Morphological and Optical Properties of Polylactic Acid Bionanocomposite Film Reinforced with Oil Palm Empty Fruit Bunch Nanocrystalline Cellulose

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Abstract. Nanocrystalline cellulose (NCC) was derived from oil palm empty fruit bunch (OPEFB) by soda pulping and followed by 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) oxidation reaction method. The NCC was used as reinforcing agent in Polylactic acid (PLA) biopolymer film matrix with 0 to 20% loadings. Bionanocomposite film was prepared by dilution in Chloroform and casted on the flat glass with 0.03-0.05 mm casting thickness. TEM shows that the nanocrystalline cellulose (NCC) has a rod like shape of 2-6 nm width and 200-500 nm length. SEM micrograph shows that the surface of PLA-NCC bionanocomposites has a relative good dispersion at low NCC loading (1, 3 and 5 wt.%), and a rougher surface at higher NCC loadings. The PLA bionanocomposites film as obviously seen exhibits decrease in transparency as the NCC content increased. The transparency of neat PLA film has higher transmission value compare to other PLA-NCC and tend to reduce the transmission percentage as the NCC loading increase, especially for 10 and 20%.

1. Introduction
The use of biopolymer is growing as more concerns on environmental impacts of petroleum based plastics. One of the most valuable biopolymer is polylactic acid (PLA) due to some advantage properties, for instances renewability, biodegradability, compatibility and excellent in transparency [1]. However PLA has shortcoming such as low thermal resistance, brittles, and poor gas and water vapor permeability [1]. To extend its applications, improvement of its properties is required. One of the most promising material to enhance the properties of the PLA is cellulose as many researches have shown recently [2-5].

In general, preparation of biodegradable plastics requires fillers as reinforcing phase made of bioresources. Many studies have shown that various forms of nano-size cellulose have been incorporated into PLA matrix have contributed to improved mechanical and barrier properties of the biocomposites [6, 7]. 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 exhibits some disadven-tages, for instance, high moisture absorb-tion, poor wettability, incompatibility with most of polymeric matrices, and limitation of processing temperature. Another problem emerges when the nanosized particle incorporated with PLA tend to reduce the transparency of the polymer matrix.

As other researchers observed using cellulose from non-oil palm sources, they also found that aggregation or poor dispersion of the cellulose has contributed to lesser the transparency of the biocomposite. In the present work, we are exploring the use of nanocrystalline cellulose (NCC) to enhance PLA biocomposite properties. NCC was isolated from oil palm empty fruit bunch (OPEFB) by pulping process and followed by TEMPO catalysed oxidation and sonication.

Haafiz [8] used micro-crystalline cellulose (MCC) to prepare PLA biocomposite film and found the transparency was good, but some white spot are visible in biocomposite film and clearly observed as the MCC loading increased. The white spots are related to the poor dispersion of MCC due to MCC aggregation. However, there is no report regarding the transparency of PLA bionanocomposite reinforced with nanocrystalline cellulose that isolate from oil palm empty fruit bunch (OPEFB) using UV-Vis. This optical property is needed for some application for example in food packaging. Therefore, in this research, we study the optical properties of PLA reinforced with nanocrystalline cellulose

2. Experimental

2.1 Material

NCC was prepared from Oil Palm Empty Fruit Bunch (OPEFB) obtained from SABUTEK Company, Malaysia. All chemicals used throughout the experiments were analytical grade and obtained from QReC (Malaysia), except 4-acetamido-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) pro-cured from Sigma Aldrich (USA).

2.2 Preparation of oil palm empty fruit bunch nanocrystalline cellulose

The OPEFB pulp was prepared using the procedure described by Wanrosli [9]. OPEFB strand was cut cut into 4–5cm lengths which was then washed and dried at room temperature. Soda pulping process was started with pre-hydrolysis with water at high pressure and followed by screening to remove unwanted fine materials.

NCC was produced via TEMPO mediated oxidation as prescribe by Rohaizu and Wanrosli [10]. The OPEFB pulp was mix with TEMPO (0.24 mmol/g cellulose) and sodium bromide (1.02 mmol/g cellulose) and place into ultrasonic bath (Model 8510, Branson). The 60 mL sodium hypochlorite solution was drop wise and pH controlled at 10± 0.2 by the addition of NaOH. The reaction was at room temperature for 4 h and stop by adding a 100 mL ethanol. Post oxidation of oxidized pulp was conducted by addition of 40 mL of sodium chloride and acetic acid (5 M) solutions at 70°C for 2 h. TEMPO Oxidized pulp was sonicated for 1 h in an ice bath the separate with the supernatant by centrifuge at 3500 rpm for 1 h. The NCC suspension was oven-dried overnight and used for bionanocomposite preparation. The NCC were also transferred to chloroform by solvent method according to the procedure described by Indarti [11].

