The potential of mango peel utilization for cellulose extraction by hydrothermal pretreatment

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Abstract

The aim of this work is to isolate cellulose from mango peel as a new cellulose source which abundantly found in food processing industries in Thailand and to assess the potential of hydro-thermal, steam explosion method combined chemical treatment for cellulose extraction to reduce the chemical use. The chemical composition of fibers in different processing stages revealed the α-cellulose content from mango peel increased to 89%, while hemicellulose and lignin content were significantly decreased during extraction processes. It was found that those methods showed great potential for removing of hemicellulose and lignin. Fourier transform infrared (FTIR) spectroscopy analysis can confirm about the removal of lignin and hemicellulose from treated fibers. Thermogravimetric analysis (TGA) found that the cellulose extracted from mango peel exhibited the high thermal property (329 °C). Therefore the great thermal property of cellulose from mango peel can be applied in various thermal processes.

Keywords: cellulose extraction, steam explosion, industrial waste, mango peel

1. Introduction

Nowadays, the growing of synthetic materials based petroleum has raised a number of environmental and human health concerns. A numerous researchers has been studied on an increasing efficiency of using resources and developing of bio-based materials from industrial and agricultural waste residues and search a new materials obtained from renewable resources. Moreover, agricultural wastes and industrial wastes have gained tremendous interest due to high volume, easily available and low cost (Zuluaga et al. 2007), which act as a main source of cellulosic materials. Therefore, a number of significant technology developments, in the area of cellulose extraction have been extensively reported (Cherian et al. 2010).

Cellulose is one of biopolymers, which the most abundant renewable biopolymer available on the earth (around 10^{15} kg) (Uma Maheswari et al. 2012). It is widely used in commercial biopolymer because of it has unique properties such biodegradability, biocompatibility, non-toxic and high mechanical properties. From cellulose advantageous properties, the cellulose application has been continuously increasing with the demand of raw materials for cellulose extraction. Thus, many studies attempt to find a new cellulose source that low cost and easy available. The peel of the fruit is one of lignocellulosic materials that composed of cellulose around 20-40%, depending on species. Mango is a fruit that grows in almost all tropical regions of the world. In Thailand, food-industry has been utilized mango for food and also generated a huge of mango peel in every years.

Peel is a major waste obtained during processing of mango production, which is constitutes about 15-20% of total weight (Henrique et al. 2013). The chemical compositions of mango peel have cellulose as main component. Thus, the utilization of mango could be creating a new cellulose sources.

Cellulose from lignocellulosic materials or plant-based cellulose has been extracted from a variety of lignocellulosic materials which is well-known that consists of complex structure. The cellulose in plant cell wall is embedded to amorphous non-cellulosic materials including, lignin, hemicellulose, and other polysaccharides (Abraham et al. 2011). Hence it is necessary to eliminate non-cellulosic materials using chemical or physico-chemical treatments. . The different approaches have been applied to isolate cellulose from different materials, depending on the cellulose sources and processes use (Klemm et al. 2005; Klemm et al. 2011; Lu and Hsieh 2012). Several processes have been used to extract highly purified cellulose from cellulosic materials. In research about cellulose extraction, there are many traditional methods of cellulose extraction based on the use of many chemical solvents, which used to remove the non-cellulosic materials such as lignin, hemicellulose and other polysaccharides. For instance chemical extraction methods, alkaline extraction, alkaline peroxide extraction, lime extraction, organic solvent extraction and acid hydrolysis (Sun and Cheng 2002; Mosier et al. 2005). The chemical extraction is effective method to extract cellulose due to low cost and easy to control, however, these methods also generate the chemical wastes that effect on environment, resulting in the growing research about the use of environmental friendly methods for reduce or replace the chemical extraction. Steam explosion is main methods developed recently to isolate cellulose from hardwood and agricultural waste residues, especially for the production of bioethanol (Abraham et al. 2013). Recently, this method has been used in the modification of cellulosic fibers such as flax, banana fibers (pseudo stem), and pineapple leaf. The advantages of steam explosion include a significantly lower environmental impact, lower energy consumption, lower capital investment, and less hazardous process chemicals, compared with chemical treatments (Mosier et al. 2005; Cherian et al. 2008).

Therefore, the objective of this study is to utilize mango peel for cellulose extraction obtained by steam explosion combined with bleaching treatments for assess the potential of mango peel in a new cellulose source.

