

# POLYLACTIC ACID NANOCOMPOSITES REINFORCED WITH CELLULOSE NANOWHISKERS ISOLATED FROM OIL PALM EMPTY FRUIT BUNCH

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## Abstract

*The objective of this study is to prepare polylactid acid (PLA) nanocomposites filled with cellulose nanowhiskers (CNW) isolated from oil palm empty fruit bunch microcrystalline cellulose (MCC) by using chemical swelling treatment. The produced cellulose nanowhiskers (CNW) displayed nanoscale structure as revealed by transmission electron microscopy with 88 % crystallinity index. Meanwhile, the nanocomposites films were prepared by incorporating 1, 3 and 5 part per hundred of the obtained CNW into the PLA matrix by solution casting method. The tensile strength and Young's modulus of nanocomposites improved with addition of CNW. However the elongation at break decreased dramatically with the increase of CNW loading. Interestingly the additions of CNW into PLA significantly increased the thermal stability of PLA nanocomposites.*

## 1. Introduction

Due to growing concerns over sustainability and environmental protection, nowadays efforts have been emphasized to produce biodegradable polymer composites based on, for example, poly(lactic acid) [1] poly(hydroxybutyrate) [2] starch [3], cellulose [4], and poly(hydroxyoctanoate) [5]. Among this one of the most promising candidates for biodegradable polymers is polylactic acid (PLA). PLA is bio-degradable thermoplastic aliphatic polyester which can be derived from renewable resources such as starch [6,7]. It can be used in various fields, such as industrial packaging, biomedical applications, such as tissue engineering, drug delivery, and dental, sanitary products and diapers, as well as in automotive applications [8]. Although PLA is an eco-friendly bioplastic with good biocompatibility, poor hardness, low thermal stability, slow degradation, hydrophobicity and medium gas barrier properties limit its application [8]. In order to overcome these inherent shortcomings reinforcing fillers are now incorporated to improve these properties while maintaining their inherently good properties such as transparency and biodegradability [8,9].

The used of nanoclays fillers as reinforcement for polymeric materials have been extensively studied. In order to produce a fully degradable and renewable nanocomposite, substituting the

clay with cellulose based reinforcement is the best alternative [8,9] As the main structural component in the cell walls of all plants, cellulose is a fibrous, tough, water-insoluble, widely available, low energy consumption and is widely considered to be the most abundant biodegraded polymer on the planet which has even good mechanical properties as compared to other inorganic reinforcing fillers [10,11]. Another advantage of cellulose is its fibrous nature which can align and orient along matrix axis improving mechanical properties with less weight compared to clay based fillers. It also has high sound attenuation and comparatively easy processability due to its nonabrasive nature, allows high filling levels which in turn results in significant cost savings [12]. In nature, the cellulose molecular chains are biosynthesized and self-assembled into microfibrils, which are composed of crystalline and amorphous domains [13]. These aggregated cellulose molecules are stabilized laterally by hydrogen bonds between the hydroxyl groups and oxygens of adjacent molecules [13]. The amorphous regions of native cellulose can be readily hydrolysed, with almost no weight loss, when subjected to strong acid hydrolysis [6]. Typically when wood sources are used, the particles of hydrolysed cellulose obtained are ~100–300 nm in length and ~3–10 nm in width [14]. These nanoparticles are referred to as "nanocrystalline cellulose" or "cellulose nanowhiskers" because of their nanoscale cross sectional dimension [15].

Cellulose nanowhiskers (CNW) are renewable and biocompatible nanomaterials that have evoked much interest in the research world because of its versatility in various applications (e.g. green nanocomposites, tissue engineering scaffolds) [16]. CNW are highly ordered crystalline regions of cellulosic materials. Isolated nanowhiskers are rod shaped nanocrystals that have unique electrical, optical, magnetic and conductive properties [14]. Even though CNW can be obtained from a variety of natural resources such as hemp, wheat straw, and wood pulp by acid hydrolysis, these nano entities however are not as commercially popular as other nanomaterials like carbon nanotubes. One major challenge in the use of CNW in commercial applications is their limited availability and low yield when isolated from natural resources [14]. This study is the first attempt to isolate CNW from the microcrystalline cellulose (MCC) produced from oil palm empty fruit bunch total chlorine free pulp by chemical swelling method using *N,N*-dimethylacetamide (DMAc) containing 0.5 % LiCl solutions as swelling agent. The obtained CNW was then used as a reinforcing element in order to assess the value of this filler to enhance the thermal and mechanical properties of the PLA matrix. To the best of our knowledge, no study on production of CNW from oil palm biomass MCC has been reported in the open literature and use as reinforcement filler in PLA. From the results, CNW exhibit novel significant potential in coatings, membranes, and food agro based packaging as well as in the automotive applications.

