Characterisation of Biocomposite Film with Napier based Nanocrystalline Cellulose

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Abstract. Nowadays, biocomposite polymers are widely used in daily life based on their ability which is composable, recyclable and sustainable. This paper presents biocomposite film's characterisation with different concentrations of nanocrystalline cellulose (NCC) (0 wt.%, 0.5 wt.%, 1.0 wt.% and 1.5 wt.%). Several techniques were used to review biocomposite film's characterisation, such as X-ray diffraction (XRD), Fourier transformed infrared spectra (FTIR) and biodegradable test. In the XRD study, the reinforcement PLA with NCC shows the improvement of crystallinity from 43.00% to 46.09% and decrease to 45.87% due to agglomeration of excessive NCC. FTIR shows the same chemical structure for each samples. As a result of the biodegradable test, the increasing concentration of NCC in the PLA increased the percentage of weight loss. Sample with NCC 1.5 wt.% shows the highest weight loss value (6.223%) compared to neat PLA (3.646%). Hence, PLA reinforced with nanocrystalline cellulose shows high potential and practical implementation as a biomaterial commercial application.

1. Introduction
In the last few years, food industry has attempted to investigate biocomposite polymer film based on growing environmental awareness, e.g. environmental sustainability, human health, and food safety [1]. Thus, expected waste products from food packaging such as non-biodegradable and disposable plastic that affects ecological sustainability and ecosystems can be reduced. The biocomposite polymer film is the reinforcement of natural fibres which is nanocrystalline cellulose (NCC) with Polylactic acid (PLA) matrix polymer. In this study, Pennisetum Purpureum, called Napier grass, is a source of natural fibre to extract NCC [2]. This type of grass consists of cellulose (46%), hemicellulose (34%) and lignin (20%) [3]. Extraction of NCC was done by acid hydrolysis treatment as stated in our previous study [4]. NCC from traditional fibres has many advantages over synthetic fibres, it has high surface area, high crystallinity, high mechanical properties and biodegradability [4]. Similar studies on PLA/nanocrystalline cellulose biocomposite was done using different sources like coffee silverskin, hemp, flax and jute [5]. PLA is a natural biomaterial with huge advantages compared to petrochemical-based polymers as they are biodegradable, renewable, affordable, and widely available [6]. Physical structure of PLA is transparent, glossy appearance, brittle, low heat distortion, high rigidity, and high crystallisation rate. PLA is however limited in processing temperature, high linear coefficient thermal expansion, and moisture sensitivity [7]. By reinforcing with natural fibres, PLA can improve their physiochemical properties. Characterisation of reinforcement PLA with NCC of different concentration
was conducted through Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD) and Biodegradability.

2. Experiment

2.1. Material and chemical

NCC extracted from *Pennisetum purpureum* from Bukit Kayu Hitam, Kedah, Malaysia. PLA (4032D) acquired from NatureWorks LLC. Chloroform from R&M Chemicals.

2.2. PLA/NCC biocomposite fabrication

Polyactic acid was prepared with different weights depends on the concentration of NCC at 0%, 0.5%, 1.0% and 1.5%, respectively (Table 1). Next was the preparation example of PLA/NCC mixture for PLA/NCC 1.0%. 2.975g of PLA was mixed with 40 ml of trichloromethane (CHCl3) followed by mechanical stirring (Favorit Stirring Hotplate) at 45°C for 120 min. The concentration of 1 wt.% NCC solution was prepared and slowly mixed into PLA solution until created homogenous dispersion solvent under mechanical stirring at 45°C. This was called solution casting method. The solution of PLA/NCC was poured into a petri dish, and the cast solution was closed with aluminium foil. Then, placed the petri dish with casting solution on flat surface to create the even thickness and leave the samples to evaporate the CHCl3. The same technique was applied for the reinforcement of PLA/NCC with different concentrations.

| Films         | Amount of NCC, (g) | Amount of PLA, (g) |
|---------------|--------------------|--------------------|
| PLA           | 0.00               | 3.000              |
| PLA/NCC 0.5%  | 0.015              | 2.985              |
| PLA/NCC 1.0%  | 0.030              | 2.975              |
| PLA/NCC 1.5%  | 0.045              | 2.955              |