2.3 Preparation of PLA-NCC biocomposite films

PLA-NCC film was prepared by solvent casting as prescribe by Indarti [12]. The semi crystalline PLA was used as polymeric matrix with density 1.24 g/cc. PLA and NCC were dissolved in chloroform (table 1) in a 500 ml round bottom flask under vigorous stirring at room temperature. The flask was equipped with a reflux condenser and a paddle-type stirrer. The neat PLA film was prepared by pouring the solution onto the flat glass, and then allowed to dry for about 24 h. For the preparation of the biocomposite films, dried NCC with 1, 3, 5, 10 and 20% concentration in 10 mL chloroform was sonicated in ice bath for 5 minutes. The NCC suspension was then mixed with 20 mL PLA solution and stirred for 4 hours. The PLA-NCC solution was casted on the flat glass with 0.03-0.05 mm casting thickness. Finally, the films were left to dry at room temperature overnight.
Table 1. Material formulation of bionanocomposites composition

| Material  | Master batch | NCC (g) | Solvent (ml) | Final Composition (%) |
|-----------|--------------|---------|--------------|-----------------------|
| PLA       | 1            | -       | 30           | Neat PLA               |
| PLA-NCC1% | 0.99         | 0.01    | 30           | (99/1) 1              |
| PLA-NCC3% | 0.97         | 0.03    | 30           | (97/3) 3              |
| PLA-NCC5% | 0.95         | 0.05    | 30           | (95/5) 5              |
| PLA-NCC10%| 0.90         | 0.10    | 30           | (90/10) 10            |
| PLA-NCC20%| 0.80         | 0.20    | 30           | (80/20) 20            |

a. Solvent were evaporated during drying of the biocomposites film

2.4 Characterization of NCC and its biocomposite films

Surface morphology of bionanocomposite film were observed using scanning Electron Microscope (SEM) with Energy Dispersive X-Ray (EVO® MA 10, Carl Zeiss NTS GmbH). The very thin film sample was scattered onto the mount with adhesives or tape. Prior to morphological examination, all samples were sputter-coated with gold. The accelerating voltage used was 10 kV, and the current changed with the vacuum of observed circumstances.

The characterization of NCC dimension was used a transmission electron microscope (TEM), (Philips CM12 with an Image Analyzer, Amsterdam, Holland). Before analysing, the sample was coated with phosphotungstic acid (wt. 2%) by dropping onto the small amount of NCC suspension (1% w/v), that placed on carbon stained electron microscope grids and allowed to dry. The average width and length were calculated as a mean of 100 measurements of NCC.

2.4 Transparency

Transparency of the bionanocomposites film was determined using UV-Vis single beam spectrophotometer (Thermo Scientific Corporation Evolution 300) at room temperature. The data was collected in visible and infrared spectrum range between 300 to 700 nm wave lengths. Meanwhile, visual observation of the bionanocomposite film using background image was evaluated using camera CANON (SX600 HS).

3. Results and Discussion

3.1 Morphology of Nanocrystalline Cellulose

In figure 1(a), there are shown that the SEM of single fiber of OPEFB pulp has dimension of 8.6 µm width and 310 µm length. After TEMPO oxidation and sonication treatment, the dimension of NCC was observed using TEM. From TEM exhibit the dimension of NCC into 2-6 nm width and 200-500 nm length as shown in figure 1(b). The average axial ratio of OPEFB pulp is 25 and become 45 for NCC. It reveals TEMPO oxidation process attack the surface of C6 primary hydroxyl group of cellulose and replace into carboxyl groups, this will cause the weakening inter molecule bond among the cellulose fibril avoid the formation of strong inter fibril bonds. Thereby, during the sonication in the aqueous phase process allowing the liberation of inter molecule fibril bonds [13-15]
Figure 1. SEM image of single of OPEFB-pulp fiber (a) and TEM of Nanocrystalline Cellulose of OPEFB (b)

Prior to the fabrication of PLA-NCC bionanocomposite, the dried OPEFB-NCC was redispersed in chloroform. Dispersing the NCC in chloroform followed by one hour sonication prior to mixing with the PLA solution is not able to completely redispersed all agglomerated NCC. The TEM observation reveals that some agglomerates exist signed with red dash lined in figure 1b. To ensure maximum dispersion in the PLA matrix, the OPEFB-NCC suspension was immediately used after redispersion.

