ENHANCED MECHANICAL PROPERTIES OF ORGANIC-INORGANIC CHITOSAN/NANO SILICA COMPOSITE FILM

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ABSTRACT: Composites made from organic and inorganic materials are already well-known in exhibiting potential properties as bio-materials. In this study, nano silica was mixed with chitosan solution to fabricate degradable and mechanically robust organic-inorganic composite biomaterial films. The various chitosan and nano silica powder ratio were used to find the optimum amount of each material to get the best film properties. Nano silica was successfully incorporated into chitosan, confirmed by FTIR results, which showed a new peak at 486.06 cm-1 and vibration shift in the area around 1000-1100 cm^{-1}. The film thickens with an increasing amount of nano silica. The lowest swelling degree and degradation ratio were observed in film mixtures containing 5% nano silica. Samples with the same composition also showed the highest tensile strength. Overall, incorporation of nano silica led to promising results for enhancing film-shaped chitosan composite properties.

KEYWORDS: *Chitosan; Nano Silica; Composite; Mechanical Strength*

1.0 INTRODUCTION

Polymers from natural materials (biopolymers) with excellent properties such as biocompatible, biodegradable, and non-toxic are commonly utilized to be applied in many application areas, including agriculture, food, medical, and pharmaceutical [1]. One of the biopolymers that attract a lot of attention to be used as a bio-material is chitosan. Chitosan is a natural polysaccharide and can be found abundantly in crustaceans' exoskeleton [2-4]. This compound has anti-bacterial properties, non-toxic, and easy to modify. Chitosan is a polymer that has a positive charge (poly-cation). In the application which requires a form of film (fertilizer coating or drug delivery matrix), this property is found to be helpful as it will improve the adhesive properties (ability to attach) of the film [5-6]. However, in its application, chitosan has a drawback. One significant deficiency of chitosan and other biopolymers is their high tendency to swell (the occurrence of swelling when the film is in a liquid system). This high level of swelling will trigger an initial burst release of the coated material [7]. Therefore, efforts are needed to modify the film from this material to improve its characteristics.

One way to improve the properties of chitosan is to blend it with inorganic ingredients. The formation of organic-inorganic composite film offers an opportunity to combine the film-forming properties of organic polymers and the stability of inorganic compounds to make a highly functional material. The combination will combine the advantages of the inorganic material and the organic polymer leading to improved materials' properties. Previous studies even showed that this method could enable the control of crystalline structure in composites. These approaches to the fabrication of organic-inorganic composites provide necessary biomedical materials with novel functions [8-11].

In this study, nano silica will be incorporated with chitosan as an inorganic part for composite film making. The incorporation aims to modify the structure of chitosan film. Thus, reduce the degree of swelling or increase the mechanical strength. Even though there may be many studies about chitosan-based film synthesis, one with silica powder with a simple mixing method and focusing on studying in mechanical properties is still very rare. In this paper, the authors would like to observe the effects of the addition of nano silica powder in a simple way to the properties of chitosan film and investigate the optimal condition to get the best film properties.

2.0 METHODOLOGY

2.1 Materials

Chitosan (powder form, low molecular weight, 75-85% deacetylate) and nano silica (powder form, 10-20 nm, 99.5% trace metal basis) Sigma Aldrich grade. Acetic acid glacial 100% (Merck, Germany). Phosphate Buffer Saline (PBS: pH 7.4) was provided by Faculty of Dentistry, Universitas Gadjah Mada (made by dissolving NaCl, KCl, Na_2HPO_4, KH_2PO_4, and HCl into distilled water).

2.2 Film Preparation

Chitosan (low molecular weight) was poured and stirred in 1% mL acetic acid/mL distilled water at room temperature for 3 hours to ensure the chitosan was homogeneously dissolved. A certain amount of nano silica powder (0%; 2.5%; 5%; 7.5%; 10% weight of nano silica/weight of chitosan) was mixed in the solutions and stirred at room temperature for four hours. Five mL each of the finished solution was poured into Ø11 cm polyethylene petri dishes and dried for 48 hours at 30°C

2.3 Fourier Transform Infra-Red Spectroscopy

The drug delivery films were analyzed by Fourier Transform Infra-Red (FTIR) Spectrophotometer (8201PC Shimadzu) with a territory of wave number between 4000-400 cm^{-1}. FTIR could prove nano silica and curcumin content in the films by showing some shifting in the obtained films' spectra. Besides, FTIR analysis could also give information about interaction force between substances, which is very important to understand the film's mechanism better.