2. Methodology

2.1 Materials

Mango peel was cleaned by distilled water. Then, the mango peels were chopped into uniform size of approximately 2-3 cm and dried at 50 °C for 12 h. All chemical regents were purchased from Ajax Chemical (New Zealand).

2.2 Steam explosion

The untreated fibers were treated with steam explosion (Nitto Koatsu, Japan) under 1.5 MPa at 200 °C for 4 min (adapted from Deepa et al. (2011). Then, the untreated fibers - steam exploded fibers - were washed by distilled water and dried at 50 °C for 24 h.

2.3 Bleaching

Steam exploded fibers were treated with 5% (v/v) sodium hypochlorite at ambient temperature under continuous agitation for 1 h and repeated for six times. Next, the bleached fibers were washed by distilled water until pH of water became neutral. After that, the bleached fibers were dried at 50 °C for 24 h.

2.4 Characterization

2.4.1 Chemical composition

Chemical constituents of fibers were determined according to standard method by Technical Association of Pulp and Paper Industry (TAPPI). α-cellulose (TAPPI T202 om-88), lignin (TAPPI T222 om-98), The hemicelluloses content was calculated from the difference between holocellulose (α-cellulose + Hemicellulose) values. The cellulose, hemicelluloses and lignin of the fiber in the untreated, steam exploded, and bleached fibers were determined.

2.4.2 Structural analysis by Fourier transforms infrared (FT-IR) spectroscopy

FT-IR spectra were obtained by using Bruker Tensor 27 spectrometer (USA). Untreated and treated fibers in different processing stages were analyzed. The samples were ground and mixed with potassium bromide (KBr). The mixture was compressed into pellet form and FTIR spectra analysis was performed within the wave number rage of 4000-400 cm^{-1}.

2.4.3 Thermal analysis by Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) (Mettler Toledo, Model TGA/DSC1) was used to investigation of the thermal behavior profile of each fiber in different processing stage. (Temperature range from 50 – 600 °C and heating rate 10 °C/min)

3. Results and Discussion

3.1 Chemical composition and possible mechanism

The chemical composition of fibers in different processing stage was determined followed by TAPPI standard and reported as cellulose, lignin and hemicellulose content. From TAPPI standard, we can be assess the potential of mango peel use for a new cellulose source. The chemical composition of mango peel was summarized in Table 1, the mango peel fibers presented the high cellulose content around 38% that can indicate about mango peel is suitable for use as a new cellulose sources that presented the high cellulose content similar to other traditional cellulose sources. For example, sugarcane bagasse around 40-45% (Mandal and Chakrabarty 2011), wheat straw at 30-35% (Alemdar and Sain 2008) and rice straw at 30-32% (Jiang et al. 2011).

Moreover, the efficiency of extraction methods was determined by chemical composition of each fiber in different processing stages, as summarized in Table 1. In untreated fibers, the mango peel presented high hemicellulose and lignin content at 13.90% and 27.90%, respectively, while cellulose content presented 38%. After steam explosion, hemicellulose content were decreased from 13.90 to 8.41%, while cellulose content were increased from 38% to 52%. This is due to the hydrothermal steam explosion has directly effect on hemicellulose structure in fibers. The main reason about greatly decreasing of hemicellulose content is related to high temperature and high pressure during steam explosion. However, after steam explosion, the lignin content was slightly decreased from 27.90% to 21.84%. This can be confirmed about the steam explosion has little effect on lignin content in untreated fibers. This is due to the strong bonding between cellulose and lignin more than hemicellulose. During steam explosion, hemicellulose are partially hydrolyzed and lignin depolymerized, giving rise to sugars and phenolic compounds that are soluble in the water (Cherian et al. 2011; Deepa et al. 2011). Moreover, the steam explosion treatment can removed some loose substance from the hard structure that was difficult to dissolve in the caustic solution (Deepa et al. 2011), resulting in the steam-exploded fibers is more susceptible to react with caustic solution. During steam explosion, the process involved the hemicellulose is partially hydrolyzed and the depolymerized of lignin results in soluble in water (Deepa et al. 2011). The high temperature and high pressure held for a period of time (minutes) as well as the rapid reduction of the pressure significantly eliminated hemicellulose and some lignin by the auto-hydrolysis of hemicellulose fraction and depolymerization of lignin. Mosier et al. (2005) reported about the mechanism of steam explosion also involved the hemicellulose is thought to be hydrolyzed by acetic acid and other acids released during steam explosion. The acetic generate from hydrolysis of acetyl groups associated with the hemicellulose may further catalyzed hydrolysis and glucose or xylose degradation (Deepa et al. 2011; Johar et al. 2012). However, the complete removal of non-cellulosic materials does not take place. Thus, the utilization of bleaching treatment is to remove remaining of lignin and other impurities. The bleaching treatment is the most methods that use as the part of cellulose extraction processes. The main aim of bleaching process is to remove the lignin in the steam exploded fibers by oxidation reaction of lignin that leads to lignin dissolved in solution, to obtain the white precipitated, called cellulose. The bleaching by chlorite solution has been attributed to its ability to react with various aromatic ring structure of lignin, resulting in the lignin will be destroyed and converted into carboxylic acid results in soluble in water. The suggested results showed that the percentage of lignin in steam-exploded fibers was decreased from 21.84% to 7.42%, while the percentage of cellulose after bleaching process was increased to 89.21%. It can be concluded that the combination of steam explosion and bleaching treatment are the effective methods for cellulose extraction.

