INFLUENCE OF DIFFERENT ACID CONCENTRATION ON PHYSICOCHEMICAL PROPERTIES OF MICROCRYSTALLINE CELLULOSE OBTAINED FROM OIL PALM BIOMASS BY ACID HYDROLYSIS

T.M. Hassan[a],
M.K.Mohamad Haafiz[a*]
I.Mazlan[a],
M.R Nurul Fazita[a],
M.M.Marliana[b]

ABSTRACT

In this present work the influence of different acid concentration on physicochemical properties of microcrystalline cellulose (MCC) obtained from oil palm empty fruit bunch (OPEFB) by acid hydrolysis was evaluated. The OPEFB was first subjected to the environmental friendly pulping and fiber-total chlorine free (TCF) bleaching sequence prior to the acid hydrolysis process. Fourier transform infrared (FT-IR) spectroscopy indicates the pulping and bleaching sequence used are able to remove lignin component inside OPEFB at the peak FTIR show $1735cm^{-1}$ in OPEFB spectra indicated as hemicellulose and $1514cm^{-1}$ indicated as lignin, after bleaching sequence both peak were disappeared it proof the hemicellulose and lignin was successfully remove from OPEFB. Furthermore, FTIR also indicates that the acid concentration does not affect the chemical structure of resultant MCC. The scanning electron microscopy (SEM) displayed a compact and a rough surface morphology structure for all MCC after hydrolysis. X-ray diffraction (XRD) analysis showed that the crystallinity of MCC is inversely proportional to acid concentration where decreased with increase in acid concentration where the highest acid concentration 4.5 N HCl displayed 18 % reduction in crystallinity as compared to MCC produced with 2.5 N HCl. The thermogravimetric analysis (TGA) meanwhile, revealed that the acid concentration influenced the thermal stability of MCC, where the MCC obtained from 2.5 N HCl exhibited the highest thermal stability (T_{20}=328 °C and T_{50}=349 °C) as compared to, 3.5 N HCl and 4.5 N HCl. The MCC obtained from 2.5 N HCl have potential as a good green filler in biocomposites with this form of MCC.

Keywords: Oil palm empty fruit bunch, microcrystalline cellulose, acid hydrolysis, thermal properties, crystallinity index

1. INTRODUCTION

The oil palm empty fruit bunch (OPEFB) is a renewable lignocellulosic biomass which has been generated from the oil palm mills after oil has been extracted (Haafiz, Eichhorn, Hassan, & Jawaid, 2013). This material is abundantly available for the production and isolation of cellulose and its derivatives (Haafiz et al., 2013; Wanrosli, Rohaizu, & Ghazali, 2011). Generally, it was estimated that more than 19.03 million tonnes (weight basis) of OPEFB were generated annually in Malaysia. OPEFB is considered as a valuable biomass residue which displayed a potential to be converted not only into energy but also as a raw material for the production of higher value added materials such as panelling and composites, fine chemicals, pulp and paper as well as compost and bio-fertilizer. This material comprised of 38.3 % cellulose, 22.1 % lignin, and 35.3 % hemicellulose, which made this material the greatest raw material for the isolation and production of cellulose based product (Kelly-Yong, Lee, Mohamed, & Bhatia, 2007; K. H. Rosnah Mat Soom, K H , & WH, 2002).

Cellulose is the most abundant and ubiquitous biopolymer in nature, which is produced by plant and microorganism (Haafiz et al., 2013; Klemm, Heublein, Fink, & Bohn, 2005). It is a linear homopolymer of glucose $(C_6H_{10}O_5)_n$ with repeating units containing of d-glucose in $^4C_1$ conformation, which is can be decomposed by microbial and fungal enzymes but unsolvable in water (Haafiz et al., 2013; Li et al., 2009). Cellulose, which can be found in the pure form was isolated from cotton, and from other lignocellulosic materials such as wood, bamboo, sugarcane, baggase, kenaf, etc. It has been used in a wide range of industries, such as in paper industry, board industry, pharmaceutical industry as well as in automotive industry (Haafiz et al., 2013; Hussin et al., 2016). Cellulose is the main component for pulp and paper production and being utilized as a starting material for the production of regenerated cellulose fibers such as rayon, microcrystalline cellulose and other cellulose derivatives, especially esters and ethers (Sixta, 2006).