2.3. X-ray diffraction (XRD) analysis

XRD analysis is to determine the crystallinity of the sample using Bruker D2 Phaser. The scattersation of diffractometer in the 2θ was between 5° to 45° at a speed of 1 °/min. The sample was tested with an acceleration voltage of 30kV and 10mA at room temperature. The file that generates by Bruker D2 were analysed by using OriginPro and X’Pert HighScore [8]. Equation 2.1 shows the formula to determine the index of crystallinity of the sample.

\[
\text{Crystallinity} = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks (crystalline + Amorphous)}}
\]  

2.4. Fourier transformed infrared spectra (FTIR) analysis

FTIR analysis determines the spectroscopic (chemical structure) of the sample. This analysis was conducted by using FTIR-PerkinElmer, where the infrared spectra collected the data of 16 scans for a range between 4000 cm⁻¹ to 650 cm⁻¹.

2.5. Biodegradability test

Biodegradability analysis determines the degradation of the biocomposite polymers where the sample was buried in the soil. The samples of the same size (30mm x 30mm) were placed in the soil, and the humidity was maintained at 95%. The biodegradability test was conducted for 45 days, and water spraying was done every day to maintain the moisture. Then, the samples were weighed on a scheduled
period. The initial and final weight of the sample were recorded. Equation 2.2 shows the formula to determine the degradability of the biocomposite polymers.

\[
\text{Biodegradability, \%} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100
\]  

(2.2)

3. Result and Discussion

3.1. Crystallinity of composite

The crystallinity pattern of polylactic acid reinforced with nanocrystalline cellulose was presented in Figure 3.1, and the calculated crystallinity index (CI) shown in Table 2. The prominent diffraction peak for PLA/NCC scattered at 16.8°, 19.19°, 22.63° and 34.3°, corresponds to the crystallographic plane (110), (010), (200), and (004) were grafted at cellulose Iβ crystalline structure [9][10]. PLA has shown the lowest crystallinity value of 43%, with the highest peak at 16.8° and smallest peak at 22.63° and 34.3°. PLA/NCC 1.0% presented the highest crystallinity with 46.09%. The slightly higher peak 22.63° probability due to a good dispersion of NCC on PLA matrix compared to other samples; leads to highest crystallinity. This is because of the crystallisation nucleation points appeared in large amount where the cellulose served nucleating agent that accelerate the crystallisation [11]. However, PLA/NCC 1.5% has slightly decrease CI (45.87) due to agglomeration of NCC causes by excess of NCC; weak efficient to favour crystallinity[12][13].

![Figure 3.1](image_url)

**Figure 3.1.** The crystallinity pattern of polylactic acid reinforced with nanocrystalline cellulose.

| Sample       | Crystallinity index (%) |
|--------------|-------------------------|
| PLA          | 43.00                   |
| PLA/NCC 0.5% | 43.87                   |
| PLA/NCC 1.0% | 46.09                   |
| PLA/NCC 1.5% | 45.87                   |

3.2. Chemical structure

FTIR is a technique to interpret the chemical structure between polylactic acid with nanocrystalline cellulose. The spectrum absorbing wavenumber divided into four region; fingerprint region (1500 – 600 cm⁻¹), double bond region (2000 – 1500cm⁻¹), triple bond region (2500 – 2000 cm⁻¹), and single bond region (4000 – 2500cm⁻¹) [14]. Figure 3.2 shows the spectra distribution of PLA, PLA/NCC 0.5%, PLA/NCC 1.0%, and PLA/NCC 1.5%, while Table 3 shows the summarised peak of the four different
concentrations. PLA/NCC's broad peak chemical structure of PLA/NCC observed at 1755 cm$^{-1}$ was assigned as C=O stretching vibration were located at double bond region. Band vibration of C=O corresponds to the acetyl and uronic ester group of hemicellulose and the ester linkage of the lignin carboxyl group [10]. The peak bending vibration was observed at 1456 cm$^{-1}$ indicates -CH3 while band stretching at 1361 cm$^{-1}$ was assigned as O-H related to the water group [15]. The peak at 870 cm$^{-1}$ represents a $\beta$-glycosidic bond, and the sharp peak bend at 1046 cm$^{-1}$ indicated C-OH, while the peak at 1087 cm$^{-1}$ represents C-O-C glycoside [14]. Comparing the result between neat and reinforced PLA, it can be observed that slightly decrease in intensity banding at -CH3 as concentration increase. These differences indicated the interaction occurs between the ester and carboxyl group [16].

