A study of microcrystalline cellulose prepared from parawood (*Hevea brasiliensis*) sawdust waste using different acid types

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Abstract

Microcrystalline cellulose (MCC) from parawood sawdust (PWS) was successfully prepared by acid hydrolysis method. In this work, parawood sawdust waste was obtained from furniture factory. Initially, PWS was subjected to an alkali pulping and bleaching processes, respectively. After that, the microcrystalline cellulose was prepared from bleached pulp using hydrochloric and sulfuric acid in order to compare the effect of acid type. The parameters for acid hydrolysis process were investigated in terms of reaction time and pulp to acid ratio at constant temperature of 80°C. The properties of obtained MCC such as functional groups, degree of polymerization (DP), crystallinity index (CrI), thermal stability and morphology were evaluated. XRD analysis, indicated native cellulose type I structure of MCC, while SEM micrographs revealed rod-like shape morphology in its aggregates. It can be observed that at the same conditions using hydrochloric acid to prepare MCC provided higher degree of polymerization and thermal stability compared to sulfuric acid. Therefore, the optimum condition for preparing PWS-MCC was to carry out the reaction for 2 h with pulp to acid ratio 1:15 using hydrochloric acid solution at 80°C.

1. Introduction

Over the past decades, much research interest was given to products made from plant fibers of wood and non-wood origin. Plant fibers show many beneficial properties such as biodegradability, renewability, low density, high strength, and high stiffness [1]. Cellulose is the most abundant biomass polymer materials on earth, representing about 1.5×10¹² tons of the total annual biomass production [2]. Cellulose, a main component of wood and non-wood fibers, is a linear homopolymer consisting of macromolecules of homopolysaccharide units called anhydroglucose linked together by β (1-4)-glycosidic linkages. It can be degraded by microbial and fungal enzymes. Cellulose structure exhibits both amorphous and crystalline regions [3]. Besides cellulose, hemicellulose and lignin are other main components of plant fibers. Hemicellulose consists of different types of cyclic saccharides while lignin is an amorphous polymer composed of aromatic units such as guaiacyl, syringyl, and phenylpropane [4].

Microcrystalline cellulose (MCC) is a purified hydrolyzed crystalline form of cellulose that appears as a white, odorless, tasteless, and crystalline powder with porous structure [5]. MCC is a useful material with excellent properties for pharmaceutical, food, cosmetic, polymer composites, and other industries [6]. MCC as reinforcing agent in composites is very interesting and gains a lot of attention because of its potential advantages such as renewability, biodegradability and high surface area for bonding with polymer resins [7]. When compared with conventional fillers such as glass fiber, silica and carbon black, microcrystalline cellulose gives benefits like low cost, low density, and low abrasion to processing equipment [8]. Thus, there are many investigations on using MCC as reinforcement in polymer matrix; for example, in poly (lactic acid) [9], polypropylene [8], poly (vinyl chloride) [10]. Due to its various applications and potential uses, there are many studies on microcrystalline cellulose from various lignocellulose sources such as soy bean husk [11], bagasse and rice straw [12], kenaf [13], waste cotton fabric [14], and waste paper [15]. However, it was
found that different sources and growth regions of cellulose resulted in different properties of the prepared microcrystalline cellulose such as crystallinity, molecular weight, moisture content, surface area, and porous structure, etc.

Parawood or rubberwood is wood from Para rubber tree which is the common name for the timber *Hevea brasiliensis*. Parawood is one of the most important economic trees in Thailand. When the ceasing latex production after 26-30 years, the trees are cut down and the wood is processed to other products. One of the biggest application of parawood is furniture which can be furniture parts, parquet, paneling, wood-based panels, medium-density fiberboards (MDF). Moreover, the sawn timber can be used for general utility and fuel [16]. Due to the large amount of processed parawood in Thailand, as high as 3 million cubic meters per year, there is a huge amount of sawdust waste generated from the wood processing mills [17]. These parawood sawdust wastes is good source of a lignocellulosic natural fiber [18].

To the best of author’s knowledge, no work has been performed to study in detail microcrystalline cellulose from parawood sawdust waste generated from furniture factory. Thus, this study was aimed to prepare and characterize microcrystalline cellulose from parawood sawdust by acid hydrolysis method. Pulping process was carried out before acid hydrolysis process. The effect of acid type, pulp to acid ratio, and the hydrolysis time on the properties of microcrystalline cellulose has been investigated. The prepared microcrystalline cellulose was characterized by infrared spectroscopy (FTIR), degree of polymerization (DP), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The comparison of the prepared microcrystalline cellulose and commercial microcrystalline cellulose was also established.

