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Hydrogel Preparation from Shrimp Shell-Based Chitosan: The Degree of Crosslinking and Swelling Study

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Abstract. Chitosan is a natural polymer derived from different starting materials such as fish scales, crab and shrimp shells. Due to the advantages like biocompatibility and biodegradability, chitosan has been widely used in hydrogel development. This current study aims to make chitosan from shrimp shells, synthesize hydrogel from chitosan, and observe the effect of various chitosan preparation treatments on the properties of the hydrogel. The preparation of chitosan was carried out through demineralization, deproteinization, and deacetylation process. HCl concentration during demineralization and NaOH concentration during deproteinization were varied (1; 1,5; 2) M and (1; 1,5; 2) M, respectively. Chitin deacetylation was conducted using 60% (w/v) of NaOH at the temperature of 90°C for 120 min, and chitosan was resulted. Chitosan based hydrogel was then synthesized with the addition of alginate and glutaraldehyde. The effect of HCl and NaOH concentrations during demineralization and deproteinization on the deacetylation degree of chitosan was observed. The effect of deacetylation degree of chitosan on the degree of crosslinking and swelling property of the hydrogel were also evaluated. Chitosan resulted from this study has the optimum degree of deacetylation at 57.28 %, resulting from demineralization by using HCl 2M and deproteinization with NaOH 2 M. Higher deacetilation degree of chitosan causing the increase of the degree of cross-linking and decrease of the swelling capacity of the hydrogel. The highest degree of cross-linking is 78.85 %, and the swelling capacity is 47 %.

Keywords: Alginate, Chitosan, Glutaraldehyde, Hydrogel, Swelling, Shrimp

INTRODUCTION

Biobased polymer products have been studied among researchers and industrialists for use in versatile applications over the recent past (Rahmayetty et al. 2017, Galiano et al. 2018, Melendres et al. 2019, Sivakanthan et al. 2020). Polysaccharides have drawn excessive attention and have been recognized as the most promising materials in recent years owing to their outstanding

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benefits. They are easily available, non-toxic, biocompatible, biodegradable, and easily modified (Yang et al. 2015). Chitosan, a deacetylated derivative of chitin, is the second most abundant polysaccharide existing in nature after cellulose (Younes et al. 2014, Kumari et al. 2017). Chitosan plays a great role in food protection (Berger et al. 2020), agricultural (Sathiyabama et al. 2016, Sharma et al. 2020, Jayakumar et al. 2022), water treatment (Bertoni et al. 2018, Pakdel and Peighambardoust 2018, Seedao et al. 2018), textile (Kundu et al. 2020), and biomedical technology (Younes et al. 2014, Naghizadeh et al. 2018). The important assignment of this natural polymer in various industries comes from its unique properties such as nontoxicity, biocompatibility, biodegrada-bility, antimicrobial activity (Younes et al. 2014, Muxika et al. 2017), and high absorption capacity (Bertoni et al. 2018, Tolesa et al. 2019).

Chitin and chitosan are commercially extracted from cuticles of various crustaceans, especially shrimps and crabs (Younes et al. 2014, Kumari et al. 2017, Tolesa et al. 2019). In recent years, chitin and chitosan are also found in the cellular walls of fungi (Berger et al. 2020), exoskeletons of insects (Hahn et al. 2020), and mollusks (Mohan et al. 2019, Balitaan et al. 2020). However, the results of a study showed that based on all physicochemical properties, shrimp shell was the best choice for chitosan preparation compared to other commercial starting materials. Furthermore, the XRD and FTIR patterns of chitosan from shrimp shells were also confirmed to be very similar to commercial chitosan (Kumari et al. 2017).

