of cellulose fibers in the sago starch matrix. In addition, the presence of hydrogen bonding between fiber and matrix, where hydroxyl group of cellulose interacted with hydroxyl group from starch matrix [21] further enhanced the strength. Thus, it allowed better stress transfer between fibers and matrix. The transparency of the films reduced from 91.4% to 89.9% when the fibers are added into the matrix. The addition of fibers prevented light transmittance and led to decrease in transparency of the film. The decrease in transparency could also be ascribed to agglomeration of the fibers. However, the SFSW films still can be categorized as transparent.

Table 3. Effect of TSW addition on the tensile stress, Young’s modulus, elongation and transparency of starch films compared to the neat SF. Values are given as mean ± standard deviation.

| Sample   | Stress, MPa | Young’s Modulus, MPa | Elongation, % | Transmittance, % |
|----------|-------------|----------------------|---------------|------------------|
| SF       | 38.66 ± 1.37| 1710 ± 0.07          | 3.85 ± 0.27   | 91.4             |
| SFSW     | 40.70 ± 0.85| 1713 ± 0.04          | 4.62 ± 0.35   | 89.9             |

Cellulose fibers and starch matrix are both hydrophilic and compatible with each other. Thus, the fiber has good adhesion with starch to allow a stress transfer from the matrix to the fiber [22]. This explained the increase in properties of starch films reinforced with cellulose fibers as compared to the properties of the starch film without cellulose fibers.
4. Conclusions

Sago waste cellulose fibers were successfully extracted using chemical treatment. Morphological analysis indicated a reduction in size from 300 μm to 20 μm, with cleaner and smoother surface of TSW observed. The thermal stability and crystallinity of TRW fibers increased upon alkaline hydrolysis. The hemicelluloses and lignin in sago waste have been successfully removed. Sago starch/treated sago waste fiber films were prepared via solution casting. The addition of TSW into SF has improved its performance. The thermal stability and tensile properties increased contributed by good interfacial adhesion between the fibers and the matrix. FESEM results indicated that chemical treatment on fibers plays an important role in enhancing the interfacial bonding between fiber and matrix. The treated fiber showed good adhesion between fiber and matrix. The present work demonstrates the cellulose extracted from sago waste are compatible with starch matrix and can be used as reinforcement in sago starch films.

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