Effect of Cellulose and Titanium Dioxide on the properties of Chitosan film

Rahmi1, *, S Lubis1 and N Az-Zahra1

1 Chemistry Department, Faculty of Mathematics and Natural Sciences, Universitas Syiah Kuala, Banda Aceh, Indonesia.

* E-mail: rahmi@fmipa.unsyiah.ac.id

Abstract. Chitosan film has attracted attention due to its advantages; it is easily modified due to numerous active sites. However, the use of chitosan film alone has limited applications. Therefore, it is necessary to modify chitosan film. In this study, chitosan was modified through addition of titanium dioxide and cellulose, extracted from grass (imperata cylindrica). Chitosan-cellulose-titanium dioxide composite film was prepared with different compositions of chitosan, cellulose and titanium dioxide. The result of the tensile test showed the addition of cellulose and titanium oxide improved tensile strength of the chitosan film. FTIR and XRD analysis confirmed the formation of chitosan-cellulose-TiO2 composite film.

1. Introduction
Several industries have begun developing composite materials, especially environmentally friendly composites. A composite is a combination of two or more macroscopically different materials with better properties than the initial materials. Composites consist of a matrix as a binding element and filler as reinforcement. The addition of fillers to the composite matrix aims to improve its mechanical properties, such as tensile strength. In this way, its properties can be designed for certain applications.

The adsorbent properties of chitosan composite are of primary concern. Used alone as an adsorbent, chitosan is easily damaged due to its weak mechanical properties. Some researchers have modified chitosan to form composites with other materials [1]. In this study, chitosan was modified by addition of cellulose and titanium dioxide (TiO2) particles. Cellulose is a natural polymer formed by linear chains of glucose units with β-(1,4)-glycosidic bonds[2]. Cellulose was chosen as a filler in the chitosan matrix because its chemical structure is similar to chitosan. The similarity in chemical structure contributes to strong adhesion force and a compact material. TiO2 particles were also added to the chitosan matrix in order to improve chitosan’s ability to remove dye from water, as TiO2 can decompose dye into harmless molecules.

This study investigates the effect of cellulose and TiO2 addition on chitosan film, especially its mechanical properties. Chitosan-cellulose-TiO2 composite films were prepared with different compositions and then characterized by tensile test, FTIR, and XRD.
2. Materials and Methods

2.1 Materials
Chitosan (deacetylation degree: 75-85%) was purchased from Tokyo Chemical Industry Co., Ltd. Japan. Cellulose was isolated from grass following the same procedure described in our previous work [3].

2.2 Methods
Preparation of chitosan-cellulose-TiO$_2$ composite film was conducted by dissolving chitosan with acetic acid (20 mL, 2%) for 2 hours at room temperature. This was followed by the addition of cellulose extracted from grass and colloidal TiO$_2$ particles (dispersed in distilled water) at varied concentrations, as shown in Table 1. The solution was then poured into a glass plate and dried in an oven at 40°C. The obtained composite films were characterized with tensile test, FTIR, and XRD.

Table 1. Chitosan, cellulose and TiO$_2$ compositions for composite film preparation.

| Film | Chitosan (g) | Cellulose (g) | TiO$_2$ (g) |
|------|-------------|---------------|-------------|
| 1    | 1           | -             | -           |
| 2    | 0.9         | 0.100         | -           |
| 3    | 0.9         | -             | 0.100       |
| 4    | 0.9         | 0.025         | 0.075       |
| 5    | 0.9         | 0.050         | 0.050       |
| 6    | 0.9         | 0.075         | 0.025       |

3. Results and Discussion
This study compared only two films, namely, chitosan film and chitosan-cellulose-TiO$_2$ composite film, in order to observe the difference between chitosan films with and without cellulose and TiO$_2$. Chitosan and chitosan-cellulose-TiO$_2$ composite films show slightly different appearances. Chitosan film is more transparent than chitosan-cellulose-TiO$_2$ composite film. Cellulose is visible in the chitosan-cellulose-TiO$_2$ composite film, while TiO$_2$ is not visible (Figure 1).

Figure 1. Chitosan film (a) and chitosan-cellulose-TiO$_2$ composite film (b).
Figure 2. FTIR spectra of chitosan (a) and chitosan-cellulose-TiO$_2$ composite film (b).

