Effect of glutaraldehyde as crosslinker on the properties of cellulose nanocrystal/chitosan films

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Abstract. Cellulose nanocrystals (CNC) were isolated from the empty fruit bunch as the reinforcing filler to enhance the tensile and thermal properties of chitosan films. The addition of CNC has greatly increased the tensile strength of the chitosan films from 32.9 MPa for neat chitosan film to 50.9 MPa for 5 wt% CNC/chitosan films. The addition of glutaraldehyde as crosslinker has further improved the tensile property of chitosan films. However, the incorporation of CNC and glutaraldehyde has a negative effect on the elongation at break of the films due to restricted polymer chain mobility. Besides, the addition of CNC also enhanced the melting temperature of the chitosan films. The crosslinking process has further increased the melting temperature to 112.8\degree C with the addition of 5 wt% CNC. Therefore, the crosslinked CNC/chitosan films display greater property reinforcements than non-crosslinked films.

1 Introduction

Increasing of public concerns regarding the environmental pollution throughout the world has led to the utilization of biodegradable and environment friendly polymer such as chitosan. Chitosan can be used as an alternative for the fabrication of biodegradable polymer composites to replace the synthetic polymers. However, chitosan is brittle and has poor mechanical properties. Therefore, cellulose nanocrystal (CNC) is introduced as the reinforcement filler to enhance its properties.

There are various methods for preparing CNC, with sulphuric acid hydrolysis being the most commonly used technique [1]. Isolation of CNC using sulphuric acid forms a negatively charged crystallite surface resulting from esterification by sulphate ions which lead to a more stable CNC dispersion. Isolation of CNC from renewable sources has earned the greatest interest lately due to its excellent mechanical properties (high specific strength and modulus), exceptional crystallinity, light weight and high aspect ratio compared to micro-sized cellulose [2]. The concept of using nanocellulose as reinforcement material in polymer matrix has been proven as the efficient approach for enhancing the tensile

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properties of biopolymers by forming the hydrogen bonding network between the filler and the matrix [3].

Aside from adding reinforcing filler, the performance of chitosan can also be enhanced through crosslinking reaction. Crosslinking is an important procedure in the production of composite films as the properties such as mechanical strength are dependent on the crosslinking degree of composites [4]. The crosslinking reaction normally takes place between the functional group of crosslinker and the amine group of chitosan [5]. Among the crosslinkers, glutaraldehyde (GA) is the most common crosslinker used in chitosan matrix due to its high stability and proven ability in improving the tensile and thermal properties of chitosan films [6, 7]. Most of the crosslinkers require heating for the crosslinking reaction to take place. The thermal crosslinking of film is generally performed by using conventional heating in which the thermal energy is directly transmitted to the film via conduction. The properties of crosslinked films can be further enhanced through the conventional heating by forming a more stable network between the crosslinker and polymeric matrix [8].

The aim of this study is to fabricate the glutaraldehyde-crosslinked CNC/chitosan films with different CNC content using conventional heating. The tensile and thermal properties of both non-crosslinked and glutaraldehyde-crosslinked CNC/chitosan films were investigated and compared.

2 Methodology

2.1 Materials

Empty fruit bunch (EFB) was provided by Taclico Company Sdn. Bhd. Chitosan powder was supplied by Cleo Shanghai Pharmaceutical, China. Acetic acid and glutaraldehyde were purchased from Sigma-Aldrich whereas sulphuric acid and glycerol were purchased from Merck. Sodium chlorite was supplied by Acros Organics. Potassium carbonate was provided by HmbG Chemicals.

2.2 Isolation of CNC from EFB

EFB fibres were treated with deep eutectic solvent (DES) at 80 ℃ for 2 hours. DES was made up of potassium carbonate and glycerol at a molar ratio of 1:7. Bleaching was then carried out 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 CNC/Chitosan Films

Chitosan powder was dissolved in 2 v/v% acetic acid solution and heated at 60 ℃ for 4 hours. Glycerol (10 wt%) and CNC were added into the chitosan solution and heated for another 1 hour. The solution was poured into a plastic mold and dried in a non-air-circulating oven at 50 ℃. For crosslinked composites, 5wt% of glutaraldehyde was added. Conventional heating was carried out at 110 ℃ for 20 minutes using a Memmert UF100 universal oven.
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. Samples 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 Differential Scanning Calorimetry (DSC)

DSC was performed using a Shimadzu DSC-60 to investigate the melting behaviors of composites. The scanning was performed in a temperature range between 30 to 200℃ at a heating rate of 10°C/min under nitrogen gas flow of 50 mL/min.