Table 1: Chemical composition of untreated and treated fibers in different processing stage

Samples	Chemical composition (%)		
	α-cellulose	Hemicellulose	Lignin
Untreated mango peel fibers	38.35	13.90	27.90
Steam exploded fibers	51.28	8.41	21.84
Bleached fibers	89.21	0.42	7.42

3.2 Structural analysis by Fourier transforms infrared (FT-IR) spectroscopy

The effect of extraction methods on the functional groups of each fiber was determined by FT-IR. Fig. 2 showed the FT-IR spectra of each fiber in different processing stages. All samples exhibited a broad band near 3400-3100 cm^{-1} represented that the free hydroxyl group (-OH) stretching vibration of the OH groups, due to the water absorbed in sample. On the other hand, an increasing of cellulose content during extraction process is evident from the increased intensity of the peak between 3400-3100 cm^{-1} bands (Neto et al. 2013). As previous results in chemical composition analysis, untreated fibers mainly consist of cellulose, hemicellulose and lignin as well as extractives (other polysaccharides, waxes and oil) (Klemm et al. 2005). These components are mainly consisted of esters, aromatic ketones and alcohols, with different oxygen-containing functional groups. The FT-IR spectra has many peaks because it consists of several components. The predominant peak at 1740 cm^{-1}, 1640 cm^{-1}, 1540-1510 cm^{-1} and 1240 cm^{-1} are related to C=O stretching vibration and C=O stretching vibration of the acetyl and uronic ester groups, from pectin hemicellulose or the ester linkage of carboxylic groups of ferulic and coumaric acids of lignin and/or hemicellulose (Abraham et al. 2011; Deepa et al. 2011). Those components are presented in untreated mango peel fibers, which is consistent with chemical composition results.

After steam explosion, steam exploded fibers revealed the disappearance of peak around 1740 cm^{-1} corresponding to the C=O stretching of the aromatic ring in hemicellulose (Rosa et al., 2010) and a decrease in the peak at 1510 cm^{-1} and 1450 cm^{-1} are attributed to C=O stretching vibration of the acetyl and uronic ester groups, from pectin hemicellulose or the ester linkage of carboxylic group of ferulic and coumaric acids of lignin, indicating in the most of the hemicellulose and some lignin were removed after steam explosion. After bleaching, the intensity around 1510 cm^{-1} corresponding to aromatic C=C stretching in lignin structure (Sun et al. 2005; Rosa et al. 2010; Neto et al. 2013) were disappeared in the spectra of bleached fibers because the oxidation reaction between lignin and chlorite solution, resulting in the lignin residues were dissolved in the caustic solution (Deepa et al. 2011). This indicated that the bleaching can remove the remaining hemicellulose and lignin in the components (Johar et al. 2012). Moreover, the intensity peak refers to cellulose structure involves the dominant peak at 1371 cm^{-1}, 1060 cm^{-1} and 898 cm^{-1} were attributed to the OH bending vibration, C-O-C pyranose ring stretching vibration and C-H deformation vibration contribution of cellulose (Alemdar and Sain 2008), respectively. These peaks appeared in the FTIR of each sample and also increased, indicated that and increasing of the purity of cellulose.

