Reinforcement of Chitosan Based Composite Film Using Chitin Nano-Whiskers and The Effects of Heat Treatment For The Wing Membrane of Biomimetic Micro Air Vehicle (BMAV)

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Abstract-- This work investigates the effects of heat treatment on chitosan films reinforced with chitin nano-whiskers and tannic acid as a crosslinker. These films will be used as a wing membrane for the state of the art biomimetic micro air vehicle (BMAV). Films were created using casting-evaporation technique. Samples of non-heat treated nanocomposites films were used as a control and compared with samples that were heat treated. Films mechanical properties were significantly changed when compared to non-heat treated samples. Fourier-transform-infrared spectroscopy (FTIR) were used to investigate molecular interaction of the film. X-ray diffraction (XRD) studies revealed crystallinity changes on the film (both with and without heat treatment). Moisture and wettability studies were conducted to investigate the effects of heat treatment on hydrophobicity of the film.

Index Term— Chitosan film; Heat treatment; Chitin Nano-whisker; Tannic acid; Nanocomposite

I. INTRODUCTION

The need for high performance biodegradable composite materials has driven many researchers to develop strong rigid materials to cater for structural and packaging requirements. Polysaccharide based composites offer the potential to replace non-bio compatible synthetic polymers [1]. Although some biodegradable synthetic materials exist (such as polylactic acid or polyhydroxybutyrate), these materials are more expensive to produce when compared to cellulose or chitin, which are the most abundant polysaccharides available in nature [2].

This research is focused on developing a nanocomposite thin film for use as a wing membrane in biomimetic micro air vehicles (BMAV). This is necessary to make an ultra-lightweight wing with adequate mechanical strength. BMAV are a new class of micro-scaled, ultra-lightweight aircraft that mimics the flying characteristic of insects, by flapping its wings to obtain lift [3, 4]. Due to its small size and weight requirement, BMAV can only carry a small power supply which limits its flight endurance and range.

Therefore it is desirable to deploy BMAV on one-way flight missions to maximize these energy constraints. This necessitates the design of disposable BMAV with low cost, biodegradable parts.

Polysaccharides, such as chitin, act as a reinforcing material for crab and shrimp shells. Despite its wide availability, chitin is underutilized due its insolubility with organic solvents [5]. Chitosan is formed through deacetylation of chitin. Chitosan has an excellent film forming capability and is flexible and biodegradable. The disadvantages of chitosan are its poor tensile strength and high moisture sorption, which leads to gel-like formations [6]. Previous studies have been made to increase its mechanical and physicochemical properties by adding nanocrystalline cellulose as a physical reinforcement and tannic acid as a chemical reinforcement [7]. This improves the chitosan film’s mechanical properties and water resistivity.

Although polymers can be crosslinked and reinforcement material can be added in the matrix, there is a threshold of how much reinforcing material can be added to achieve desired properties. Polymers can also be heat treated to enhance specific properties. Several researchers have used dry heat treatment techniques to increase the water resistance for chitosan film. Positive results have been attained by exposing samples in a high temperature environment for specified times [8, 9].

This experimental work is an on-going series of investigation on heat treated of chitosan nanocomposite film. Previously published article Rubentheren et al. [10] was based on nanocrystalline cellulose and tannic acid being incorporated into chitosan film. The film samples revealed changes in chemical composition and increased in mechanical properties. This work describes the effects of heat treatment on chitosan based nanocomposite film with chitin whiskers added as a physical reinforcing agent and tannic acid used as a chemical crosslinker.
II. Methodology

A. Materials

Chitosan powder (with 75% degree of deacetylation) and chitin flakes (sourced from crab shells) were purchased from Sigma-Aldrich. Glacial acetic acid (Grade AR) and tannic acid were purchased from Friendemann Schmidt. Hydrochloric acid and other reagents were purchased from a local Malaysian supplier and used as received.