Figure 2a shows the typical FTIR spectrum of chitosan, where the absorption band of hydroxyl groups overlaps with that of amine groups appearing at wave number 3427.51 cm$^{-1}$ [4,5]. The absorption bands indicating a $-\text{CH}$ group appear at wave number of 2918.80 cm$^{-1}$ and 2851.30 cm$^{-1}$ [5-7]. At wave number 1633.71 cm$^{-1}$ absorption bands of carbonyl groups overlap with CN stretching (amide I) [8,9]. At wave number 1598.98 cm$^{-1}$ the absorption bands of $-\text{NH}$ bending (amide II) and C-N stretching can be observed [4,8]. Bands at wave number 1155.36 cm$^{-1}$, 1078.21 cm$^{-1}$, 1029.99 cm$^{-1}$ and 852.53 cm$^{-1}$ demonstrate presence of $\beta$-(1,4)-glycosidic bonds [5,8,10,11]. These results confirm findings by Habiba (2016) [6] and Jiang (2014) [7], where absorption bands at wave number of 1151 cm$^{-1}$, 1152 cm$^{-1}$, 1080 cm$^{-1}$, 1028 cm$^{-1}$, and 894 cm$^{-1}$ indicate the presence of chitosan saccharide groups.

FTIR spectrum of chitosan-cellulose-titanium dioxide composite film (Figure 2b) shows changes in absorption bands for $-\text{OH}$ and $-\text{NH}$ in chitosan film. The absorption band widened and shifted to a larger wave number, 3452.00 cm$^{-1}$. The widening of the band occurs due to the addition of cellulose. The shift in wave numbers occurs due to the presence of hydrogen bonds and electrostatic forces between the three components: chitosan, cellulose and TiO$_2$. Absorption band of amide I also shifted to a lower wave number. Absorption bands for Ti-OH and Ti-O appear at wave numbers 1637.58 cm$^{-1}$ and 669.79 cm$^{-1}$, respectively. These results are in accordance with the studies reported by Oliveira (2017) [12] and Saravanan (2018) [13] and confirm the formation of chitosan-cellulose-TiO$_2$ composite film.

Tensile test was conducted for all compositions shown in Table 1, using ASTM (American Standard Testing Material) D638 TYPE IV. Results are shown in Figure 3.

The study prepared films of varying compositions: chitosan-cellulose-TiO$_2$, chitosan, chitosan-cellulose and chitosan-TiO$_2$. The aim was to investigate the effects of each filler on the mechanical properties of chitosan. Figure 3 shows the addition of cellulose can increase the tensile strength of chitosan film. A similar result was also found by addition of TiO$_2$ particles, which increased tensile strength of chitosan composite more than cellulose particles. One probable cause is that TiO$_2$ particles are smaller than cellulose particles, resulting in better adhesion force and producing more compact material. The tensile strength of chitosan film was 12.33 kgf/mm$^2$. The tensile strengths of chitosan-cellulose film and chitosan-TiO$_2$ film were 14.00 kgf/mm$^2$ and 15.42 kgf/mm$^2$, respectively. The highest tensile strength (16.17 kgf/mm$^2$) was obtained by chitosan-cellulose-TiO$_2$ film containing 0.9 g chitosan, 0.05 g
cellulose and 0.05 g TiO$_2$, where the weight of both fillers are the same. Hydrogen bonding between chitosan, cellulose and TiO$_2$ increases the tensile strength of the film. However, when the weight of one of the fillers is higher than 0.05 g, the composite’s tensile strength decreases because fillers tend to interact with themselves, reducing adhesion force and thus decreasing tensile strength [14].

![Figure 3. Tensile strength of composite films with different compositions](image)

XRD analysis was also performed to study the effect of cellulose and titanium dioxide on chitosan crystallinity (Figure 4). A broad peak with high intensity at 20=20° is typical of chitosan, illustrating its crystalline and amorphous phases (Figure 4a) [15]. After forming a composite film with cellulose and titanium dioxide, the crystallinity of chitosan reduces, wherein the typical peak intensity of chitosan decreases and results in a new amorphous material. A new peak was observed at 20=24.78°, which is typical of titanium dioxide. These results confirm the formation of chitosan-cellulose-TiO$_2$ composite film. The obtained amorphous material offers several applications, such as an adsorbent.

