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ISOLATION AND CHARACTERIZATION OF MICROCRYSTALLINE CELLULOSE (MCC) FROM RICE HUSK (RH) AND KENAF : A COMPARISON STUDY

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ABSTRACT

Microcrystalline cellulose (MCC) was successfully isolated from rice husk (RH) and kenaf via acid hydrolysis process by using nitric acid (HNO_3). RH and kenaf were undergone alkali and bleaching treatment for removal of non-cellulosic materials. The extracted MCC-RH and MCC-kenaf were characterized to study their functional groups, thermal stability and percentage crystallinity. Analysis of Fourier transform infrared (FTIR) spectroscopy showed the successive elimination of non- cellulosic constituents in both MCC-RH and MCC-kenaf. Differential scanning calorimetry (DSC) displayed 58% and 89% crystallinity of the extracted MCC-RH and MCC-kenaf respectively. X-ray diffraction (XRD) analysis showed MCC-kenaf exerted the highest crystallinity index value of 64%. The results indicated MCC isolated from RH and kenaf were extracted with high purity, crystallinity index and posed higher percentage crystallinity that able to be utilized in the biocomposite preparation.

Keywords: Acid hydrolysis; microcrystalline cellulose; rice husk; kenaf; thermal stability; crystallinity

INTRODUCTION

MCC is a refined wood pulp that derived from cellulose which appears as inert white crystalline powder with no odor and tasteless. It is generally applied in pharmaceutical, cosmetics, food industries and acts as a water retainer, suspension stabilizer and reinforcement filler in composite preparation [1]. MCC poses excellent properties such as biodegradability, renewability, low density and high surface area which make it as alternative filler in the composite preparation [2].

Generally, MCC is isolated from wood pulp and purified cotton linters. Recent studies reported that MCC also can be obtained from the agricultural wastes such as coconut husk fiber [3], banana rachis [4], groundnut husk [5], rice straw [6] and rice husk [7]. The properties of MCC obtained from different sources vary with respect to porosity, crystallinity, surface area, morphology [8].

RH is a by-product from paddy production. The paddy is made up of 78% rice, 8% bran and 22% husk. RH can be used as fertilizer, building material and heat insulator [9]. However, only small amount of RH are recycled, whilst large quantities of RH are burn in open air which can cause air pollution. RH is composed of 33% cellulose, 26% hemicelluloses and 7% lignin [10]. Kenaf or *Hibiscus cannabinus L.* is a common wild plant found in tropical and subtropical countries such as Asia and Africa. It is employed in industry sector as an abundantly available renewable annual fiber crops. It is mainly used as building materials, textiles and composite preparation. Kenaf core fiber contains higher lignin and holocellulose whilst its bast fibers contains plenty of α-cellulose and ash content [11]. In this study, nitric acid was used over strong acids due to its miscibility in water and less corrosive characteristic. The significance of this research is to compare the MCC production isolated from RH and kenaf using acid hydrolysis by nitric acid. Characterization study such as FTIR, DSC and XRD were done to characterize the isolated MCC. FTIR spectroscopy was done to identify the successive elimination of non-cellulosic constituents in MCC. DSC was implemented to measure the thermal stability of the extracted MCC while XRD was performed to determine the percentage crystallinity of the MCC samples after undergo pre-treatments and acid hydrolysis process.

EXPERIMENTAL

Materials

RH was collected from BERNAS, a local rice mill in Simpang Empat, Perlis. Kenaf was supplied from Lembaga Kenaf Malaysia in Kelantan. NaOH and NaOCl were applied as bleaching agents while HNO_3 was used for acid hydrolysis process. All chemicals were purchased from Fluka and were used without further purification.

Alkaline and bleaching treatment of RH and kenaf

The alkaline treatment was performed to solubilize hemicellulose. 10g of RH was reflux with 120 mL of 1M NaOH at 80 ^oC for 1h 30 min and then washed using distilled water to remove the solubilized components until pH7 was achieved. Following the alkaline treatment, the alkaline treated RH was undergoing bleaching treatment with 140mL of 5% sodium hypochlorite (NaOCl) reflux at 80 °C for 18 min [12]. The cellulose pulp obtained was washed using distilled water until pH7. Then, the treated RH was dried at 70 ^oC for 24 h in oven. Lignin become soluble in the alkaline medium and oxidized during bleaching. The alkaline and bleaching treatments then repeated to treat 10g of kenaf.

