



## The Effect of Nanocrystalline Cellulose (NCC) Filler on Polylactic Acid (PLA) Nanocomposite Properties

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**Abstract.** This paper discusses the effect of nanocrystalline cellulose (NCC) when used as filler on polylactic acid (PLA)-based nanocomposites and on its mechanical properties and permeability. NCC was produced from commercial cellulose and another cellulose source, i.e. oil palm empty fruit bunch, by hydrolysis of microcrystalline cellulose with sulphuric acid and by oxidation with ammonium persulfate. The nanocomposites were made by adding nanocrystalline cellulose with varying compositions into PLA. A solvent casting method was used to produce a nanocomposite film with 5% v/v triacetin as a coupling agent. Both methods produced crystalline celluloses within the micro and nano range with mean particle size at 99.5 nm and 157.9 nm for the sulphuric acid hydrolysis and the ammonium persulfate oxidation method, respectively. The utilization of NCC as PLA composite filler increased the percentage of elongation at break with a highest percentage 19.02% for addition of 1% NCC filler. However, higher compositions of cellulosic filler resulted in a decreasing trend of tensile strength and elongation at break. Higher content of NCC filler in the PLA matrix increased the nanocomposite's water vapor permeability.

**Keywords:** *mechanical properties; nanocrystalline cellulose; oil palm empty fruit bunch; permeability; PLA-NCC nanocomposite;*

### 1 Introduction

The continuing increase of plastic usage in the world causes growing accumulation of waste because conventional petroleum-derived plastics cannot be naturally degraded in a relatively short time. To support a green environment, biodegradable or bioplastics derived from biomass have been extensively developed. One bioplastic material that is commonly used is polylactic acid (PLA), which can be derived from renewable resources [1]. However, PLA has a brittle characteristic, with elongation at break less than 10%, low toughness, and slow degradation. Hence, neat PLA should be supplemented with filler or other additives to get a material with high plastic

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deformation in high stress and a higher rate of degradation [2,3]. An alternative way to overcome the weaknesses of PLA is by synthesizing PLA nanocomposites, for example, clay-based, carbonaceous-based, metal/metallic (hydr)oxide-based PLA, or nanocellulose-based nanocomposites, among others [4]. The components of both PLA and nanocellulose can be synthesized specifically from biomass [5,6]. The use of filler such as NCC will significantly improve PLA's properties. Nanocrystalline cellulose (NCC) can be synthesized by oxidation with ammonium persulfate or by hydrolysis of microcrystalline cellulose (MCC) with sulphuric acid [5,7,8]. NCC has an extraordinary axial Young modulus, low density, high aspect ratio, high surface area, and modifiable surface properties due to reactive –OH side groups. Moreover, its dimension (nanoscale) opens a wide range of possible properties to be discovered [5].

However, PLA and cellulose are not compatible with each other. Therefore, a coupling agent, in this case triacetine, is used to form a better interaction between them. Further, adding cellulose as filler to the PLA matrix will increase its biodegradability. Using cellulose as filler in a biocomposite also increases its mechanical strength [9]. When the particle size of cellulose is at the nano-scale, it can significantly change the nanocomposite's properties, either physically or chemically [10]. Hence, nanocrystalline cellulose (NCC) can be used as alternative filler for the PLA matrix in order to overcome PLA's weaknesses.

Unfortunately, according to Raquez [4], final outcomes and uses of nanocellulose-based PLA composites have been rarely reported. This is due to the difficulty of obtaining a good dispersion of the nanoparticles within the matrix [4]. This has led to several researches on PLA-cellulose nanocomposite. Haafiz [3] and Sullivan [11] have reported the mechanical properties of PLA-NCC prepared by using a solvent exchange method and by using a melt blending method, respectively. Further, Pirani [12] reported the mechanical properties of electrospun PLA-NCC composite prepared by aqueous mixing and freeze drying. However, a comparison of NCC synthesis methods has not yet been made with regard to PLA-NCC properties.

