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Extraction of nanocellulose from pineapple leaves by acid-hydrolysis and pressurized acid hydrolysis for reinforcement in natural rubber composites

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Abstract. This work aimed to study the extraction of nanocellulose (CNC) from pineapple leaves (PL) for using as a reinforcing filler in the natural rubber. PL mainly consists of cellulose so it is properly used for nanocellulosic extraction. The extractions were performed by acid-hydrolysis and pressurized acid-hydrolysis methods. The morphology and structure of the extracted nanocelluloses were compared and investigated using transmission electron microscope, Fourier transformed infrared, and X-ray diffraction analysis. It was found that pineapple leave has 27.64% of α-cellulose. The size of celluloses, which were extracted and hydrolyzed by acid- hydrolysis and pressurized acid hydrolysis, were reduced to 130 and 117 nm, respectively. And the shape was rod-like. The crystallinity index (CrI) of CNC was increased to 92.95 % and 91.24 % when it was treated by acid hydrolysis and pressurized acid hydrolysis, respectively.

1. Introduction

Pineapple is one of the most popular tropical fruits but only its fruit part is focused in food industry. The other parts especially leaves are considered as agricultural waste which is abundant and inexpensive. Its main chemical composition is cellulosic compound [1]. Cellulosic is well known and attractive material due to their various extraordinary properties such as high mechanical properties, biocompatibility and biological degradability [2, 3]. The size of micro cellulose (MCC) was reduced into nanocellulose (CNC), which retain unique properties of cellulose with the smaller size leading to their higher incorporated ability with polymer matrices [4]. In this work, CNC was extracted from pineapple leaves by used alkali treatment followed by bleaching treatment. The extracted cellulose was used to synthesize the nanocellulose using two different methods which are the acid hydrolysis and pressurized acid hydrolysis.

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These two extracted nanocelluloses were investigated by transmission electron microscopy, Fourier transformed infrared, and X-ray diffraction analysis. It was further used as reinforcing filler in the natural rubber.

2. Experimental

2.1 Materials
Pineapple leaves was supplied from amphoe Bang Saphan, Prachuap Khiri Khan in Thailand. 97% purity sodium hydroxide (NaOH) was purchased from Ajax Finechem. 10% (w/v) sodium chlorite ($NaClO_2$) was purchased from local industry in Thailand. Acetic acid (CH_3COOH) was purchased from Quality Reagent chemical. 98% sulfuric acid (H_2SO_4) was purchased from Merck, Germany. And NR latex (60%DRC) was provided by Rubber Authority of Thailand.

2.2 Extraction of cellulose
First, raw pineapple leaves were washed in fresh water then chopped into approximately 2 cm × 5cm, dried in oven at 90 ºC, and grinded into 250 μm pineapple leave powder. After that, the cellulose was extracted from pineapple leave powder by alkali treatment using 50 g of pineapple leave powder to 1 L of 1 M (4 w/v %) NaOH at 80 °C for 2 hrs under stirring condition. Then, bleaching treatment was carried out three times using 2.5 %w/v $NaClO_2$ at 100°C for 1 hr using the ratio of material to liquid was 1:20 (g/ml). At the end the cellulose was neutralize by distilled water and dried in oven at 70°C overnight.

2.3 Acid hydrolysis
The extracted cellulose was hydrolyzed to obtain CNC through acid hydrolysis method. First, 1 g of extracted cellulose was added into 10 ml of 64 %w/w sulfuric acid to form a suspension. It was continued hydrolyzed at 45 °C for 1 hr. At the end of reaction, the suspension product was filled with 5 fold water for stop reaction and then centrifuged at 8,000 rpm for 10 min to separate the gel suspension and remove the excess acid. The gel was adjusted to neutral by filtering through dialysis membrane and immersed in water. Finally, neutral gel was sonicated by ultrasonic sonicator.

2.4 Pressurized acid hydrolysis
The dried pineapple leave powder was treated with 2 %w/v NaOH at 80 °C for 1 hr under autoclave. Then alkali cellulose was bleached with $NaClO_2$ at 90 °C for 2 hrs. The bleaching was repeated a few times. Finally, the bleached cellulose was hydrolyzed with 10 %w/w sulfuric acid at 45 °C for 4 hrs.

2.5 Characterization
Determination of compositions such as holocellulose, α-cellulose, hemicellulose, lignin, extractives and ash by TAPPI standard methods and acid chlorite method of Browing were carried out [5, 6]. The Fourier-transformed infrared spectroscopy (FT-IR) was used to investigate functional group in samples. The XRD pattern of samples was recorded to calculate crystallinity index (CrI) by using $I_c = (I_{crys+am}-I_{am})\times100/ I_{crys+am}$ where I_C is the crystallinity index (CrI), $I_{crys+am}$ is parts of crystalline and amorphous at 2θ = 22º, and I_{am} is the intensity peak of only amorphous region at 2θ around 18º. Transmission electron microscopy (TEM) was used to examine the shape and the size of extracted cellulose and nanocellulose.

3. Result and discussion

3.1 Chemical composition

The chemical composition of pineapple leave powder is shown in Table1. It consisted of 44.60% holocellulose that was classified to 27.64% α-cellulose, 16.96% hemicelluloses, 8.03% of lignin, 39.42% of extractives, and 5.80% ash.

