Evaluation of Cross-Linked Chitosan as Filler on Mechanical Properties of Chitosan-Based Bio-Composites

Nurhidayatullaili Muhd Julkapli, Hazizan Md Akil & Zulkifli Ahmad

School of Material and Mineral Resources Engineering, Universiti Sains Malaysia, Pulau Pinang, Malaysia
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The cross-linked chitosan (XCs) was applied as a filler for chitosan (Cs) matrix. The composites film was prepared by solution casting at 0 to 12 wt% content of XCs filler and characterized under tensile analysis. The tensile strength (TS) and Young Modulus (YM) increased linearly with the content of XCs filler (2 to 8 wt%). Contrarily, tensile strain (EB) and toughness (K) reduced correspondingly to similar content of filler. The Fourier Transform Infra-Red (FTIR) and Field Emission Scanning Electron Microscope (FESEM) analysis proved, such results were influenced by the inter hydrogen bonds and electrostatic interactions between Cs and XCs.

**Keywords** Chitosan; Composites; Cross-linking; Mechanical properties

**INTRODUCTION**

Chitosan (Cs) is a natural bio-polymer with unique properties that is high potential to be used in various applications. Apart from naturally abundant Cs is a non-toxic, able to form networks and biodegradable polymer[11-4]. However, due to poor mechanical properties[2,5] high crystallinity[6], high hydrophilicity[7-9] and insolubilities in several acid solutions[10,11] make applications of Cs limited.

Numerous methods are available for improving the properties of Cs film. Incorporation of synthetic and/or organic fillers has been reported to significantly increase the mechanical properties of Cs composites[12-20]. The synthetic filler such as metal[21-23], silica[24], oxide based[25,26] and carbon-based filler[12] induced the Cs composites with more rigidity properties. For example, the addition of 3 wt% of silica oxide (SiO₂) increased the modulus of Cs film up to 3.0 GPa[26].

Other studies reported the mechanical properties of carbon nanotube (CNTs)-filled Cs and concluded that the well dispersion of CNTs gave the Cs composites with dramatically increment in Young's Modulus and tensile strength as compared to native Cs film. Contrarily, the elongation at breaks of Cs film is reduced with addition of CNTs[12]. However, most of the synthetic fillers are not compatible with the Cs matrix, because only mechanical interactions such as interlocking[22] and gripping[24] occurred at the interfacial area of composites components.

Apart from synthetic filler, organic fillers such as plant fiber[27], polysaccharide-based[28] ceramic[13] and mineral[29] have also been used as filler in Cs composites. It was proved that the organic filler are more compatible with Cs matrix than synthetic filler[29-39]. The polar groups and biological characters of organic fillers induced not only mechanical[38] but chemical and physical interactions[37,39] at the interfacial regions of composites components[29-33]. However, the main drawbacks of using organic filler are; first, the harvesting and processing of organic filler is not as straightforward[31,32], and the properties are vary largely depending on geographical locations, processing methods and others. Second, the organic filler is always associated with the lacks in rigidity properties as compared to synthetic filler[32-38].

One way of ensuring a good level of compatibility between filler and matrix is to derive filler from similar origin of that of the matrix. It has been reported that a significant increase in mechanical and stability properties of Cs-based composites using cross-linked Cs (XC) as filler[37,39]. The increase was attributed to the improvement in compatibility between the XCs (as filler) and Cs (as matrix), where the rigidity and homogeneity of the Cs composites system were increased simultaneously. The increased in compatibility is thought to be brought about by the good interaction between the polar groups of Cs matrix and XCs filler[34,37,39].

In this article, the XCs with different cross-linking agent were used as fillers in Cs composite films. The XCs was synthesized using 3,3',4,4'-diphthalic anhydride (X) as the cross-linking agent. Then, a series of XCs-filled Cs composites films were prepared by varying the content of the XCs filler from 0 to 12 wt/v%. Last, the compatibility, homogeneity and rigidity effect of this incorporation was qualitatively investigated through its mechanical properties under tensile analysis.
MATERIALS AND METHODOLOGY

Cs powder was purchased from Hunza Phamarceutical (M) Sdn Bhd having a degree of deacetylation of 67%. The acetic acid (AcOH), N-methyl pyrrolidone (NMP), sodium hydroxide (NaOH), methanol and chloroform were purchased from Merck. All these organic solvents were used without further purification. The XCs filler was synthesized with accordance to the previous reports[11,34]. The chemical structure of the Cs matrix and the XCs filler are illustrated in Fig. 1a and Fig. 1b.

