Water resistance and biodegradation properties of conventionally-heated and microwave-cured cross-linked cellulose nanocrystal/chitosan composite films

## **Abstract**

The cross-linking of [cellulose nanocrystals](https://www.sciencedirect.com/topics/chemistry/cellulose-nanocrystals) (CNC)/chitosan composite films with glutaraldehyde (GA) as the cross-linking agent, was carried out by using conventional heating and microwave curing, respectively. The addition of 5 wt% CNC has significantly reduced the water vapor permeability (WVP) of chitosan films by 30% compared to the neat chitosan film. The decline in the swelling and solubility were also observed in the CNC/chitosan composite films. Moreover, the cross-linking has further enhanced the water resistance by reducing the WVP, swelling and solubility of CNC/chitosan films, especially for microwave-cured GA-cross-linked CNC/chitosan films. The biodegradation testing was performed by the soil burial experiment. The cross-linked chitosan composite films were found to have a lower degradability rate compared with the uncross-linked composites especially for the microwave-cured CNC/chitosan composite films. The composite films-degrading microorganisms were identified as Ophiocordyceps heteropoda, Enterobacter kobei and E. roggenkampii, by the molecular analysis via polymerase chain reaction and DNA sequencing. This study demonstrated that the CNC/chitosan composite films especially microwave-cured composite films could be the suitable materials to be employed as the food packaging with outstanding water resistance property and moderate biodegradability.

## **Introduction**

A new generation of food packaging which based on biopolymers, has garnered a high level of interest in recent years and represent a better alternative compared to the conventional food packaging. Chitosan is a biodegradable polysaccharide produced by the deacetylation of chitin, the second most abundant natural polysaccharide after cellulose [1]. The excellent properties, biodegradability, biocompatibility and non-toxicity of chitosan allow its potential application in the food industry as food packaging or coatings to enhance the food conservation by resorting to its antimicrobial property [2]. However, comparing the properties of biopolymers (such as chitosan) with the petrochemical-based plastics, biopolymers have inferior water barrier property, which restricts their applications in various fields especially in food packaging field. Recently, the chitosan films are doped with various nanofillers to improve the water resistance properties. Among all, cellulose nanocrystal (CNC) has attracted significant attention due to its excellent mechanical properties (high specific strength and modulus), large specific surface area and high aspect ratio [3]. Previous research has proven that the mechanical and water resistance properties of chitosan composite films could be enhanced by the addition of small amounts (<10 wt%) of CNC into the polymer matrix. CNC offers high surface area and reactive hydroxyl groups which alter the composite properties [4]. The properties of composite films could be significantly enhanced through the strong interfacial adhesion between the filler and polymer matrix, as well as the homogeneous dispersion of CNC in the polymer matrix [5].

Another promising way to overcome the poor water resistance property of chitosan film is to modify the physical properties through physical or chemical treatments that induce the intra- and inter-molecular chemical bonding [6]. The treatments alter the polymer network via crosslinking of polymer chains between the functional group of the crosslinker and the amino group of chitosan and thus enhance the degradation and water resistance of films [7]. Among the cross-linkers, glutaraldehyde is the most popular cross-linking agent employed for chitosan due to its great stability and proven ability in enhancing the properties of chitosan composite films in spite of its cytotoxicity [8,9]. Numerous studies have reported that the addition of glutaraldehyde as cross-linking agent can enhance the mechanical and thermal properties of chitosan composite films [10,11].

Aside from the addition of cross-linking agent, curing could also be applied to strengthen the polymeric network structure and improve the properties of composite films. Microwave curing provides a convenient and rapid method for heating that reinforce the intermolecular reaction between the cross-linker and polymer matrix [12]. Microwave curing converts the electromagnetic energy into heat by the intermolecular interactions with the electromagnetic field. The microwave irradiation penetrates the composite films and generates heat in a volumetric manner [13]. Furthermore, microwave curing has also been known as an environmental-friendly technique as it offers numerous advantages over the conventional heating method such as higher crosslinking rate, shorter reaction time, the reduction of hazards and pollution, better heat uniformity and higher product yield compared to conventional thermal curing [14].

Application of biodegradable composite films as alternative materials to petroleum-derived plastics are important as they can be fully decomposed in the environment. The biodegradation properties of composite films are influenced by the environmental conditions, the diversity of microorganisms and the chemical structure of the polymeric composite films [15]. The degradation of chitosan can take from a few weeks to months, depending on its degree of acetylation, molecular weight, environmental relative humidity, and temperature [16]. The biodegradation of composite films comprises two stages: the degradation via hydrolysis followed by the attack of microorganisms on the fragmented composite films and convert it into microbial biomass, carbon dioxide and water [17]. Microorganisms play an important role in the biodegradation process as more than 90 species of bacteria, fungi, and actinomycetes can degrade the plastics [18]. Numerous researches have reported the biodegradability of the chitosan film. However, the effect of conventional heating and microwave curing on the biodegradation properties of CNC/chitosan composite films and associated film-degrading microorganisms have not been thoroughly investigated.

The current study is the extension of our previous research [19], in this CNC are incorporated in chitosan matrix to enhance the water resistance properties of chitosan composites. The main objective of this work was to study the effect between the reinforcement and cross-linking on the water resistance and biodegradation properties of CNC/chitosan composite films. The water resistance properties of the composite films, such as water vapor permeability (WVP), swelling, and film solubility were investigated. Besides, the degrading microorganisms of chitosan composite films were also isolated and identified via polymerase chain reaction (PCR).

## **Section snippets**

## **Materials**

Oil palm empty fruit bunch (EFB) was procured from Taclico Company Sdn. Bhd., Malaysia. EFB was ground and sieved with a 125-µm sieve and then cleaned and dried at 60°C. Glutaraldehyde (25% concentration) and glacial acetic acid were supplied by Sigma-Aldrich (St Louis, MO, USA) while sodium chlorite was obtained from Acros Organic (Geel, Belgium). Potassium carbonate, calcium chloride, sodium chloride, ethanol absolute, magnesium sulphate and ammonium chloride were purchased from HmBG

## **Water vapor permeability**

WVP values of the chitosan composite films is displayed in Fig. 2. The WVP of chitosan composite films was improved by the addition of CNC into the polymer matrix. The WVP of neat chitosan composite film was 5.670 g.mm/m2.day.kPa. It decreased remarkably for 15%, 26% and 30% when 1, 3 and 5 wt% of CNC was added in the chitosan matrix, respectively. The good interfacial adhesion between CNC and chitosan created the tortuous pathway within the composite films and slowed down the water vapor

## **Conclusion**

GA-cross-linked CNC/chitosan composite film has been successfully prepared by using conventional heating and microwave curing, respectively. The WVP, swelling property, and solubility of chitosan films were found to be decreased by the addition of CNC due to the formation of the tortuous pathway within the composite film. The cross-linked chitosan films exhibited a lower WVP, swelling and solubility compared to uncross-linked films, especially for the microwave-cured cross-linked chitosan

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## **CRediT authorship contribution statement**

**Pei Gie Gan:** Writing – original draft. **Sung Ting Sam:** Supervision, Writing – review & editing. **M.F. Abdullah:** Funding acquisition. **Mohd Firdaus Omar:** Visualization, Resources. **Wai Kian Tan:** Writing – review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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