Effect of glutaraldehyde to the mechanical properties of chitosan/nanocellulose

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Abstract. Research on making films using chitosan, nanocellulose from pineapple leaf fiber, and glutaraldehyde were carried out as an effort to obtain alternative biodegradable plastics. Chitosan has low mechanical, therefore nanocellulose is added from pineapple leaf fibers and glutaraldehyde additives. This research was conducted to obtain the optimum glutaraldehyde additive variable that functions as a crosslinker. What chitosan used was 2% (w/v solution) and nanocellulose 3% (w/w chitosan) based on optimum results from previous research. The method used a casting method, chitosan and nanocellulose are dissolved and heated in acetic acid 1% then glutaraldehyde is added during cold and cast. Variable of glutaraldehyde added by 0%, 0.5%, 1%, 2%, and 3% (w/w chitosan). Tensile strength, elongation, functional groups, and absorbance were used to characterize film. The results showed that the results of FT-IR were a spectrum of chitosan and indicated the crosslinking between chitosan and glutaraldehyde. The tensile strength values change with the addition of glutaraldehyde. The optimum value of adding glutaraldehyde is 1% based on the results of tensile strength and the lowest absorbance.

1. Introduction

During the last decades, much research and development have been focused on renewable raw materials to produce biodegradable packaging. One of the approaches is to use renewable biopolymers such as cellulose, chitosan, chitin, and starch. Using biopolymer for packaging has been limited because it has weak mechanical properties for the film. Many research studies have focused on improving the mechanical properties of biopolymers based film [1].

Chitosan is a natural linear polysaccharide consisting of (1-4)-2-amino-deoxy-β-D-glucan and obtained from deacetylation of chitin [2]. Chitosan is film-forming ability, nontoxic, biodegradable, biofunctional, biocompatible, aqueous adsorption capabilities, and suitable for food packaging (antibacterial ability) [1], [3], [4]. Chitosan is an ideal polymer for a wide variety of fields and industrial applications including textiles, medical, agricultural,
ophthalmology, and food. Chitosan soluble in dilute organic acids, such as acetic, formic, succinic, lactic, and malic acids [4].

Blended biopolymers (with others polymer including biopolymer) can enhance the weak properties of biopolymers. One of the strategies is to use reinforcement agent (natural cellulose fiber) in polymeric composite materials [5]. Pineapple leaf fiber exhibits high specific strength and stiffness. Pineapple leaf fiber has high cellulose content made it has superior mechanical properties and can be used as reinforcement agent in composites materials [6]. Cellulose consist of D-glucopyranose unit joins together by β-(1→4)-glycosidic bonds[2]. Dimensions of nanocellulose are less than 100 nm [7]. Nanocellulose made lightweight and robust nanocomposite[2].

Cross-linking that commonly used on chitosan film is glutaraldehyde. Glutaraldehyde leads to the formation of covalent linkages between the chitosan chain [8]. Pristine chitosan crosslinked with glutaraldehyde is autofluorescent, that has limitation such as brittle and poor barrier properties [9]. To improve its properties, chitosan-glutaraldehyde blending with nanocellulose.

Several studies on chitosan-nanocellulose film, such as studied nanocellulose reinforced chitosan composite [2], [10], [11], nanocomposite film chitosan-nanofibrillated cellulose [12], properties chitosan-nanocrystalline cellulose [1], [3], [13]. And previous research have reported the use of crosslinker on chitosan film, such as glutaraldehyde-chitosan and poly (vinyl alcohol) blends [9], chitosan films reinforced by nanocellulose and cross-linked by adipic acid [8], chitosan nanofibers cross-linked by glutaraldehyde[4], and crosslinking chitosan into H₃PO₄/HNO₃–nano oxidized cellulose [14]. Much of the interest has been focused on combining chitosan with nanocellulose and chitosan cross-linked by glutaraldehyde, but there is no data about combining chitosan with nanocellulose pineapple leaf fiber and glutaraldehyde as a crosslinker to increase properties film. This research is to investigate the influence of glutaraldehyde as a crosslinker on chitosan-nanocellulose film. Nanocellulose that used in this study is nanocellulose isolated from pineapple leaf fiber.

2. Materials and Method

2.1. Materials

The materials used for the research includes chitosan, nanocellulose pineapple leaf fiber, glutaraldehyde, acetic acid. Chitosan powder, having deacetylation degree of 95%, was purchased from PT Biokitosan Indonesia. Nanocellulose pineapple leaf fiber isolated from pineapple leaf fiber was obtained from CV HasanahNiaga Bandung. Acetic acid glacial and glutaraldehyde 25% were provided by Merck, Co.

2.2. Chitosan/Nanocellulose Film Preparation

Chitosan/nanocellulose film was prepared by a casting method. Certain amounts of chitosan (2% w/v) dissolved in aqueous solution of acetic acid 1% (100 mL), stirring was conducted at 80 °C for 1 h. The nanocellulose pineapple leaf fiber (3% w/w) was added while stirring, and the solution was mixed for at least 1 h. Glutaraldehyde (0%, 0.5%, 1%, 2%, and 3% w/w) were added into a solution of chitosan-nanocellulose, solution were mixed for at least 1 h. The solutions (35 mL) were cast on the plexiglass plate (20 x 20 cm²) and place on the room temperature. It needed 48 h for film formation. The dried film was removed from plexiglass plate and then stored in aluminum foil.

2.3. Tensile Strength

Tensile strength testing was performed on a Universal Testing Yasuda Seiki Auto Strain Machine. Tensile strength is determined based on the maximum load when the films break.
The tensile strength was calculated by dividing the maximum load for breaking fill by cross-sectional area.