In this paper, the main objective was to study the effect of nanocrystalline cellulose (NCC) as filler on the properties of polylactic acid nanocomposite with two methods of NCC synthesis. The two methods of synthesis of NCC were compared through oxidation of cellulose with ammonium persulfate and through hydrolysis of microcrystalline cellulose (MCC) with sulphuric acid. Triacetine was used to increase the compatibility of the two components. Note that commercial cellulose was used and from other sources, such as oil palm empty fruit bunch (OPEFB). Further, the synthesized NCC's were used as filler to produce PLA-NCC nanocomposite film by applying a solvent casting

method. The films were then characterized to study the effects of the NCC filler from two kinds of celluloses towards the properties of PLA-NCC nanocomposite, especially its mechanical properties and water vapor permeability.

## **2 Experimental Method**

### **2.1 Materials**

Poly(lactic acid) (PLA), trade name PLA Ingeo 2003D, was supplied by NatureWork, USA. Oil palm empty fruit bunch (OPEFB) in powdered form was supplied by the plantation of PT Perkebunan Nusantara VII, Indonesia. Triacetine (TAc) 99% as coupling agent, cellulose (powder), ethanol 96%, and n-hexane were purchased from Sigma-Aldrich. Sulphuric acid, chloroform, and acetone were supplied by Merck, Inc.

### **2.2 Synthesis of Nanocrystalline Cellulose**

#### **2.2.1 Oxidation of MCC with Sulphuric Acid and Extraction of Nanocrystalline Powder**

MCC was hydrolyzed in sulphuric acid (60 wt%) with an acid to cellulose ratio of 10 and then stirred robustly. The reaction temperature was 45 °C and the duration of the reaction was 60 min. Hydrolysis was stopped by adding the solution onto a tenfold volume of cold water. The suspension was then centrifuged at a rate of 3,200 g and washed with demineralized water, NaHCO<sub>3</sub> 5 wt%, and further re-washed with demineralized water. The washing was repeated until the pH of the suspension was equal to 6 with a solid concentration of 2-3 wt%. The suspension was then sonicated for 10-20 min followed by evaporation under vacuum at a temperature of 80 °C to a concentration of solids in the suspension of 10-15 wt%. This suspension was analyzed with a particle size analyzer (PSA). NCC powder was extracted by washing consecutively with ethanol, acetone, and pure hexane with centrifugation at each wash. The final suspension in the form of solids in hexane was then dried at a temperature of 50 °C over a specified time range until there was no more mass change in the sample, indicating that the sample was fully dry [7]. The obtained white powder was then analyzed using scanning electron microscopy (SEM).

#### **2.2.2 Ammonium Persulfate Oxidation of OPEFB**

The operating conditions of synthesis of the nanocrystalline cellulose by this method were based on Ref. [7]. OPEFB, mainly lignocellulosic, was fed into

1 M of ammonium persulfate (APS) with feed mass ratio to APS solution volume at 1 g / 100 mL. The reaction was carried out at 60 °C for 10 hours under isothermal conditions. The solution of the reaction product was then directly analyzed using a Delsa <sup>TM</sup> Nano Particle Analyzer.

### 2.3 Synthesis of PLA/Nanocrystalline Cellulose Nanocomposite Film

PLA nanocomposite films were made by solvent casting. About 3 gr of PLA were dissolved in 40 mL of chloroform at room temperature with strong stirring. The dried NCC was then added with a certain percentage to obtain the PLA/NCC nanocomposite. The mixture was added with triacetin and stirred for a while and then poured onto a glass plate. The mixture was allowed to dry for 24 hours in order for the solvent to evaporate completely. The resulting nanocomposite was then analyzed for its mechanical properties using a Universal Testing Machine (Lloyd Instrument, LRX Plus) [13].

### 2.4 Characterization

The characteristics of the produced NCC were analyzed by SEM (Motic, BA 310) and PSA. Furthermore, the properties of the PLA/NCC nanocomposite were characterized by mechanical testing using a Universal Testing Machine (Lloyd Instrument, LRX Plus) and a water vapor permeability test.