In nature, cellulose molecular chains are self-assembled into microfibrils, which are contains of crystalline and amorphous regions (Fernandes et al., 2011; Nishiyama, 2009). The structural characteristics were determined by chemical constituents that make up the cell wall of wood fiber. Lignin and hemicellulose have only amorphous substances, whereas crystalline and amorphous regions are composing in cellulose (A. Rosnah Mat Soom, Astimar Abd & Wan Hasamudin, 2009; Zickler, Wagermaier, Funari, Burghammer, & Paris, 2007). The amorphous region from cellulose can be removed by using mild acid hydrolysis technique and leave behind the insoluble crystalline region and this material mostly referred as microcrystalline cellulose (MCC) (Adel, El-Wahab, Ibrahim, & Al-Shemy, 2011; Haafiz et al., 2013).

MCC is white, fine, odourless, crystalline powder and a biodegradable material which can be isolated from pure cellulose through acid hydrolysis approach. This method is able to remove and eliminate the amorphous region of cellulose which

consequently increase the crystallinity index of obtained MCC (Haafiz et al., 2013; A. Rosnah Mat Soom, Astimar Abd & Wan Hasamudin, 2009). The typical range of crystallinity values MCC as reported earlier from 55 % to 80 % as determined by X-ray diffraction (XRD) (Chuayjuljit, Su-uthai, & Charuchinda, 2010). MCC has been used as a suspension stabilizer and water retainer, in the cosmetics, food and direct compressor in development of tablets and soluble drugs in pharmaceuticals industries (Chuayjuljit et al., 2010; El-Sakhawy & Hassan, 2007; Hussin et al., 2016).

The production and isolation of MCC from other materials such as from jute cellulose (Jahan, Saeed, He, & Ni, 2011), peel of pear fruits (Habibi, Mahrouz, & Vignon, 2009) mulberry barks (Li et al., 2009),wheat and cereal straws (Alemdar & Sain, 2008a), sugar cane bagasse (Bhattacharya, Germinario, & Winter, 2008), flax fibers and flax straw (Bochek, Shevchuk, & Lavrent'ev, 2003), and soybean husk (Uesu, Pineda, & Hechenleitner, 2000) have been studied and reported. The isolation of MCC from oil palm biomass residue by using acid hydrolysis (HCl) method has been reported by (Haafiz et al., 2013). Motivate from previous work reported by aforementioned author. This current work focusing on the characterization the properties of MCC obtained from OPEFB with different acid concentration. To date, no information and research have reported yet on the physicochemical properties of MCC obtained from OPEFB by different acid hydrolysis concentration. This article therefore reports for the first time the effect of difference acid concentration on MCC from OPEFB which has a potential to be used as green filler for the bio-composite application.

2.0 EXPERIMENTAL
2.1 Materials

Fibrous strands of OPEFB were supplied by United Oil Palm Sdn Bhd, Nibong Tebal, Penang. Reagents used in this work were 37 % hydrochloric acid (HCl), magnesium sulphate ($MgSO_5H_2O$), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2). The chemicals used were purchased from Merck, Malaysia.

2.2 Methods
2.2.1 Preparation of microcrystalline cellulose

MCC was prepared from OPEFB-pulp according to the technique described by Haafiz et al. (2013) and Chuayjuljit et al. (2010) based on the original procedures patent by Battista (1950). OPEFB-pulp was first obtained from total chlorine free (TCF) pulping and bleaching sequences, as described by Leh, Rosli, Zainuddin, and Tanaka (2008). The resultant OPEFB-pulp was hydrolyzed with three difference acid concentrations 2.5, 3.5 and 4.5 N HCl. The process was conducted with the ratio of 1:20 (OPEFB-pulp to acid), from temperature 105˚C for 15 minutes under reflux. The obtained MCC was washed, with plenty of distilled water to rinse the mixture until it was free from acid and it will dry and powdered using rotary ball mill. The resultants MCC was produced in snowy-white in appearance and were noted as 2.5 N MCC, 3.5 N MCC and 4.5 N MCC.