The presence of chitin in crustacean shells, generally is very closely related to proteins and minerals. Various techniques have been developed to isolate chitin to achieve the highest purity. The most common chemical processing applied for chitin extraction consists of deproteinization and demineralization (Younes et al. 2014, Kumari et al. 2017, Muxika et al. 2017, Tolesa et al. 2019). Deproteinization is the process of removing proteins by adding alkaline solutions, and demineralization is the elimination of minerals in the form of calcium carbonate by treatment using acid solutions (Leceta et al. 2014). In addition, a decolorization and purification step is often conducted to remove pigments and get a pure product without impurities (El Knidri et al. 2018). Finally, chitosan is obtained by partial deacetylation of chitin through chemical conversions or enzymatic reactions (Muxika et al. 2017, El Knidri et al. 2018). However, the chemical process involving chitin treatment with hydroxides at high temperatures is preferable because it is low cost and suitable for mass manufacture (Muxika et al. 2017).

The molecular weight and the deacetylation degree especially characterize Chitosan. These specifications influence chitosan's physicochemical and biological properties, such as solubility, hydrophilicity, crystallinity and cell response (El Knidri et al. 2018, Bakshia et al. 2020). Plenty of reactive amino and hydroxyl groups are in chitosan's structure, which leads to the possibility of physical and chemical modifications for numerous applications (El Knidri et al. 2018, Bakshia et al. 2020, Negm et al. 2020). Many studies were reported for its combination with other organic and inorganic materials through sundry methods to achieve some desirable properties (Naghizadeh et al. 2018, Kundu et al. 2020, Kaya et al. 2020).

Hydrogel is a rising material due to its unique properties such as hydrophilicity, soft texture, non-toxic, insoluble in water, a

porous structure, excellent biocompatibility, and biodegradability. Today, chitosan has gained a special place in the field of hydrogels preparation in a wide range of potential and practical uses (Naghizadeh et al. 2018, Pakdel and Peighambardoust 2018, Onat et al. 2019, Bagher et al. 2020). Over the past few years, a variety of studies have been conducted on enhancing the physical, chemical, and biological properties of chitosan-based hydrogels through cross-linking, grafting, impregnation, incorporating of hard fillers, blending, interpenetrating, and ion-imprinting techniques (Pakdel and Peighambardoust, 2018). Several studies have shown that cross-linked hydrogels of chitosan and alginate can have good elasticity property (Naghizadeh et al. 2018), high porosity, biodegradable, and non-toxic (Bagher et al. 2020). One material that is well known and is often combined with chitosan in the manufacture of hydrogels is alginate.

Most studies on the application of chitosan have focused on chitosan concentration and combined treatment (Onat et al. 2019, Jayanudin et al. 2022). Therefore, it is meaningful to explore the effects of deacetylation degree on the mechanical properties and functional characteristics of chitosan hydrogel. The present work prepared chitosan from shrimp shell through demineralization, deproteinization, and deacetylation by using different concentrations of acid and alkaline sodium hydroxide NaOH solutions during demineralization and deproteinization. The aims of this study are: to produce chitosan from shrimp shell waste through the process of demineralization, deproteinization, and deacetylation, to investigate the effect of different concentrations during demineralization and deproteinization to the percentage of demineralization, percentage of deproteinization and deacetylation degree of chitosan, also to evaluate the effect of deacetylation degree of chitosan to the degree of cross-linking and swelling property of the hydrogel.

MATERIALS AND METHODS

Materials

Processed shrimp shells waste was collected from several seafood restaurants in Cilegon, Banten Province of Indonesia. Shrimp shell waste was mixed and treated simultaneously to ensure the raw material's consistency in each variation. Analytical grades of hydrochloric acid (HCl) (38% purity, Sigma-Aldrich, USA) and sodium hydroxide (NaOH) (98% purity, Sigma-Aldrich, USA) were used for chitosan production. Sodium alginate food grade as one of the raw materials for hydrogel synthesis was purchased from PT. Graha Jaya Pratama Kinerja, Jakarta, Indonesia. Glutaraldehyde solution (50% in H2O, Sigma-Aldrich, USA) was applied as a crosslinking agent, and acetic acid glacial (99.8% purity, Sigma-Aldrich, USA) was employed for chitosan dissolution. Distilled water was used in all experiments.

