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# Structural and Thermal Properties of Extracted Cellulose Treated with 1-Butyl-3-Methylimidazolium Chloride

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**ABSTRACT**. In this work, alpha cellulose extracted from Mahang wood were successfully pretreated with BMIMCl. The structural and thermal properties of microcrystalline cellulose (MCC), untreated alpha cellulose and BMIMCl treated alpha cellulose at 2 wt.%, 5 wt.% and 8 wt.% were analyzed by X-ray diffraction (XRD), Fourier transform infrared analysis (FTIR) and thermogravimetric analysis (TGA) analysis. The results showed that the crystal structures of cellulose were transformed from cellulose I to II with different degree of crystallinity after BMIMCl pretreatment. FTIR and X-ray diffraction analyses indicated that the regenerated cellulose was a mixture of amorphous and crystalline cellulose. The thermal stability of cellulose decreased after BMIMCl ionic liquid treatment. The used of high amount of BMIMCl during pretreatment can be potentially produce regenerated cellulose that is very correlate to the real properties and characteristics of nanocellulose (NCCs).

***Keywords:*** *Ionic liquid, Pretreatment, Regenerated cellulose, Crystallinity*

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## 1. INTRODUCTION

Cellulose is abundantly found on earth especially in wood and other lignocellulosic biomass. There are many sources of cellulose that can be isolated and extracted from various types of plants [1]. Mahang (*Macaranga spp.*) is a pioneer and soft-wooded tree species that consider as light density wood types and have abundant quantity in the logged-over forest in Southeast Asia [2]. Apart from fast-growing ability, Mahang also has the great advantages such as exotic colours and texture, cheaper price and also abundance availability. From the other sides, Mahang is still under-utilized plants due to it poor properties and the information regarding the species is also limited, but it can greatly contribute the great potential in composite production by added value into the wood types [3].

Recently, ionic liquid has been used widely as the new type of green solvent pretreatments used in lignocellulosic field. Many researchers proved that ionic liquids can dissolve cellulose and have great versatility in the field of cellulose technology. Pretreatment with ILs more environmentally friendly than other pretreatment methods such as mechanical milling, steam explosion, acid, base, or organic solvent processes.Many researchersproved that ionic liquids can dissolve cellulose and have great versatility in the field of cellulose technology [4]. By the addition of water, ethanol or acetone, cellulose can be easily generated from its ionic liquid solutions [5].

In this study BMIMCl is used to dissolve the alpha cellulose extracted from Mahang wood. The effect of BMIMCl on structural and chemical properties of alpha cellulose extracted from Mahang wood will be investigated.

## 2. MATERIALS AND METHODS

Cellulose was extracted from Mahang wood according to TAPPI Test Method T204. The alpha cellulose was then dissolved in BMIMCl at 2 wt.%, 5 wt.% and 8 wt.%. The solutions were then heated in an oil bath at 80 ºC under continuous vigorous stirring for 12 hours. The solutions were then cooled at room temperature and regenerated using distilled water. The regenerated cellulose was freeze dry for 24 hours prior the characterization process. Thestructural and thermal properties of the regenerated cellulose were analyzedusing XRD, FTIR and TGA and were then compared to the microcrystalline cellulose (MCC) and untreated alpha cellulose.

**2.1** ***X-ray Diffraction (XRD).*** The crystalline phase and crystallinity index of the samples were studied using an X-ray diffractometer (D2-Phaser Bruker XRD) equipped with a monochromatic CuKα radiation source (λ = 0.154 nm). The samples were scanned in the step-scan mode with a 2θ angle ranging from 5º to 60º with a step of 0.01º and a rate of 1º $min^{-1}$ under room temperature. The operating voltage was 40 kV and the current was 40 mA. The crystallinity of the samples, the crystallinity index (CI) was determined based based on the reflected intensity data using method of Segal et al. [6]:

$$CI\ (\%) = 100\times(I_{002} - I_{am})/I_{002} \quad (1)$$

Where $I_{002}$ is the maximum intensity for the crystalline portion in samples (i.e., cellulose) at about 2θ=22º and $I_{am}$ is the intensity attributed to the amorphous portion of samples (i.e., hemicellulose and lignin) at 2θ= 18º.