Table1. Chemical compositions in pineapple leaves.

Chemical compositions	Percentage (%)	Standard
Holocellulose	44.60	Acid chlorite Method of Browing
α-cellulose	27.64	TAPPI T203
Hemicellulose	16.96	Holocellulose - α-cellulose
Lignin	8.03	TAPPI T222
Extractives	39.42	TAPPI T204, T264 and T264
Ash	5.80	TAPPI T211

3.2 Fourier-transformed infrared spectroscopy (FT-IR)
FT-IR spectroscopy was used to investigate the functional groups in samples including bleached and hydrolyzed cellulose to confirm the successful of treatment in each step. FTIR images are shown in Figure 1. It was found that cellulose existed in all samples. The bonds referred to peaks of celluloses were at 3328, 2911, and 1634 cm^{-1} which assigned to –OH stretching vibrations of hydroxyl group and aliphatic C–H stretching. Peak around 1620 cm^{-1} assigned to carboxylate groups that absorbed some water [7, 8]. The result could confirm that cellulose was remained in the sample after treatment in each step.

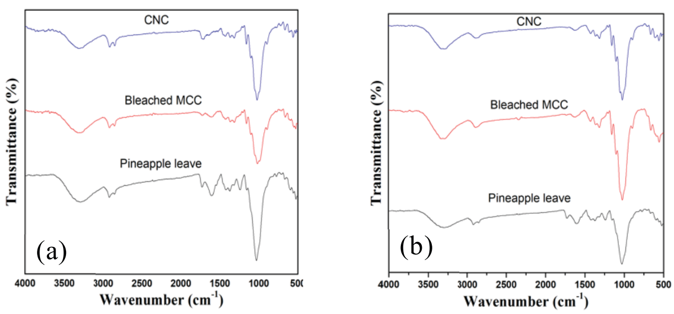

Figure 1. FTIR spectra image of pineapple leave, bleached MCC and CNC from acid hydrolysis (a) and pressurized acid hydrolysis (b**).**

3.3 X-ray diffraction (XRD)
XRD spectra exhibited the diffraction patterns of pineapple leave, bleached MCC, and hydrolyzed CNC (figure 2). At 2θ of around 18°, it referred to amorphous parts. At 2θ of around 22°, it assigned to amorphous and crystalline regions. The crystallinity index (CrI) of samples was calculated by Eq (1). The CrI of hydrolyzed CNC was increased to 92.95% and 91.24 % for acid hydrolysis and pressurized acid hydrolysis, respectively.

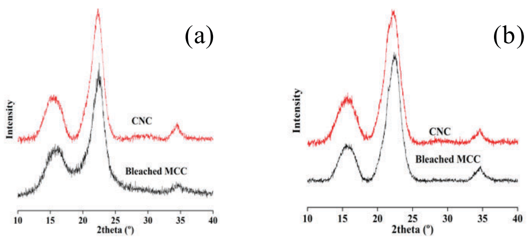

Figure 2. Image XRD patterns of MCC and CNC treated by acid hydrolysis (a) and pressurized acid hydrolysis (b).

3.4 Transmission electron microscopy (TEM)

The characteristic and shape of CNC hydrolyzed by the acid hydrolysis is shown in figure 3(a-c). The shape of CNC was found to be rod-like with the average length × width of 130.02 ± 48.55 nm × 5.14 ± 2.03 nm. In addition, CNC from pressurized acid hydrolysis is revealed in figure 3(d-e). The shape of CNC was similar to that hydrolyzed CNC. And average dimension was 3.52 ± 0.8 nm in width and 117.14 ± 24.75 nm in length.

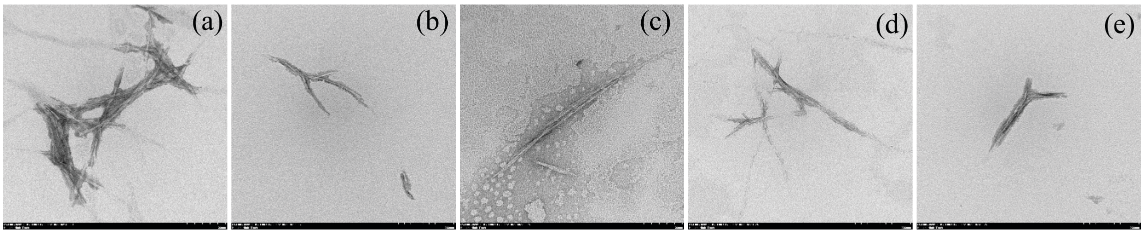

Figure 3. TEM images for CNC treated by acid hydrolysis (a - c) and pressurized acid hydrolysis (d - e).

4. Conclusion

This work studied cellulose extraction processes by alkali treatment and bleaching. CNC was hydrolyzed by acid hydrolysis and pressurized acid hydrolysis. The size of CNC was reduced into nano scale. It was found that the crystallinity index was increased. Therefore, CNC was suitable to be reinforcing agent in composites such as natural rubber. It will be used as filler in natural rubber composites for further study.

5. References

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