Effect of Adipic Acid as Crosslinker on the Tensile and Thermal Properties of Rice Straw Cellulose Nanocrystals/Chitosan Nanocomposites

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Abstract

The effect of chemical crosslinking on the tensile and thermal properties of cellulose nanocrystals (CNC)/chitosan nanocomposites was investigated. Adipic acid (AA) was employed as crosslinking agent in this study. CNC reinforced chitosan-based nanocomposites were prepared by solution casting. The inclusion of AA enhanced the tensile strength and modulus of elasticity of CNC/chitosan nanocomposites significantly compared to the non-crosslinked nanocomposites. However, elongation at break decreased notably upon the addition of CNC and AA. The fractured surface of the CNC/chitosan nanocomposites was studied by the scanning electron microscopy (SEM). The behaviors of thermal property of chitosan nanocomposites was investigated by using differential scanning calorimetry (DSC). DSC analysis showed that the AA-crosslinked chitosan nanocomposites has a higher melting point than the non-crosslinked chitosan nanocomposites.

Keywords: Cellulose nanocrystal, chitosan, crosslink, composite, adipic acid.

Article Info

Received 25th November 2019
Accepted 22nd March 2020
Published 1st April 2020
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ISSN: 1823-7010, eISSN: 2600-7444

Introduction

The global plastic production was increased rapidly due to its ease of processing, good barrier properties, and low cost [1]. However, the increased concern for environmental sustainability stimulates the use of renewable resources for producing biodegradable and environmental-friendly composites that could replace the synthetic polymers.

Chitosan [cationic (1-4)-2-amino-2-deoxy-β-ᴅ-glucan] is a natural biopolymer produced from the deacetylation of chitin [2]. Chitosan can be considered as the alternatives in resolving the environmental issues resulted by the plastic products due to its excellent properties such as non-toxicity, anti-microbial activity and barrier property [3]. However, the poor mechanical property of chitosan has limited their usage when compared to synthetic polymer, especially in packaging field [4].

The addition of cellulose as reinforcing agent to biopolymer is of particular interest due to their abundant source, renewability and biodegradability [5]. Cellulose materials with diameters in the nanometer range named cellulose nanocrystals (CNC) is developed. CNC is prepared by strong acid hydrolysis of cellulose, to produce a rod-like crystalline cellulose with a diameter between 10 – 20 nm [6]. The production of CNC has garnered significant interest of researchers owe to its remarkable characteristics such as high aspect ratio, outstanding tensile properties and high thermal resistance [7].

Crosslinking is a significant process in the production of CNC/chitosan nanocomposite as the properties such as mechanical strength of the film are dependent on the crosslinking degree. Sionkowska et al. [8] used tannic acid as crosslinking agent for nanocellulose/chitosan nanocomposites and they observed that the mechanical properties were enhanced notably. While, Khan et al. [9] studied the effect of genipin on the anti-microbial property of chitosan composites. The results showed that the genipin-crosslinked chitosan composite has a higher antimicrobial property compared to non-crosslinked composite. Thus, in order to enhance the tensile properties of chitosan nanocomposites, additives such as crosslinker and fillers are necessary. Adipic acid (AA) was applied as the crosslinker for the CNC/chitosan nanocomposites in the present study. AA is a non-toxic dicarboxylic acid. It is generally applied in the food industry as flavorant and gelling aid [10]. In this work, the influence of the addition of AA as crosslinker on the tensile properties of chitosan nanocomposites were studied. The melting point of nanocomposites was assessed by the differential calorimetry scanning (DSC) analysis. The CNC/chitosan nanocomposite could offer a great potential in various applications especially in food packaging and biomedical field.

Materials and Methods

Materials

Rice straw was collected from the paddy field in Arau, Perlis, Malaysia. Chitosan was purchased from Zhejiang Golden-Shell Pharmaceutical Co. Ltd., China. Sodium chlorite, acetic acid and sodium hydroxide were purchased from Sigma-Aldrich (St Louis, MO, USA). Sulphuric acid and adipic acid were supplied by Merck (Darmstadt, Germany).