***2.2 Fourier transform infrared analysis (FTIR).*** The FTIR spectra of the samples were recorded on a FTIR instrument (Nicolet iZ10 FT-IR Microscope) in the range of 4000-400$cm^{-1}$ with a resolution of 4 $cm^{-1}$.

***2.2 Thermogravimetric analysis (TGA).***The thermal stability of the samples was determined using a Mettler Toledo thermogravimetric analyser (TGA/DSC) under the following operational conditions: sample weight approximately 7 mg was transferred into the alumina, temperature range 25 to 550 ºC and heating rate 10 K $min^{-1}$. In order to prevent any premature thermoxidative degradation, all measurements were performed under a nitrogen atmosphere with a gas flow rate of 20 $cm^3$ $min^{-1}$.

## 3. RESULTS AND DISCUSSION

The crystallinity of samples was characterized by XRD. Fig. 1 showed all of the XRD patterns with ordered structure of crystalline and amorphous region. Three characteristics peaks of MCC showed at 2θ = 14.9°, 16.5°,and 22.6° which corresponded to crystallographic plane of crystals (110), (110), and (002) respectively. Alpha cellulose showed a slightly different pattern which more amorphous and less sharp at 2θ = 19.75°compared to MCC. The differences are probably due to the disrupted of ordered structure of the crystalline region of the alpha cellulose by the extraction process. It is clearly shown that BMIMCl treated alpha cellulose at 2 wt % has high crystalline cellulose pattern with the occurrence of a most intense and sharp peak (002) at 2θ = 26.10°. On the other hand, 5 wt.% and 8 wt.% of regenerated celluloses indicate amorphous pattern after IL pretreatment because the peak (101) disappeared and the peak (002) became broader and weaker (Fig.1).

The intense and sharper peak pattern of 2wt. % alpha cellulose (Fig. 2) compared to the others is very correlate to the real properties and characteristics of nanocellulose (NCCs) which is high crystallinity. Besides, 2wt.% alpha cellulose pattern indicates that the regenerated cellulose obtained with high amount of IL have more crystalline region because BMIMCl has selectively removed the amorphous region pattern. The higher crystallinity of 2 wt.% alpha cellulose may due to the highest amount of ionic liquid treated ratio compared to 5 wt.% and 8 wt.%.

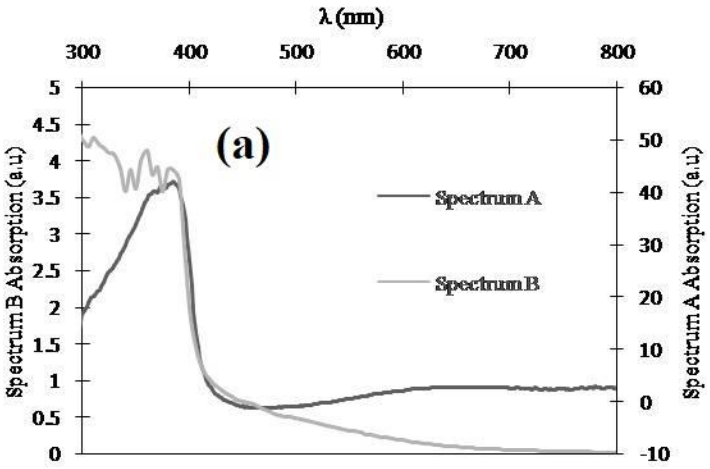


**Fig.1**XRD pattern of (a) MCC,(b) alpha cellulose,(c) 2 wt.%alpha cellulose,(d) 5 wt.%alpha cellulose and (e)8 wt.%alpha cellulose