3.0 CHARACTERIZATION
3.1 Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra of the produced MCC were recorded using Nicolet Avatar 360 ESP FTIR spectrometer. The oven dried powder of MCC were mixed with Potassium bromide (KBr) with ratio 1:100 and pressed into a pellet. The pellet was then scanned in the spectrometer within the range of 500 to 4000 cm^{-1}. The positions of significant transmittance peaks were determined using the "find peak tool" provided by the Nicolet OMNIC 5.01 software.

3.2 Scanning electron microscope

Scanning electron microscope (SEM) was used to observe the surface morphological appearance of MCC sample. The samples were observed using a scanning electron microscope Model Supra 50 VP with an accelerating voltage of 15 kV. MCC were coated with thin layer of gold and palladium to avoid charging using a Polar on SC515 SEM coating system (Fisons Intrusment) prior observation.

3.3 X-ray diffraction

X-ray diffraction (XRD) was carried out using KristalloflexD-5000 X-ray diffraction system (Siemens, Germany) and Ni-fltered Cu Kα radiation at an angular incidence of 10–60∘ (2θangle range). The operating voltage and current were 40 kV and 40 mA, respectively. The crystallinity of the samples was calculated from diffraction intensity data using the empirical method for native cellulose (Rosa, Rehman, de Miranda, Nachtigall, & Bica, 2012). The crystalline-to-amorphous ratio of materials was calculated by using Equation. (1).

$$C_r.I(\%) = ((I_{002} - I_{am})/I_{002}) \tag{1}$$

$C_r.I$ = crystallinity index,
I_{002} = maximum intensity (in arbitrary units) of the diffraction from the 002 plane at 2θ = 22.6∘.
I_{am} = intensity of the background scatter measured at 2θ= 19∘.

3.4 Thermogravimetric analysis

The thermogravimetric analysis (TGA) of MCC samples was analysed by using a Mettler Toledo TGA/SDTA851e thermogravimeter (Mettler Toledo Corp., Switzerland) with STARe software (version 9.20). The samples were scanned from 30°C to 800°C at a rate of 20°C/min^{-1} under a nitrogen gas atmosphere.

4.0 RESULTS AND DISCUSSION
4.1 Fourier transform infrared analysis

FT-IR spectra of OPEFB, OPEFB-pulp, and MCC samples are presented in Fig. 1. The peak assignments were summarized in Table 1. From Fig.1 all samples shown two main absorbance regions which is fingerprint region and functional group region (Fahma, Iwamoto, Hori, Iwata, & Takemura, 2010; Rosa et al., 2012). From Fig.1, the absorption band which corresponds to either acetyl or uronic ester groups of hemicelluloses (normally appears in the region of 1700-1740 cm^{-1}) was absent, indicate the TCF was successfully remove the hemicelluloses part similar observation reported early by other author (Alemdar & Sain, 2008a; Nuruddin et al., 2011; Rosa et al., 2012). Meanwhile, the absorption at 1510cm^{-1} which could be observed in OPEFB which correspond to C=C aromatic skeletal vibration is completely absent for bleached pulp as well as MCC samples indicate the complete removal of lignin component in OPEFB sample. This result is in agreement with work published earlier by Haafiz et al. (2013) when producing MCC from OPEFB.

