THE STUDY OF GLUTINOUS STARCH-CHITOSAN BLEND AS A BIOMEDICAL MATERIAL

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Abstract
Chitosan/starch blend films were successfully prepared by using acetic acid as a solvent. Starch was used as filler in chitosan films of biopolymer. In this study, two types of starches which are black glutinous rice and regular rice was used to see the differences of its effect to the biopolymer films. The structure and properties of the film were studied by water absorption test, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analysis. The results of water absorption test showed that the sensitivity of the chitosan's film to the water was lowered by addition of starch. The results for FTIR and SEM analysis showed that both polysaccharides were compatible. These results proved that the interaction between chitosan and starch molecules exist in the blend films. The sensitivity of water was lowered when chitosan and starch were blended by volume ratios of 5:5, 7:3, and 3:7, in which the best result was achieved for composition of 3:7 chitosan/starch. Among these two starches, the best result was given by starch from regular rice with the ratio of 3:7 chitosan/starch films which is the lowest percentage of water absorption by the film (1.33x10^{3} %) was achieved.
Keywords: *Chitosan; Starch Films; Biopolymer; Water sensitivity*

I. Introduction

Food, pharmaceutical and waste water treatment are the examples of many industrials applications where polysaccharides materials have a high potentials. Polysaccharides are abundant in nature and known to be renewable, biodegradable, and nontoxic [1-4]. These natural polymers have a huge potential to replace the uses of synthetic polymer. Among polysaccharides, chitosan which are widely used in blend films especially to improve the structural strength of the polymer [5]. Chitosan, poly-β-(1→4)-2-amino-2-deoxy-D-glucose, is an aminopolysaccharide derived from the N-deacetylation of chitin [6]. It comes from deacetylation of seafood's waste product, as chitin is a biopolymer that is the third easiest to find in nature after cellulose and hemicellulose. Chitin can be found from exoskeleton of crustaceans such as crab, lobster and shrimps [7]. Chitosan are able to form as food packaging or coating since it's able to form as film by itself without the need to combine with other chemicals and the presence ofchitosanase which is a degradable enzyme that gave chitosan its biodegradability property [8, 9]]. Thus, it is one of the best candidates to replace petroleum-based plastics since petroleum-based plastics is unable to decay in short time and this can be harmful to the environment [10]. Chitosan potential as a biomedical material can be attributed to its outstanding bio-compatibility, anti-microbial action, and non-poisonous [11-15]. It also might be used as antitoxic packaging for food [16] and many pharmaceutical applications such as drug packaging or as coating for medicine [17]. Unfortunately, the application of chitosan still has some limitation. For instance, it cannot easily set as film especially for packaging since chitosan has high sensitivity to water or moisture [18-20]. Thus, blending chitosan with pure polymer [21-22] or by using modifying agents [22-24] could improve the performance of the chitosan-based films. Starch could be used to support chitosan to form film [26]. Starch is a natural biopolymer which made up of two homopolymers: amylase and amylopectin. The combination of chitosan and starch can be used to develop biodegradable film or plastics for packaging materials [13]. Corncob starch, cassava starch, potato starch, and gelatinize starch are suitable candidates to produce biocomposite film to partially or entirely replace plastic polymers due to their abundance [25]. However, it needs element of support to form a film since it cannot stand as a film by itself and the application of starch film is limited due to its water solubility and brittleness [26]. Hence, chemical modification is one of the ways to overcome these poor properties of starch. Starch may be blended with different proteins to reduce the wettability of the film and to increase their tensile strength [14].

The aim of this project is to examine the effect of different types of starch on the chemical properties of chitosan/starch biocomposite films and to examine the improvement of chitosan/starch biocomposite film in term of water sensitivity based on different types of starch. There are three types of materials blended with different percentage of starch was used to investigate its effect to the biocomposite film. The films produced were characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red (FTIR) and water adsorption test to investigate the film's wettability, chemical interaction, and morphology.

II. Materials and Methods

A. Materials

Chitosan was obtained from Acros Organics with molecular weight average of 100,000-300,000 g/mol. Regular rice and black glutinous rice were purchased from a local market in Perlis, Malaysia. Firstly, all the grains were separately crushed into powder form and dried at 70 °C for 24 hours.

B. Films Preparations

Chitosan/starch films were prepared by using solvent casting method. 1 w/v % of chitosan solution were prepared by dissolving chitosan into 2 v/v % acetic acid. The solution was stirred at room temperature for 30 minutes. Next, starch solution of regular rice was prepared by dissolving starch with 2 v/v % of acetic acid. The starch solution was stirred for 2 hours. After that, chitosan solution was mixed with different ratio of starch solution as shown in Table 1. The cast films were dried at room temperature for 72 hours. The procedure was repeated by using the black glutinous rice. Pure chitosan films were used as control. All the samples were tested in duplicates and each experiment was repeated three times.