Preparation of Cs/XCs Composites Film

The fine powders of XCs filler (2 to 12 wt/v%) were uniformly dispersed into AcOH solution (in 0.1 M; 100 ml AcOH) using the magnetic stirrer (4 h; 50 rpm). After 4 h of vigorous stirring, the Cs powder (2 g) was slowly added into the mixture. The mixing process was then continued for another 6 hours. The homogenous mixture was then cast into a Teflon container (10 x 10 x 1 cm) and dried at 35°C for 48 h to form a thin film (thickness ≈10 μm). The composite film was further dried at 35°C for 24 h under vacuum. The thickness of the composite film was controlled by pouring a constant amount of composites mixture during wet casting.

The composites mixture was poured onto the centre of the plate and spread uniformly. The conical flasks containing the composite mixture was then sealed with rubber stopper and degassed using a vacuum pump in order to avoid the formation of air bubbles during casting. After drying, the composite films were immersed in 1% NaOH solution for 4 h, and then washed with distilled water until the pH of composites film was neutral. Each composite film was abbreviated as M-XCs (where M gives the wt/v% of XCs).

Tensile Testing of Cs/XCs Composites Film

In order to study the force holding ability of the composites, their mechanical properties via tensile testing was analyzed. The tensile test of the composites film was performed according to the ASTM procedure D 882 (ASTM 1995) using Universal Testing Machine [Instron Model 1122]. Samples (100 x 15 mm) were cut from the composites film and the thickness of the films were measured as the average of five points using the micrometer [Digital Caliper; Model Metatoyo].

Field Emission Scanning Electron Microscopy Analysis of Cs/XCs Composites Films

The microstructures of the fractured surface of the composites films were evaluated using Field Emission Scanning Electron Microscopy [FESEM, Model Zeiss Supra 35 VP]. The excitation energy used was 5 keV. To achieve good electrical conductivity, all the composites films were first carbon sputtered and followed by sputtering of gold palladium mixture before scanning.

RESULTS AND DISCUSSION

Proposed Interactions Between the Cs Matrix and XCs Filler

Two types of interactions are proposed for the interfacial bonds of the Cs matrix and XCs filler; electrostatic interactions and inter hydrogen bonds (Figs. 2 and 3). The electrostatic interactions are occured between the NH₃⁺ ions (from the protonization of NH₂ groups of Cs

![FIG. 1. (a) The chemical structure of Cs matrix. The Cs matrix consists of two copolymer units (X) deacetyl glucosamine (Y) acetyl glucosamine; (b) The chemical structure of XCs derived from the cross-linking process of Cs with 3,3',4,4'-diphtathalic anhydride as cross-linking agents.](image)

![FIG. 2. The proposed electrostatic interactions between NH₃⁺ ions (Cs matrix) with COO⁻ ions (XCs filler).](image)
matrix) with COO\(^{-}\) ions (from the dissociation of COOH groups of XCs filler) (Fig. 2). The inter-hydrogen bonds occurred between the NH\(_2\), OH and CH\(_2\)OH groups (of the Cs matrix) and COOH, NH-R, OH and CH\(_2\)OH groups (of the XCs filler) (Fig. 3).

Fourier Transform Infrared Analysis of Cs/XCs Composites Film

To identify the possible interaction between the Cs matrix and XCs filler, the FTIR spectra for the Cs/XCs composites film is analyzed and showed in Fig. 4. Generally, the FTIR spectrum of the Cs and XCs molecules are identified as follows; 3445 cm\(^{-1}\) (very strong OH and NH), 2923 cm\(^{-1}\) (very strong CH), 1610 cm\(^{-1}\) (the coupling of very strong C=O and N-H), 1735 cm\(^{-1}\) (COOH), 1701 cm\(^{-1}\) (C=O), 1660 cm\(^{-1}\) (NH-R), 1620 cm\(^{-1}\) (-NH-R), 1585 cm\(^{-1}\) (NH\(_2\)) and 1058 cm\(^{-1}\) (very strong C-O) and 880 cm\(^{-1}\) (very strong glucose ring).