2.4 Mechanical Strength Test

One of essential parameters in making a hybrid material is the change of mechanical ability. The mechanical performance measured in this experiment was tensile strength and percentage of elongation. The tensile strength test was executed using standard ASTM D 638M–84 procedures, and the elongation percentage was measured using Universal Testing Instrument (UTI).

2.5 Swelling Degree Measurements

The degree of swelling (SD) was observed by cutting the film by a punch with a diameter of 1.25 cm and then placed in a desiccator to remove the remaining free water. The dried film was then weighed

(Mo) and immersed in a test liquid (PBS pH 7.4) at room temperature. After a particular time, the film was taken out from the liquid and immediately weighed (Ms). The degree of swelling was calculated in percentage using Equation (1) such as

$$\text{Swelling Degree} = \frac{(\text{Ms-Mo})}{\text{Mo}} \times 100\% \tag{1}$$

2.6 Degradation Rate Measurements

Degradation rates are closely related to the swelling behavior of the material. The higher swelling degree leads to the increase of degradation rate. This test was conducted by cutting the film by a punch with a diameter of 1.25 cm and then placed in a desiccator to remove the remaining free water. The dried film was then weighed (Mo) and then immersed in test liquid (PBS pH 7.4) under room temperature for a total time of six (6) days. At certain times, the film was removed from the solution, dried using an oven at 50°Cfor three hours, and then weighed (Md). The calculation of degradation rate was using Equation (2).

$$\text{Degradation Rate} = \frac{(\text{Mo-Md})}{\text{Mo}} \times 100\% \tag{2}$$

3.0 RESULTS AND DISCUSSION

3.1 FTIR Characterization Result

A composite film made from chitosan and nano silica was successfully fabricated. The presence of each material, including chitosan and nano silica in the film, can be observed from FTIR analysis results in Figure 1. Furthermore, the possible interaction between each material also can be predicted. FTIR spectra in Figure 1(a) shows some common characteristics for chitosan as there appear peaks in 2924 cm^{-1} which represents alkyl C-H stretching, and 1152 cm^{-1} which indicates a C-O-C bond. There is also a broad stretching area around 3300 cm^{-1} that can be interpreted as OH and/or NH bond. Nano silica in the film can be noticed by inspecting the FTIR spectra in Figures 1(a) and 1(b). A new peak around 486 cm^{-1} appeared due to Si-O-Si bands' characteristics in the chitosan/nano silica film. The vibration shift in around 1000-1100 cm^{-1} is broad due to the presence of Si-O-Si stretching and Si-OH vibration [9]. This result shows that nano silica exists in the film.

Previous observation using the digital microscope conducted by Imani et al. [12] showed that nano silica addition resulted in the film's rougher surface.