Fig. 1: FT-IR spectra a) OPEFB b) OPEFB-pulp c) 2.5N MCC d) 3.5N MCC e) 4.5N MCC
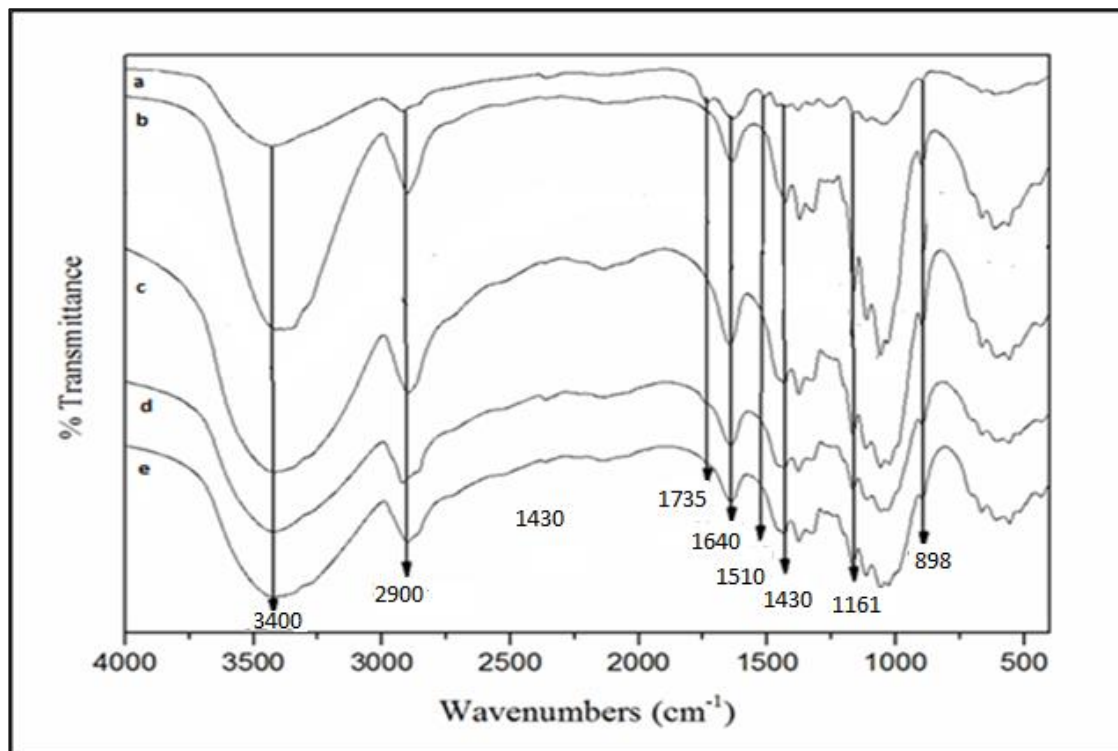
From Fig. 1 the broad absorption band located from 3400cm^{-1} to 3500 cm^{-1} is due to stretching of –OH groups and an absorption at 2900 cm^{-1} is related to CH_2 groups (Jahan et al., 2011; Rosa et al., 2012; Satyamurthy, Jain, Balasubramanya, & Vigneshwaran, 2011). The absorption at 1640cm^{-1} in all samples is indicative as absorption of water molecules due to a strong interaction between cellulose and water(Johar, Ahmad, & Dufresne, 2012; Rosa et al., 2012). The absorption band at 1425 cm^{-1} is associated to the intermolecular hydrogen at the C_6 (aromatic ring) group (Haafiz et al., 2013; Kumar, de la Luz Reus-Medina, & Yang, 2002). The absorption band at 1163 cm^{-1} corresponds to C-O-C stretching, and the peak at 896 cm^{-1} is associated to C-H rock vibration of cellulose (anomeric vibration, specific for β-glucosides) observed in OPEFB, OPEFB-pulp, and MCC samples similar results has been reported earlier by Haafiz et al. (2013).

The FT-IR spectra displayed similar pattern and peak position for all MCC samples. This indicated that the different acid concentration used in acid hydrolysis does not affect the chemical structure of the cellulosic fragment of MCC, the morphological and thermal stability could be affected.

Table 1: FTIR spectral peak assignments for OPEFB, OPEFB-pulp, and MCC

Peak Frequency(cm^{-1})	Peak assignment
3400-3500	OH-bending
2800-2900	CH_2 groups

1700-1740	acetyl or uronic ester groups
1645	O-H stretching
1509-1609	C=C aromatic skeletal vibrations
1425	CH_2 bending
1163	C-O-C stretching
896-900	C-H

4.2 Scanning electron microscopy (SEM)

The MCC samples surface morphology structure after hydrolysis treatments were observed by means of SEM and presented in Fig. 2. From the figure, it can be clearly seen that the MCC obtained displayed irregular, rough and dense surface morphological structure. Interesting to note that, even though different acid concentration has been used the resultant MCC samples showing a similar morphological pattern (irregular and dense structure). Similar morphologies have been observed during isolation of MCC from OPEFB with 2.5 N HCl as reported by Haafiz et al. (2013) and isolation of MCC from OPEFB α-cellulose by A. Rosnah Mat Soom, Astimar Abd and Wan Hasamudin (2009).According to Mathew, Oksman, and Sain (2006), the production of MCC via hydrolysis can caused the irregularity of MCC surface morphology and Trache, Donnot, Khimeche, Benelmir, and Brosse (2014) also reported the chemical treatment during acid hydrolysis caused roughness of MCC. As reported earlier by de Menezes, Siqueira, Curvelo, and Dufresne (2009), cellulose produced from different sources and different hydrolysis displayed different in overall appearances either in particle size, surface morphology and/or crystallinity percent.

