Reinforcement of chitosan film using cellulose isolated from grass (*imperata cylindrica*)

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**Abstract.** Cellulose from grass (*imperata cylindrica*) had been used as reinforcement in chitosan film preparation. Cellulose was obtained from grass through hydrolysis process. Hydrolysis was conducted with different concentration of sulfuric acid at room temperature for 2 h. The results show that the highest crystallinity of cellulose was obtained at sulfuric acid concentration of 40% (v/v) on hydrolysis process. The isolated cellulose with the highest crystallinity was used as reinforcement on chitosan film preparation. Mechanical test shows addition of isolated cellulose into chitosan film improved the tensile strength. The FTIR analysis confirmed the interaction between components in the film.

1. **Introduction**

Chitosan is a chitin derivative natural polymer compound isolated from fishery waste, such as shrimp shells and crab shells. Chitosan has several advantages such as biocompatible, biodegradable, environmentally friendly and has high adsorption capacity [1,2]. However, chitosan film is a hydrogel that easily swells in water, and has low chemical and physical stability [3,4]. Therefore, a modification is needed to improve the weakness of chitosan. Chitosan has hydroxyl and amino groups that allow it to be modified and potentially used in composite preparation. Some researchers have reported the use of cellulose as a filler of chitosan in order to improve mechanical properties of chitosan. Cellulose is a glucose polymer with β-1,4-glucoside bonds in a straight chain. Cellulose was chosen as a filler because it is a biopolymer material with a chemical structure similar to chitosan. The similarity of the chemical structure of chitosan and cellulose will make both biopolymers compatible and have good adhesion, where cellulose acts as reinforcement. Most studies reported the use of commercial cellulose as reinforcement of chitosan which produced relatively expensive material. While, it is known that many cellulose sources are available in nature. One of cellulose source that available in the environment is *imperata cylindrica*.

*Imperata cylindrica* is an Indonesia native grass which is very easy to grow and develop. *Imperata cylindrica* is a type of sharp leaf grass that is often a weed on agricultural land. *Imperata cylindrica* has been used in several applications such as raw material for medicines, paper raw materials, fertilizers, and the remains are disposed because it inhibits the growth of major plants. *Imperata cylindrica* contains cellulose which can be utilized as a filler in composite preparation. Isolation of cellulose from natural resources can be conducted using various physical and chemical processes including hydrolysis, bleaching and drying. According to Leite [5], hydrolysis using concentrated acids will produce cellulose with high crystallinity and remove amorphous parts, and the process can be operated at low temperatures. However, at a very concentrated acid the hydrolysis process can decompose crystalline...
part of cellulose. Therefore, in this study hydrolysis of cellulose from *imperata cylindrica* was performed using H$_2$SO$_4$ with different concentrations in order to obtain the best concentration of H$_2$SO$_4$.

In this study, chitosan was used as a matrix and cellulose from grass as filler. They were combined to form a new material (composite) with the aim to produce new material with better mechanical properties. The composite obtained was characterized using tensile test (tensile strength), and FTIR.

2. Method

2.1. Isolation of cellulose from grass

Grass (imperata cylindrica) was collected in Aceh, Indonesia. It was washed with water, dried and cut into pieces with a size of about ± 2 cm. The small pieces of grass were grounded into powder and then sifted using a 100 mesh sieve in order to obtain a uniform powder size. Powdered grass was hydrolysed using sulphuric acid with various concentrations (20, 30, 40, 50 and 60%). The hydrolysis process was conducted at 45°C for 90 minutes. Hydrolysis process was stopped with addition of cold water. The mixture was filtered and washed until neutral pH was reached using distilled water and then dried at 40°C. The hydrolysed grass was then bleached using 30% of H$_2$O$_2$ solution. The bleaching process was performed at 45°C for 90 minutes under stirring with a magnetic stirrer on the hot plate. The bleaching process was conducted twice in order to completely remove the remnants of lignin and hemicellulose. The obtained cellulose was then filtered, washed with distilled water, and dried at 40°C.

2.2. Preparation of chitosan-cellulose composite film

Chitosan (obtained from shrimp skin with a degree of deacetylation is 75-85%) was purchased at Tokyo Chemical Industry Co., Ltd. Japan with code number C0831. Chitosan (0.9 g) was dissolved in 100 mL of acetic acid (2%) at room temperature for 2 hours. Cellulose was dispersed in distilled water and then added to chitosan solution. The mixture was stirred for 3 hours and then poured into the glass plate. After drying, the composite film was peeled from the glass plate. The obtained composite film was characterized with tensile test and FTIR.