2.4. Elongation
The elongation of the film is tested using ASTM- D882 (2013) on a Universal Testing Yasuda Seiki Auto Strain Machine. Elongation is the increase in the gauge length, measured after fracture of the specimen within the gauge length, usually expressed as a percentage of the original gauge length.

2.5. Fourier Transform Infrared Spectroscopy
Infrared spectra for the chitosan-nanocellulose and chitosan-nanocellulose-glutaraldehyde before and after crosslinking were measured on Seri Nicolet iS5 FTIR spectrometer. The selected spectral range is 4000 cm\(^{-1}\) until 500 cm\(^{-1}\).

2.6. UV Vis
Composite film plastic is taken absorbance measurement to find out the absorption of light at specific wavelengths in the sample to be tested using a UV-Vis [Thermo UV-Vis 10 S Genesys] spectrophotometer at a resolution of 1 nm with a wavelength range of 200-800 nm.

3. Results and Discussion

3.1. Chitosan/Nanocellulose visual appearance
After adding glutaraldehyde to the solution of chitosan-nanocellulose, color changes occur. The color of the solution becomes more brown with the higher the concentration of glutaraldehyde added (seen in figure 1), this shows the occurrence of crosslinking between chitosan and glutaraldehyde [15]. Glutaraldehyde has high reactivity toward the amine groups of chitosan [16].

![Figure 1](image)

*Figure 1. The color of the solution of chitosan-nanocellulose pineapple leaf fiber with the addition of glutaraldehyde*

3.2. Tensile Strength
The tensile strength curves of the crosslinked chitosan-nanocellulose film are plotted in figure 2.
Figure 2. Effect of glutaraldehyde in the tensile strength of the chitosan-nanocellulose pineapple leaf fiber

Based on figure 2, the addition of glutaraldehyde to chitosan-nanocellulose pineapple leaf fiber makes the tensile strength increase, the higher the concentration of glutaraldehyde added, the higher the tensile strength. However, on the addition of glutaraldehyde by 2% and 3%, the tensile strength value is smaller. The optimal amount of tensile strength was obtained at the addition of 1% glutaraldehyde concentration. The addition of glutaraldehyde causes cross-linking, so that the matrix gets closer. Glutaraldehyde in chitosan causes crosslinking between amine groups (NH$_2$) and glutaraldehyde. Cross-linking between aldehyde groups is very reactive to free amino groups in chitosan, so when reacted the aldehyde group binds covalently to amine groups and connects between chitosan polymers. The higher the concentration of glutaraldehyde added, the higher the strength of the gel. This is because of the function of glutaraldehyde in the manufacture of gels as a form of crosslinking [17]. But on the addition of glutaraldehyde by 2% and 3%, the tensile strength is smaller because films become brittle for glutaraldehyde 2% and 3%. Crosslinked chitosan-glutaraldehyde has several limitations, such as fragility [18], [15]. Even though the bonds that form are getting more compact with increasing glutaraldehyde concentrations, there is likely to be an $\sim$NH$_2$ group that is not crosslinked with glutaraldehyde. As a result, there is a strong repulsion between groups, which decreases the strength of the gel matrix [19].

3.3. Elongation

The elongation curves of the crosslinked chitosan-nanocellulose film are shown in figure 3.
Figure 3. Effect of glutaraldehyde in the elongation of the chitosan-nanocellulose pineapple leaf fiber

Based on figure 3, the elongation value was found to be 105.71% for pure chitosan-nanocellulose pineapple leaf fiber and with the addition of 0.5%, 1%, 2%, and 3% glutaraldehyde decreased the elongation value. Such a decrease in elongation values indicated that incorporation of nanocellulose and glutaraldehyde into chitosan matrix resulted in strong interactions between filler, crosslinker, and matrix, which restricted the motion of the matrix and hence decrease elongation values [1][17].

3.4. Optical properties

The curves of optical properties (the crosslinked chitosan-nano cellulose film) are plotted in figure 4.

Figure 4. Effect of glutaraldehyde in the optical properties of the chitosan-nanocellulose pineapple leaf fiber
The film composite chitosan-nanocellulose-glutaraldehyde 1% has the lowest absorbance, indicated that it is most transparency.

3.5. Fourier Transform Infrared Spectroscopy

FTIR spectra were taken of the chitosan and chitosan-nanocellulose before and after cross-linking with glutaraldehyde. Figure 5 displays the spectra of chitosan, chitosan-nanocellulose, and chitosan-nanocellulose-glutaraldehyde.

![FTIR spectra of chitosan, chitosan-nanocellulose, and chitosan-nanocellulose-glutaraldehyde](image)

**Figure 5.** FTIR spectra of chitosan, chitosan-nanocellulose, and chitosan-nanocellulose-glutaraldehyde

The characteristics of the effect of adding a crosslinker to the chitosan-nanocellulose film and the IR band and its shift due to crosslinker interaction was carried out by FTIR analysis. Based on figure 5, it can be seen that the FTIR spectrum analysis formed is a spectrum of chitosan. On the addition of glutaraldehyde, indicated the crosslinking between chitosan and glutaraldehyde evidenced by a reduction of the peak at 1556.27 cm\(^{-1}\) which is due to the NH\(_2\) group being bonded during crosslinking [20].

4. Conclusion

The addition of glutaraldehyde crosslinkers with a variable of 0% to 3% (w/w chitosan) influence the characteristics of the mechanical chitosan-glutaraldehyde-nanocellulose film properties. Characteristics of chitosan-nanocellulose-glutaraldehyde which are the optimum and meet the requirements to be applied as the biodegradable plastic matrix are shown by the addition of glutaraldehyde as much as 1% (w/w chitosan) where the tensile strength is 35.16 MPa and has the lowest absorbance.

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