4 Results and Discussion

4.1 Tensile properties

Table 1 tabulates the tensile strength and elongation at break of non-crosslinked and crosslinked chitosan films with different CNC loading. The non-crosslinked neat chitosan film exhibited the lowest tensile strength. The tensile strength increased significantly with the addition of CNC from 37.4 MPa (1 wt% CNC) to 50.9 MPa (4 wt% CNC). The enhanced tensile strength of chitosan films was effective stress transfer between CNC and chitosan matrix. However, the incorporation of 5 wt% CNC has reduced the tensile strength to 37.9 MPa. The reduction in tensile strength could be resulted by the agglomeration of CNC which acted as the stress concentrator and resulted in the uneven stress transfer between the filler and polymeric matrix.

| Samples                        | CNC Content (wt%) | Tensile Strength (MPa) | Elongation at Break (%) |
|--------------------------------|-------------------|------------------------|-------------------------|
| Non-crosslinked chitosan films | 0                 | 32.9                   | 38.6                    |
|                                | 1                 | 37.4                   | 34.7                    |
|                                | 2                 | 41.7                   | 30.3                    |
|                                | 3                 | 45.8                   | 26.8                    |
|                                | 4                 | 50.9                   | 24.4                    |
|                                | 5                 | 37.9                   | 21.5                    |
| Glutaraldehyde-crosslinked chitosan films | 0 | 44.1                   | 30.3                    |
|                                | 1                 | 48.5                   | 37.1                    |
|                                | 2                 | 53.4                   | 24.3                    |
|                                | 3                 | 55.1                   | 21.4                    |
|                                | 4                 | 60.8                   | 28.9                    |
|                                | 5                 | 50.6                   | 16.5                    |
The crosslinking of the films with glutaraldehyde was found to increase the tensile strength of the chitosan films significantly. The enhancement in strength could be attributed to the formation of stable crosslinked network between aldehyde group of glutaraldehyde and amine group of chitosan which enhanced the intermolecular reaction within chitosan matrix [11]. This results was in agreement with Jose and Al-Hathi [12] in which the tensile strength increased remarkably by the addition of crosslinker.

The addition of CNC and glutaraldehyde had a negative impact on the elongation at break of the chitosan films. The addition of rigid CNC reduced the polymer chain mobility and made the film become stiffer [13]. Hence, the CNC/chitosan film become stiffer and less stretchable compared to the neat chitosan film. Furthermore, the addition of glutaraldehyde has further reduced the elongation at break of the films. This was due to the formation of the more compact and rigid crosslinked network which reduced the mobility of polymer chains and resulted in the declination in elongation at break [14]. The result was in concurrent with Yang et al. [15], who reported the reduction of elongation at break in bacterial cellulose/poly(vinyl alcohol) composite after crosslinking.

4.2 Differential Scanning Calorimetry (DSC)

The DSC thermogram of CNC/chitosan films is depicted in Figure 1. The non-crosslinked chitosan films with 0 wt%, 1 wt% and 5 wt% CNC were labelled as XC0, XC1 and XC5, whereas the glutaraldehyde-crosslinked chitosan films with addition of 0 wt%, 1 wt% and 5 wt% CNC were labelled as CH0, CH1 and CH5.

![Figure 1: DSC Thermogram of non-crosslinked and glutaraldehyde-crosslinked CNC/chitosan films.](image-url)

The DSC thermogram of neat chitosan composite film presented an endothermic peak at 92.4°C which was attributed to the dissociation process of intermolecular hydrogen bonding of chitosan [16]. The addition of CNC enhanced the melting point ($T_m$) from 95.7°C to 100.4°C as the content of CNC increased from 1 to 5 wt%. The enhancement in $T_m$ could be attributed to the addition of highly crystalline CNC which acted as the nucleating agent and promoted the crystallization of polymeric composite films [17]. This result was
concorded with Atef, Rezaei, & Behrooz [18] in which the incorporation of CNC greatly increased the $T_m$ of agar composite film.

The crosslinking reaction has further enhanced the melting temperature. The glutaraldehyde-crosslinked chitosan composite films have a denser crosslinked network and stronger intermolecular bonding compared to non-crosslinked composite films, which required a higher temperature and heat energy to disrupt the crosslinked network [19].

5 Conclusion

CNC/chitosan film were successfully fabricated and chemical crosslinked using glutaraldehyde by conventional heating. The tensile and thermal properties of chitosan films were greatly improved by the addition of CNC and crosslinker. However, the incorporation of CNC and glutaraldehyde has a negative impact on the elongation at break of the chitosan films due to the reduction in polymer chain mobility.

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