The FTIR spectrum of electrostatic interactions between the Cs matrix and XCs filler is presented by increment of intensity and blue-shift of the 2500 cm\(^{-1}\) (NH\(^{+}\)), 1735 cm\(^{-1}\) (COOH), 1650 cm\(^{-1}\) (C=O and N-H) and 1450 cm\(^{-1}\) (asymmetric COO\(^{-}\)) and 1408 cm\(^{-1}\) (symmetric COO\(^{-}\)) bands with addition 2 to 8 wt/v% content of the XCs filler.

The FTIR spectrum of inter hydrogen bonds between the Cs matrix and XCs filler is presented by alteration in the intensity and shiftment of 3500 to 3200 cm\(^{-1}\) (OH and NH\(_2\)), 1735 cm\(^{-1}\) (COOH), 1701 cm\(^{-1}\) (C=O), 1660 cm\(^{-1}\) (NH-R), 1620 cm\(^{-1}\) (-NH-R), 1585 cm\(^{-1}\) (NH\(_2\)) and 1072-1139 cm\(^{-1}\) (-C-O-) bands with addition 2 to 8 wt/v% content of the XCs filler.

Tensile Properties of Cs/XCs Composites Film

The tensile strength (TS), elongation at break (EB), Young Modulus (YM) and Toughness (T) of the Cs/XCs composites film are measured under tensile mode (Figs. 5 and 6). At the XCs content of 0 to 8 wt/v%, the tensile properties of the composite films are linearly related to the

![FIG. 4. The FTIR spectrum of Cs/XCs composites film at different corresponding bands: (i) 4000 to 3500 cm\(^{-1}\), (ii) 3500 to 3000 cm\(^{-1}\), (iii) 1770 to 1700 cm\(^{-1}\), (iv) 1665 to 1616 cm\(^{-1}\), (v) 1563 cm\(^{-1}\), (vi) 1450 cm\(^{-1}\), (vii) 1150 to 890 cm\(^{-1}\).]

![FIG. 5. The stress-strain curves (under tension mode) of Cs/XCs composites film at different content of the XCs filler (0 to 12 wt/v%).]
content of the XCs filler, with the stress-strain curve shows a gradual transition from rubbery to plastic nature (Fig. 5).

In this case, the TS and YM values of the composites' film increased almost 50 and 80%, respectively (Fig. 6). The most noticeable change in the TS and YM values occurred when changing the XCs filler from 6 to 8 wt/v%. On the contrary, the EB and T values of composite film decreased 43 and 62% with the similar content of XCs filler. However, at 10 to 12 wt/v% XCs filler content, the behavior of the composite film corresponded to the relatively brittle material (Fig. 5). Therefore, the TS, YM, EB and K values of the composites’ films showed 12, 67, 2, and 74% of reduction, respectively (Fig. 6).

The increments in TS values are contributed mainly by the compatibility between the Cs matrix and XCs filler. The compatibility of these components is influenced by two main factors. Firstly, the factor may be ascribed to the increment on the number of polar groups into the composites’ film through the addition of the XCs filler. The respective polar groups are responsible for the formation of electrostatic interaction and inter hydrogen bonds. Therefore, the combination of the XCs filler in Cs matrix would produce the composite film with dense intermolecular interactions. The Cs and XCs molecules are physically and chemically linked, consequently, produced more rigid composite film. Second, the molecular similarity between these components in the presence of the glycosidic linkage in their back bone allowed predicting the same behavior under tension mode. Therefore, the load is easily and efficiently transferred from the Cs matrix to the XCs filler and reduced the load resistance within the composites’ film.

The reduction in EB values of the Cs/XCs composites film is due to the deformation of the XCs filler, which is generally much less than that of the Cs matrix. As the content of the XCs filler increased, the chain flexibility of the composites’ film corresponded to the relatively brittle material (Fig. 5). Therefore, the TS, YM, EB and K values of the composites’ films showed 12, 67, 2, and 74% of reduction, respectively (Fig. 6).