Preparation of CNC from Rice Straw

40g rice straw powder was pre-treated with sodium hydroxide followed by bleaching at a temperature of 80 ℃ for 120 minutes. Both pre-treatments were repeated twice to remove any non-cellulosic constituents. Then, the rice straw cellulose was hydrolysed by 64 wt% sulphuric acid at 45 ℃ for 45 minutes. The obtained CNC suspension after sulphuric acid hydrolysis was centrifuged and washed with distilled water. The CNC suspension was then sonicated and preserved in refrigerator under 4 ℃ for further analysis.

Synthesis of CNC/Chitosan Nanocomposites

Chitosan solution was prepared by adding 2 wt% of chitosan into 2 v/v% of acetic acid solution and stirred at 60 ˚C for 4 hours with a speed of 400 rpm. After that, 10 wt% of glycerol as plasticiser and CNC were added into the chitosan solution and stirred for another 1 hour. The mixture was sonicated for 10 minutes before it was poured into a plastic dish and dried in an oven at 50℃. As for crosslinked chitosan composites, 5 wt% of AA was added together with glycerol and CNC. The solution was mixed vigorously for 1 hour using magnetic stirrer until it was homogenized.

Characterization

Tensile Properties

The tensile properties were assessed using 5569-universal tensile testing machine (UTM) (Instron Universal, USA) at 10mm/min according to ASTM D882-A. The specimens were cut into rectangular shape with a length of 10 cm and width of 1 cm. A total of 5 measurements were carried out for each formulation.

Scanning electron microscopy (SEM)

The fractured surface of non-crosslinked and AA-crosslinked neat chitosan and CNC/chitosan nanocomposites was studied by JSM-6460 LA SEM (JEOL Ltd., Japan). Prior to examination, the specimens were coated with a thin layer of platinum. The morphology of samples was determined under a 5-kV accelerating voltage with a magnification of 2000

Differential Scanning Calorimetry (DSC)

DSC was performed using a Shimadzu DSC-60 (USA) 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.

Results and Discussion

Tensile Properties

Tensile properties of non-crosslinked and AA-crosslinked chitosan nanocomposites with different CNC are shown in Figure 1. The tensile strength of chitosan nanocomposites exhibited a significant increase with the incorporation of CNC. The increment could be caused by the increase of hydrogen bonding by the addition of high crystallinity index CNC [11]. Besides, the enhancement in stress transfer between CNC and chitosan and strong filler-matrix interaction had led to a remarkable improvement in the tensile strength. The incorporation of AA has further enhanced the tensile strength by establishing a dense crosslinking network between crosslinker and chitosan matrix [12]. The good performance of crosslinked nanocomposites indicated the favorable interactions among crosslinker, filler and matrix. The reduction in tensile strength for the chitosan nanocomposites with the incorporation of 4 wt% and 5 wt% CNC was attributed to the agglomeration of CNC that reduced the reinforcing effect [13].

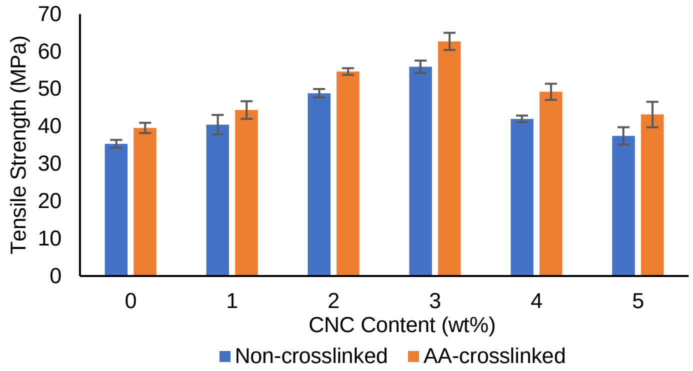

Figure 1: Tensile Strength of Non-crosslinked and AA-crosslinked CNC/Chitosan Nanocomposites

However, the addition of CNC and crosslinkers had a negative effect on the elongation at break of the nanocomposites significantly as shown in Figure 2. According to Ching et al. [14], the incorporation of CNC developed a stable intramolecular and/or intermolecular hydrogen bonds with chitosan and resulted in the decline of elongation at break. Furthermore, the crosslinking reaction has restricted the polymer chain mobility of nanocomposites and decreased the elongation at break.