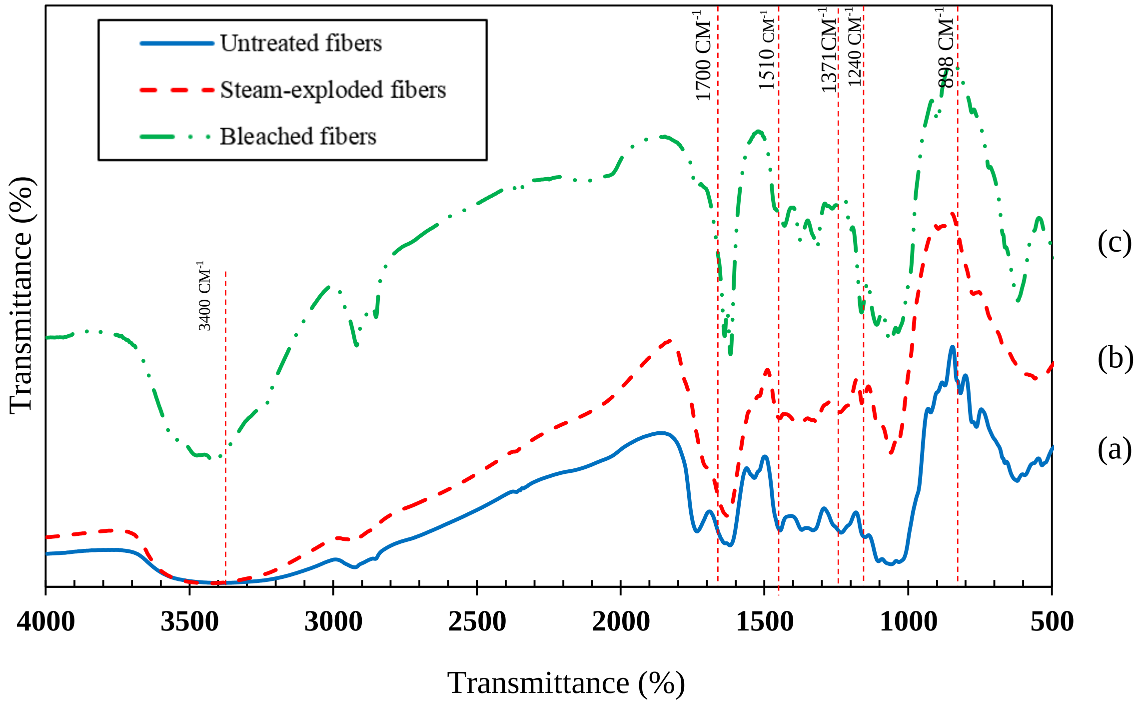

Figure 2: FT-IR spectra of each fiber in different processing stages.

3.3 Thermal behavior

The thermal stability of cellulose from mango peel was investigated by Thermogravimetric Analysis (TGA) in order to evaluate their suitability as reinforcement for application in composites. TGA is commonly used to investigate the change in weight of the sample as a function of temperature. All samples presented the first initial weight loss in the region 50-120 °C due to the evaporation of water in the substance (Rosa et al. 2010), reflecting the moisture content in the samples. The temperature around 50-120 °C is able to destroy interaction of hydrogen bonding between water and fibers and hydrogen bonding between water molecules resulted in water vapored from the fibers. These results were therefore in agreement with the FTIR analyses involves FTIR spectra of all samples present a broad peaks around 3400-3200 cm^{-1} corresponding to –OH groups, related to the water containing in fibers.