Fig. 2: Scanning electron micrographs of (a) 2.5 N MCC, (b) 3.5 N MCC, (c) 4.5 N MCC
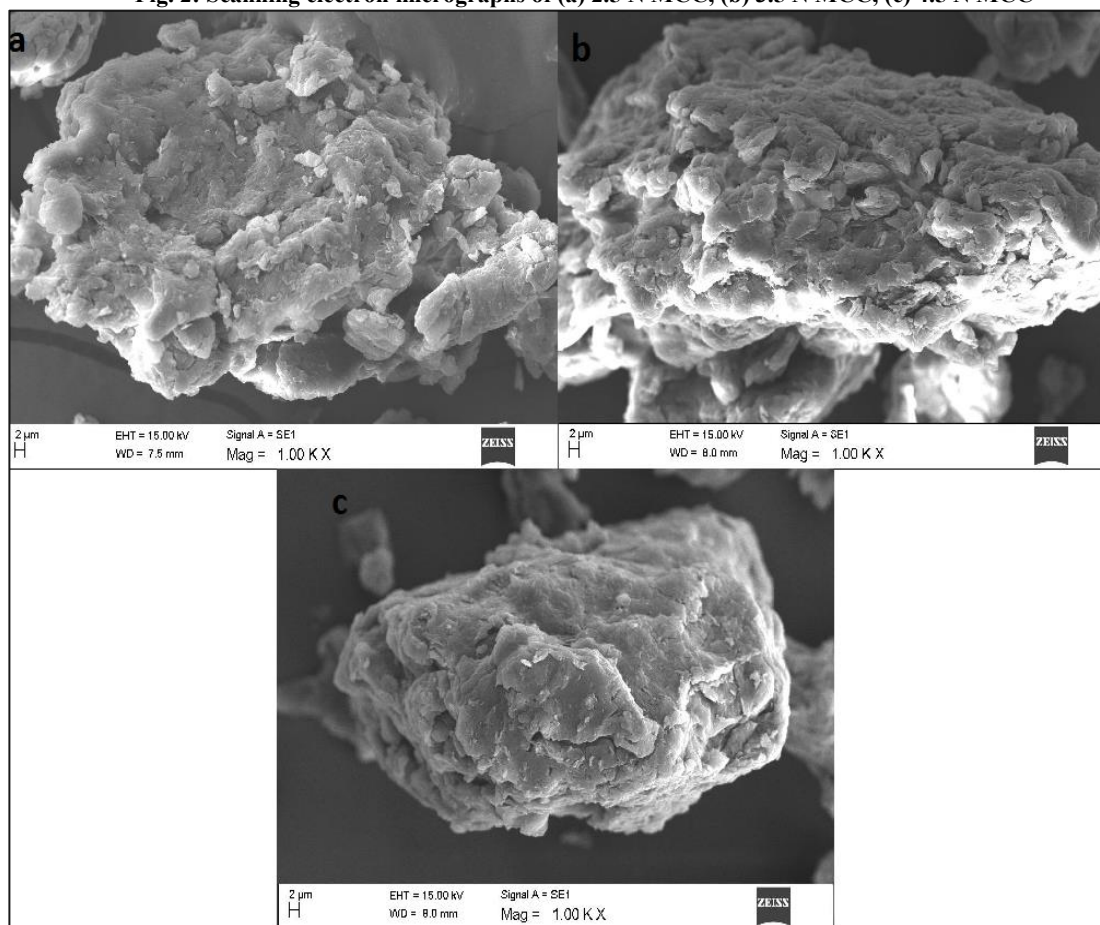
4.3 X-ray diffraction