Table 1. Ratio of the Biocomposites Solution

No	Types of starches	Composition	
		Chitosan solution (ml)	Starch solution (ml)
1	Regular rice	5	5
2		3	7
3		7	3
4	Black glutinous rice	5	5
5		3	7
6		7	3

C. Characterizations

Fourier transform infrared spectroscopy (FTIR) analysis was done by using Perkin Elmer, Model L1280044 instrument. Next, the scanning electron micrograph (SEM) was taken by using SEM (JEOL JSM-6460LA). Lastly, water adsorptions test was conduct to test the porosity and wettability of the sample. The test was conducted by immersing 3 cm^2 of biocomposite film into 20 ml distilled water about 30 minutes. The initial and final weight of the film was recorded and the percentage of water adsorption was calculated as below:

$$\%\,water\ adsoption = \frac{(final\,weight\,of\,film - initial\,weight)}{initial\,weight\,of\,film}\ x\ 100$$

Results and Discussion

1. Water Adsorption Test

The amount or the percentage of water adsorption for pure chitosan film is very high compared to the other biocomposite film which is 9.14x103 %. By blending chitosan with starch, the water sensitivity of the films was reduced significantly. Between these two types of starch that had been mixed with chitosan, regular rice had better adsorbtion criteria compared to black glutinous rice. However, for 3:7 and 7:3 ratios, mixtures of chitosan/regular rice starch gave a better result compared to other composition. From the graph in Figure 1, it is clearly seen that for each types of starch, the best ratio is chitosan/regular rice starch with ratio of 3:7 since the percentage of water adsorption is the lowest compared to the other two ratios (7:3 and 5:5).

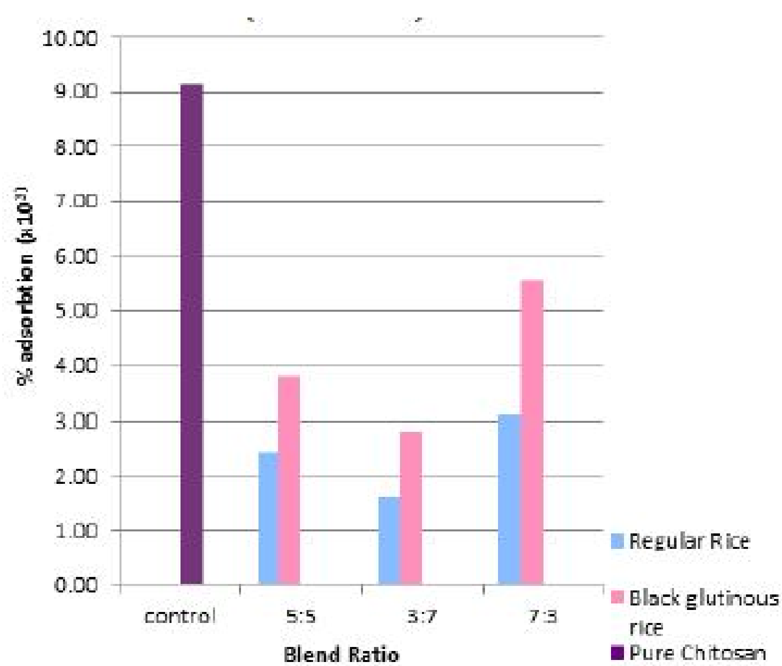
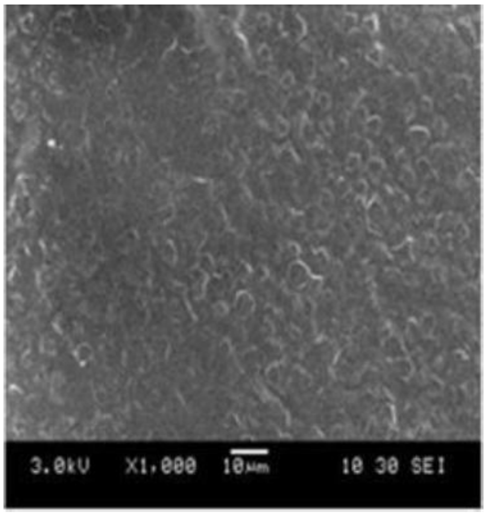


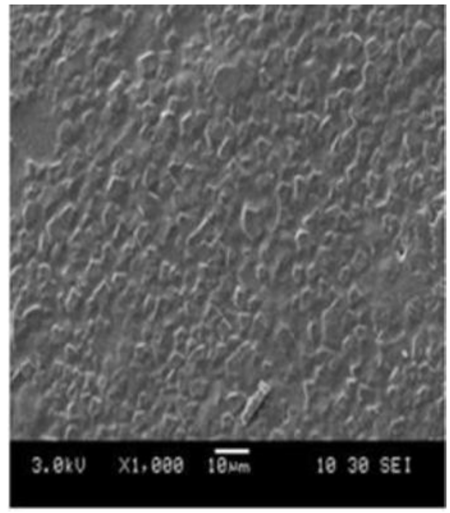
Fig. 1: The Results for Water Adsorptions Test