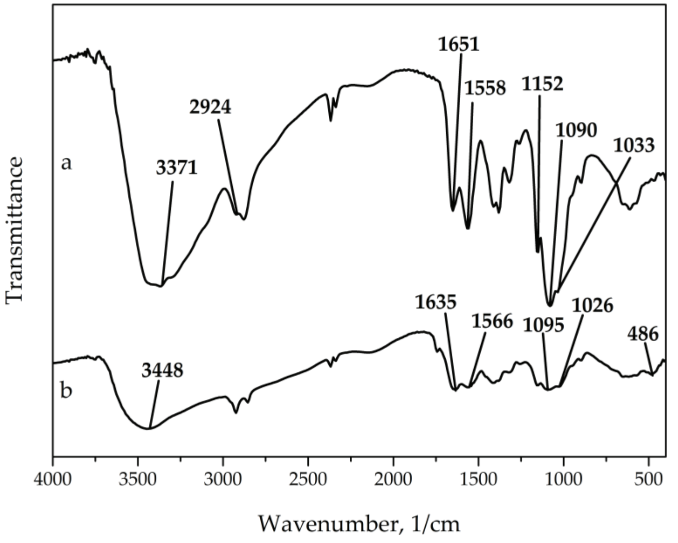

Figure 1: FTIR result of (a) chitosan film and (b) chitosan/nano silica film

3.2 Swelling Behaviour of Chitosan/Nano Silica Films

Swelling degree (SD) is a parameter that represents the swelling ability level of a material that causes the pore size of the material to increase. The size of the SD in a material is closely related to the strength of the chemical bond in the material, the original pore size, and the level of crystallinity of the material itself. As shown in Figure 2, the SD values of the overall composite film were reduced in the presence of nano silica. Addition of 2.5%, 5%, or 7.5% g nano silica/g chitosan has a significant effect ($p < 0.05$) on the difference of SD values of the obtained films. In this study, the addition of nano silica makes the bonds between molecules in the film stronger, so that the swelling test liquid becomes more difficult to diffuse into the film. In addition, the adsorption ability of chitosan film itself was also reduced because the functional group of chitosan, which was previously free, has undergone interaction with nano silica [13-14].

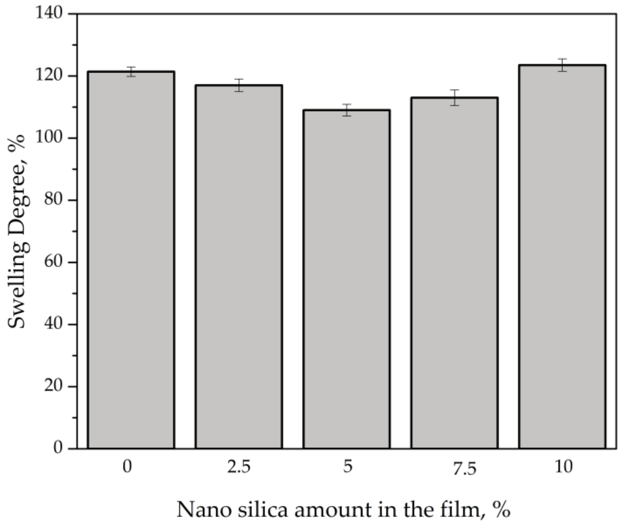

Figure 2: Swelling profile of composite films

3.3 Tensile Strength Measurement

One of the important parameters in film-forming is the thickness of the film. The thicknesses of obtained films with various concentrations of nano silica are presented in Figure 3. As the content of nano silica was increased, resulting composite film became thicker. The statistical analysis result showed that the addition of 5%, 7.5% and 10 % of g nano silica/g chitosan give a significant effect ($p<0.05$) on the thickness. The larger amount of nano silica added into the solution may have increased possibility of aggregation. The aggregates of nano silica would make the solution unevenly dispersed and resulted in non-homogenously casted thick films.

The results for mechanical tests in Table 1 show that the addition of nano silica up to 5% could increase the film's tensile strength, but further addition will reduce the value of its tensile strength. This increase in tensile strength values is explained by nano silica causing the film to become more rigid and the film structure became more robust. The bond between hydroxyl groups of silica and amine groups in chitosan can also strengthen the composite films that have been made. The result is in good accordance with swelling experiments shown in Figure 2.

The decrease in tensile strength in films with more than 7.5% nano silica may have caused by excessive nano silica leading to the agglomeration due to poor interfacial bonding that made the nature of the inorganic-organic film (chitosan/nano silica) to be more to the inorganic side, such as strong yet rigid and brittle [15].