Acid hydrolysis

The purified RH cellulose was hydrolyzed with 140 mL of 1M HNO_3 at 80 ^oC for 30 min under continuous stirring. Then, it was washed repeatedly with distilled water to neutralize the pH. The MCC obtained from purified RH cellulose was dried in a vacuum oven at 100 ^oC until constant weight was achieved. The resultant MCC were grounded into fine powder by using rotary ball mill after the washing and drying process. Finally, the mass of the MCC-RH were recorded and the same acid hydrolysis

steps were repeated with the purified kenaf.

Fourier Transform Infrared (FTIR) Spectroscopy
FTIR was used to determine the functional group that present in the isolated MCC. FTIR analysis was carried out using Perkin Elmer FTIR spectrometer 1650 with scanning ranges of 4000 cm^{-1} to 400 cm^{-1} to achieve an acceptable signal-to signal ratio. FTIR spectra of the samples were recorded using Nicolet's Avatar 360 at 32 scan with the spectra resolution of 4 cm^{-1}.

Differential Scanning Calorimeter (DSC)
DSC analysis was implemented to measure the thermal transition of MCC using a Perkin Elmer Instrument Pyris DSC. About 5 to 10 mg of samples were used in this analysis. All samples were set with flow rate 35 mL/min of nitrogen atmosphere. The samples were held for 5 ^oC for 5 min, heated at 10 ^oC/min to 250 ^oC at first cycle, subsequently held for 5 min to erase the thermal history. Then they were cooled at rate of 10 ^oC/min to -10 ^oC on the second cycle. The glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (H_m) were determined from the second heating. T_m was taken as the peak temperature of the melting endotherm while T_g was taken as the inflection point of the specific heat increment at the glass-rubber transition. Degree of crytallinity was calculated using Eq. 1 below:

$$X_c = \frac{\Delta H_m(treated)}{\Delta H_m^{\circ}(untreated)} \times 100\% \quad (1)$$

where, ΔH_m is the treated MCC of 1M HNO_3, and ΔH°_m is the untreated RH and kenaf.

X-ray Diffraction (XRD)
X-ray diffraction was performed to determine the crystallinity of the MCC samples after different treatments. PANalytical X'Pert PRO Multi-Purpose Diffractometer with Cu K radiation was used to obtain the diffraction patterns. 40 kV voltages with current 40 mA were used. The crystallinity index (CrI) was calculated using Eq. 2:

$$CrI = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \quad (2)$$

where, I_{002} is the maximum intensity of the 0 0 2 peak at about 2 = 22^o and I_{am} is the intensity corresponds to the peak at about 2 = 18^o

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RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR).

Figure 1 shows the FTIR spectra for untreated RH, treated MCC-RH with 1M HNO_3, untreated kenaf and MCC-kenaf treated with 1M HNO_3. For untreated RH and treated MCC-RH spectrums, broad bands appear at 3100-3600 cm^{-1} due to –OH stretching vibration that gives information about the hydrogen bonds. The band at 2800-2900 cm^{-1} which appeared in the spectra shows the presence of C-H group. The band from 1640-1650 cm^{-1} in the spectra is indicative of the absorption of water. This band indicates the bending of water molecules due to the interaction of water and cellulose [13]. Therefore, these indicate that the cellulose components were present in RH fibres and it is not removed during the chemical treatment.

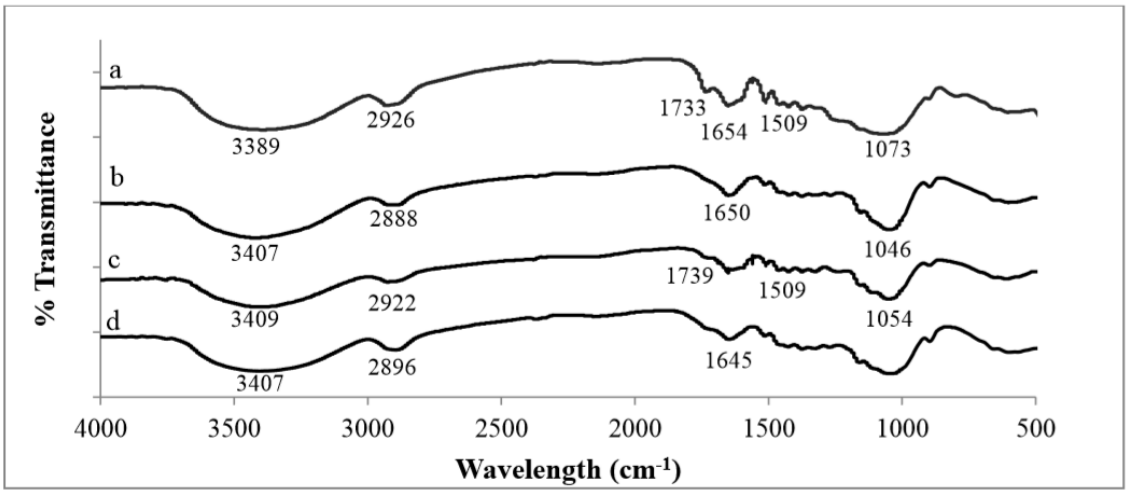

Figure 1: FT-IR spectra of (a) untreated RH (b) MCC-RH treated with 1M HNO_3 (c) untreated kenaf and (d) MCC-kenaf treated with 1M HNO_3