![Figure 4. XRD patterns of chitosan film (a) and chitosan-cellulose-TiO$_2$ composite film (b).](image)
4. Conclusions
Chitosan was successfully modified using grass-derived cellulose and titanium dioxide. The addition of cellulose and titanium dioxide improved the mechanical properties of the chitosan film. FTIR and XRD analysis confirmed the formation of chitosan-cellulose-titanium dioxide film. The addition of cellulose and titanium dioxide reduced the crystallinity of chitosan film.

References
[1] Lin S, Chen L, Huang L, Cao S, Luo X and Liu K 2015 Novel antimicrobial chitosan–cellulose composite films bioconjugated with silver nanoparticles Industrial Crops and Products 70 395-403
[2] Loerbroks C, Rinaldi R and Thiel W 2013 The Electronic Nature of the 1,4- β- Glycosidic Bond and Its Chemical Environment: DFT Insights into Cellulose Chemistry Chemistry A European Journal 19 48 16282-16294
[3] Az-Zahra, Rahmi and Lubis S 2019 Reinforcement of chitosan film using cellulose isolated from grass (imperata cylindrica) J. Phys.: Conf. Ser. 1402 055039
[4] Almeida E V R, Frollini E, Castellan A and Coma V 2010 Chitosan, sisal cellulose, and biocomposite chitosan/sisal cellulose films prepared from thiourea/NaOH aqueous solution. Carbohydrate Polymers 80 655-664.
[5] Karthikeyan K T, Nithya A and Jothivenkatachalam K 2017 Photocatalytic and antimicrobial activities of chitosan-TiO₂ nanocomposite Journal of Biological Macromolecules 104 1762-1773
[6] Habiba U, Islam M S, Siddique T A, Affifi A M and Ang B C 2016 Adsorption and photocatalytic degradation of anionic dyes on chitosan/PVA/Na-Titanate/TiO₂ composites synthesized by solution casting method Carbohydrate Polymers 149 317-331.
[7] Jiang X, Sun Y, Liu L, Wang S and Tian 2014 Adsorption of C.I Reactive Blue 19 from aqueous solution by porous particles of the grafted chitosan Chemical Engineering Journal 235 151-157
[8] Zhao T, Che Z, Lin X, Ren Z, Li B and Zhang Y 2018 Preparation and characterization of microcrystalline cellulose (MCC) from tea waste Carbohydrate Polymers 184 164-170
[9] Zheng X, Li X, Li J, Wang L, Jin W, Liu J, Pei Y and Tang K 2018. Efficient removal of anionic dye (Congo red) by dialdehyde microfibrillated cellulose/chitosan composite film with significantly improved stability in dye solution Biological Macromolecules 107 283–289
[10] Behera S S, Das U, Kumar A, Bissoyi A and Singh A K 2017 Chitosan/TiO₂ composite membrane improves proliferation and survival of L929 fibroblast cells: Application in wound dressing and skin regeneration Journal Biological Macromolecules 98, 329-340.
[11] Maity J and Ray S K 2014 Enhanced adsorption of methyl violet and congo red by using semi and full IPN of polymethacrylic acid and chitosan Carbohydrate Polymers 104, 8-16.
[12] Oliveira A C De M, Santos M S, dos Brandao L M S, de Resende I T F, Leo I M, Morillo E S, Yerga R M N, Fierro J L G, Egues S M da S and Figueiredo R T 2017 The effect of cellulose loading on the photoactivity of cellulose-TiO₂ hybrids for hydrogen production under simulated sunlight Journal of Hydrogen Energy 42, 28747-28754.
[13] Saravanan R, Aviles J, Gracia F, Mosquera E and Gupta V K 2018 Crystallinity and lowering band gap induced visible light photocatalytic activity of TiO₂/CS (chitosan) nanocomposites. Journal of Biological Macromolecules 109, 1239-1245.
[14] Fröhlich J, Niedermeier W and Luginsland HD 2005 The effect of filler–filler and filler–elastomer interaction on rubber reinforcement Composites Part A Applied Science and Manufacturing 36(4):449-460
[15] Karimi M H, Mahdavinia G R, Massoumi B, Baghbani A and Saraei M 2018 Ionomically crosslinked magnetic chitosan/k-carrageenan bioadsorbents for removal of anionic eriochrome black-T International Journal of Biological Macromolecules 113: 361–75.