

# Thermal Stability of Oil Palm Empty Fruit Bunch (OPEFB) Nanocrystalline Cellulose: Effects of post-treatment of oven drying and solvent exchange techniques

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**Abstract.** Nanocrystalline cellulose (NCC) from biomass is a promising material with huge potentials in various applications. A big challenge in its utilization is the agglomeration of the NCC's during processing due to hydrogen bonding among the cellulose chains when in close proximity to each other. Obtaining NCC's in a non-agglomerated and non-aqueous condition is challenging. In the present work NCC's was isolated from oil palm empty fruit bunch (OPEFB) using TEMPO-oxidation reaction method. To obtain non-agglomerated and non-aqueous products, the NCC's underwent post-treatment using oven drying (OD) and solvent exchanged (SE) techniques. The thermal stability of all samples was determined from TGA and DTG profiles whilst FTIR was used to analyze the chemical modifications that occurred under these conditions. NCC-SE has better thermal stability than the NCC-OD and its on-set degradation temperature and residue are also higher. FTIR analysis shows that NCC-SE has a slightly different chemical composition whereby the absorption band at  $1300\text{ cm}^{-1}$  (due to C-O symmetric stretching) is absent as compared to NCC-OD indicating that in NCC-SE the carboxylate group is in acid form which contribute to its thermal stability. (*Keyword: Nanocrystalline cellulose, oil palm empty fruit bunch, thermal stability, oven drying, solvent exchange*)

## 1. Introduction

Cellulose is the world most abundant natural renewable biodegradable polymer and has been predicted that globally around  $10^{12}$  tons are synthesized and destroyed every year [1]. The use of non biomaterial will cause a serious environmental problem since they are not easily degraded in the environment after use. Many studies have shown that cellulose nanoparticles could be used as filler to improve mechanical and barrier properties of biocomposites. Growing interest in nanocomposites has been related to several



reasons, among them are possible to design and create new materials and structures with exceptional flexibility and physical properties, almost free of defects when used as nanoscale fillers, and presenting a large volume of interfacing matrix material due to high specific surface area. For reinforcement applications, however, cellulose nano or microfibrils present some disadvantages, for instance, high moisture absorption, poor wettability, incompatibility with most of polymeric matrices, and limitation of processing temperature.

Cellulose can be extracted from natural fibers and through systematic approach it can be converted to produce cellulose nanoparticles. There are various mechanical and chemical treatments offered depending on the source of lignocellulosic and properties to be achieved. Properties of cellulosic fibers are strongly influenced by different sources of plant, part of plant [2]. Agro-based material such as plant fibers is an example that is abundantly available in nature and more often are in the form of agro waste. Malaysia and Indonesia have abundance of this agro waste which is obtained from the oil palm (OP) industry of which the empty fruit bunch (EFB) is the largest available. Oil palm biomass comprise of 45-70% complex carbohydrate cellulose and hemicellulose. Therefore, this cheap and abundant biomass could compete with other plant biomass to produce cellulose microfibrils or microfibrils at competitive price.

One of the most important fields of cellulose application in composite material is as reinforcement of biopolymer matrix [3]. However, certain drawbacks of the application are incompatibility with the hydrophobic biopolymer matrix, especially during processing it tend to form aggregates and water-swelling nature of cellulose [4]. Some research has recently stated that the addition of renewable and high biodegradable fillers like cellulose or cellulose derivatives could optimize cost performance balance and improve the mechanical and thermal behaviors [5]. More recently, there has been an increase use of cellulose nanowhiskers or nanocrystals as the load bearing constituent in developments in new and inexpensive biodegradable materials due to their high aspect ratio, good mechanical properties [6] and fully degradable and renewable character. Some of biopolymer or biocomposite has low thermal stability, and also still limited and high production cost, therefore the use of cellulose, especially in nano size and crystalline form has a good potential to become the reinforcement [7]