## 2. Experimental

### 2.1 Material

Polylactic (NatureWork<sup>TM</sup> PLA 300ID) in pellet form was obtained from NatureWork® LLC, Minnetonka, MN USA. It has a specific gravity 1.24 g/cm<sup>3</sup> and melt flow index (MFI) around 15 g/10min (190 °C/2.16 kg). A cellulose nanowhisiker (CNW) was produced from oil palm empty fruit bunch (OPEFB) microcrystalline cellulose as the reinforcement filler. All chemicals were used as received and were secured from Merck, Malaysia.

## 2.2 Swelling and separation of cellulose nanowhiskers

MCC was swelled and partly separated to whiskers by chemical and ultra sonification treatments using same method described by Pereda et al.[17] based on original procedures described by Oksman et al. [18]. A *N, N*-dimethylacetamide (DMAc) with 0.5 % LiCl solutions was used as swelling agent. The initial concentration of MCC in DMAc/LiCl was 10 wt %. MCC was agitated using a mechanical stirrer inside the water bath for 12 hours at 70 °C. Then the slightly swelled particles were sonicated in Branson 2510 bransonic bath for 3 h over a period of 5 days with long intervals between each sonication treatment, to separate the CNW. The resultant CNW were repeatedly washed with distilled water then freeze-dried.

## 2.3 Preparation of PLA and PLA/CNW nanocomposite

A 10 wt % solution of PLA pellets in chloroform was prepared by stirring the solution inside the water bath at 60 °C for 2 hours until the pellets were fully dissolved [8]. The PLA solution was immediately cast on the clean glass plates and left for the solvent to evaporate at ambient temperature for 48 hours. The thickness of the cast solution was approximately 100 µm and noted as pure PLA. To prepare the PLA/CNW nanocomposite, 10 wt % solution of PLA was mixed with different amounts of CNW (1, 3 and 5 phr) and the mixture was kept at 60 °C with strong agitation until the PLA pellets were fully dissolved. The nano filler used in this stage was in suspension form. Therefore solvent exchange was done through centrifugation by using Universal 32 Hettich (Newport Pagnell, England). In this stage water was exchanged with acetone and acetone was exchanged with chloroform. The filler was then sonicated in a Branson 2510 bransonic bath for 5 minutes to make sure the CNW is dispersed homogenously inside the chloroform. The dispersed CNW-S was then transferred into PLA with strong agitation approximately 2 hours. The dissolved PLA containing CNW was then sonicated for another 5 minutes. The solution was then casted on a clean glass plate. The nanocomposite with approximately 100 µm in thickness was obtained by solvent evaporation at surrounding temperature for 48 hours before analysis. The PLA nanocomposites were designated as PLA/CNW1, PLA/CNW3 and PLA/CNW5.

## 3 Characterization

### 3.1 X-ray diffraction

X-ray diffraction (XRD) analysis was carried out to study the crystallinity of the samples using an X'Pert X-ray diffractometer (SIEMENS XRD D5000) and Ni-filtered Cu K $\alpha$  radiation at an angular incidence of 5° to 50° ( $2\theta$  angle range). The operating voltage and current were 40 kV and 50 mA, respectively. The crystallinity of the samples was calculated from diffraction intensity data using the empirical method for native cellulose [19]. The crystalline- to-amorphous ratio of materials was determined using Eq. (1).

$$C_{cr}(\%) = [(I_{200} - I_{am})/I_{200}] * 100\% \quad (1)$$

### 3.2 Transmission electron microscopy

Transmission electron microscopy (TEM) model LEOLIBRA was used to observe the size distribution of the sample specimens.