The broad absorption band at 3409 and 3407 cm^{-1} for untreated kenaf and MCC-kenaf respectively indicate the presence of –OH group. The –OH groups of untreated kenaf slightly shifted toward lower wavelength after the treatment. This is probably due to weakening of hydrogen bonding in cellulose during acid hydrolysis process [14]. The absorption band presents at 1739 cm^{-1} for untreated kenaf is in line with [15] and in which signifies the presence of C=O stretching vibration of carbonyl and acetyl group in the hemicelluloses. Whilst for MCC, the absent band of the C=O stretching indicates a complete removal of hemicelluloses during alkaline treatment. According to previous work [16] the band appears within the range of 1509 - 1609 cm^{-1} is correspond to C=C aromatic skeletal vibrations, indicates the presence of lignin. Hence, the absence of C=C aromatic skeletal vibrations band from the MCC spectrum proves that lignin had been completely removed out of the MCC.

Differential Scanning Calorimeter (DSC).

The melting endotherms of all samples are presented in Figure 2. From the graph, the onset temperatures of the decomposition as well as midpoint temperatures data for treated MCC-RH increases from the untreated RH. The higher thermal stability is s associated with, the higher value of the onset temperatures. This behaviour can be attributed to the high degree of crystallinity of MCC. Treated MCC-RH showed 58% of percentage crystallinity which is in line with the recent study [17], reported that 59% crystallinity on nanofibers from OPEFB via H_2SO_4 was recorded. On the other hand, the percentage for crystalline region in MCC-kenaf calculated is 89%. This value confirmed that the extracted MCC-kenaf contains high crystallinity which is important for the reinforcement of MCC in composite preparation. The onset temperature for both kenaf fiber and MCC is at 4.47 °C.