The thermal properties are important to investigate in order to know the material application for biocomposite processing at high temperature [8]. Most of biocomposite was in the nonpolar form and hydrophobic that very good in water resistant properties, but weak in the thermal resistance, heat distortion temperature and rate of crystallization. Therefore the use of nano filler is potential to overcome the weakness of 'those' properties [9]. Some of researches have been reported one of biopolymer such as PLA low thermal properties, toughness, water vapor than gas barrier are inferior to those non biopolymers [10-12]. The challenge of crystalline nano fiber (CNF) used in industrial is to overcome the weak capability in hydrophobic material in order to enhance the dispersion and to increase the stress transfer towards the matrix. Most of the bio-polymeric or biocomposite are non-polar that cannot directly use NCC suspension in very polar or hydrophilic properties. Some research related to drying of NCC has been reported [13-16]. But NCC mostly in the form in water suspension and the use of the NCC as reinforcing is in solid state and suspension form also inconvenient during transportation. The problem is NCC tend to agglomeration during drying process and difficult to redisperse. Meanwhile the drying of NCC also has potential for next process and easier handling and reuse as a filler. Therefore the aim of this work is to study the thermal behavior of dried NCC as a reinforcement, heat barrier potential to overcome the weak thermal properties in most biocomposites. The NCC is prepared from OPEFB microcrystalline cellulose via the TEMPO-oxidation reaction technique and later underwent post-treatments using the oven drying and solvent exchange methods.

## 2. Experimental

### 2.1 Material

Oil Palm Empty Fruit Bunch (OPEFB) was obtained from SABUTEK Company, Perak, Malaysia while 4-acetamido-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) procured from Sigma Aldrich (USA). All other chemicals in the experiment were purchased from QReC (Malaysia).

### 2.2 Preparation of Totally Chlorine Free Bleached OPEFB Pulp and OPEFB Microcrystalline Cellulose

OPEFB fiber as raw material was cut into 4-5 cm lengths, then washed and dried and kept in polyethylene bags. Before pulping, OPEFB was first pre-hydrolyzed with water and later pulped using 26% NaOH at a temperature of 170°C for 2 h [17]. The obtained pulp is further bleached using a totally chlorine free (TCF) sequences of oxygen (O), ozone (Z) and peroxide (P) [18]. The final TCF OPEFB pulp has a Kappa no. of 1.4. Microcrystalline cellulose (MCC) was prepared according to Wanrosli et al. (2011). Briefly, the TCF OPEFB pulp was hydrolyzed with 2.5M HCl at a solid liquor ratio of 1:20 and refluxing at 105±2°C for 15 min. The MCC was thoroughly washed with distilled water before air drying. MCC powder was obtained by grinding the sample in a ball mill and subsequently kept in a desiccator.

### 2.3 Isolation of NCC

Nanocrystalline cellulose (NCC) was prepared using TEMPO- oxidation reaction [20]. 5 g of MCC was reacted with 4-acetamido-TEMPO (2,2,6,6-tetramethylpiperidin -1-oxyl) 98% (0.11 mmol/g) and sodium bromide (0.617 mmol/g) in 500 ml distilled water in an ultrasonic bath (Model 8510, Branson) for 4 hours. In the post-oxidation step, the mixture was reacted NaClO<sub>2</sub> at 70°C in water bath for 1 hour. The mixture was then washed with distilled water and unfibrillated with Sonicator (Sonifier 450, Branson). The suspension was centrifuged at 3500 rpm and the upper phase was separated as the NCC product.

### 2.4 Drying and solvent exchange of NCC

The Oven Drying (OD) process was conducted at 50°C for 24 hours in an air circulated oven dryer. Dried NCC was gently crushed with mortar and sieved to obtain uniform size. For solvent exchange, the procedure of Fujisawa et al (2013) was followed. NCC suspension was mixed with 1 M HCl to obtain pH 2, then stirred at slow speed at room temperature for 30 minutes. Then the mixture was washed with water and solvent exchanged to ethanol.

### 2.5 Characterization

#### 2.5.1 TGA

The thermal stability was carried out using A Mettler TG 50 Module equipped to Mettler TC 11 4000 thermal Analyzer (USA). The specimen was analyzed in a nitrogen atmosphere at a flow rate 50 ml/min. The temperature was set from 30 to 800°C at a rate of 20°C per minute.