3. Results and discussion

3.1. Cellulose isolated from grass

XRD analysis was performed in order to study the crystallinity of the samples. Figure 1 is the XRD patterns of cellulose isolated from grass with different sulfuric acid concentration in hydrolysis process. It shows typical XRD pattern of cellulose, where each XRD pattern exhibits peak at 2θ = 15.24° and 21.96° [6] with different degree of crystallinity (Table 1). Degree of crystallinity was determined using the segal method [7] as shown in equation 1.

\[
X_c (%) = \frac{A_c}{A_c + A_a} \times 100
\]  

(1)

Where Ac and Aa are area under the sharply resolved peaks and remaining area under curve above background [8,9].

![Figure 1. XRD patterns of cellulose isolated from grass with different concentration of H$_2$SO$_4$ (20, 30, 40 and 50%).](image)
Table 1. Crystallinity of cellulose isolated from grass with different concentration of H$_2$SO$_4$.

| H$_2$SO$_4$(%) | Crystallinity of cellulose (%) |
|---------------|------------------------------|
| 20            | 39.23                        |
| 30            | 42.49                        |
| 40            | 48.75                        |
| 50            | 46.00                        |

Table 1 shows the crystallinity of cellulose increases by increasing sulfuric acid concentration. However, when sulfuric acid concentration was 50% the crystallinity decreases. At concentrations of 20% and 30% of sulfuric acid, the low crystallinity values were obtained due to the hydrolysis process has not been worked optimally. Where the acid was not enough to break down or degrade other components such as lignin, hemicellulose or other amorphous substances. However, the crystallinity decreases when the concentration of sulfuric acid increases (50%). A decrease in the crystallinity index is associated with decrystallization. The high concentration of sulfuric acid not only causes degradation of the amorphous portion but also causes degradation of the crystalline parts and hydrogen bonds between cellulose chains [10,11]. Acid hydrolysis at high concentrations can reduce cellulose crystallinity, where acid will cause cellulose chain decomposition which affect the chain rearrangement from the original arrangement and results in low crystallinity. The low degree of crystallinity causes the low mechanical properties of cellulose. Based on the result the highest crystallinity of cellulose was obtained at 40% of sulfuric acid concentration and this cellulose was used as reinforcement of chitosan film.

Figure 2 is FTIR spectrum of cellulose isolated from grass. It shows typical absorption bands of cellulose. Absorption band at wavenumber 3407.28 cm$^{-1}$ correlated with stretching vibration of –OH functional group. Absorption band at wavenumber 1653.01 cm$^{-1}$is carbonyl group (C = O) vibration and water absorption in cellulose [12-16]. The absorption band at 1462.05 cm$^{-1}$ shows an interaction between hydrogen molecules in the C1-O-C2 group [17]. The absorption band of CO stretching of lignin appears at wavenumbers 1262.90 cm$^{-1}$ [18]. Strong absorption bands appeared at 1163.09 cm$^{-1}$, 1109.08 cm$^{-1}$ and 1059.89 cm$^{-1}$ show stretching vibration of pyranose ring COC [19] and bands at range of 900-809 cm$^{-1}$ show β-1,4-glycosidic bonds between D-glucose units in cellulose. These results are similar to FTIR spectrum of cellulose isolated from jackfruit reported by Sundarraj [20].

![Figure 2. FTIR spectrum of cellulose isolated from grass.](image)

3.2. Chitosan-cellulose composite film

In order to study the influence of cellulose loading on the mechanical properties of chitosan-cellulose composite film, the tensile test was performed. The result shows the tensile strength of chitosan film increases after cellulose loading (Figure 3). The increase was due to good adhesion between chitosan as matrix and cellulose as filler. The result implies that cellulose isolated from grass is a good reinforcement of chitosan film.
Figure 3. Tensile strength of chitosan composite film and chitosan-cellulose composite film

Figure 4. FTIR spectra of chitosan film (a) and chitosan-cellulose composite film (b)

In order to confirm the interaction between components in the composite, the FTIR analysis was performed. Figure 4a shows FTIR spectrum of chitosan which exhibits typical absorption bands of chitosan. Absorption band at wave number 3427.51 cm\(^{-1}\) indicates stretching vibrations of -OH functional group which overlap with the –NH vibration (amine group) [21]. The absorption bands at wave number 2918.80 cm\(^{-1}\) and 2851.30 cm\(^{-1}\) show stretching vibrations of –CH [22,23]. Absorption bands at wave number 1633.71 cm\(^{-1}\) corresponds with carbonyl group (C = O), where the amide group CO stretching overlaps with CN stretching (amide I). The C-N stretching and –NH bending groups (amide II) appear in the wave number of 1598.98 cm\(^{-1}\). Aliphatic compounds (C-H bending and C-N stretching groups) appear at wave numbers 1379.10 cm\(^{-1}\) and 1319.31 cm\(^{-1}\). Special absorption bands of \(\beta\) (1.4)-glycosidic (COC) bonds in glucose units and CO stretching vibrations are found at wave number 1155.36 cm\(^{-1}\), 1078.21 cm\(^{-1}\), 1029.99 cm\(^{-1}\) and 852.53 cm\(^{-1}\) [24].