### 3.3 Thermogravimetric analysis

The samples were characterized to determine their thermal stability using a thermogravimetric analyzer (TGA) model 2050, (TA Instruments, New Castle, DE). The specimens were scanned from 30°C to 600°C at the rate of 10°C/min and analyses were performed under a nitrogen gas flow.

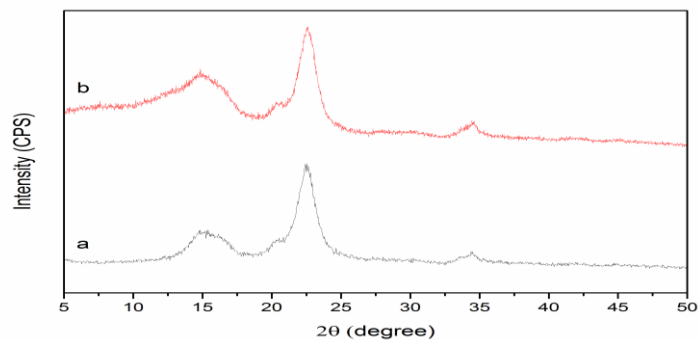
### 3.4 Mechanical test

Mechanical test was done using the Instron 4400 Universal Tester to measure the tensile strength at the point of breakage for each sample. Tensile tests were carried out at room temperature, according to the ASTM D882 type V. A fixed crosshead rate of 10 mm/min was utilized in all cases and the results were taken as an average of five tests.

## 4. Result and Discussion

### 4.1 X-ray X-ray diffraction

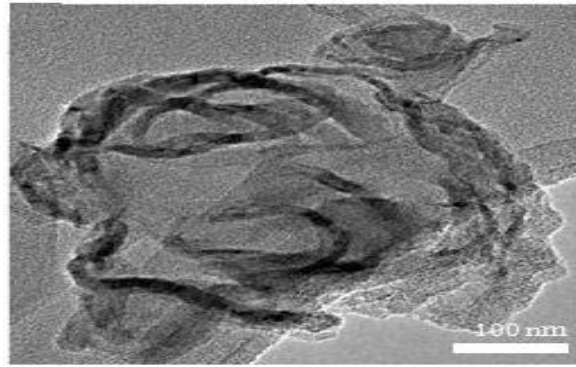
The x-ray diffraction (XRD) patterns of MCC and CNW are presented in Figure 1. The crystallinity value of CNW increased slightly to 88 % (Figure. 1a), as compared to MCC, which exhibited 87 % crystallinity (Figure. 1b). An increase in the crystallinity is related to increases in the rigidity of the cellulose structure, which can lead to a higher tensile strength of fibers [18]. XRD diffraction data suggested the both samples were highly crystalline native Cellulose I, with no Cellulose II present; indicated by the absence of the doublet located at 22.6° [19]. CNW produced from chemical swelling method in our study possess a higher degree of crystallinity compared to nanocellulose produced from OPEFB by a chemo-mechanical technique (69 %) [20].



**Figure 1.** X-Ray diffractograms from a) MCC and b) CNW

### 4.2 Transmission electron microscopy

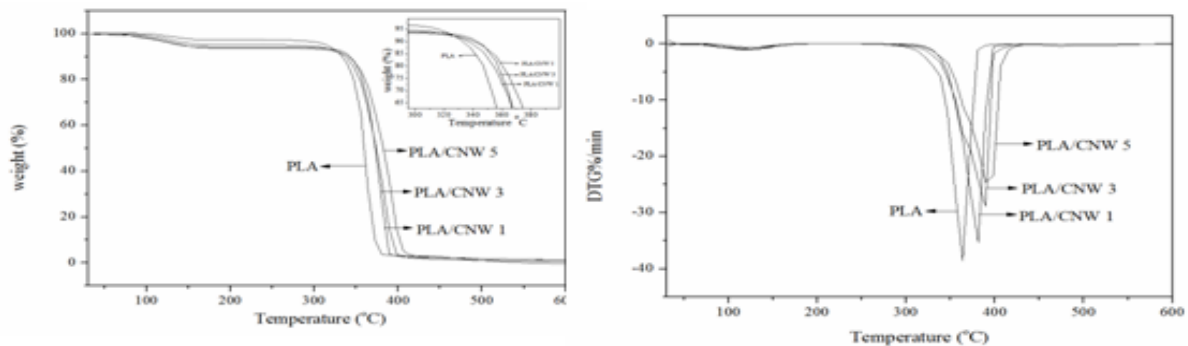
The morphology of CNW was investigated by transmission electron microscopy (TEM). TEM technique was used to observe the dispersion of individual crystallites or whiskers and the morphology of MCC after chemical swelling treatment. Typical TEM images of CNW are shown in Figure. 2. The figure shows that the separation of whiskers in nanometer scale. The size of whiskers was estimated to be less than 20 nm width and 300nm in length.