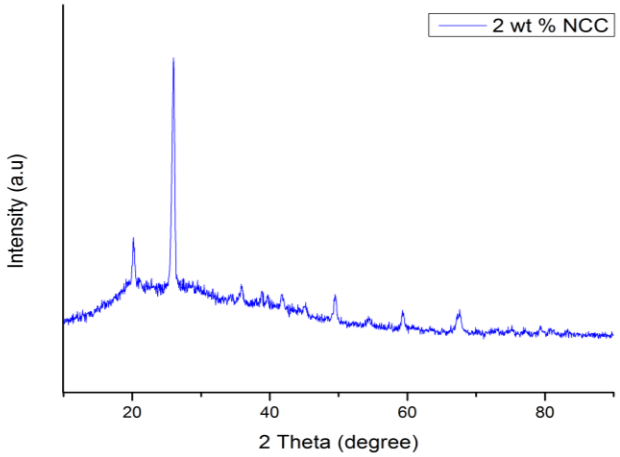


**Fig. 2** XRD pattern of 2 wt.% BMIMCl treated alpha celluloses

The crystallinity index (%)of all samples has been tabulated in Table1. As shown in Table 1, the crystallinity index (Crl) and crystallite size of MCC are higher than the alpha cellulose. This indicates alpha cellulose has lower amount of crystallinity compared to MCC. Except for 2 wt.% that shows high crystallinity index, both 5 wt.% and 8 wt.%, exhibit lower crystallinity index relative to its origin, alpha cellulose.

The crystallite size of 2 wt.% of regenerated cellulose also is the largest size which is 15.22 nm compared to 5 wt.% and 8 wt.% of regenerated cellulose which are only 0.40 nm and 0.32 nm respectively. The improved crystallinity index for 2 wt.% of regenerated cellulose can attributes to the elimination of the amorphous parts as the amount of BMIMCl increased [7]. Dissolution of the amorphous regions is predominant as it is more prone to IL treatment than the crystalline parts.

Fig. 3 illustrates the FTIR spectra of MCC, alpha cellulose and BMIMCl treated alpha celluloses. It was observed that the bands in the five spectra are somewhat similar, implying the similar structure of the cellulosic samples either with or without ionic liquid treatment. All the cellulosic samples show the almost identical basic structure which suggested no changes in the functional groups. However, a slight difference can be detected in the infracted spectra in term of different absorbance value and shapes of bands and also their location.

**Table 1** The crystallinity index (Crl) of MMC, alpha cellulose and cellulose treated with ionic liquid at 2 wt.%, 5 wt.% and 8 wt.%

| Sample | Crystallinity index (%) |
|---|---|
| MCC | 78.10 |
| Alpha cellulose | 59.74 |
| 2 wt.% | 74.76 |
| 5 wt.% | 56.33 |
| 8 wt.% | 35.90 |

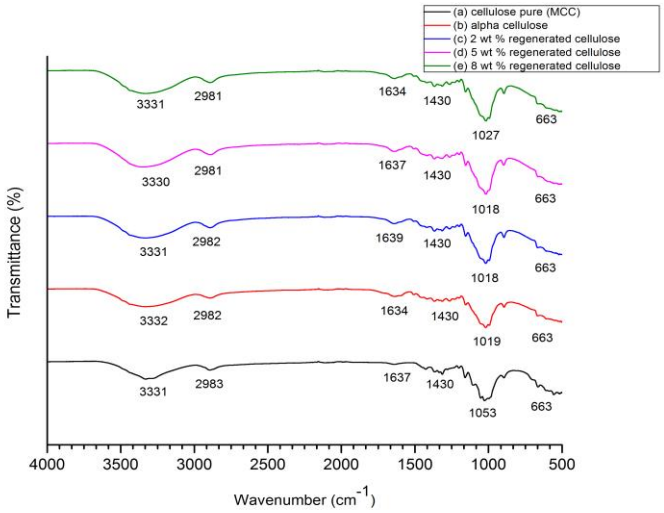


**Fig.3.**FTIR Spectra of (a) MCC, (b) alpha cellulose, (c) 2 wt.%alpha cellulose, (d) 5 wt.%alpha cellulose and (e)8 wt.%alpha cellulose

Spectra of all the cellulosic samples show the strongest absorption band at about 1019 $cm^{-1}$. This band corresponds to the stretching vibration of the C-O-C pyranose ring (antisymmetric in phase ring) of cellulose molecules [8].The peak near 3331 $cm^{-1}$, which was observed in all spectra, is attributed to characteristic hydrogen bond O-H stretching vibrations due to the presence of water. The absorption around ~2982 $cm^{-1}$observed in the five spectra which indicates the aliphatic saturated C-H stretching associated with methylene groups in cellulose. Moreover, the O-H bending of absorbed water bound to the cellulose structure gave rise to peak at 1637 $cm^{-1}$.Besides that, the absorption bands are clearly observed around 895 $cm^{-1}$corresponding to β-glycosidic linkages. In addition, the absence of peaks of IL (BMIMCI) in the spectra implied the complete removal of IL during the washing process [9].