Methods

Chitin Extraction from Shrimp Shells

Shrimp shells were washed thoroughly with water, then dried under the sunlight at ambient temperature for 48 h. The cleaned and dried shrimp shell samples were milled into coarse powder by using a blender machine to make particles of about 2 mm in size. The coarse powder samples were demineralized by treating them with various percentages of HCl solution (1-2 M, 1:15 w/v) in temperature range 55-65°C with constant stirring for 2 h. The demineralized samples were filtered and washed several times using

distilled water to remove the remaining HCl. Afterward, they were dried by using an oven at 100°C for 1 h. The dried demineralized samples were then deproteinized by treating them with various percentages of NaOH (1-2 M, 1:10 w/v) in a 45-55°C with a fixed stirring speed. After 2 h of stirring, the deproteinized samples were filtered, washed with distilled water until to neutrality, and processed for the production of chitosan. Both the demineralization and deproteinization steps were carried out according to the method used by previous researchers (Al Hoqani et al. 2020, Al Shaqsi et al. 2020) with few modifications.

Chitosan Preparation from Chitin

The obtained chitin was deacetylated to produce chitosan by the previous method (Trung et al. 2020) with slight modifications. Chitin samples were incubated in 60% NaOH solution (1:20 w/v) at 90°C for 2 h. Chitosan was obtained by washing with distilled water and drying in sunlight. The produced chitosan was weighed and characterized.

Degree of Deacetylation Determination of Chitosan

The FTIR spectra of chitosan samples were obtained using the Shimadzu IR Prestige-21 spectrometer model 800 series in the range of 4000-400 cm^{-1}. The degree of deacetylation (DD) of the chitosan samples was calculated according to Eq. (1) (Kumari et al. 2017):

$$\mathrm{DD}\ (\%) = \left[100 - \left\{\left(\frac{A_{1654.6}}{A_{3341.2}}\right) x \left(\frac{100}{1.33}\right)\right\}\right] \quad (1)$$

Table 1 shows the symbols and descriptions for the variables used in this study.

Table 1. Labeling of material

No.	Symbols	Definition
1	Chitosan 1	Chitosan was treated withdemineralization using 1 M HCl and deproteination with 1 M NaCl
2	Chitosan 2	Chitosan was treated with demineralization using 1 M HCl and deproteination with 1.5 M NaCl
3	Chitosan 3	Chitosan was treated with demineralization using 1 M HCl and deproteination with 2 M NaCl
4	Chitosan 4	Chitosan was treated with demineralization using 1.5 M HCl and deproteination with 1 M NaCl
5	Chitosan 5	Chitosan was treated with demineralization using 1.5 M HCl and deproteination with 1.5 M NaCl
6	Chitosan 6	Chitosan was treated with demineralization using 1.5 M HCl and deproteination with 2 M NaCl
7	Chitosan 7	Chitosan was treated with demineralization using 2 M HCl and deproteination with 1 M NaCl
8	Chitosan 8	Chitosan was treated with demineralization using 2 M HCl and deproteination with 1.5 M NaCl
9	Chitosan 9	Chitosan was treated with demineralization using 2 M HCl and deproteination with 2 M NaCl

Hydrogel Synthesis

Chitosan-based hydrogel was synthesized with glutaraldehyde as a cross-linking agent (Yu et al. 2017). First, 20 mL of chitosan solution with a concentration of 2% (m/v) was prepared by diluting it in 1% (v/v) of aqueous

acetic acid solution. An amount of 38.1 mL alginate solution with a concentration of 0.5% (w/v) was then added and stirred at of 70 rpm until homogeneous. After that, 2 mL of glutaraldehyde at a concentration of 4% was added to the mixture. Addition was done dropwise with stirring for 60 min for uniformity. The hydrogel solution, which has been produced, was poured into a cast container, then dried for 24 h at room temperature. Finally, the hydrogel was re-dried using an oven at 100°C to constant weight.