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other words, the incorporation of the XCs filler into Cs matrix resulted in strong interaction between the XCs filler and Cs matrix, which restricted the motion of the Cs matrix while only micro phase separation occurred under the applied force.

However, the interactions are destroyed for the formation of aggregates of the fillers with the further increase of the XCs filler content. Therefore, as composition of the XCs filler rose up to 10 wt/v%, the insolubility of the XCs filler was observed. At this composition, the composite film was very delicate and cracked during manipulation, resulted from the decrease in cohesion between the molecules of the XCs filler and Cs matrix. This may be caused by the weaker intermolecular forces between the XCs filler and Cs matrix. The XCs filler tended to form inter hydrogen bonds between themselves rather than Cs matrix and brought to the reduction of TS, EB, YM, and K values of composites film.

Field Emission Scanning Electron Microscopy Analysis on Fracture of Cs/XCs Composites Film. Figures 7(a, b, and c) show the fractured surface of the composites’ film with various content of the XCs filler, conditioned at 50% RH and tested under tensile loads up to breakage. In this case, the appearance of the fractured surfaces is strongly affected by the content of the XCs filler. Figure 7a shows that the planes of the fracture are smooth when composites film was filled with a lower content of the XCs filler. The fractured surface became smooth due to the rapid relaxation of the materials as stress is introduced (Fig. 7b). At the higher content of the XCs filler (8 to 10 wt/v%), the fractured surface became discontinued and sharper.

In contrast to the Cs film, the XCs filler can be easily identified in these images (Fig. 7c). The XCs filler appears as round dots when the concentration of the XCs filler on the surface of the composite film increases in content. It is more difficult to observe the individual XCs filler dispersion in Cs matrix for the composites film with the lesser amount of the XCs filler (less than 4 wt/v%), due to its small particle size. There is homogenous distribution of the XCs filler in the Cs matrix can be observed in the composites film as the content of XCs filler is lower than 8 wt/v%, illustrating good adhesion between the interfacial region of the XCs filler and Cs matrix.

However, some larger spots, which are attributed to the XCs filler aggregates, appear in composites film with 10 wt/v% of XCs filler. Generally, upon fracture, most of the XCs filler, regardless of the XCs filler content, is broken instead of being simply pulled out of the Cs matrix. This observation definitively indicated that the XCs filler has good compatibility or linkage within Cs matrix. It has already been proven that the hydrogen bonds and electrostatic interactions ensure the compatibility of the dispersion of the XCs filler in the Cs matrix. This latter phenomenon greatly contributed to avoid the agglomeration of non-bound XCs filler and any potential microscopic phase separation in the composites film.

Additionally, some very small holes are observed in the interior of the Cs/XCs composites film, having the size in the order of 200 nm. These holes are not related to the content of XCs filler in Cs matrix, since it also appeared in Cs film of equal size and aspect. Instead, they may have been formed and trapped during the drying step by eliminating of the AcOH solvent. A part of these features, the micrographs obtained a featureless surface proper of Cs as compared to the Cs/XCs composites film regardless of the content of the XCs filler.
CONCLUSION
In this study, the compatibility, homogeneity and rigidity of Cs composites was achieved by using a new types of cross-linked Cs (XCs) as a filler. From the results obtained, the following conclusion can be drawn:

1. The FTIR analysis proved that, the compatibility of the composites components is occurred by formation of inter-hydrogen bonds and electrostatic interaction. The formation of these interactions proved by alterations of the 3500 cm\(^{-1}\) (OH and NH\(_2\)), 1735 cm\(^{-1}\) (COOH), 1705 cm\(^{-1}\) (COO\(^-\)) and 1512 cm\(^{-1}\) (–NH\(_2\)) bands in the IR spectrum of the Cs/XCs composites film.

2. The FESEM analysis showed that, the homogeneity of composites film component is achieved due to the well distribution of the XCs filler in Cs matrix.

3. The tensile testing indicated that, the reinforcement effect of the XCs filler into the Cs matrix provides the composites film with better rigidity properties. The TS and YM increased almost 50% to 80% with incorporation of 2 to 8 wt/% of the XCs filler. Meanwhile, the EB and K values of Cs film showed a slightly reduction at the similar composition of the XCs filler.

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