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# Adipic Acid Crosslinked Nanocrystalline Cellulose/Chitosan Composite: Tensile Properties and Crystallinity

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**Abstract**. In the present study, empty fruit bunch derived nanocrystalline cellulose (NCC) was prepared and employed as a reinforcing agent to improve the tensile properties of the chitosan composites. Adipic acid was added as a crosslinker. The incorporation of NCC has greatly improved the tensile properties of composites. The crosslinking reaction has further improved the tensile properties. 3 wt% NCC/chitosan composites displayed the highest tensile strength which is 48.7MPa and 65.3 MPa without and with the addition of crosslinker respectively. The X-ray diffraction (XRD) results showed that the crystalline peak of chitosan composites was significantly improved by the addition of NCC however the crystallinity peak was decreased by the incorporation of adipic acid.

## 1. Introduction

In recent decades, renewable polymeric materials from natural resources have been widely explored as the substitutes for the non-renewable polymers. Chitosan is such an alternative due to its excellent film-forming capability, non-toxic, biodegradability and anti-microbial activity make it an ideal alternative for reducing the environmental problems caused by synthetic polymers. Chitosan is the second most abundant polysaccharide which obtained from the deacetylation of chitin [1]. The attractive properties of chitosan have inspired the researchers in the development of chitosan-based film composites where chitosan is utilized as a polymeric matrix and reinforced with other nanoparticle fillers.

Among the biopolymers, cellulose is of particular interest to be utilized as reinforcing agent due to their wide variety of source, low cost and biodegradability [2]. Thus, cellulose with diameters in the nanometre range known as nanocrystalline cellulose (NCC) is developed. NCC is a rod-like crystalline cellulose prepared from acid hydrolysis with a diameter between 5 – 70 nm [3]. Among the acids, sulphuric acid is the most common acid used. The use of sulphuric acid could lead to the formation of negatively-charged sulphate group on the surface of NCC which produced a highly stable NCC suspensions by electrostatic repulsion [4]. NCC as a reinforcing agent has been extensively applied in various polymer matrices for different applications due to its remarkable properties such as remarkable strength and stiffness, high aspect ratio and high biodegradability.

Crosslinking had been an important procedure in the formation of NCC/chitosan film in improving the properties of chitosan composites film. Yeng et al. [5] used epichlorohydrin as a crosslinker for chitosan composites and found out that the mechanical properties were improved significantly compared to non-crosslinked set. Therefore, in order to improve the mechanical properties of chitosan film composites for certain application, chemical modification by using crosslinker is introduced. In this study, adipic acid was employed as crosslinker for the production of NCC/chitosan film. The main

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objectives of the study are to compare the tensile properties, morphology and crystallinity of both non-crosslinked and adipic acid crosslinked chitosan film composites with and without the addition of NCC.

## 2. Experimental

### *2.1. Material*
Empty fruit bunch (EFB) was supplied by Taclico Company Sdn. Bhd. was purchased from Cleo Shanghai Pharmaceutical, China. Acetic acid, sodium hydroxide, adipic acid and sodium chlorite were purchased from Sigma-Aldrich whereas sulphuric acid was purchased from Merck.

### *2.2. Preparation of NCC from EFB fibres*
EFB fibres were treated with 4wt% sodium hydroxide solution at 80 ℃ for 2 hours. After that, the fibres were bleached at 80 ℃ for 2 hours. Both treatments were repeated thrice. Acid hydrolysis was performed by using 60 wt% sulphuric acid at 45 ℃ for 1 hour. The suspension obtained was washed with distilled water and centrifuged repeatedly till the supernatant become turbid. The suspension was then sonicated and stored in refrigerator at 4 ℃.

### *2.3. Preparation of NCC/Chitosan Composites*
Chitosan powder was dissolved in acetic acid solution and heated at 60 ˚C for 4 hours. Glycerol (10 wt%) and NCC were mixed with the chitosan solution and heated for another 1 hour. The solution was poured into a plastic petri dish and dried in a non-air-circulating oven at 50 ℃. For crosslinked composites, 5wt% of adipic acid was added.