Compare between five spectrums, there were small differences of absorbances in spectrum of BMIMCl treated alpha cellulose. The peak around 896 $cm^{-1}$, assigned to C-O-C stretching at β-1-4-glycosidic linkages, increased in intensity in the amorphous samples, compared to the other samples. The increase in the

intensity of the peak around 896 $cm^{-1}$for 2 wt.%, 5 wt.% and 8wt.% regenerated cellulose compared to untreated cellulose as shown in Fig.3 indicates the structure of cellulose become more amorphous after BMIMCl pretreatment. The intensity around 896 $cm^{-1}$band is very sensitive to the amount of crystalline versus amorphous structure of cellulose. The higher intensity of this band reflects higher amounts of disordered structure [10].

Figs. 4 and 5 show the thermogravimetric (TG) and its derivatives (DTG) of all samples. At the temperature below 100 °C, all of the samples had an initial small amount of weight loss that indicates to the evaporation of water [6]. Decomposition MCC and alpha cellulose took place at the temperature of (310 °C-380°C) and (250 °C-370°C) respectively which both illustrated one step pyrolysis process. Conversely, the decomposition of the regenerated cellulose occured within a wider range of weight percentage with two distinct pyrolysis process that well separated in close proximity. The first pyrolysis of regenerated cellulose occurred from 220°C to 280 °C with the $T_{max}$ peak at 240°C that attributes to the decomposition of amorphous regions, while the second pyrolysis had greater dominance over the first pyrolysis, ranging from 280 °C to 350 °C with $T_{max}$ at 325 °C that represented to the breakdown of the crystal interior [6].

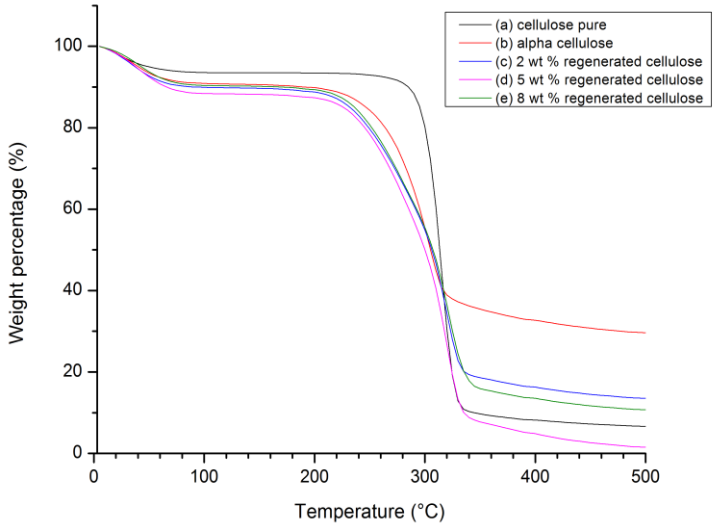


**Fig.4**TG curves for (a) MCC, (b) alpha cellulose, (c) 2 wt.%alpha cellulose, (d) 5 wt.%alpha cellulose and (e) 8 wt.% of BMIMCl treated alpha cellulose

The value of $T_{max}$ derived from TGA data represents the temperature at which the maximum decomposition occurs. Hence, $T_{max}$ is used to evaluate the impact of IL pretreatment on the thermal stability of samples. This difference in thermal degradation was probably due to the degree of crystallinity. Besides, the two peaks that observed in two-step pyrolysis process could be due to the presence of both crystalline and amorphous components in the regenerated cellulose. In general, it is easier to breakdown the amorphous region at a lower temperature followed by weight loss due to the crystalline components, which decompose at high temperature.