Untreated fibers presented three weight loss regions, the first degradation peak was found to be around 50-120 °C that related to the water evaporation. The second degradation region around 200 °C are mainly attributed to thermal depolymerization of hemicellulose and the cleavage of glycosidic linkages in cellulose chain (Klemm et al. 2005; Morán et al. 2008; Deepa et al. 2011). The third region at 230 °C also related to the hemicellulose decomposition. It is well known that the hemicellulose will be degraded before lignin and cellulose due to existing of acetyl groups (Deepa et al. 2011; Johar et al. 2012). The final peak at 341 ˚C (mass loss 46%) represented to thermal decomposition of the cellulose in the components (Alemdar and Sain 2008). The steam-exploded fibers in mango peel exhibited three main degradation peaks included the temperature region approximately 60-90 °C, 200-260 °C and 340 ˚C. It is well known that the degradation temperature below 120 °C refers to the evaporation of water. The presence of a broad region around 200-260 ˚C are attributed to the hemicellulose residue decomposition (Morán et al. 2008). Moreover, the degradation rate of these peaks (around 200-260 ˚C) was smaller than untreated mango peel fibers because of the most hemicellulose fraction degraded during steam explosion. This was consistent with suggested chemical composition and FTIR analysis. . The major degradation temperature of cellulose from plant fibers has found to be ranging from 310 ˚C to 380 ˚C, depending on cellulose source and extraction process used (Alemdar and Sain 2008).

The bleached fibers (cellulose fibers) exhibited three weight loss regions. The initial weight loss at 75 ˚C referred to the water in fibers. The major degradation temperature at 329 ˚C corresponded to the thermal decomposition of α-cellulose (mass loss 39.68%). The shoulder peak at 450 ˚C may be attributed to some lignin residue in the fibers. At the same way, several authors proposed this degradation peak (above 425˚C) was attributed to the oxidation and breakdown of the charred residue to lower molecular weight gaseous products (Neto et al. 2013).

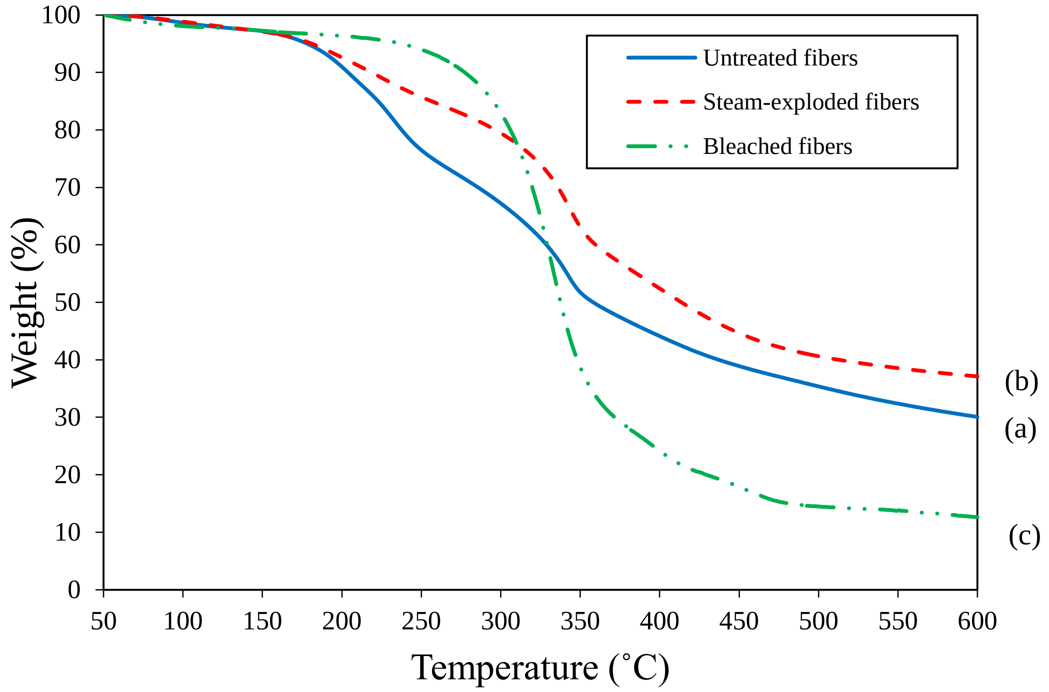

Figure 3: Thermal behavior of each fiber in different processing stages

4. Conclusion

The objective of this work was to use the environmental friendly method for the effective utilization of mango peel. The chemical composition of fibers in different processing stages reveal the α-cellulose content from mango peel increase to 89%, while hemicellulose and lignin content were significantly decreased during extraction processes. FT-IR and TGA results also supported the removal of lignin and hemicellulose. Therefore, the steam explosion combined with bleaching treatments proved to be an effective method for cellulose extraction. In addition, mango peel can be a new potential source for cellulose extraction.

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