## 3. Characterization

### *3.1.* Tensile properties
The tensile test was performed using Instron universal tensile testing machine (UTM). A crosshead speed of 10mm/min was used in the test. Specimens of size 10 x 1 cm were cut from the films. The thickness of specimens was measured randomly using a micrometer and the average thickness was recorded. The data were averaged over at least 5 samples.

### *3.2. Field emission scanning electron microscopy (FESEM)*
The fractured surface of non-crosslinked and adipic acid crosslinked NCC/chitosan film composites were observed by using FESEM. Gold-coated samples were analyzed using NOVA NANOSEM 450 with 5000x magnification and 10 kV accelerating voltage.

### *3.3.* X-Ray Diffraction (XRD)
The crystalline structure of non-crosslinked and adipic acid crosslinked neat chitosan and NCC/chitosan film composites was examined by a desktop D2 Phaser X-ray diffractometer (Bruker Corporation, USA). The samples were scanned within the range of 5° to 40° with a speed of 0.1 s/step.

## 4. Results and Discussions

### *4.1. Tensile properties*

Tensile properties of non-crosslinked and adipic acid crosslinked neat chitosan and NCC/chitosan film composites are presented in Figure 1. In general, the tensile strength of chitosan composites showed a significant improvement with the addition of NCC up to 3 wt%. The increment could be due to the good interaction between NCC and chitosan matrix. Besides, the reinforcing effect occurring through effective stress transfer between fillers and polymeric matrix also enhance the tensile strength significantly [6]. Nevertheless, the addition of higher concentration of NCC declined the tensile strength of the composites. It could be resulted by the agglomeration and uneven dispersion of NCC

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within the chitosan matrix. The addition of crosslinker has even improved the tensile strength by developing a more stable network between adipic acid and chitosan [7]. The non-crosslinked and adipic acid crosslinked composites with the addition of 3 wt% NCC displayed the highest tensile strength which is 48.7 MPa and 65.3 MPa, respectively.

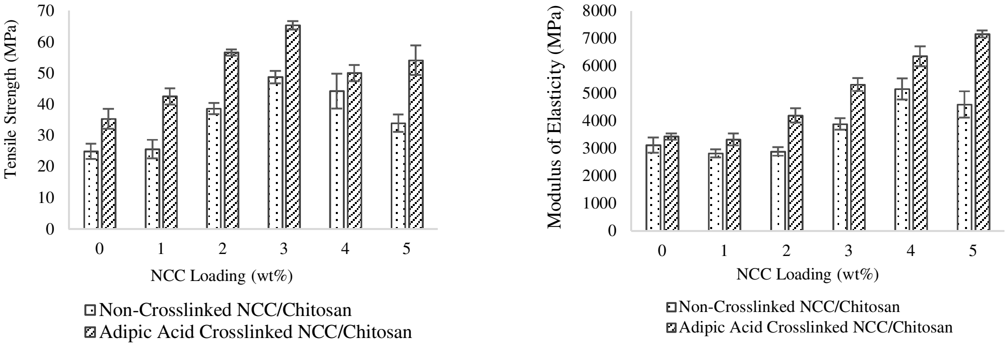


**Figure 1.** The (a) tensile strength and (b) modulus of elasticity of non-crosslinked and adipic acid crosslinked neat chitosan and NCC/chitosan film composites

The modulus of elasticity also displayed a similar trend as tensile strength in which the incorporation of NCC improved the modulus of elasticity significantly. The addition of highly crystalline NCC formed a strong intramolecular or intermolecular hydrogen bonding with matrix and improved the modulus of elasticity remarkably [8]. Moreover, the crosslinking process has further restrained the flexibility and chain mobility of polymer composites and increased the modulus of elasticity.