The WVP was calculated based on the following equations:

$$WVTR = \frac{wms_1 - wms_0}{A \times t}$$

$$WVP = \frac{WVTR \times L}{\Delta P}$$

where  $wms_0$  and  $wms_1$  are initial mass of water adsorbent and water adsorbent mass after  $t$  period of time, respectively. WVTR is the difference between  $wms_1$  and  $wms_0$  divided by the water reduction time for each  $m^2$  of film used ( $g/m^2s$ ).  $L$  is the thickness of the film (in m) and  $\Delta P$  is the pressure difference between the two sides of the film. Note that WVP has a unit  $g.m/m^2.s.Pa$ .

## 3 Results and Discussion

### 3.1 Synthesis of Nanocrystalline Cellulose (NCC)

As mentioned above, two methods of NCC synthesis were applied. The first method utilizes MCC through hydrolysis to produce nanocrystalline cellulose (NCC) by adding sulphuric acid ( $H_2SO_4$ ). This method is commonly applied for obtaining nanocrystalline cellulose. Paracrystalline or irregular areas of

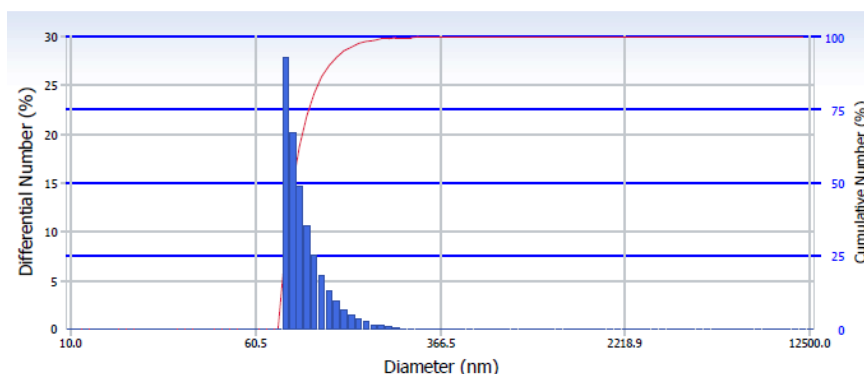
cellulose are selectively hydrolyzed over crystalline regions that have a higher resistance to acid attack, leaving cellulose crystals that have a similar crystallinity on the original cellulose fibers [14]. The other method uses ammonium persulfate to convert OPEFB into nanocrystalline cellulose through oxidation using ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), commonly referred to as APS, which is preferably used due to its higher solubility in water compared with any other persulfate compounds, such as sodium persulfate and potassium persulfate [15].

The synthesized nanocrystalline cellulose's particle sizes from each method were analyzed. Note that the analysis produced a particle size distribution based on amount (number), volume, and intensity. The average NCC particle size results are presented in Table 1 for both methods.

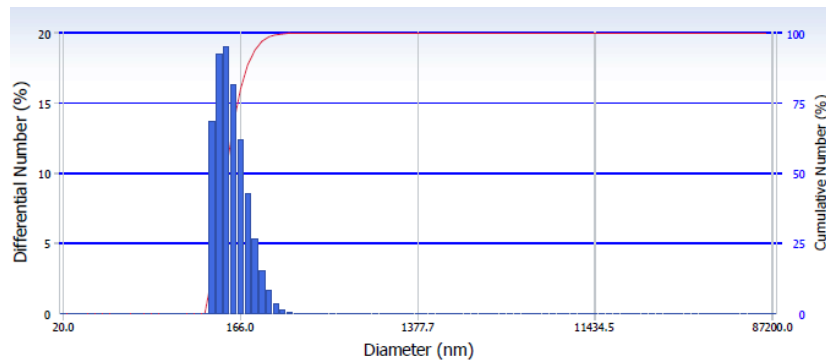
**Table 1** Mean and cumulative sizes of synthesized nanocrystalline cellulose.