B. Scanning Electron Microscopy (SEM)

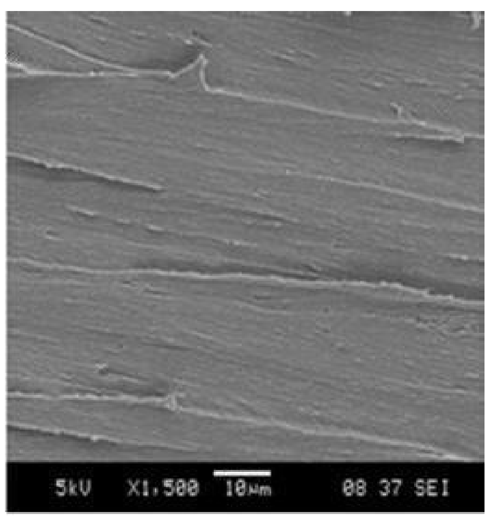
Figure 2 shows the morphological differences of the pure chitosan film and chitosan/starch film surfaces for with different type of starches. Black glutinous rice gave the roughest surface compared to regular rice. The roughness of the film’s surface could have improved the water sensitivity and this is verified by our observation. Hence, chitosan/ black glutinous film has the lowest percentage of water adsorption due to its rough surface.



(a)



(b)



(c)

Fig. 2: SEM Images of (a) Chitosan (b) Chitosan/Glutinous Rice with Ratio 3:7 (c) Chitosan/Normal Rice with Ratio 3:7

C. Fourier Transform Infra Red (FTIR)

The spectrum of control, chitosan/starch (black glutinous rice) and chitosan/starch (regular rice), are shown in Figure 3. The spectrum of chitosan obtained from previous research [27-28]. The broad band for pure chitosan at 3497 cm-1 was the OH stretching and it happened to shift to 3450 cm-1 for black glutinous rice and 3493 cm-1 for regular rice. It can conclude that there were some interaction happened between chitosan and both types of starch molecules that may due to the existent of intermolecular hydrogen bands in the molecules of the composite [29].

The peak at 1556 cm-1 for pure starch was shifted after the addition of starch due to the energy absorbed caused by NH bending (amide II). The peak was shifted to 1506 cm-1 for addition of black glutinous rice starch. While the addition of regular rice starch, the peak was shifted to 1515 cm-1. The bands at 1647 cm-1 for control shifted to 1647 cm-1 for black glutinous rice and to 1651 cm-1 for regular rice were assign to some interaction between starch and chitosan molecules may be due to formation intermolecular O-H bending of water [30]. This shows that the sensitivity of the film to the water was improved by adding the starches.

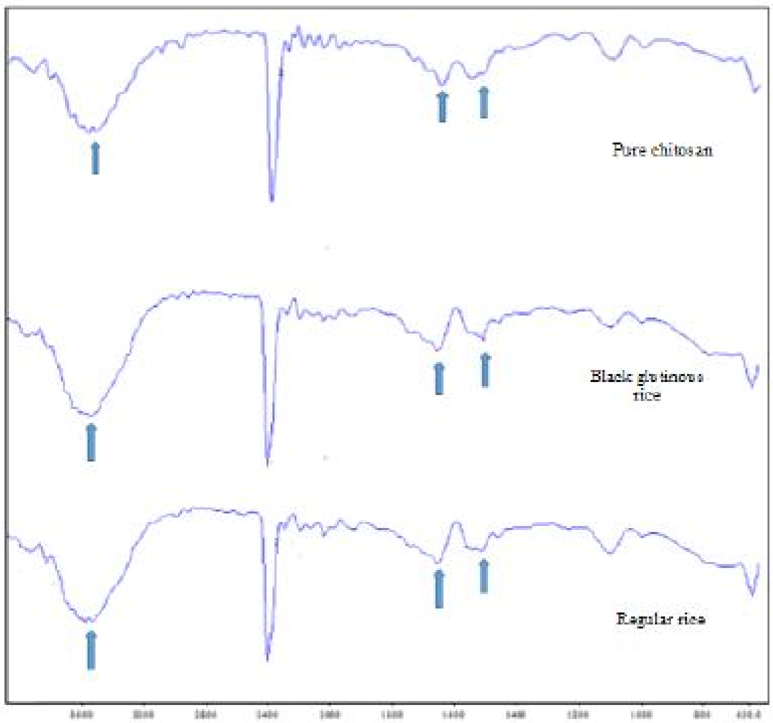


Fig. 3: The FTIR spectra of 3:7 chitosan/starch blend

IV. Conclusion

Chitosan/starch films where made from blends of two types of starch either black glutanous rice and regular rice in order to test the improvement of film’s properties for each types of starch can gave. The addition of starch to chitosan had improve the roughness surface of chitosan thus lowered the sensitivity of film to the moisture or water since it was able to adsorb more liquid on it surface. The best adsorbent between these two composite is chitosan/ black glutinous strach with ratio 3:7. The chitosan also able to act as supporter for starch to stand as a film since starch is unable to became a film by itself.

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