B. Preparation of chitin whiskers

Chitin flakes were subjected to a hydrolysis process to remove the amorphous region in the chitin molecule network. Chitin flakes were dispersed into 150 ml of 3 N HCl (weight ratio of 1:30) in a flat bottom flask. [11]. The mixture was then stirred and heated at its boiling temperature under reflux for 180 min. A light brown solution with fine particles was observed at the end of the hydrolysis process. Next, the suspension was centrifuged at 6000 RPM for 10 min. Excess hydrochloric acid was removed from the container and distilled water was added to dilute it. This process was repeated 3 times. A white slurry suspension was then collected and transferred to a dialysis bag and soaked in running water for 2 h, followed by another soaking for 24 h in distilled water to neutralize the suspension. Once neutralized, dilute hydrochloric acid was added (drop by drop) until a pH of 2.5 was obtained. The suspension was then separated into several beakers (30 cm³ volume each) and treated with an ultrasonic bath for 10 min followed by the addition of 5 drops of chloroform to prevent fungal growth. They were then stored in an air tight container at 6 °C. The final concentration of chitin whiskers was 3.3 wt% in the suspension.

C. Preparation of chitosan nanocomposite

Chitosan solution was prepared by adding 2 wt% of chitosan powder into 2% v/v of acetic acid solution and magnetically stirred for 90 min. Once the chitosan powder completely dissolved, chitin whiskers were added using a burette and stirred for an additional 60 min. The mass ratio of chitin whiskers to chitosan was kept at 10:90. For crosslinking purposes, 20 mg of tannic acid was added into chitosan solution and stirred for another 60 min. Finally, the mixed solutions were cast into petri dishes and left overnight at room temperature to eliminate bubble formation as it solidified. Then, the petri dishes were placed into a convection oven at 45 °C for 48 h to obtain dry composite films with a thickness of 90 micrometres.

D. Heat treatment on chitosan composite

The dried films were then heat treated using a convection oven. Samples of pure chitosan film, crosslinked chitosan film, chitosan film with chitin whiskers and crosslinked chitosan film with chitin whiskers were placed in the convection at 180 °C for 30 min. Also untreated treated samples were kept as control specimens.

The film nomenclature used in this article is: C for chitosan film, CX for crosslinked chitosan film, CC for chitosan film with chitin whiskers, CCX for crosslinked chitosan film with chitin whiskers. All heat treated specimens have the letter “H” assigned at the end of their label.

E. Fourier Transform Infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy of the films was recorded using a Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer. A wavelength range of 4000 cm⁻¹ - 400 cm⁻¹ was used with a total scan of 32 and resolution of 4 cm⁻¹.

F. X-ray Diffraction (XRD)

Treated and untreated specimen were analyzed by an XRD machine (PANalytical EMPYREAN) equipped with Cu Kα radiation source (k = 1.54060 Å) operating at 40 kV and 40 mA (at room temperature). The relative intensity was recorded in the scattering range of (2θ) 5°–80° with a step size of 0.1.

G. Mechanical properties

Mechanical properties for all film samples were obtained using a Shimadzu AGS-X series with 500 N load cell and a crosshead speed of 1 mm/min. Composite films were cut in a rectangular shape (50 mm by 8.5 mm). Tensile strength, elongation-at-the-break and Young’s Modulus were calculated according to the ASTM D882−02 method. At least three samples were tested for each film.

H. Water uptake test

The film was cut into 15 x 12 mm pieces. Samples were weighed to the nearest 0.0001 g in a dry state after heating in a convection oven at 105°C for 1.5 h. Water uptake was measured by immersing the dried film pieces in 75 ml of distilled water (under constant agitation) for 1 h at 25°C. The samples were then recovered and dried with filter paper to remove excess surface water and weighed again. The average value of water uptake was calculated using Equation (1) where Ws is the weight of the swollen sample and Wi is the weight of the sample after heating it in a convection oven.

\[
\% \text{ water uptake} = \left[ \frac{W_f - W_i}{W_f} \right] \times 100 \tag{1}
\]

I. Wettability

Measurement of the water contact angle on the film surface reveals the wettability of the film. Samples were prepared as described in section 2.8. The contact angle of the water and film were viewed using the Dataphysics Tensiometer Model OCA 15EC. Samples were preconditioned in dry cabinet before test. Needle tip dispersion were set to 2 μL. Distilled water was used as a liquid medium. The contact angle was measured were captured after 5 s after water contact was established. At least 3 repetitions were performed for each sample to collect the average value.
III. RESULTS AND DISCUSSION