Crystallinity of cellulose is related in rigidity of cellulose, an increase in the crystallinity it indicate increased in rigidity of cellulose which could enhanced the tensile strength of cellulose fiber (Alemdar & Sain, 2008a; Haafiz et al., 2013). Cellulose contains two regions which is crystalline and amorphous region (Klemm et al., 2005). The amorphous region could be eliminated by acid hydrolysis leaving behind the crystalline region (Adel et al., 2011; Haafiz et al., 2013). According to Rosa et al. (2012) the mechanical properties of composite were expected will increase if high crystallinity index of cellulose fiber used as reinforcement agent. The X-ray diffraction patterns for MCC samples were displayed in Fig. 3 and the crystallinity of each sample is summarized in Table 2. Based on the analysis preformed, it can be concluded that the acid concentration effect the crystallinity values of obtained MCC. The crystallinity of MCC decreased when the acid concentration increased up to 4.5 N. The crystallinity value decrease when high concentration acid hydrolysis was used, suggesting that the hydrolysis process not only able to remove the amorphous phase but also to eliminate some part of the cellulose crystalline region. Similar result were reported earlier by other authors Rozmarin (1977) and Chuayjuljit et al. (2010), the result presented higher concentration acid used more low crystallinity index, it similar result according studied by Rozmarin (1977) increase in acid concentration the crystallinity index decreased rapidly. By this XRD result on Table 2, it show the crystallinity value decrease when high concentration acid hydrolysis was used, suggesting that it the hydrolysis process not only able to remove amorphous phase but also eliminate some part of the cellulose crystalline region. Similar result was reported that hydrolysis of cellulose not only dissolves the amorphous regions, but also some crystalline regions (Mandal & Chakrabarty, 2011).

Fig 3: X-ray diffractograms of 2.5N MCC, 3.5N MCC and 4.5 N MCC.
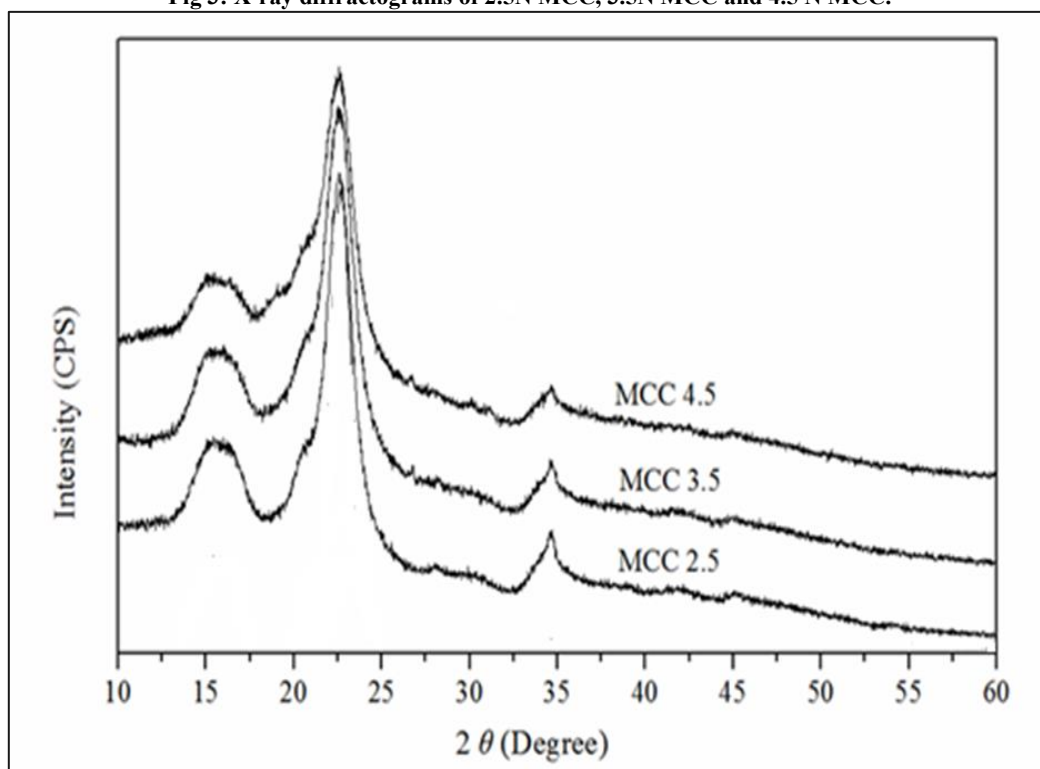