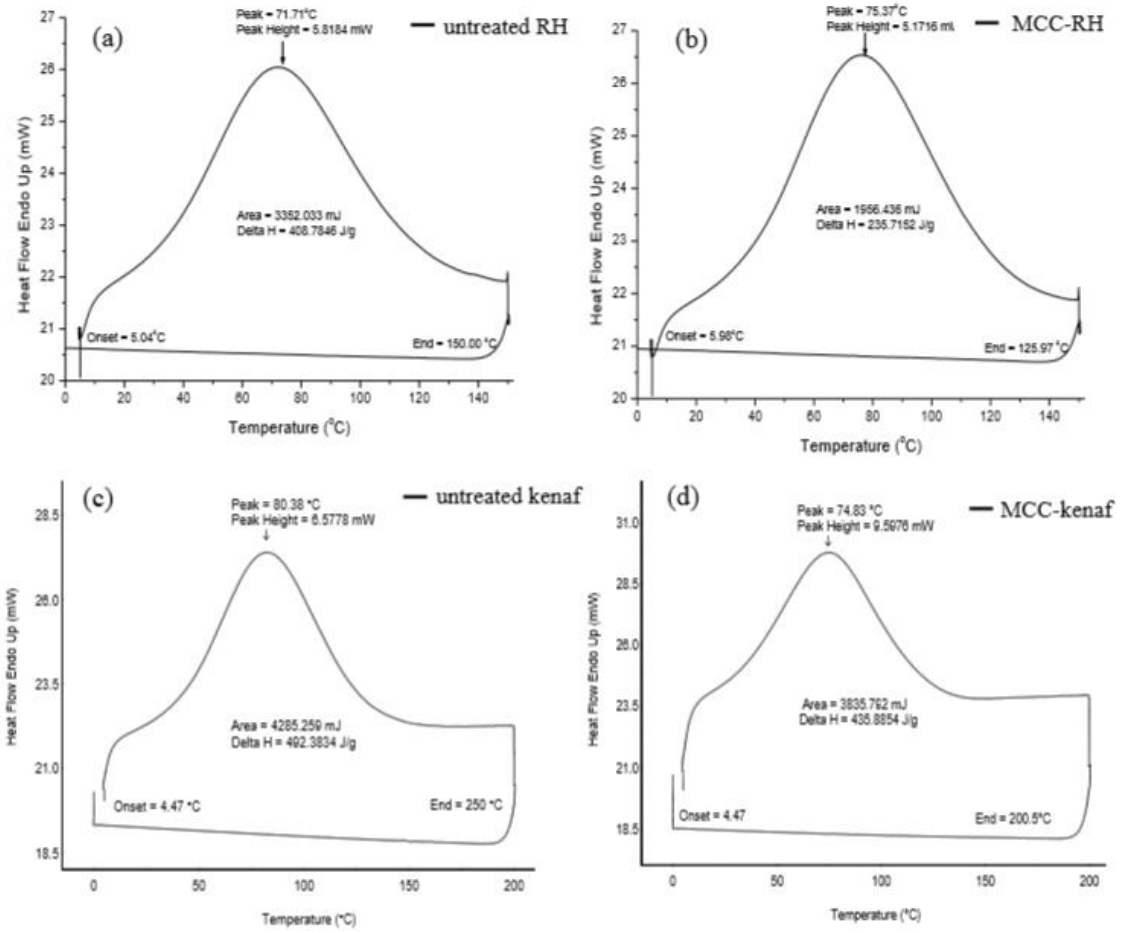

Figure 2: DSC curves of (a) untreated RH, (b) treated MCC-RH with 1M HNO_3, (c) untreated kenaf and (d) treated MCC-kenaf with 1M HNO_3

X-ray Diffraction (XRD).

Figure 3(a) shows treated MCC-RH produced the highest peak at 2 = 22º. The crystallinity values of untreated RH and treated MCC-RH were 39% and 42% respectively. The increase in crystallinity is due to the increase in the rigidity of cellulose structure [18]. From Figure 3(b) it is clear that the diffraction peak located at 22.6º belongs to the treated MCC-kenaf displayed the sharpest and strongest peak indicating increases in crystallinity. The crystallinity values of untreated kenaf and treated MCC-kenaf were 33% and 64% respectively. The previous study [19] stated that the crystallinity index for OPEFB-pulp is high due to removal of hemicellulsoe and lignin, which existed in amorphous regions leading to realignment of cellulose molecules. Based on the obtained results, MCC- kenaf display the highest crystallinity value compared to MCC-RH. The result is in line with [20] in which, the highest crystallinity index obtained for OPEFB-MCC is thought to be due to the removal of the amorphous regions of cellulose by acid hydrolysis process, which prompts the hydrolytic cleavage of glycosidic bonds and finally releasing individual crystallites.

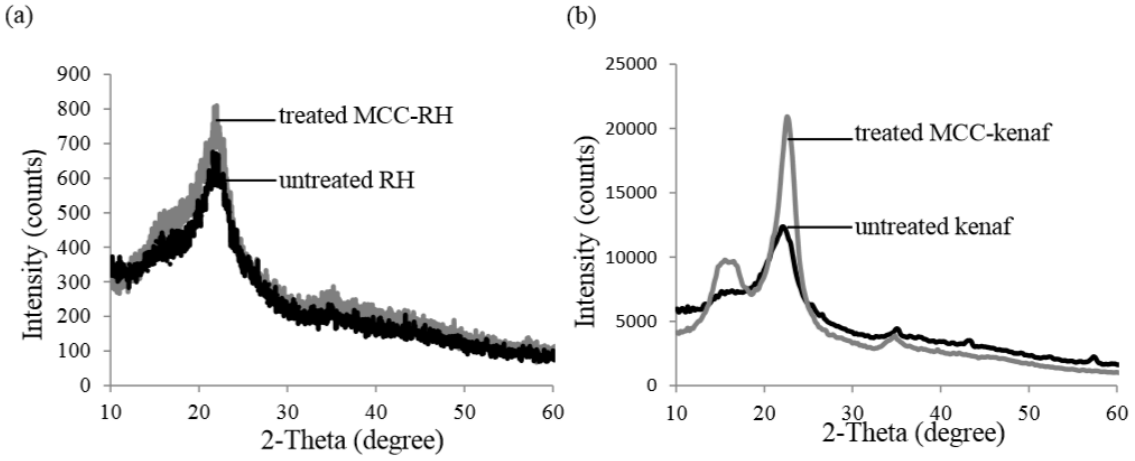

Figure 3.XRD patterns (a)untreated RH and treated MCC-RH, (b)untreated kenaf and treated MCC-kenaf

CONCLUSION

MCC has been successfully isolated from RH and kenaf using chemical treatments involving alkaline, bleaching and acid hydrolysis treatments of nitric acid. The extracted MCC samples enhanced their physical characteristic in term of purity, thermal stability and higher crystallinity that able to be utilized as reinforcing filler for polymeric composite material preparation. This study has proved that isolation of MCC from RH and kenaf are successful and making the extracted MCC as a promising candidate to be used in many field.

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