A. Materials Fourier-transform-infrared spectroscopy (FTIR)

Figure 1 shows both heat treated and untreated specimens FTIR spectra for all samples. Interestingly, the heat treatment process significantly changes the absorbance for certain wavelengths. Figure 1(a) shows sample C having a significant difference within the wavenumber of 3600-3000 cm\(^{-1}\). This band is associated with the O-H and N-H stretching vibration \[12\]. The heat treated chitosan film produces a narrow and sharper band across the wavenumber. This is due to the dehydration process that the heat treated film undergoes in a high temperature environment \[13\]. In this work all samples that were subjected to heat treatment show a narrower band compared to non-heat treated samples within the wavenumber of 3600-3000 cm\(^{-1}\). Spectra of crosslinked chitosan film (CX CCX) for both treated and untreated samples (Figure 1(b) and (d)) show more prominent narrowness in the region of 3600-3000 cm\(^{-1}\). This suggests that tannic acid plays a crucial role in causing chemical changes in the chitosan film which is further accelerated by heat treatment. Other bands located at 1700-1500 cm\(^{-1}\) show similar modifications due to the heat treatment process.

An absorption peak at 1560 cm\(^{-1}\) is associated with the formation of carboxylate groups. All heat treated samples exhibited a decrease in this wavenumber band intensity. This was due to the gradual disappearance of the chitosan amino groups in a chemical reaction due to heat treatment \[14\]. Absorptions peak at 1650 cm\(^{-1}\) associated with (C=O stretching in amide group, amide I band) shows a significance increase in absorption for heat treated film with respect to the band of 1158 cm\(^{-1}\) (anti-symmetric stretching of the C-O-C bridge). This is due to an increase of new amide and/or imide groups in the film \[12\]. For the addition of chitin whiskers in sample CC and CCX, (Fig. 1(c) and (d)) no significant differences were observed for the heat treated film. The result obtained by FTIR shows distinct changes in the chemical composition. This explains the changes in film color, mechanical and moisture content properties.

B. X-ray Diffraction (XRD)

X-ray diffractograms provide insight on the molecular structure of the film. Neat chitosan film, both with and without heat treatment, is shown in Figure 2(a). These results show some changes in the peaks. Non-heat treated film exhibits two major peaks at 2θ=22.6° and 11.4° which is associated with the characteristic of hydrated “tendon” conformation \[15\] and two

Fig. 1. : FTIR spectra of all treated and untreated samples, (a) Sample C, (b) Sample CX, (c) Sample CC, (d) Sample CCX
minor peaks located at 2θ=18.1° and 9.3°. Heat treatment of the chitosan film diminishes the peak at 11.4° and shifts another peak to higher 2θ values in the region of 18° to 24° [8]. It has also been postulated that this shift to anhydrous conformation of chitosan, which is similar to the crosslinked samples [13, 15], see Figure 2(b). All heat treated samples experience disappearance of the peak at 2θ= 11.4°. Crosslinked chitosan film (Figure 2b) shows a peak at 2θ=15° which is associated with the characteristic of anhydrous crystalline conformation. Heat treated samples of crosslinked chitosan film shows flattening effects at 2θ=15° [16]. This indicates a synergic effect of tannic acid and heating of the chitosan film.

Figure 2(c) and d show a significant peak rise due to the addition of chitin whiskers. Two major peaks are located at 2θ=19.3° and 9.3° and two minor peaks are located at 23.5° and 21.1°. These are the typical peaks associated with α-chitin [17]. Heat treatment of this film gives a slight reduction on peak intensity at 23.5°. The change of this peak reflects a change in the mechanical properties of the heat treated films.

![XRD diffractograms of, (a) Sample C, (b) Sample CX, (c) Sample CC, (d) CCX](image-url)
C. Mechanical properties

Figure 3(a) shows the tensile strength of both treated and untreated films. The control samples show an increase in tensile strength when additives are introduced. Neat chitosan film C exhibits the lowest tensile strength of 34.32 MPa. The crosslinked sample CX shows an increased strength of 43.98 MPa. Addition of 10% nano sized chitin whiskers also increases the tensile strength of the film by 6.87 MPa. The highest strength achieved by non-heat treated film was sample CCX with a strength of 47.34 MPa. These results are similar to previous observation by Rubentheren et al. [18]. Figure 3(b) shows the percentage of elongation-at-break. The addition of physical and chemical additives decreases the elongation-at-break. However, insignificant changes were observed for sample CC and CCX for this measurement. Sample C has greater ductility than sample CCX, which is more brittle. Figure 3(c) shows Young’s Modulus of both treated and untreated samples. The addition of tannic acid and chitin whiskers increases the stiffness of the chitosan matrix.