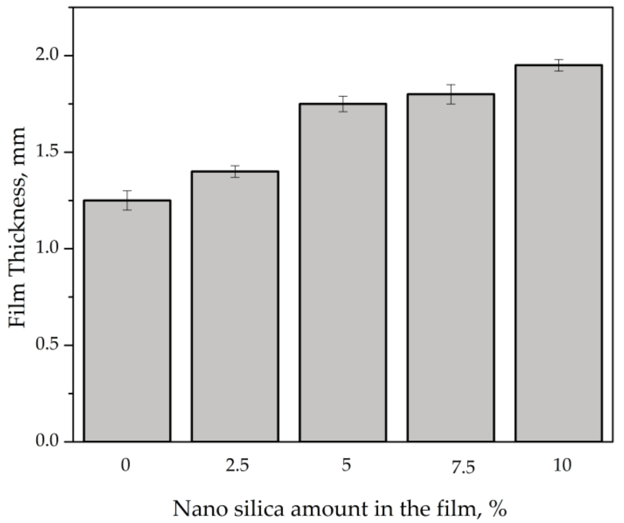

Figure 3: Film thickness of composite films

Table 1: Tensile strength of composite films

Nano silica amount (% nano silica/chitosan)	Tensile strength (10^{-3} MPa)
0	1.56 ± 0.03
2.5	2.84 ± 0.02
5	3.14 ± 0.03
7.5	2.08 ± 0.03
10	0.6 ± 0.05

This study's result is inline with Liu et al. [9], which stated that, up to a point, nano silica would be dispersed as filler in the interspace of chitosan network. Using the hydrogen bond, the nano silica has a function to become a junction to reinforce the network structure of chitosan-based film [9]. On the other side, the percentage of elongation tends to be stable because there was no additional plasticizer on the matrix as plasticizer is the main factor deciding the film's elasticity.

3.4 Degradation Rate of Chitosan/Nano Silica Film

The graph in Figure 4 shows that with the addition of nano silica, the film took a longer time to degrade. This is indicated by the lower degradation percentage of the four hybrid films compared to films made only of chitosan. The effect of adding nano silica to the reduction of this film's degradation percentage was analyzed by ANOVA analysis. The result was a film with the addition of 5% g of nano silica/g chitosan had a significant effect ($p<0.05$). Stronger resistance against degradation was possibly because of stronger bonds between molecules that exist in hybrid films and stronger structure of the hybrid films [16]. Although all hybrid films showed lower degradation percentages compared with a chitosan only film, the addition of nano silica with 7.5% and 10% g nano silica/g chitosan gave higher degradation percentages compared with that of 5% g nano silica/g chitosan. This happened probably because the addition of nano silica more than 5% g nano silica/g chitosan made the film not homogeneously dispersed as we discussed before. The inhomogeneous films have many nano silica aggregates on the surface. During the degradation test, when nano silica aggregates were released from the film, it would lead to a larger film mass reduction. This may have contributed in higher degradation percentage observed.

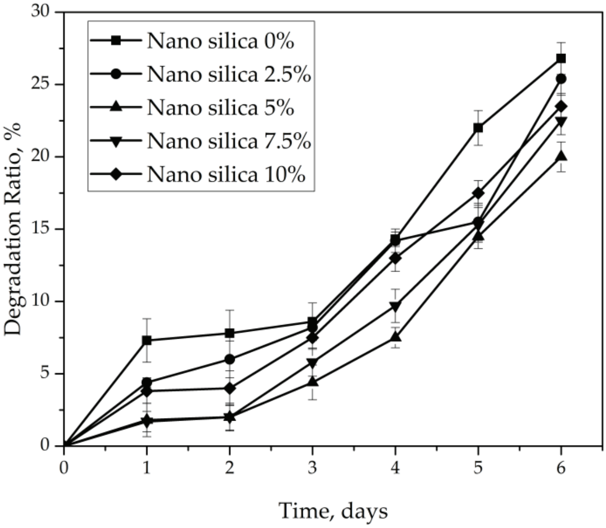

Figure 4: Degradation rate of chitosan/nano silica films

4.0 CONCLUSION

The incorporation of organic and inorganic materials in this study resulted in a promising result with a film-shaped composite. The addition of nano silica up to 5 % nano silica/chitosan to the matrix was proven to enhance the chitosan-based film's properties. The degree of swelling decreased by as much 13% and the tensile strength increased compared to films made of chitosan alone. The presence of silica has also been shown to reduce the degradation rate of the film. This preliminary discovery can be explored further, especially in biomaterial applications, by evaluating its performances through biological and pharmaceutical tests.

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