#### 2.5.2 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

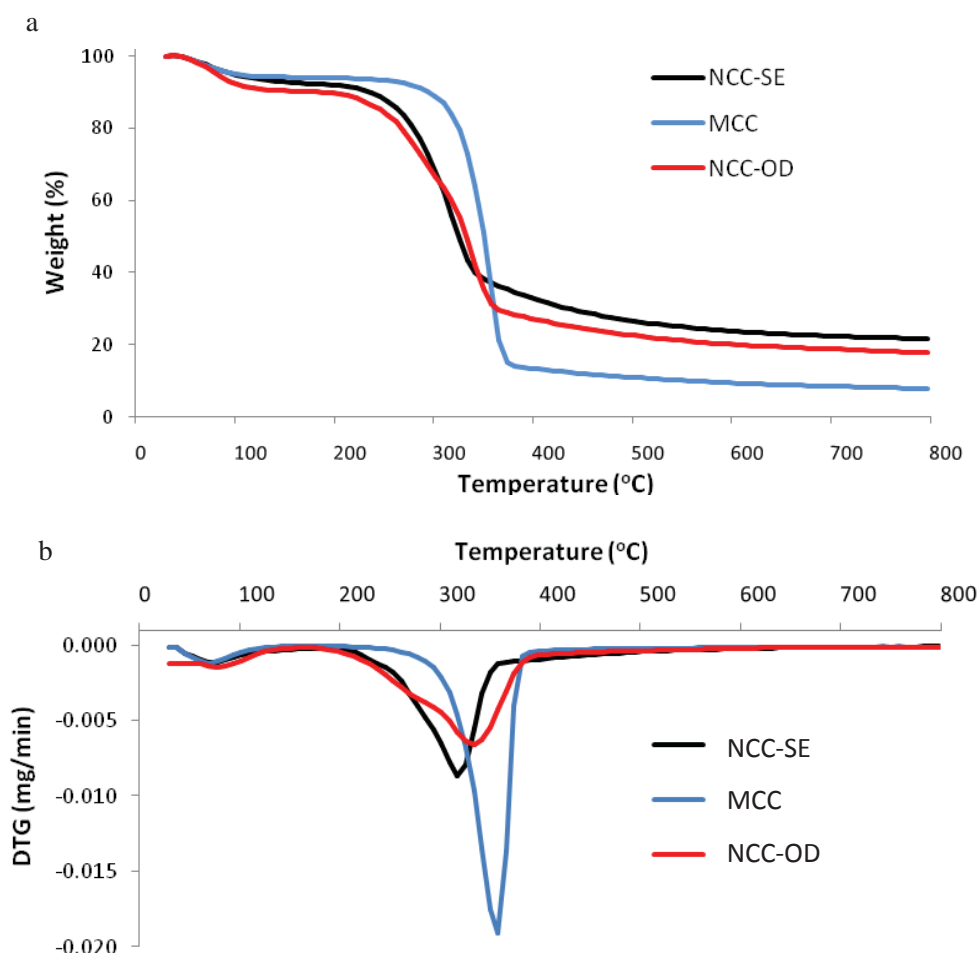
FTIR analysis was carried out using a FTIR spectrometer (Nicolet iS10, Thermo Scientific). The films were cut around 3 cm and directly loaded for analyzing the transmittal spectra within the range of 4000–400 cm<sup>-1</sup>.

## 3. Results and Discussion

### 3.1 Thermogravimetric analysis

Thermal properties of NCC-OD, NCC-SE and MCC, with the later as a control, were studied by thermogravimetric (TGA) and derivative thermogram (DTG). The TGA and DTG curves for all samples are shown in Figure 1. The thermal condition of degradation at T<sub>on</sub>, T (50%) and the residual weight at

400°C and 700°C are presented in Table 1. A small weight loss for all samples occurs between 40-70°C which is attributed to the removal of absorbed water in cellulose [22]. As depicted in 1, the NCC-OD sample initiates a slightly more pronounced degradation process at around 255°C while for NCC-SE a more pronounced degradation process occurs at 290°C. The extremely high slope for all samples in the range of 240°C to 350°C is due to the high degradation or decomposition step of the cellulose. In this stage the cleavage of the glycosidic linkages of cellulose reduces the polymerization degree leading to the formation of CO<sub>2</sub>, H<sub>2</sub>O and a variety of hydrocarbon derivatives [23]. It can also be seen that based on weight percentage as a function of temperature, the first initial mass loss portion was found between 25°C to about 125°C. No thermal degradation occurred in this region. The loss of weight in this region is about 5-10%, which is mainly caused by evaporation of loosely bound moisture on the surface of the NCC's [15, 24, 25].



**Figure 1.** Typical TGA (a) and DTG (b) of MCC, NCC-OD and NCC-SE from palm oil empty fruit bunch

It can be seen that both processes of oven drying and solvent exchange treatment affected the thermal stability of NCC. NCC-OD and NCC-SE both have a lower degradation temperature ( $T_{on}$ ) compared to MCC.

as a control. However, the NCC - SE has better thermal stability than the NCC-OD. This higher decomposition temperature is caused by the presence of free carboxylic group that is formed during the solvent exchange process. During the isolation of NCC using TEMPO-oxidation, the hydroxyl groups were replaced by the carboxylate groups. In the solvent exchange process (because of the acid condition where the pH was set to 2 by the addition of 1 M HCl at room temperature) these carboxylate groups were converted to free carboxyl groups [16, 21] leading to a viscous and flowable gel as compared to only a dispersible state for unprocessed NCC. On the other hand, NCC that is processed by oven drying is still in the form of sodium carboxylate salt. Thus, this different content of carboxylic group is responsible for the thermal behavior differences of both NCC.