### 2. Experimental

#### 2.1 Materials

Parawood sawdust (PWS) used in this work was a waste from local furniture factory in Thailand. Sodium hydroxide (99%, RCI Labscan) was used as chemical treatment of fiber while sodium hypochlorite (10%, Aldrich) was applied as bleaching reagent. The hydrolysis agents were hydrochloric acid (37%, RCI Labscan) and sulfuric acid (96%, RCI Labscan). These chemicals were used without further purification. Commercially available MCC, Avicel® PH101, Fluka, supplied by Sigma Aldrich, USA, with a particle size of ~50 μm was used as reference which was designated as Ref-MCC.

#### 2.2 Preparation of parawood sawdust pulp

Parawood sawdust was treated with 0.5 M NaOH using the liquor ratio of 1:10 at a temperature of 80°C for 2 h. The fibers were thoroughly washed with deionized water until the solution reached pH 7. The fibers were then dried in a hot air oven at 80°C overnight. The dried parawood sawdust fibers were bleached using 5% sodium hypochlorite with liquor ratio of 1:10 at room temperature. Each bleaching step took 2 h and the process was repeated 3 times. After bleaching, the fibers were thoroughly washed with deionized water until the solution became neutral. The bleached fibers were dried in a hot air oven at 80°C for 24 h. The obtained fibers were white pulp.

#### 2.3 Preparation of microcrystalline cellulose

MCC was prepared from hydrolyzed parawood sawdust pulp using 2 N hydrochloric acid or 2 N sulfuric acid in glass reactor. The reaction temperature was set at 80°C while the ratio of pulp over liquor was 1:10 and 1:15. The reaction time was 2 h and 4 h. The agitation speed was set at 180 rpm. The reaction mixture was filtered at room temperature, and washed repeatedly with deionized water until it was free from acid. The MCC obtained from parawood sawdust pulp was dried in a hot air oven at 80°C until constant weight was achieved. The dried MCC was ground into a fine powder by using pulverizer. The obtained MCC was snow-white in appearance. The prepared MCC hydrolyzed by hydrochloric acid and sulfuric acid was designated as PWS-MCC-H and PWS-MCC-S, respectively.

#### 2.4 Characterization of microcrystalline cellulose

The composition of raw PWS and PWS-MCC was evaluated according to TAPPI T204-OM-97, TAPPI T264-OM-97, and TAPPI T207-OM-93, respectively. The functional group and chemical structure were examined by FTIR spectroscopy
(Vertex 70, Bruker, Ettlingen, Germany) with KBr method. FT-IR spectra were recorded in a spectra range of 500-4000 cm\(^{-1}\) using 32 scans with resolution of 4 cm\(^{-1}\). X-ray diffraction was carried out to determine the crystallinity of parawood sawdust microcrystalline cellulose (PW3710, Phillips diffractometer, Almelo, Netherlands) with CuK\(\alpha\) radiation from a sealed tube operated at 40 kV and 30 mA. The diffraction pattern was recorded between 20 = 10-40\(^{0}\). The crystallinity of the samples was calculated based on the reflected intensity data following the method of Segal et al. [19]. The crystallinity-to-amorphous ratio of materials was determined using equation (1)

\[
CrI(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100
\]  

Where CrI is the crystallinity index, \(I_{002}\) is the peak intensity corresponding to both the amorphous and crystalline fraction of cellulose I at about 2\(\theta\) = 22.5\(^{0}\) and \(I_{am}\) is the lowest intensity assigned to the amorphous fraction at 2\(\theta\) value near 18.5\(^{0}\). The degree of polymerization (DP) was analyzed by viscosity measurement of the samples dissolved in a cupriethylenediamine (CED) solution using Cannon-Frenske viscometer. Each experiment was measured in triplicate according to ASTM D1795. The thermal decomposition temperature was investigated using a thermogravimetric analyzer (TGA) (Mettler Toledo, TGA/DSC, Greifensee, Switzerland). About 20 mg of each sample was heated under a nitrogen atmosphere from 30\(^{0}\)C to 900\(^{0}\)C at a heating rate of 20\(^{0}\)C-min\(^{-1}\). The morphology of parawood microcrystalline cellulose was observed using a scanning electron microscope (LEO1450VP, LEO, Oberkochen, Germany). The fiber samples were coated with gold before SEM analysis.