	<b>H<sub>2</sub>SO<sub>4</sub> Hydrolysis</b>	<b>Ammonium Persulfate Oxidation</b>
Source	Microcrystalline cellulose	OPEFB
Feed particle size	< 30 $\mu\text{m}$	< 20 mesh (841 $\mu\text{m}$ )
Avg. diameter (number distr.)	99.5 nm	157.9 nm

NCC size distribution diagrams for  $\text{H}_2\text{SO}_4$  hydrolysis and ammonium persulfate oxidation are presented in Figures 1 and 2, respectively. Based on the particle size analysis, the nanocrystalline cellulose from sulphuric acid hydrolysis had a size distribution of 76.1-1,440.3 nm with an average particle size of 99.5 nm. Further analysis on the NCC powder from this method using SEM resulted in rod-shaped nanocrystalline cellulose, as shown in in Figure 3.



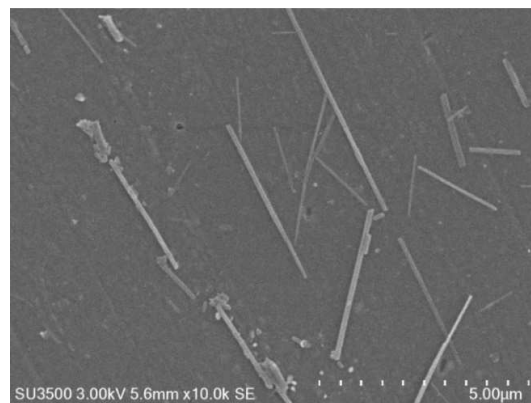
**Figure 1** Particle size analysis of NCC by sulphuric acid hydrolysis.



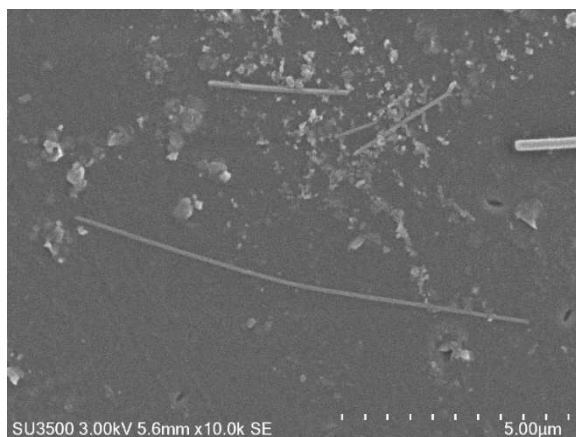
**Figure 2** Particle size analysis of NCC by APS oxidation.

The results supported the study conducted by Ioelovich [7], who produced rod-shaped nanocrystalline cellulose with dimensions of about 150-200 x 10-20 nm from an MCC feed of 50µm with an H<sub>2</sub>SO<sub>4</sub> concentration of about 60% -wt. Specifically, oxidation with APS for 10 hours produced cellulose particles with sizes between 118.3 and 2,4495.1 nm and an average size of 157.9 nm based on the amount of NCC obtained.

A fairly large particle size distribution can be caused by lignocelluloses that have not been fully oxidized and thus a reaction time of more than 10 hours should be considered. This may be also due to the cellulose source influencing the APS oxidation time. APS is a powerful oxidant, which converts cellulose contained in a natural material, especially lignocellulose, in one stage without need for pretreatment [10]. The SEM analysis for NCC from APS oxidation can be seen in Figure 4. It also revealed rod-shaped particles.