It was also reported that the carbonation of the sodium carboxylic group degrade at a lower temperature than that of cellulose. Similar study also found for carboxymethyl cellulose that contain of sodium carboxyl groups [26]. The pathway of thermal decomposition is influenced by many chemical and physical factors such as temperature, type of atmosphere, size and texture of cellulose, and crystallinity [27].

Comparatively, MCC has a higher degradation behavior temperature than both NCC-OD and NCC-SE. The maximum of the DTG peak of MCC ( $T_{max} = 358^{\circ}\text{C}$ ) is higher than the NCC-OD and NCC-SE of  $334^{\circ}\text{C}$  and  $318^{\circ}\text{C}$  respectively. This is probably due to the difference of the outer surface structure of each MCC and NCC resulting from the different processes that were used to prepare the materials. The NCC in this research was produced directly from OPEFB TCF pulp whereas MCC was produced by acid hydrolysis from the pulp with HCl. It has been reported that the chloride anions contributed to these differences because they affected the swelling of cellulose chains and breakage of hydrogen bonds in cellulose [28]. Hydrolysis process did not only dissolve the amorphous region, but also some crystalline region that caused more vulnerable degradation as temperature increased [29, 30]. There are two different degradation mechanism in cellulose. First is dehydration of cellulose by an endothermic process to form dehydrocellulose at  $200\text{--}280^{\circ}\text{C}$  and second is depolymerization of cellulose in competition with dehydration between  $280\text{--}340^{\circ}\text{C}$  that yield the volatile matter [15]. The mechanism of depolymerization occurs in very fast rate as shown very big slope on this stage. Decomposition of dehydrocellulose formed into gases and char residue becomes dominant at about  $320^{\circ}\text{C}$ . At temperature above  $500^{\circ}\text{C}$ , the levoglucosan breakdown to produce varying low molecular weight, including hydrocarbons and hydrogen as well as  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [15, 32].

**Table 1.** Thermal properties of MCC, NCC-OD and NCC-SE

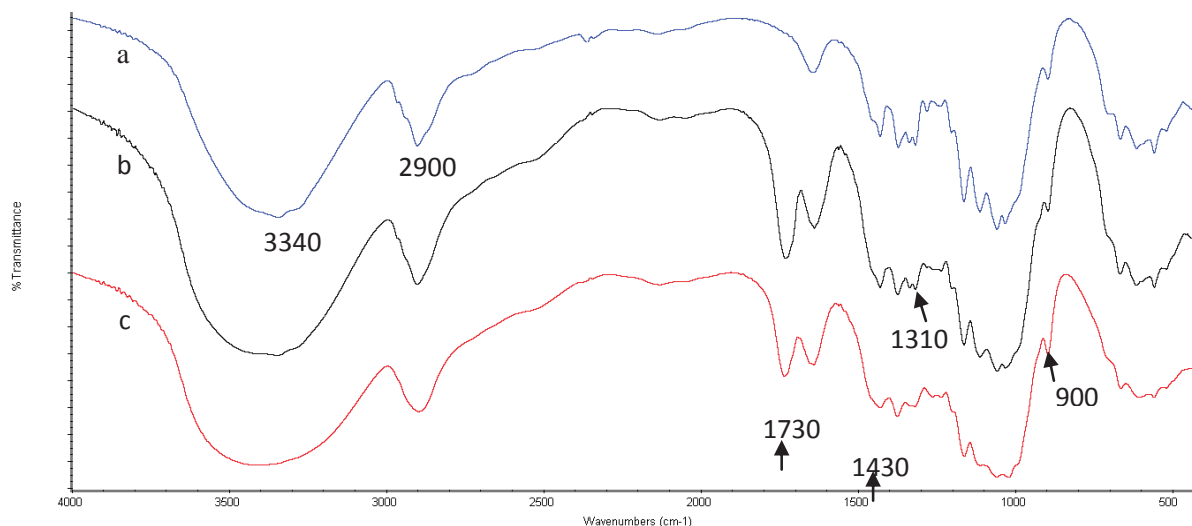
Samples	Degradation temperature ( $^{\circ}\text{C}$ )		DTG Peak Temp ( $^{\circ}\text{C}$ )	Residue weight (wt %)	
	$T_{on}$	$T_{(50\%)}$	$T_{max}$	$T_{400}$	$T_{700}$
MCC	327.96	350.64	358	13.44	8.49
NCC/OD	254.40	332.83	334	27.20	18.85
NCC/SE	289.05	324.69	318	32.88	22.42