**Figure 2.** Typical transmission electron microscopy of CNW

#### 4.3 Thermogravimetric analysis

In order to investigate the thermal performance of the PLA and PLA/CNW nanocomposites thermogravimetric analysis (TGA) were performed. The TGA and DTG curve reveal the weight loss of material when heated. Figure. 3 shows the TGA (weight % vs. temperature°C) and DTG (derivative thermograms) of pure PLA and PLA/CNW nanocomposites with various CNW contents (phr). The value of thermal behavior of this materials were summarized in Table 1, using the on-set decomposition temperatures ( $T_{on}$ ) and temperature at which various weight losses of the samples were achieved.



**Figure 3.** Typical TGA and DTG curves for PLA and PLA/CNW nanocomposites

Figure.3 depicts that all samples showed initial weight loss at about 100°C to 150°C. The weight loss was resulted from evaporation of moisture or other volatiles inside the materials and similar observation were observed earlier by Hossain et al. [21]. Figure.3 clearly shows an improvement in thermal stability of the PLA/CNW as compared to pure PLA. It can be seen that the onset decomposition temperature ( $T_{on}$ ), for all PLA/CNW nanocomposite were higher than pure PLA (295.93°C) as well as the  $T_{10\%}$  and  $T_{50\%}$  decomposition temperatures which indicated the presence of a certain amount of CNW can improve thermostability of the nanocomposite. On the other hand this behaviour probably may be due to the highest decomposition temperature of CNW [22]. Apparently from Table 1 at temperature 600°C both PLA/CNW nanocomposites displayed highest char residue as compared to pure PLA which degrade without forming any residue, as the quantity of the CNW increased the residue was also increased due to very high thermal stability of the CNW. Beside that this behavior is probably due to the presence of a higher amount of crystalline cellulose I from CNW produced which has an intrinsically flame resistant property. Furthermore the improvement in

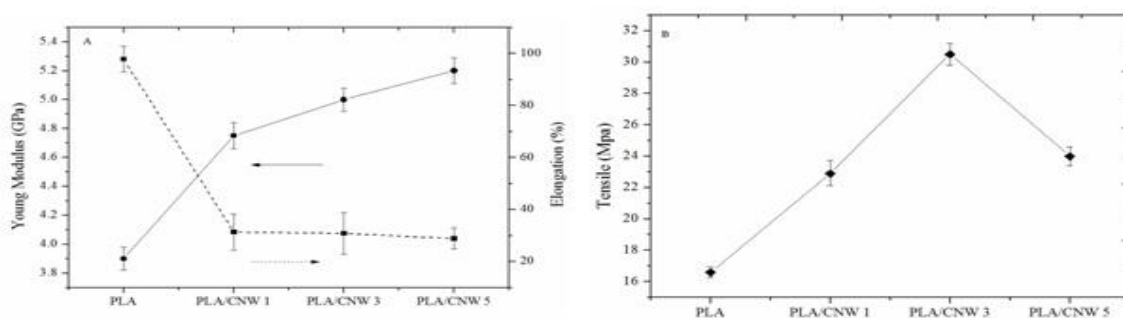
thermal stability could be attributed to uniform dispersion of nanofiller in PLA matrix. Similar conclusions were arrived from other studies [23]. The dispersion of CNW in PLA matrix is discussed in detail in microscope analysis section. From the above result it can be concluded that incorporation of CNW is able to induce the thermal stability of pure PLA. The maximum decomposition ( $T_{max}$ ) for PLA/CNW shift to higher temperature as the content of filler increased suggest that their interaction might have significant influence on improving thermal properties of PLA.