3. Results and discussion

3.1 Chemical composition of raw PWS and PWS-MCC

The chemical compositions of raw PWS and PWS-MCC are presented in Table 1. It could be observed that raw PWS had the lowest content of cellulose. After alkaline treatment, the content of cellulose increased. In addition, pulp PWS from bleaching process had percentage of cellulose of 76.75% while hemicellulose, lignin, and extractives were significantly reduced. Thus, lignin, hemicellulose and extractives were removed by alkaline treatment [20]. In addition, PWS-MCC form different acid type presented a similar chemical composition to that of pulp PWS. The results indicated that PWS-MCC from acid hydrolysis did not affect to chemical composition of pulp PWS.

3.2 Functional group of PWS microcrystalline cellulose

FTIR analysis was carried out to characterize the functional groups present in each sample. The comparison between FTIR spectra of PWS-pulp and PWS-MCC are shown in Figure 1.

![Figure 1. FTIR spectra of a) raw PWS, b) bleached PWS pulp, c) PWS-MCC-H, d) PWS-MCC-S, and e) ref-MCC.](Image)

The spectra of all samples showed broad absorption band in the 2800-3600 cm\(^{-1}\) region which was attributed to O-H group stretching vibration present in the main component of cellulose and a peak at 1641 cm\(^{-1}\) which was associated with the H-O-H bending of absorbed water molecule [21]. The peak in the region of 2900-2940 cm\(^{-1}\) was assigned to C-H stretching of cellulose [22]. The spectrum of raw PWS exhibited a dominant peak at 1740 cm\(^{-1}\) which was assigned to the C=O stretching in the acetyl and uronic ester groups of hemicellulose or the carboxylic ester group of the ferulic and p-coumaric unit of lignin [23]. This peak was absent after bleaching with sodium hypochlorite. The other absorption bands of lignin at 1504 cm\(^{-1}\) related to lignin aromatic ring [24] also disappeared in the bleached pulp and PWS-MCC. This peak did not observe in ref-MCC spectrum either. This indicated that lignin was
removed from pulp during pulping process. In addition, peaks at 1429 cm\(^{-1}\) and 1330 cm\(^{-1}\) were observed in the spectra of raw PWS, bleached PWS-pulp, PWS-MCC, and ref-MCC which were assigned to the saturated C-H bending and wagging vibration, respectively [25]. The absorption band at 1163 cm\(^{-1}\) was attributed to C-O-C stretching, and the peak at 897 cm\(^{-1}\) was assign to C-H rocking vibration of cellulose [22]. It can be seen that using different acid type to hydrolyze bleached PWS pulp did not affect the chemical structure of cellulose. Both PWS-MCCs hydrolyzed from either hydrochloric acid or sulfuric acid exhibited similar FT-IR spectra as ref-MCC.

3.3 Hydrolysis of bleached parawood sawdust pulp

The effect of different acid hydrolysis conditions (i.e., acid type, reaction time, and pulp to acid ratio) on the degree of polymerization (DP) of the prepared microcrystalline cellulose was studied. The reaction temperature was set constant at 80\(^{\circ}\)C for all reactions. Initially, DP value of raw PWS was 850 but after acid hydrolysis, DP values of PWS-MCC decreased due to the degradation of the glycosidic bond of cellulose chain catalyzed by the H\(^{+}\) ions of dilute acid solution [13]. The DP values of PWS-MCC prepared from different acid hydrolysis conditions are displayed in Table 2. The results showed that DP values of PWS-MCC hydrolyzed using hydrochloric acid were higher than in the case of using sulfuric acid. Theoretically, no difference in DP value was expected when using both acids. However, using sulfuric acid for hydrolysis could cause esterification of cellulose and introduce sulfate groups into the cellulose molecule [5]. These sulfate groups on MCC will be ionized in solution and caused repulsion between chains leading to easier flow or shorter flow time than PWS-MCC prepared with hydrochloric acid during viscosity measurement [12]. Consequently, PWS-MCC prepared using sulfuric acid has shorter flow time and results in low viscosity value and therefore lower DP. Besides, it can be seen that the DP values of PWS-MCC prepared from both acids were reduced with increasing pulp to acid ratio because higher acid to cellulose ratio promotes the rate of hydrolysis [26] leading to faster depolymerization of cellulose. However, increase of reaction time resulted only in slight reduction of DP because extended hydrolysis time was compensated by slower rate of degradation. The hydrolysis of cellulose was fast at the initial time of reaction followed by slow degradation rate [27].