The NNC-SE and NCC-OD also has a higher residue at  $T_{400}$  and  $T_{700}$  compare to MCC. Similar trends were also reported from OPEFB nanocellulose whisker [32]. Moreover the NCC-SE has a higher residue at  $T_{400}$  and  $T_{700}$  (32.88% and 22.42%) compared to NCC-OD (22.42% and 18.85%). Again the probable reason for this observation is due to the presence of carboxylic form in NCC-SE as compared to the

carboxylate form in NCC-OD. Other factors that can also affect the thermal degradation behavior are sonication time and temperature [8], both of which will be dealt in subsequent publications. It is interesting to note that in spite of the fact that both NCC-SE and NCC-OD has a lower thermal stability as compared to NCC-OD as seen in Fig.1 and Table 1, the char fraction (residue that remains after 700 °C) of the former is much higher (23 % & 19 % and 8% respectively). It is possible that the incorporation of the carboxylate functionality resulting from the TEMPO-oxidation has the flame-retardant effect which can have positive implications as a potential as a filler in lower thermal retardants in biopolimeric matrix [7].

### 3.2 FTIR Analysis

The FTIR spectroscopy is an essential technique for tracking chemical changes of the cellulose before and after treatment. The FITR spectra of MCC and NCC were presented in Figure 2. The vibrational assignments are summarized in Table 2.



**Figure 2.** Typical FTIR spectra obtained from (a) MCC, (b) NCC-OD and (c) NCC-SE

In Figure 2, the broad peak for all samples observed in the region 3300-3400  $\text{cm}^{-1}$  is due to stretching vibration of O-H (Hydroxyl) groups [34]. The absorption around 2900  $\text{cm}^{-1}$  is attributed to stretching of C-H groups of cellulose [25, 35, 36]. When spectra of MCC are compared with those of NCC-OD and NCC-SE, the most different is a new appearance of the vibration peak observed at 1730  $\text{cm}^{-1}$  from spectra on NCC-OD and NCC-SE. The appearance of this peak is indicated by the C=O stretching of carboxylic group of TEMPO-oxidation nanocrystalline cellulose [37]. Meanwhile the MCC from OPEFB using HCl showed no C=O bond formation. Similar result were also reported by Wanrosli et al. (2011) that compares OPEFB MCC with pure cellulose before converting to cellulose phosphate. Comparatively, this C=O peak is lower in NCC-SE than NCC-OD which is a consequence of pH reduction causing the presence of the free carboxylic group during solvent technique. This observation suggests that the higher content of



carboxyl content in NCC-OD contributed higher thermal retardant in NCC-SE and the absence C=O bond MCC will cause the lower thermal retardant compare to both NCC post oxidation technique.

**Table 2.** FITR Spectral peak assignment for (a) MCC, (b) NCC-OD, (c) NCC-SE

Peak frequency (cm <sup>-1</sup> )			
Peak assignment	MCC	NCC/OD	NCC/SE
OH Bending	3343	3345	3413
CH <sub>2</sub> Group Bending	2901	2901	2898
C=O stretching	-	1732	1735
O-H stretching	1640	1639	1641
CH <sub>2</sub> Bending	1430	1430	1430
C-O symmetric stretching	1318	1318	-
C-O-C Stretching	1113	1164	1163
C-H	897	898	897

#### 4. Conclusion

Nanocrystalline cellulose (NCC) was obtained from oil palm empty fruit bunch (OPEFB) by TEMPO oxidation. The resulting suspension was then dried or solvent exchanged as the way to prepare NCC for the next processing. In this work, the effect of drying and solvent exchange method on thermal stability of the OPEFB-NCC was studied. It reveals that the choice of between drying process and solvent exchange treatment of NCC determined thermal stability of NCC. The NCC prepared by either method has a lower degradation temperature ( $T_{on}$ ) compare to MCC as a control. However, their thermal resistance properties are better than MCC as revealed from lower thermal degradation rate and higher residues. The NCC-SE has better thermal stability compared to NCC-OD due to the presence of the free carboxylic group during solvent exchange process, resulted from a reduction in the carboxyl group in NCC. FTIR spectra revealed such chemical change of the cellulose before and after different treatment. In addition to its function as filler, the result suggests NCC could contribute to better thermal properties of biocomposite. Future works will include development of the NCC as a filler of biocomposite by improving its interaction with the polymeric matrix without losing its thermal resistance properties.

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