Degree of Cross-linking and Swelling Study of The Hydrogel

Hydrogel was weighed (W_o) and immersed in 1% acetic acid solvent for 24 h. The hydrogel weight after immersion was recorded as W_t. Afterwards, the hydrogel was oven-heated at 60°C to dry, then weighed (W_1). The hydrogel product's degree of cross-linking and swelling capacity was determined using Eq. (2) and Eq. (3), respectively (Jayanudin et al. 2022):

$$\text{DC}\ (\%) = \left(\frac{W_1}{W_0}\right) x100 \qquad (2)$$

$$\text{Swelling capacity}\ (\%) = \left(\frac{W_t - W_0}{W_0}\right) x100 \qquad (3)$$

RESULTS AND DISCUSSION

Extraction of Chitin

In this study, chitin extraction from shrimp shells was carried out with the demineralization stage and then continued with deproteinization. Based on previous research (Al Hoqani et al. 2020), differences in the concentration of chemicals used during the demineralization and deproteination processes affect the yield of chitin obtained. In the demineralization process, three samples of shrimp wastes were treated individually with HCl using various concentrations (1, 1.5, 2 M). Figure 1 shows the effect of HCl and NaOH concentrations on the percentage of demineralization and deproteinization.

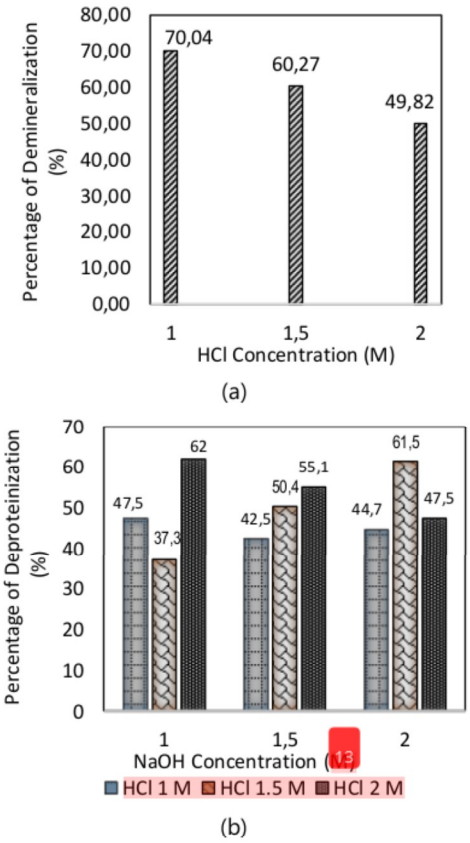


Fig. 1: Effect of different chemicals concentrations on the (a) percentage of demineralization, (b) percentage of deproteinization

The yield of the demineralization product was calculated based on the mass of biomass (shrimp shells). From figure 1 (a), it can be seen that the percentage of demineralization depends on the HCl concentration. In this experiment, the highest percentage of

demineralization is obtained by using 1 M HCl and the lowest result of using 2 M HCl. This result differs from studies's data showing that a higher concentration of HCl resulted in a higher percentage of demineralization and a lower percentage of yield (Al Shaqsi et al. 2020). The material used in this study is the rest of the restaurant in the form of shrimp shell waste that has gone through the previous cooking process, so a lot of mineral content has been dissolved and wasted due to heating.

The demineralized product of three HCl treatments with the same amount was treated separately using NaOH solution with varying concentrations for protein removal. The effect of HCl concentration in the demineralization process and NaOH concentration in the deproteinization process to the percentage of deproteinization is shown in Figure 1 (b). The use of different concentrations of HCl and NaOH has a significant effect on percentage of deproteinization. In this study, the 1 M HCl concentration and 1 M NaOH concentration result in the highest percentage of deproteinization, which reach 62%.

Deacetylation of Chitin to Chitosan

The content of free amino groups in polysaccharides is mainly determined by the value of the degree of deacetylation. The importance of degree of deacetylation of chitosan is due to its enormous influence on the physical, chemical, and biological properties of chitosan. Chitin deacetylation to chitosan is generally complete after treatment using concentrated sodium or potassium hydroxide solutions (40-50%) normally at a temperature of 100°C or higher for 30 min or more (Kumari et al. 2017). With treatment using concentrated NaOH (60%) at 90°C for 2 h, this study produces chitosan from the extracted chitin from shrimp shells with the FTIR spectras and degrees of deacetylation as shown in Figure 2 and Figure 3, respectively.