3.4 Crystallinity of PWS-MCC

It is well known that cellulose consists of both crystalline and amorphous regions [28]. The acid hydrolysis is a protonation of glycosidic oxygen by H\(^{+}\) resulting in breaking of β-1,4-glycosidic bond of cellulose polymer by the water addition [29]. In order to observe effect of hydrolysis on crystallinity, X-ray diffraction was carried out. The crystallinity index of samples calculated from X-ray diffraction pattern (Figure 2) is presented in Table 2. The CrI of bleached PWS was 60\%, indicating higher crystallinity than raw PWS which had only 33\% CrI value. The increase of CrI of bleached PWS can be a result from the removal of hemicellulose and lignin during the chemical treatment. After hydrolysis, CrI values of PWS-MCC samples were around 60\% which were similar to that of bleached PWS pulp, indicating that acid hydrolysis conditions used in this study did not affect crystalline structure of PWS. In addition, it can be observed that there were three main diffraction peaks at 2θ = 15.2\(^{\circ}\), 16.4\(^{\circ}\), and 22.7\(^{\circ}\) for all samples. These patterns revealed a typical crystal form of cellulose I and displayed highest scattering intensity at 22.7\(^{\circ}\) [30]. It is obvious that all of the obtained MCC samples from different conditions showed similar diffraction pattern but a slight difference in intensity. It can then be concluded that acid hydrolysis did not destroy crystalline structure of PWS pulp and the selected hydrolysis conditions did not affect PWS-MCC as well.

![Figure 2. X-ray diffraction pattern of a) bleached PWS pulp, b) PWS-MCC-H, c) PWS-MCC-S, d) ref-MCC, and e) raw PWS.](image-url)
Table 1. Chemical composition of PWS and PWS-MCC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Cellulose</th>
<th>%Hemicellulose</th>
<th>%Lignin</th>
<th>%Extractives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw PWS</td>
<td>37.75</td>
<td>25.20</td>
<td>15.17</td>
<td>21.88</td>
</tr>
<tr>
<td>De-lignin PWS</td>
<td>55.96</td>
<td>18.90</td>
<td>19.87</td>
<td>5.27</td>
</tr>
<tr>
<td>PWS pulp</td>
<td>76.75</td>
<td>8.85</td>
<td>6.19</td>
<td>7.29</td>
</tr>
<tr>
<td>PWS-MCC-H</td>
<td>77.67</td>
<td>8.80</td>
<td>6.93</td>
<td>6.60</td>
</tr>
<tr>
<td>PWS-MCC-S</td>
<td>76.89</td>
<td>8.35</td>
<td>5.24</td>
<td>9.52</td>
</tr>
</tbody>
</table>

Table 2. DP and CrI values of PWS-MCC from different acid hydrolysis conditions.

<table>
<thead>
<tr>
<th>Hydrolysis condition</th>
<th>Reaction time (h)</th>
<th>DP</th>
<th>CrI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2N HCl</td>
<td>2N H2SO4</td>
<td>2N HCl</td>
</tr>
<tr>
<td>Pulp to acid ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:10</td>
<td>2</td>
<td>437</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>425</td>
<td>307</td>
</tr>
<tr>
<td>1:15</td>
<td>2</td>
<td>375</td>
<td>287</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>369</td>
<td>279</td>
</tr>
</tbody>
</table>

3.5 Thermogravimetric analysis

The thermal stability of reinforcement material is a very important factor for the processing and usage of these materials. Thus, the investigation of thermal stability by TGA was performed. It is known that thermal degradation of lignocellulose materials begins with decomposition of lignin and hemicellulose followed by decomposition of cellulose [31]. The TGA curves of the PWS, bleached PWS and PWS-MCC are displayed in Figure 3. The degradation temperature data are listed in Table 3. The TG curves show a mass loss below 100°C, which indicate the desorption of water from the polysaccharide structure [32]. It is clearly seen that raw PWS started to decompose of lower temperature than PWS-MCC. This lower thermal stability could be due to the thermal decomposition of hemicellulose [33]. The raw PWS consisted of hemicellulose, lignin, and other non-cellulosic constituents which have lower thermal stability. Thus, these components caused raw PWS to undergo earlier thermal decomposition compared to PWS-MCC. By treated with alkali solution and acid hydrolysis, non-cellulosic materials were removed. Furthermore, cellulose became more dense and compact that could also increase the onset of thermal degradation temperature. Comparing between the acid hydrolysis condition, lower thermal stability was observed from PWS-MCC prepared by using sulfuric acid. This was because of an introduction of sulfate groups onto cellulose chains during acid hydrolysis. Those sulfate groups catalyzed the thermal degradation of cellulose [14]. Moreover, using sulfuric acid for hydrolysis to obtain PWS-MCC gave lower degree of polymerization (DP) compared to hydrochloric acid as shown in Table 2, which also contributed to the lower thermal stability of PWS-MCC prepared using sulfuric acid [34]. This result is in agreement with other researchers [12,35-37]. In addition, it can be seen from the results that using different reaction times or pulp to acid ratios slightly affected thermal stability of the obtained MCC. When the hydrolysis was prolonged to 4 h, thermal degradation temperature decreased due to the reduction of DP value as indicated in Table 2.