Crosslinking the film increases the tensile strength and stiffness with a slight reduction on elongation-at-break due to the formation of a more stable network over the chitosan matrix. Similar results have been attained by adding tannic acid into gelatin films [19]. Introduction of chitin whiskers also increases the tensile strength and stiffness but significantly reduces the percentage of elongation-at-break. From the TEM results, nano-sized chitin whiskers having a rod-like shape that acts as a reinforcing agent that increases the tensile strength and act as a barrier that reduces the intermolecular mobility. This promotes brittleness in the chitosan film matrix and increases the stiffness of the film.

Heat treatment yields an increase in tensile strength and drastically improve Young’s Modulus for all of the samples. The highest difference between untreated and treated films was sample CC which gained a tensile strength and stiffness of 8.75 MPa and 281.0 MPa respectively. The increase in tensile strength and stiffness (regardless of physical and chemical additives) was due to the development of a crosslinked matrix and stabilization when chitosan is being heated [20]. The addition of tannic acid and chitin whiskers further accelerates the crosslinking process during heat treatment. Changes in chemical composition as observed in FTIR analysis suggest that there is a good miscibility and interaction between tannic acid and chitin whiskers in the chitosan matrix. Drastic changes in elongation-at-break between treated and untreated samples were due to dehydration of chitosan matrix during heat treatment and inducement of crosslinking effect makes the film more brittle.

Fig. 3. Comparison of treated and untreated film mechanical properties, (a) Tensile strength, (b) Elongation at break, (c) Young’s Modulus
D. Moisture Studies

The effects of heat treatment on moisture uptake is shown in Figure 4. The addition of tannic acid and chitin whiskers is known to improve the water resistivity. The non-heat treated samples CX, CC and CCX have a significant water resistivity improvement. This is due to addition of the chitin whiskers, which increases the concentration of nanocrystals and acts as a hydrophobic barrier preventing water absorption in the chitosan matrix. Also the addition of tannic acid as a crosslinker reduces the water resistivity. This is due to carboxylic acids in the tannic acid reacting with the amine group to form an amide, as observed in FTIR analysis. This eliminates water in the reaction [13].

Water resistivity was significantly enhanced by heat treatment. This same behaviour was recorded for all the other heat treated samples. Similar results were obtained by several researchers [21]. Other research stressed that these changes are due to fact that the chitosan matrix had evaporated moisture from the matrix at higher temperatures (150 °C – 200 °C) [22]. The chemical changes at elevated temperatures converts chitosan into a chitin-like material. At higher temperatures the crosslinking agent is more effective.

E. Wettability

Contact angle is another important parameter that can define a material's hydrophobic/hydrophilic properties. It is the measurement of tangent line at the point of contact of the liquid droplets. Figure 5 shows static water contact angle for all samples. Sample C exhibit contact angle value of 90° which is in the range comparable value produced [23]. Although chitosan is hydrophilic by nature, its wettability could be affected when blending with another material or by heat treatment. Addition of tannic acid as a crosslinker (sample CX), the contact angle yields an insignificant value of 92°. However introduction of nanomaterials translate the chitosan film to exhibit hydrophobic properties. Sample CC shows a contact angle of 99.8° (CNW based) and 100.3° (NCC based). This is due to the hydrophobic nature of nanomaterials that prevents the water molecules to slip into hydrophilic surface of chitosan matrix. Crosslinked nanocomposite chitosan film (sample CCX) exhibits a lower contact angle of 95.9°. Although these films shows better water absorption resistivity, it does not prove to be useful in wettability. The addition of chitin nanowhiskers might lead the film to have a porous surface which display a highly hydrophobic character due to the surface roughness and possibilities of air entrapped inside the pores [24]. Heat treatment counterpart shows a slight improvement on the wettability except for sample CC which shows some reduction on contact angle. This suggest that hydrophilic nature of chitosan film can be altered with physical and chemical additives.
IV. CONCLUSION

The heat treatment process on chitosan nanocomposites improves its mechanical strength and water resistivity, regardless of the additives studied. FTIR spectra shows changes in chemical composition when the film is subjected to heat treatment. The XRD pattern reveals diminishing of peaks at $2\theta = 11.4^\circ$ for heat treated samples. Heat treatment removes the water in the chitosan matrix, making the film more brittle and rigid as opposed to the highly ductile nature of chitosan. The result shows that heat treatment film possesses more suitable mechanical properties for use as a wing membrane for BMAV, as well as other applications that require robustness.

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