**Figure 3** SEM analysis result of extracted NCC powder by hydrolysis with sulphuric acid (magnification: 10,000 x).

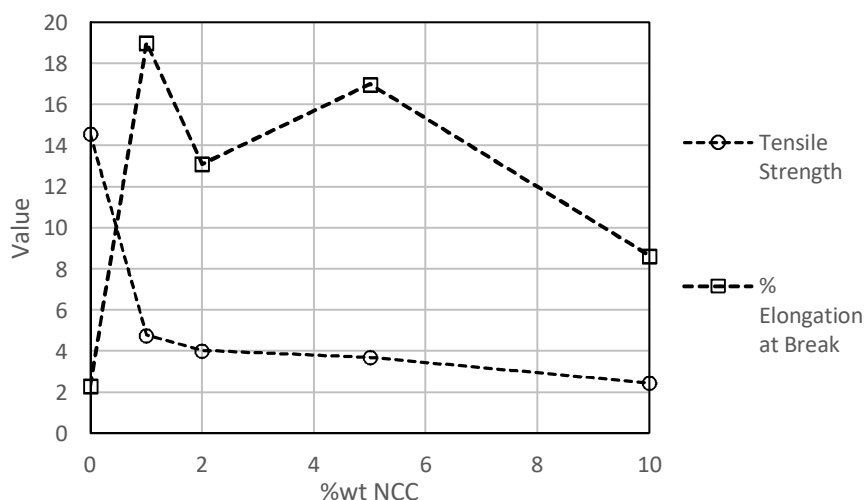


**Figure 4** SEM analysis result of NCC by APS oxidation (magnification: 10,000 x).

### 3.2 PLA-NCC Nanocomposite's Mechanical Properties

Analysis of the mechanical properties of the nanocomposites was performed by adding 1%, 2%, 5%, and 10% NCC of the total weight of the PLA. In addition, triacetin (1,2,3-triacetoxyp propane) was added at 5% overall weight as coupling agent. The results of the analysis, performed with a Universal Testing Machine, are presented in Figure 5.

Based on the experimental results above, the addition of nanocrystalline cellulose significantly increases the elongation at break but significantly decreases the tensile strength of pure PLA. The value of tensile strength has a decreasing trend with further addition of NCC compared with that of 1%-wt NCC. The value of elongation at break also has a tendency to decrease when there is further increased content of NCC filler in the PLA matrix. Oksman [16] and Jacobsen [17] have reported that the addition of nanocrystalline cellulose as compatibilizer increases the value of elongation at break but decreases the film's tensile strength. These tendencies may be due to NCC filler not bonding well with the PLA matrix because of their different properties: PLA is hydrophilic while cellulose is hydrophobic. A higher amount of cellulose causes reduced mechanical strength of the resulting nanocomposite film. Other factors may be due to poor dispersion of NCC in the PLA matrix, moisture presence in the composite, or weak NCC alignment [13]. From the experimental results, the optimum composition of NCC as filler in PLA-NCC nanocomposite is about 1%.



**Figure 5** PLA-NCC nanocomposite mechanical properties.

### 3.3 PLA-NCC Nanocomposite's Water Vapor Permeability

Water vapor permeability is a property of a material to withstand water vapor from passing through. When it is used as a wrapper, the property is crucial for the material. Water vapor permeability analysis was performed on the film in order to study the effect of NCC content on the film's ability to retain moisture. WVP analysis in this experiment was conducted for 45 hours. The film's WVP, measured after 45 hours, is tabulated in Table 2 below.

**Table 2** WVP of PLA-NCC nanocomposite.

NCC Content	WVP (g/m.h.Pa)
10%-wt	$4.7 \times 10^{-12}$
5%-wt	$3.7 \times 10^{-12}$
0%-wt	$2.69 \times 10^{-13}$

Based on the results presented in Table 2, a higher amount of NCCs in the nanocomposite film resulted in slightly higher water vapor permeability of the film, in the order of one tenth, indicating a decreased quality of the film as a wrapper compared with that of neat PLA. This may be due to the difference in properties between cellulose and PLA so that a suitable coupling agent is required.



#### 4 Conclusion

NCC was synthesized by hydrolysis of MCC using sulphuric acid and by APS oxidation of OPEFB with mean particle sizes of 99.5 nm and 157.9 nm, respectively, showing average nanosize particles were successfully produced. When used as filler in a PLA matrix, the elongation at break value will significantly increase but the tensile strength will significantly decrease compared to those of neat PLA. The utilization of NCC as PLA composite filler increased the percentage of the elongation at break with the highest percentage (19.02%) at addition of 1% NCC filler. The highest tensile strength and elongation at break was produced when 1% NCC was added as filler. Addition of more cellulosic filler resulted in a decreasing trend of elongation at break compared with that of the nanocomposite with 1% NCC filler. On the other hand, higher NCC content in the PLA matrix resulted in higher water vapor permeability.