3.2 Morphology of PLA Bionanocomposite

The surface of the PLA bionanocomposite are presented in figure 2. From SEM micrograph shows that the NCC aggregates were visible in the surface of the PLA bionanocomposiste film. Compared to pure PLA, the surface of the PLA-NCC shows that the NCC embedded and bulge out in the PLA matrix. Generally, a relative good dispersion was obtained at low NCC loading (1, 3 and 5 wt. %). However, at the10 and 20 wt. % of NCC loading show that a rougher surface compare to those with lower NCC loading (figure 2). From the figure of all PLA-bionanocomposites, it can be seen clearly that the OPEFB-NCC (Figure 2b-f) displayed large particle due to the tendency of agglomeration [16]. The same result also found by Joonobi [17] who use Cellulose nano fiber from kenaf as reinforcement. Before mix with PLA, NCC was remove water through oven drying process as describe [11, 18] to obtain a better dispersion in Chloroform. In this stage the NCC starts aggregation even the dispersion process in solvent use the sonication to reduce the aggregation. Moreover the different character of the NCC which is hydrophilic is not compatible with both Chloroform (solvent) and PLA (biopolymer matrix) which is hydrophobic [19]. From the previous research, the cross section fracture of PLA-bionanocomposite film of SEM micrograph, reveal that there is a void and cracking between NCC and PLA hence affected to other mechanical, barrier and optical properties [12]
3.3 Optical Features

Figure 3 and 4, show the photographs of the PLA composite film with different NCC loading, and also the light transmittance curves measured by UV-Vis spectrometry, respectively. The effect of NCC loading in PLA biopolymer was investigated in term of transparency. The PLA nano composite film as obviously seen exhibits decrease in transparency as the NCC content increased, this is due to the dispersion of NCC in polymer matrix [7, 20]. The reduction of UV-VIS was obtained as the increasing of NCC loading. PLA bionanocomposite with NCC loading of 1-10% are transparent and visible light transparency at 550 nm is more than 80%. For the PLA with NCC loading, it is clearly observed that the some white spots appear as the increasing of NCC content. The spots occurred due to the aggregation of NCC in PLA matrix.

The transmission degree also shows the same trend with the visual of the PLA-NCC matrix. The neat PLA film shows higher transmission value compared to other PLA-NCC. The transmission percentage trend decreases as the increasing of NCC content, especially for 10 and 20%. This property supports the application of the PLA nanocomposite film, can use for packaging material, medical material or other material that tensile and stiffness is not very important.
Figure 3. Visual comparison of the transparency of (a) Neat PLA, (b) PLA-NCC1%, (c) PLA-NCC3%, (d) PLA-NCC5%, (e) PLA-NCC10%, (f) PLA-NCC20%

Figure 4. Light transmittance curves of neat PLA and PLA-NCC based on NCC concentration (%) at different wavelength (300-700 nm)

In food packaging industry the light transmission become an important factor, where the packaged goods are light sensitive [21]. However, the transparent and colorless packaging is also crucial due to the opaque film hinder the costumer to see the product clearly, because it reduce the attractiveness for them to buy it. In addition, optical performance of bionanocomposite film is also an important parameter to assess dispersibility of nanoparticles in polymer matrix, therefore films are directly related with their nano and micro-structure [22].

4. Conclusion
NCC production by TEMPO Oxidation catalyst with the dimension of NCC into 2-6 nm width and 200-500 nm length, has been successfully used as a filler in PLA matrix by solution casting method. SEM
micrograph shows that the NCC aggregates were visible in the surface of the PLA bionanocomposite film. Compared to pure PLA, the surface of the PLANCC shows that the NCC embedded and bulge out in the PLA matrix. The effect of NCC loading in PLA biopolymer was investigated in term of transparency. The reduction of UV-VIS was obtained as the increasing of NCC loading. PLA bionanocomposite with NCC loading of 1-10% are transparent and visible light transparency at 550 nm is more than 80%. The future challenge is to find out the better and stabile dispersion of NCC in PLA to enhance the optical properties.

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