Figure 3. TGA thermograms of PWS-MCC under acid hydrolysis condition ratio 1:10 for 2 h.
Table 3. Thermal characteristic of PWS-MCC form different conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid type</th>
<th>Pulp to acid ratio</th>
<th>Time (h)</th>
<th>Td (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw PWS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>282</td>
</tr>
<tr>
<td>Ref MCC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>326</td>
</tr>
<tr>
<td>PWS-MCC</td>
<td>2N HCl</td>
<td>1:10</td>
<td>2</td>
<td>311</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:10</td>
<td>4</td>
<td>306</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:15</td>
<td>2</td>
<td>311</td>
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<tr>
<td></td>
<td></td>
<td>1:15</td>
<td>4</td>
<td>309</td>
</tr>
<tr>
<td></td>
<td>2N H₂SO₄</td>
<td>1:10</td>
<td>2</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:10</td>
<td>4</td>
<td>279</td>
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<td></td>
<td></td>
<td>1:15</td>
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<td>293</td>
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<tr>
<td></td>
<td></td>
<td>1:15</td>
<td>4</td>
<td>284</td>
</tr>
</tbody>
</table>

Figure 4. SEM micrographs of a) raw PWS, b) bleached PWS pulp, and c) ref-MCC.

3.6 Morphological analysis

The SEM micrographs of raw PWS, bleached PWS pulp and ref-MCC are displayed in Figure 4. After treatment of raw PWS with alkali solution and bleaching with sodium hypochlorite, the pulp became whiter. The SEM micrograph of raw PWS show a rough surface containing short fiber and some small particles. This roughness could be related to the presence of wax or other impurities on the surface resulting in fibers with a protective layer [38]. The average particle size of raw PWS was approximately 50-100 µm. After treatment and bleaching to remove hemicellulose, lignin, and other components, the bleached pulp became fibrillated and a smoother surface can be observed.

The effect of hydrolysis conditions on PWS-MCC are presented in Figure 5. It was found that PWS-MCC exhibits rod-like structure and smooth surface without surface layers after acid hydrolysis. Moreover, the most smooth surface can be observed when using higher pulp to acid ratio. Both acids gave the same morphology of PWS-MCC. PWS-MCCs from different acid treatment had similar particle size approximately 30-100 µm. Compared with ref-MCC, PWS-MCC demonstrated similar morphology.

Figure 5. SEM micrographs of PWS-MCC with different acid hydrolysis conditions a) PWS-MCC-H ratio 1:10, b) PWS-MCC-S ratio 1:10, c) PWS-MCC-H ratio 1:15, and e) PWS-MCC-S ratio 1:15.
It could be observed that parawood sawdust was an effective raw material for preparing PWS-MCC using acid hydrolysis method. The most suitable condition for preparing PWS-MCC was using hydrochloric acid at ratio 1:15 for 2 h at 80°C. The obtained MCC had good properties as the comparison of PWS-MCC to other MCC in Table 4, shows PWS-MCC had better thermal stability than other MCC. Degradation temperature of PWS-MCC reached 310°C which is suitable for polymer composite application. Considering the large quantity of waste parawood sawdust in Thailand, producing PWS-MCC is a suitable way to reduce parawood sawdust waste and increase value of parawood sawdust waste. Moreover, using acid hydrolysis method is a proper process for industrial-scale production of MCC.

4. Conclusions

Microcrystalline cellulose was successfully prepared from parawood sawdust (PWS) which is a waste from furniture factory via acid hydrolysis method. The results from FT-IR analysis indicated that PWS-MCC still had cellulose structure, while hemicellulose and lignin were removed during chemical treatment. The DP value of PWS-MCC was lower when using sulfuric acid and increasing pulp to acid ratio from 1:10 to 1:15 also caused reduction of the DP values. In the XRD patterns, PWS-MCC exhibited cellulose type I with crystallinity about 60%. This evidence also confirmed that acid hydrolysis did not change the cellulose structure. TGA analysis indicated that PWS-MCC had better thermal stability than raw PWS although using sulfuric acid treatment yielded MCC with lower thermal stability compared to hydrochloric acid due to the introduction of sulfate group onto cellulose chains. SEM micrographs revealed that PWS-MCC has rod-like structure similar to ref-MCC. Based on these results it can be concluded that MCCs produced from PWS by acid hydrolysis has potential to be use as a reinforcing agent for polymeric materials due to their morphology and better thermal stability compared to raw PWS.

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