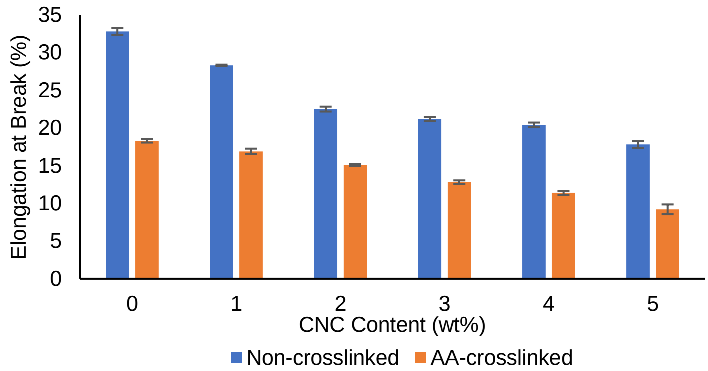

Figure 2: Elongation at Break of Non-crosslinked and AA-crosslinked CNC/Chitosan Nanocomposites

Modulus of elasticity of chitosan nanocomposites exhibited an upward trend as the content of CNC increased (Figure 3). This could be attributed to the increased of stiffness by the incorporation of CNC. The result was in concurrence with the study of Chan et al. [15] which described the enhancement of modulus of elasticity as the CNC content increase. AA-crosslinked chitosan nanocomposites presented higher modulus than non-crosslinked composites. The addition of AA as crosslinking agent formed the amide bonding between AA and chitosan which led to the denser crosslinked networks and boosted the enhancement in the modulus of elasticity [16].

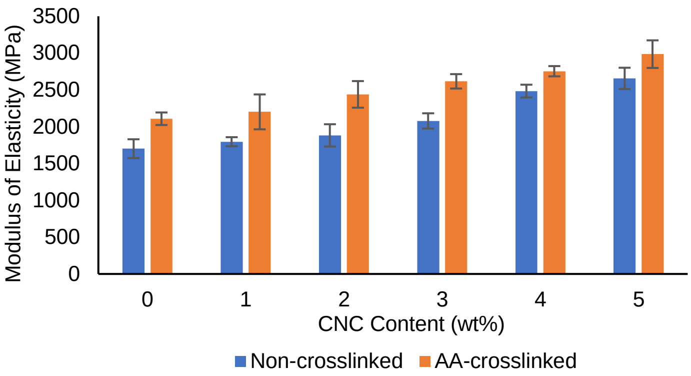

Figure 3: Modulus of Elasticity of Non-crosslinked and AA-crosslinked CNC/Chitosan Nanocomposites

The morphology of neat chitosan and CNC reinforced chitosan nanocomposites fracture surfaces were investigated by SEM (Figure 4). A smooth and homogeneous surface with matrix tearing could be observed in the fractured surface of neat chitosan without and with the addition of crosslinker (Figure 4 (a) and (c)). Additionally, the 5 wt% CNC/chitosan nanocomposite exhibited a rougher morphology due to the incorporation of CNC compared to the neat chitosan. On the other hand, the fractured surface of AA-crosslinked nanocomposites showed a better dispersion and homogeneous surface compared to non-crosslinked nanocomposites.