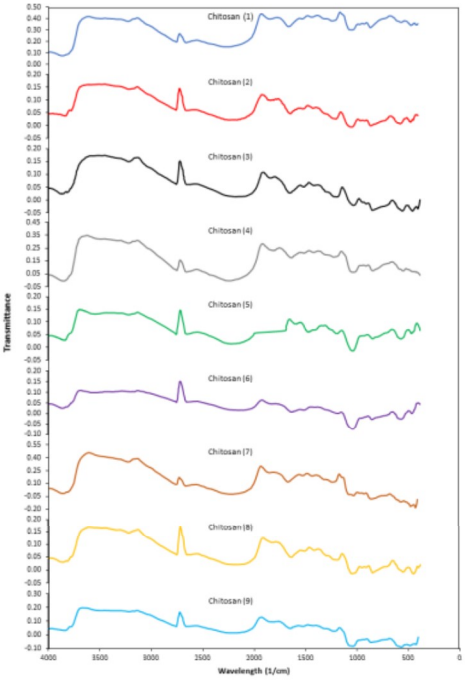


Fig. 2: FTIR spectra of treated shrimp shells

The degrees of deacetylation of chitosan products obtained from this research range from 20.47% to 57.28%. In pursuance of the literature, the deacetylation degree of chitosan depends on the crustacean species and the preparation methods, and it ranges from 50% to 100% (Sivashankari and Prabaharan, 2017). Accordingly, the degree of deacetylation in this experiment cannot yet meet the called chitosan category, but chitin. The low degree of deacetylation obtained from this test is caused by the raw material for shrimp shells which is processed leftovers from restaurants so that they still contain a lot of impurities. Figure 3 shows that the acid and alkaline treatment also influence the degree

of deacetylation during demineralization and deproteinization.

The highest degree of deacetylation is found in this study during treatment using 2 M NaOH and 2 M HCl. At 1.5 M HCl concentration, a decrease in the degree of deacetylation is seen when the NaOH concentration is increased. Meanwhile, different results are shown for 1 M and 2 M HCl concentrations where there is a trend of increasing deacetylation degree with increasing NaOH concentration. The difference in the effect of acid and base treatment is also shown in Figure 3, where at 1 M and 1.5 M NaOH concentrations, the highest deacetylation degree is obtained at 1.5 M HCl while at 2 M NaOH concentration the highest data is obtained at 2 M HCl.

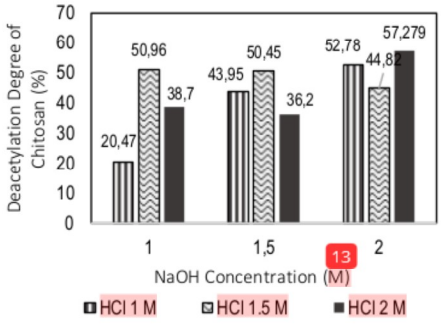


Fig. 3: Effect of demineralization and deproteinization treatments to the Deacetylation Degree of chitosan

The results of this study indicate that the highest degree of deacetylation is achieved by using the highest concentrations of acid and alkaline solution. Based on various procedures proposed and developed by many researchers, in general, the chemical methods involve using strong acids and bases at high temperature to increase the deacetylation degree and the solubility. Due to some process variables affect the physicochemical properties of chitosan making it difficult to produce good quality of chitosan with a high deacetylation degree (El Knidri et al. 2018).

Hydrogel Synthesis

Chemical cross-linking reactions between glutaraldehyde and amine or hydroxyl groups have an important role in building hydrogels from natural and synthetic polymeric materials. Previous reports have proposed the reaction mechanisms of glutaraldehyde with amino groups (Khapre et al. 2021) and amide groups (Dmitriev et al. 2015) to form cross-linked hydrogels. Figure 4 shows the mechanism of the reaction of hydrogel formation from shrimp shell-based chitosan with glutaraldehyde as a cross-linker agent. (Atangana et al. 2020).