Fig. 3 and Table 2 showed that, the 2.5 N MCC displayed the highest crystallinity value as compared 3.5 N MCC and 4.5 N MCC. The highest crystallinity value could be due to the removal of the amorphous regions of cellulose by acid hydrolysis which stimulated the hydrolytic cleavage of glycosidic bonds, and finally produce the individual crystallites (Haafiz et al., 2013; Li et al., 2009; Trache et al., 2016). The acid hydrolysis however, not only removed the amorphous region but also eliminate some of the crystalline region, therefore, the crystallinity index slightly decreased at high acid concentration (3.5 N and 4.5 N). It interesting to note that all samples displayed a single peak at theta 22.6º which are representing of cellulose I polymorph structure. It can be concluded that the different acid concentration did not affect the cellulose polymorph. Similar observation reported earlier by Haafiz et al. (2013) and Rosa et al. (2012), the thermal properties however get effected as discussed in detail in next section.

Table 2: Crystallinity of all samples MCC.

Sample(HCl)	Crystallinity %
2.5N	68%

3.5N	60%
4.5N	50%

## 4.4 Thermogravimetric analysis

In order to identify their applicability of filler to be used in the bio-composite processing especially at high range temperatures, investigating the thermal properties of the reinforcement filler is vital (Alemdar & Sain, 2008b; Haafiz et al., 2013). The thermal stability of MCC samples after hydrolysis process were studied by thermogravimetric analysis (TGA) and derivative thermogram (DTG) are presented in Fig. 3(a & b) and the degradation temperature at 20 % ($T_{20\%}$) and 50 % ($T_{50\%}$) weight loss were summarized in Table 3.

Table 3: Thermal properties of MCC samples.

Samples	Degradation Temperature (ºC)		Residual weight % at 600 °C	DTG Peak Temp (°C) T $_{max}$
	$T_{20\%}$	$T_{50\%}$		
MCC 2.5	328	349	11	350
MCC 3.5	323	347	10	350
MCC 4.5	307	339	13	342

The TGA curves for all MCC samples show two stages of thermal degradation, in Fig. 4 the first degradation stage in the range 50–150 °C due to the removal of water from the samples. Meanwhile the MCC samples show the second stage degradation in the range 250-400 °C due to the degradation process of cellulose and followed by the formation of char at 600°C (Haafiz et al., 2013; Hussin et al., 2016). From Fig. 4 it can be seen that at $T_{20\%}$ and $T_{50\%}$ degradations temperature, MCC obtained with 2.5 N HCl concentration exhibited better thermal stability with higher $T_{20\%}$, $T_{50\%}$ and $T_{max\%}$ degradation temperature 328°C, 349°C and 350°C respectively as compared to 3.5 N HCl and 4.5 N HCl as presented in Table 3. This could be due to the higher crystallinity of cellulose, which display higher thermal stability (Hussin et al., 2016; Kim, Eom, & Wada, 2010). This result can be related result discuss before on X-ray diffraction. The maximum decomposition temperature for MCC is presented in the derivative weight loss curve (Fig. 3b). The higher decomposition peak temperature of MCC is observed at 350°C, these are the degradation temperatures of cellulose. The cellulosic materials degrade at low to moderate temperatures as reported by (Jonoobi, Khazaeian, Tahir, Azry, & Oksman, 2011). Early degradation of hemicelluloses begins below 400°C followed by pyrolysis of lignin, depolymerization of cellulose, active flaming combustion and char oxidation (Haafiz et al., 2013).