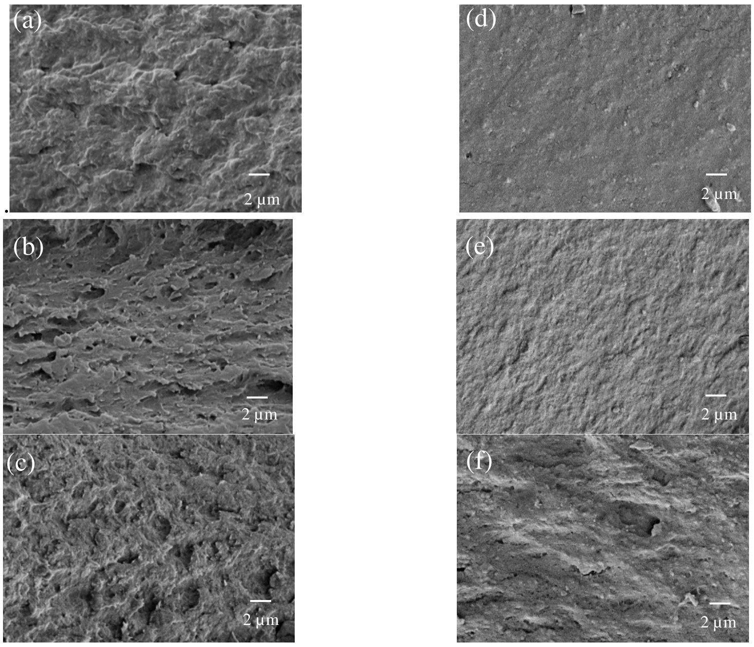


**Figure 2.** Fractured surface of the non-crosslinked (a) 0% NCC, (b) 1% NCC & (c) 5% NCC & adipic acid crosslinked (d) 0%, (e) 1% NCC & (f) 5% NCC/chitosan composites.

The fractured surface of non-crosslinked and adipic acid crosslinked neat chitosan composites in Figure 2 (a) and (e) showed a smooth and homogeneous surface. The incorporation of NCC resulted in a rougher and uneven surface with respect to the neat chitosan film. Adipic acid crosslinked NCC/chitosan composites presented smoother and more even surface compared to non-crosslinked set. The addition of adipic acid had improved the interaction between NCC and matrix. FeSEM analysis has proven that the enhanced tensile properties of composites were resulted by the NCC and crosslinking agent addition.

### *4.2. X-Ray Diffraction (XRD)*

The XRD analysis (Figure 3) of non-crosslinked and adipic acid crosslinked neat chitosan and NCC/chitosan film composites showed intense peaks at $2\theta = 12.4$□, 22.5 □ and 34.7 □, which attributed to the hydrated "tendon" conformation of chitosan [9]. The addition of NCC has enhanced the intensity of the peak at $2\theta = 22.5$ □. The adipic acid crosslinked composites showed a slightly lower peak at $2\theta = 22.5$ □ compared to the non-crosslinked chitosan composites, which showed the effective crosslinking reaction between adipic acid and chitosan matrix [10]. Crosslinking reaction interrupted the intra and inters molecular hydrogen bonds of chitosan network which resulted a lower peak of composites [11].

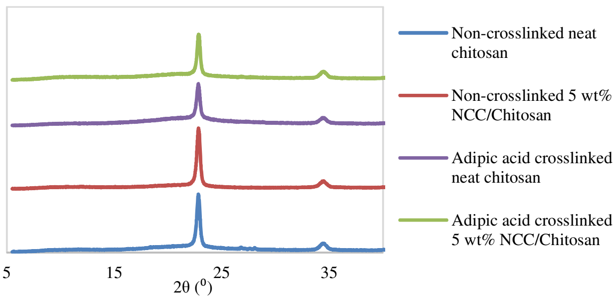


**Figure 3.** XRD pattern of non-crosslinked and adipic acid crosslinked neat chitosan and NCC/chitosan film composites

## 5. Conclusions

NCC/chitosan film composites were synthesized and chemical crosslinked using adipic acid. Tensile properties of chitosan film composites were greatly improved by adding NCC and adipic acid as crosslinker.

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