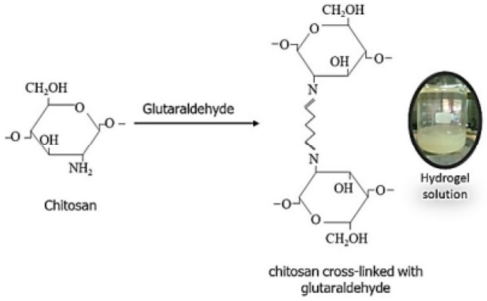
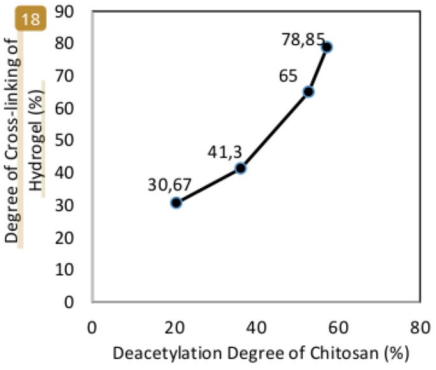


Fig. 4: Mechanism of the reaction for the formation of hydrogel crosslinks from chitosan using glutaraldehyde.

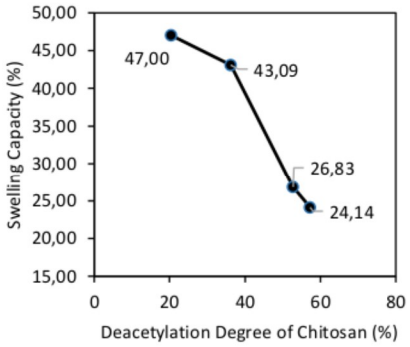
Hydrogel Characterization

The degree of cross-linking indicates the cross-linking density in the hydrogel network structure due to radiation or the addition of a chemical cross-linking agent. The hydrogel's degree of cross-linking made from chitosan with varying degrees of deacetylation with glutaraldehyde as cross-linking agent are presented in Figure 5 (a). The figure shows that the degree of cross-linking of hydrogel

has increased with the higher degree of deacetylation of the chitosan used.



(a)



(b)

Fig. 5: Effect of Deacetylation Degree of chitosan to the physical characteristics of hydrogel (a) degree of cross-linking, (b) swelling capacity

Hydrogel has hydrophilic functional groups such as amino, carboxyl and hydroxyl groups in the backbone of polymer chains that allow water absorption in hydrogel networks. The swelling capacity of hydrogels depends on the type of polymers and the type and degree of cross-linking between polymer chains (Khalesi et al. 2020). Figure 5 (b) shows the hydrogel swelling capacity which is influenced by the degree of deacetylation of chitosan. The decrease in hydrogel absorption capacity with the increasing degree of deacetylation of chitosan is caused by the high cross-linking density, making it difficult for water to enter the hydrogel networks (Erizal 2012).

The degree of cross-linking and the swelling capacity are important parameters that hydrogels must own, especially in their role as superabsorbent materials. According to Rather et al. (2022), superabsorbent hydrogels' main features are high swelling or absorption capacity, low residual monomer concentrations and low soluble content. The high degree of cross-linking implies that soluble material derived from the remaining monomer that is not converted is also low. Unfortunately, this study results in a lower absorption capacity value with an increase in the degree of cross-linking, thus making it unsuitable for application as a superabsorbent. High swelling capabilities are not profitable in many situations, especially for biomedical applications. Volume expansion due to hydrogel swelling can worsen the mechanical properties of the hydrogel and cause unwanted oppression in the surrounding tissue if applied in vivo (Zhan et al. 2021). Therefore, this research turns the disadvantages of low swelling hydrogels into advantages and provides new ideas for applying of hydrogels in biomedical fields such as tissue engineering and internal wound closure. A low swelling ratio is also desirable criteria for conductive hydrogels with great potential applications in wearable electronics, flexible printable electronics, and tissue engineering scaffolds (Zhang et al. 2022).

CONCLUSIONS

Chitosan from this study has the optimum degree of deacetylation at 57.28 %, resulting from demineralization using HCl 2M

and deproteinization with NaOH 2 M. Higher deacetylation degree of chitosan cause the increase of degree of cross-linking and decrease of the swelling capacity of the hydrogel product. The highest degree of cross-linking is 78.85 %, and the swelling capacity is 47 %.

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