Fig. 4: (a)TGA curves for 2.5 N MCC, 3.5 N MCC and 4.5 N MCC, and (b)DTG curves for 2.5 N MCC, 3.5 N MCC and 4.5 N MCC
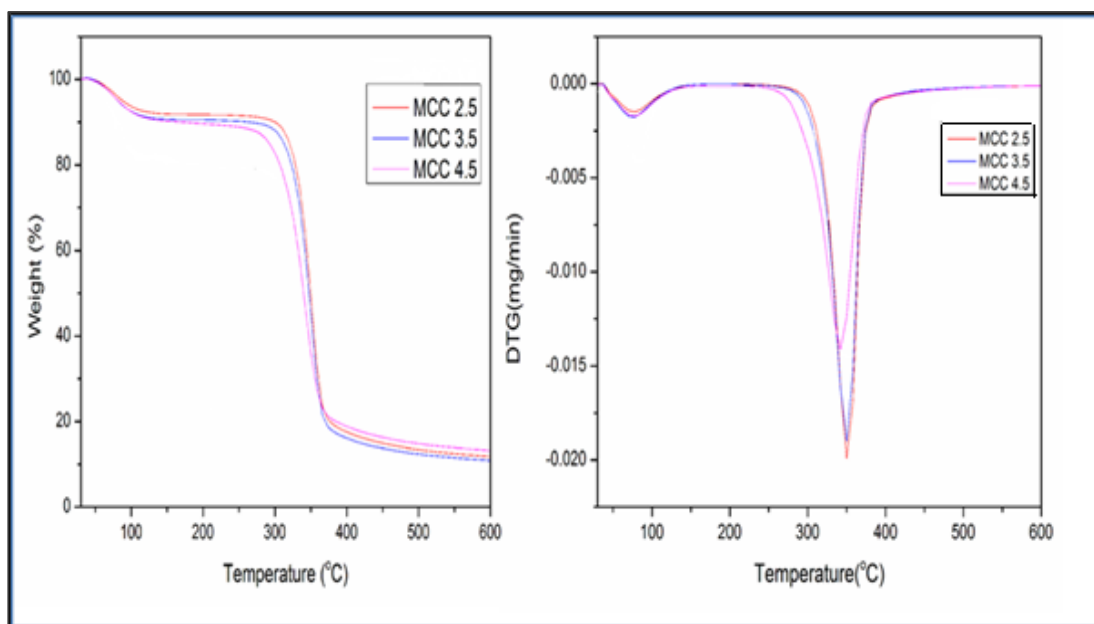
From the previous studies, Haafiz et al. (2013) reported high residual weight that means high char residue and Mandal and Chakrabarty (2011) reported the high char residue on sample is probably due on high crystalline cellulose which is flame resistant. From TGA result presented on Table 3 residual weight at 600°C, it shown all sample presented that considered as high char residue. In view of the above results, it was concluded that the MCC sample produced from OPEFB-pulp has good thermal stability and will be suitable to be used in the production of green bio-composites and MCC produced in 2.5 N HCl could be the best conditions.

5.0   CONCLUSIONS

MCC has been successfully isolated from OPEFB with different acid hydrolysis concentration. The results obtained from FT-IR analysis shows the chemical structure of the cellulosic fragments were not influenced by treatments as well as different in hydrolysis concentration. SEM analysis shows that the all sample MCC has a rough and compact surface structure morphological. Meanwhile from the XRD analysis revealed MCC produced from OPEFB was classified as cellulose I and from the results it can be concluded that the acid concentrations are inversely proportional to crystallinity index of MCC, where it decreases with increased in acid concentration. Based on these TGA result, it can be concluded that MCC with 2.5 N HCl has good thermal stability compared to others concentration acid and it has the potential to use in production of green filler biocomposites at higher range temperature. Based on this preliminary study in the acid concentration effect on the MCC produce, the detail optimization process will be carry out to find the best condition to produce MCC which will be the main challenge in this work.

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T.M. Hassan[a],
[a]*School of Industrial Technology,*
Universiti Sains Malaysia , 11800 Penang, Malaysia

M.K.Mohamad Haafiz[a*]
[a]*School of Industrial Technology,*
Universiti Sains Malaysia , 11800 Penang, Malaysia

 I.Mazlan[a],
[a]*School of Industrial Technology,*
Universiti Sains Malaysia , 11800 Penang, Malaysia

M.R Nurul Fazita[a],
[a]*School of Industrial Technology,*
Universiti Sains Malaysia , 11800 Penang, Malaysia

M.M.Marliana[b]
[b]*Department of Bioprocess and Polymer Engineering, Faculty of Chemical and Energy*
Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia

*Corresponding author. Address: Division of Bioresources, paper and coating, School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia. Tel.: +60 4 6532203; fax: +60 04-657 3678. E-mail address: mhaafiz@usm.my (M.K. Mohamad Haafiz)