Formulation	Degradation temperature (°C)				Residual weight % 600 °C
	$T_{on}$	$T_{10}$	$T_{50}$	$T_{max}$	
PLA	295.93	331.99	359.57	363.62	0
PLA/CNW 1	332.86	341.18	373.37	381.82	0.61
PLA/CNW 3	328.84	334.71	374.86	389.48	1.23
PLA/CNW 5	338.8	344.07	382.92	390.91	1.29

**Table 1** Thermal properties of PLA and PLA/CNW nanocomposites.

### 4.3 Mechanical Properties

The tensile properties of materials are strongly influence by the microstructure and provides important information about the internal structure of material [24]. The effects of CNW loading on the tensile properties of pure PLA and PLA/CNW are shown in Figure. 4 (a and b).As reported in the literature that incorporation of microcrystalline cellulose from oil palm residues into the PLA matrix did not show any improvements in both tensile strength and elongation at break of the composites as compared to pure PLA [23] but the addition of CNW in PLA matrix showed the different behaviour in tensile strength properties. Apparently from the Figure (4b), the tensile strength for the nanocomposites showed enhancement with increasing in filler loading up to 3phr before decrease with additional of CNW. According to Wang et al [24] the improvement of nanocomposite could probably due to the good dispersion, stiffness and hydrogen bond between filler and polymer matrix. Due to this concept the filler-matrix interaction becomes more pronounced and better interfacial adhesion was formed between the CNW and PLA. Therefore the stress transfer to the filler, which the load bearing entity becomes efficient, gives the good interfacial bonding between CNW, and PLA which in consequent improves tensile strength. Similar conclusion as published early by other researchers Baheti et al. [25]. However more than 3 phr, the tensile strength of nanocomposite dropped which attributes to agglomeration of CNW in PLA. The aggregation of CNW could act as stress-centralized point and reduced surface area interaction between filler and matrix which leads to decrease in tensile strength of PLA.



**Figure 4.** Effect of CNW loading on tensile properties of PLA/CNW nanocomposites: a) showing the elongation (%) and young modulus, b) showing the tensile strength of nanocomposites

The addition of CNW filler in the PLA matrix also reveals that it gives the negative impact to the elongation at break for nanocomposite, where the elongation at break of PLA/CNW decrease dramatically as compared to the PLA as shown in Fig. 3a. Fig 3a clearly depicts that the elongation at break decreased gradually as the concentration of filler increased for all formulations rendered PLA more brittle where this observations may be attributed to the stiffening action of the filler by restricting the segmental chain movement of PLA during tensile testing. Similar result has been reported by Wang et al. [24] in cooperating cellulose whisker with soy protein thermoplastic. However from Figure 4a also shows that the Young's modulus of PLA/CNW increases with increasing of CNW loading which is explained by increase in hydrogen bonding, stiffening effect and high crystallinity index of the filler which is a typical characteristics filler/polymer composite. This observation is also in agreement with the FT-IR analysis for the nanocomposite as discussed early where the hydrogen bond interaction occurred between PLA and filler, which lead to increase the rigidity of PLA and consequently increase the modulus. Also high crystallinity index of CNW found may be attributed to the increase in the Young's modulus of PLA/CNW which is in agreement with results of Liu et al. [23].

## Conclusion

Cellulose nanowhiskers were successfully isolated from oil palm biomass MCC by chemical swelling treatment. The size of whiskers produced were found to be less than 20 nm width and 300nm in length with a relatively higher degree of crystallinity. Thermogravimetric analysis results indicated that the CNW able to enhance the thermal stability of PLA, showing higher degradation temperature ( $T_{10}$  and  $T_{50}$ ). Tensile properties of the cast nanocomposites showed the optimum tensile strength of PLA/CNW was at 3 phr CNW contents. The Young's modulus increased with increasing in CNW content. However, elongation at break decreased with additional of CNW content due to poor chain restriction movement. This study showed that CNW suitable as reinforcing agents in bio-renewable nanocomposites and has the potential to be utilized in automotive, medical and food packaging applications.

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