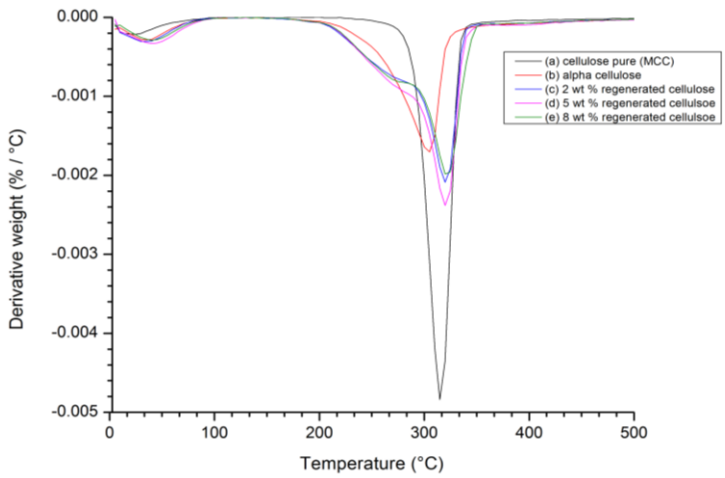


**Fig.5**DTG curves for (a) MCC, (b) alpha cellulose, (c) 2 wt.%alpha cellulose, (d) 5 wt.%alpha cellulose and (e) 8 wt.% of BMIMCl treated alpha cellulose

The decreasing trend of decomposition temperature concludes that the thermal stability of regenerated cellulose was lower than MCC. Besides, this reduction in thermal stability could be due to several factors [6] such as the thermal stability that reduces for regenerated cellulose due to the higher surface area of fiber dimensions than macroscopic cellulose which increases the heat exposure and also the delignification occurring at higher pretreatments temperature may also contribute to lower the thermal stability.

## 4. SUMMARY

In this work, alpha cellulose extracted from Mahang wood were successfully pretreated with BMIMCl. The crystal structures of cellulose were transformed from cellulose I to II with different degree of crystallinity after BMIMCl pretreatment. FTIR and X-ray diffraction analyses indicated that the regenerated cellulose was a mixture of amorphous and crystalline cellulose. The thermal stability of cellulose decreased after BMIMCl ionic liquid treatment. The used of high amount of BMIMCl during pretreatment can be potentially produce regenerated cellulose that is very correlate to the real properties and characteristics of nanocellulose (NCCs).

## REFERENCES

[1] E. Kopania, J. Wietecha, D. Ciechańska,. Studies on isolation of cellulose fibres from waste plant biomass,Fibres Text. East Eur., 96 (2012) 167-172.

[2] A. Ang, Z. Ashaari, E.S. Bakar, M.H. Sahri,. Enhancing the properties of mahang (macaranga spp.) wood through acrylic treatment in combination with crosslinker, Mod. Appl. Sci.,3(2009)2-10.

[3] A.R. Noor Azrieda,A.K. Razali, S.Rahim, K. Izran,. Physical and mechanical properties of portland cement-bonded flakeboards fabricated from macaranga gigantea and neolamarckia cadamba,Pertanika., 35(2012)783-792.

[4] H.T. Tan, K.T. Lee, A.R. Mohamed, Pretreatment of lignocellulosic palm biomass using a solvent-ionic liquid [BMIM]Cl for glucose recovery: An optimisation study using response surface methodology,Carbohydr. Polym., 83(2011)1862-1868.

[5] A.N. Frone, D.M.Panaitescu, D. Donescu,. Some aspects concerning the isolation of cellulose micro- and nano-fibers,UPB Bul. Stiint., Ser. B, 73(2011) 133-152.

[6] L. Segal, J.J. Creely, A.E. Martin, C.M.Conrad,. An empirical method forestimating the degree of crystallinity of native cellulose using the X-raydiffractometer, Text. Res. J., 29 (1959) 786-794.

[7] X.Y. Tan, S.B. Abd Hamid, C.W. Lai, Preparation of high crystallinity cellulose nanocrystals (CNCs) by ionic liquid solvolysis,Biomass and Bioenergy, 81(2015) 584-591.

[8] A. Mandal, D. Chakrabarty, Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization, Carbohydr. Polym., 86 (2011) 1291-1299.

[9] J. Han, C. Zhou, A.D. French, G. Han, Q. Wu,. Characterization of cellulose II nanoparticles regenerated from 1-butyl-3-methylimidazolium chloride, Carbohydr. Polym., 94(2013) 773-781.

[10] D. Ciolacu, F. Ciolacu,V.I.Popa, Amorphous cellulose-structure and characterization,Cell. Chem. Technol., 45 (2011) 13.