Figure 4b is FTIR spectrum of chitosan-cellulose composite film. It shows the absorption band of –OH vibration become broader and the band intensity also increases. It was due to cellulose addition in the composite film, where cellulose contains –OH functional groups. The shift of absorption band from wave number 3427.51 cm\(^{-1}\) to 3450.68 cm\(^{-1}\) was due to hydrogen bonding between chitosan and cellulose. Absorption bands at wave number 2922.66 cm\(^{-1}\) and 2853.71 cm\(^{-1}\) show stretching vibrations
of C-H. Absorption bands at wave number 1659.28 cm$^{-1}$ and 1530.04 cm$^{-1}$ indicate the presence of C=O stretching which overlaps with CN stretching (amide I), and NH bending (amide II) from chitosan and groups C=C and OH bending of cellulose, respectively [25]. Absorption bands at wave number 1102.33 cm$^{-1}$ and 898.35 cm$^{-1}$ correlate with CO stretching group and COC stretching, respectively which exhibit the existence of $\beta$-1,4-glycosidic bonds between D-glucose units of chitosan and cellulose [15,25].

4. Conclusion

Cellulose can be isolated from grass by hydrolysis process using sulfuric acid. The highest crystallinity of cellulose was obtained at concentration of sulfuric acid 40%. Cellulose loading improved tensile strength and decreased the crystallinity of chitosan film.

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References

[1] Ngah W S W, Teong L C, Hanafiah M A K M 2011 *Carb. Polym*. 83, 1446-1456
[2] Zhang L, Zeng Y, Cheng Z 2016 *J. Mol. Liq*. 214, 175-191
[3] Pandiselvi K, Thambidurai S 2013 *Colloid Surf*. 108, 229-238
[4] Yazdani M, Bhatnagar A, Vahala R 2017 *Chem. Eng. J*. 316, 370-382
[5] Leite A L M P, Zanon C D, Menegalli F C 2017 *Carb. Polym*. 157, 962-970
[6] Zhao T, Che Z, Lin X, Ren Z, Li B, Zhang Y 2018 *Carb. Polym*. 184, 164-170
[7] Segal L, Creely J, Martin A, Conrad C 1959 *Res. J. 29*(10), 786-794
[8] Vinodhini P A, Sangeetha K, Gomathi T, Sudha P N, Venkatesan J, Anil S 2017 *Int. J. Bio. Mac.* 104, 1721-1729
[9] Li J, Qiang D, Zhang M, Xiu H, Zhang X 2015 *Carb. Polym*. 129, 44-49
[10] Sheng S, Meiling Z, Chen L, Wensheng H, Zhifeng Y 2018 *Waste Management*. 82, 139-146
[11] Hou W, Ling C, Shi S, Yan Z 2019 *Int. J. Bio. Mac.* 123, 363-368
[12] Xiang L Y, Mohammed M A P, Baharuddin A S 2016 *Carb. Polym*. 148, 11-20
[13] Liu Y, Liu A, Ibrahim S A, Yang H, Huang W 2018 *Int. J. Bio. Mac.* 111, 717-721
[14] Roz A L D, Leite F L, Pereiro L V, Nascente P A P, Zucolotto V, Oliveira O N, et al. 2010 *Carb. Polym*. 80, 65-70
[15] Bonaridd S, Robles E, Barandiaran I, Saldias C, Leiva A, Kortaberria G 2018 *Carb. Polym*. 199, 20-30
[16] Hussin M H, Pohan N A, Garba Z N, Kassim M J, Rahim A A, Brosne N, et al. 2016 *Int. J. Bio. Mac.* 92, 11-19
[17] Rashid M, Gafur M A, Sharafat M K, Minami H, Miah M S J, Ahmad H 2017 *Carb. Polym*. 170, 72-79
[18] Lionetto F, Sole R D, Canoletta D, Vasapollo G, Maffezzoli A 2012 *Material* 5, 1910-1922
[19] Amin M C H, Abadi A G, Katas, H 2014 *Carb. Polym*. 99, 180-189
[20] Sundarraj A A, Ranganathan T V 2018 *J. Exp. Bio. Agr. Sci.* 6(2), 414-424
[21] Karthikeyan K T, Nithya A, Jothivenkatachalam K 2017 *Int. J. Bio. Mac.* 104, 1762-1773
[22] Habiba U, Islam M S, Siddique T A, Afi M, Ang B C 2016 *Carb. Polym*. 149, 317-331
[23] Jiang X, Sun Y, Liu L, Wang S, Tian 2014 *Chem. Eng. J.* 235, 151-157
[24] Maity J, Ray S K 2014 *Carb. Polym*. 104, 8-16
[25] Baran N Y, Baran T, Mentes A 2018 *Carb. Polym*. 181, 596-604