Furthermore, the spectra distribution of glycoside bond content similar to the previous study from the isolation of NCC through different time reaction of acid hydrolysis [4]. The IR spectrum of neat polylactic acid identically similar with PLA/NCC 0.5%, PLA/NCC 1.0%, and PLA/NCC 1.5%. The addition of NCC was an insignificant effect IR spectrum of PLA because of the lack of a new peak in the chemical structure. PLA and PLA/NCC biocomposites have a similar chemical group and thus highly potential compatibility between the two components.

**Figure 3.2.** The spectra distribution of PLA, PLA/NCC 0.5%, PLA/NCC 1.0%, and PLA/NCC 1.5%.

**Table 3.** FTIR peak for PLA, NCC 0.5%, NCC 1.0% and NCC 1.5%.

|                | PLA (cm$^{-1}$) | NCC 0.5%(cm$^{-1}$) | NCC 1.0%(cm$^{-1}$) | NCC 1.5%(cm$^{-1}$) |
|----------------|----------------|---------------------|---------------------|---------------------|
| C=O (carbonyl) | 1752           | 1755                | 1755                | 1755                |
| -CH3           | 1456           | 1452                | 1456                | 1452                |
| O-H (hydroxyl) | 1361           | 1361                | 1361                | 1364                |
| C-O-C glycoside| 1087           | 1087                | 1131                | 1084                |
| C-OH           | 1046           | 1046                | 1046                | 1046                |
| $\beta$-glycosidic | 870           | 870                 | 873                 | 864                 |
3.3. Degradability performance

The studies of polymer degradation properties are an essential factor for producing friendly material and reducing environmental impact. Table 4 shows the weight loss (wt.%) for PLA/NCC over a different soil buried period. Biodegradable testing was conducted for a period of 5-day, 10-day, 15-day, 30-day and 45-day, while humidity of the soil (95%) was controlled by a sensor. Degradation of polymers was taken over by microorganism, bacteria or other biological substance. The contact between polymers and microorganism will transform the polymers through the metabolic process to reduce molecular weight [13]. On the other hand, PLA needed multiple steps to degrade, which broken down the ester bond by cleaved hydrolytically. When the molar mass of PLA below 20,00g/mol, the PLA will become water-soluble. The degradation of PLA by microorganism will produce water, carbon dioxide, and carbon conversion into biomass[17]. From Table 4, the performance of degradation biocomposite polymers increased with increasing the concentration of NCC with total weight loss from 3.646% (PLA) increase to 6.223% (NCC 1.5%) on day 45. NCC naturally hydrophilic where readily absorb the water from the soil. The highest absorbed water rate led to microcrack where the inter and intra-molecule structure was weaker and degraded by a microorganism.[18].

Table 4. Weight loss (wt.%) for PLA/NCC over a different period of soil burial testing.

| Period | PLA (%) | NCC 0.5 (%) | NCC 1.0 (%) | NCC 1.5 (%) |
|--------|---------|-------------|-------------|-------------|
| 5      | 1.933   | 2.109       | 3.944       | 3.962       |
| 10     | 0.657   | 0.670       | 0.760       | 0.837       |
| 15     | 0.481   | 0.557       | 0.613       | 0.573       |
| 30     | 0.242   | 0.265       | 0.339       | 0.364       |
| 45     | 0.333   | 0.384       | 0.464       | 0.487       |
| Total weight loss | 3.646 | 3.985 | 6.120 | 6.223 |

4. Conclusion

The fabrication of biocomposite polymers such as polylactic acid with nanocrystalline cellulose can give an opportunity as a green product. The main objective of this study was to determine the physicochemical properties between neat PLA and PLA/NCC with different concentration. XRD result showed that the highest crystallinity was observed at PLA/NCC 1.0% with 46.09%, where improvement of about almost 3% with neat PLA. Determination of chemical structure by using FTIR does not affect the structure between neat PLA and reinforced PLA. Degradation performance can be accelerated with the presence of NCC in the matrix of PLA. The percentage of weight loss increased with the increasing value of NCC.

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