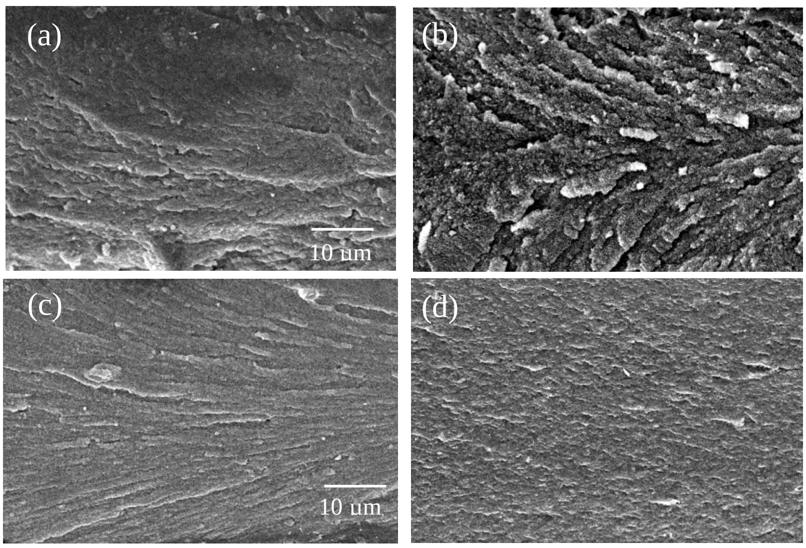

Figure 4: Fractured surface of the non-crosslinked chitosan nanocomposites with the addition of (a)0 wt% CNC, (b)5 wt% CNC; AA-crosslinked (c)0 wt% CNC, (d)5 wt% CNC at 2000X magnification.

Differential Scanning Calorimetry (DSC)

DSC thermogram of chitosan nanocomposites exhibited an endothermic peak at 105.8°C as shown in Figure 5. The inclusion of CNC showed no significant effect on the melting of chitosan nanocomposites. This could be due to the the poor crystallization of polymeric nanocomposite resulted by the poor nucleating effect induced by the agglomeration of CNC [16]. However, the addition of CNC in AA-crosslinked chitosan nanocomposites showed a higher temperature of endothermic peak. This could be attributed to the rigid crosslinked network which required higher energy and temperature for melting [17]. The result was in agreement with Detduangchan et al. [18] in which the crosslinked composites were more thermally stable compared to non-crosslinked composites. The introduction of AA as crosslinker tightened the molecular packing and reduced the polymer chain mobility and hence led to a higher melting point. This suggested that there were strong interactions among AA, CNC and chitosan matrix.

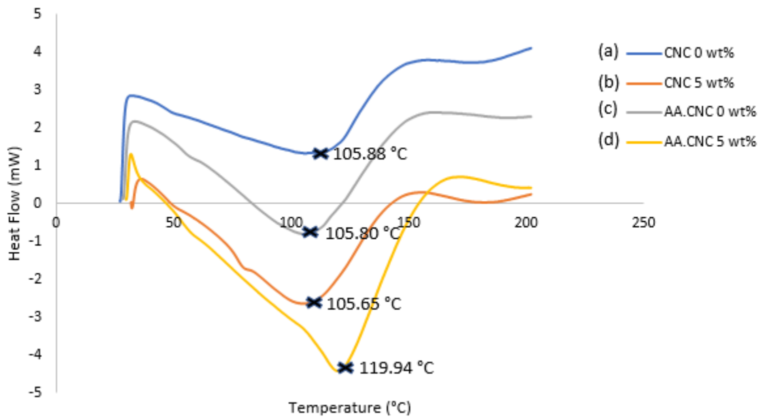

Figure 5: DSC Thermogram of Non-crosslinked and AA-crosslinked CNC/Chitosan Nanocomposites

Conclusion

CNC/chitosan nanocomposites were prepared and chemically-crosslinked with AA. Tensile properties of chitosan nanocomposites were enhanced notably by the inclusion of CNC. The tensile strength was further enhanced by the crosslinking reaction. Besides, it was found that the melting temperature of AA-crosslinked chitosan nanocomposites shifted to higher temperature compared to non-crosslinked nanocomposites.

Acknowledgment

The authors would like to thank the Ministry of Higher Education for the Fundamental Research Grant Scheme (FRGS/1/2017/TK05/UNIMAP/02/10) for financial support.

Author Contributions

All authors contributed to the data analysis, drafting and revising the paper agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors declare no conflict of interest.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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