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#### References

- [1] Lim, L-T., Auras, R. & Rubino, M., *Processing Technologies for Poly(Lactic Acid)*, Progress in Polymer Science, **33**, pp. 820-852, 2008.
- [2] Mathew, A.P., Oksman, K. & Sain, M., *Mechanical Properties of Biodegradable Composites from Poly Lactic Acid (PLA) and Microcrystalline Cellulose (MCC)*, Applied Polymer Science, **97**, pp. 2014-2025, 2005.
- [3] M.K.M. Haafiz, Hassan, A., Khalil, H.P.S.A., Khan, I., Inuwa, I.M., Islam, Md. S., Hossain, Md. S., Syakir, M.L. & Fazita, M.R.N., *Bionanocomposite Based on Cellulose Nanowhisker from Oil Palm Biomass-filled Poly (Lactic Acid)*, Polymer Testing, **48**, pp. 133-139, 2015.
- [4] Raquez, J.M., Habibi, Y., Murariu, M. & Dubois, P., *Poly(lactide (PLA)-based Nanocomposites*, Progress in Polymer Science, **38**(10-11), pp. 1504-1542, 2013.
- [5] Brinchi, L., Cotana, F., Fortunati, E. & Kenny, J.M., *Production of Nanocrystalline Cellulose from Lignocellulosic Biomass: Technology and Applications*, Carbohydrate Polymers, **94**, pp. 154-169, 2013.

- [6] Mitra, B.C., *Environment Friendly Composite Materials: Biocomposites and Green Composites*, Defence Science Journal, **64**, pp. 244-261, 2014.
- [7] Ioelovich, M. *Optimal Conditions for Isolation of Nanocrystalline Cellulose Particles*, Nanoscience and Nanotechnology, pp. 9-13, 2012.
- [8] Haafiz, M.K.M., Eichhorn, S.J., Hassan, A. & Jawaid, M., *Isolation and Characterization of Microcrystalline Cellulose from Oil Palm Biomass Residue*, Carbohydrate Polymers, **93**, pp. 628-634, 2013.
- [9] Wan, Y.Z., Luo, H., He, F., Liang, H., Huang, Y. & Li, L.X., *Mechanical, Moisture Absorption, and Biodegradation Behaviours of Bacterial Cellulose Fibre-reinforced Starch Biocomposites*, Composite Science and Technology, **69**, pp. 1212-1217, 2009.
- [10] Callister, W.D. & Rethwisch, D.G., *Material Science and Engineering*, 9<sup>th</sup> Ed., John Wiley and Sons, 670-675, 2014.
- [11] Sullivan, E.M., Moon, R.J. & Kalaitzidou, K., *Processing and Characterization of Cellulose Nanocrystals/Polylactic Acid Nanocomposite Films*, MDPI, 2015.
- [12] Pirani, S., Abushammala, H.M.N. & Hashaikh, R., *Preparation and Characterization of Electrospun PLA/Nanocrystalline Cellulose-based composites*, Applied Polymer Science, pp. 3345-3354, 2013.
- [13] Fortunati, E., Peltzer, M., Armentano, I., Torre, L., Jiménez, A. & Kenny, J.M., *Effects of Modified Cellulose Nanocrystals on the Barrier and Migration Properties of PLA Nano-biocomposites*, Carbohydrate Polymers, **90**, pp. 948-956, 2012.
- [14] Habibi, Y., Lucia, L.A. & Rojas, O.J., *Cellulose Nanocrystals: Chemistry, Self-assembling, and Applications*. Chemical Reviews, **110**, pp. 3479-3500, 2010
- [15] Weast, R.C., *Handbook of Chemistry and Physics*, 64<sup>th</sup>ed. (CRC Press, Boca Raton, Fla.), 1983.
- [16] Oksman, K., Mathew, A.P., Bondeson, D. & Kvien, I., *Manufacturing Process of Cellulose Whiskers/Poly(lactic acid) Nanocomposites*, Compos. Sci. Technol., **66**, pp. 2776-2784, 2006.
- [17] Jacobsen, S. & Fritz, H.G., *Plasticizing Polylactide-The Effect of Different Plasticizers on the Mechanical Properties*, Polym. Eng. Sci., **39**, pp. 1303-1310, 1999.