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Synthesis of Cross-Linked Konjac Glucomannan and Kappa Carrageenan Film with Glutaraldehyde

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Abstract**—**Cross-linked konjac glucomannan and kappa carrageenan film were prepared by chemical crosslinking using glutaraldehyde (GA) as the crosslinking agent. The effect crosslinking on the swelling degree was investigated. Konjac glucomannan and its mixture with kappa carrageenan film was immersed in GA solution and then thermally cured. The obtained cross-linked film was washed and soaked in the ethanol to remove the unreacted GA. The obtained film was air dried at room temperature to a constant weight. The infrared spectra and the value of swelling degree of obtained crosslinked film showed that glucomannan and kappa carrageenan was able to be cross-linked using glutaraldehyde by film immersion and curing method without catalyst. The cross-linked films were found to be pH sensitive, indicating a potential to be used in drug delivery polymer system.

Keywords**—**Crosslinking, glucomannan, carrageenan, swelling.

I. Introduction

RECENTLY, the drug delivery system materials based on natural polymers, especially polysaccharides, have been investigated extensively due to more biodegradable, less toxic, more biocompatible, renewable, and cheaper because the raw materials are locally abundant than synthetic polymer. Konjac glucomannan is a neutral polysaccharides derived from the bulbs of Amorphallus konjac. It consists of a linear chain of β 1-4 linked glucose and mannose units with a glucose mannose ratio of approximately 1.6:1 [1]. Kappa carrageenans are linear polysaccharides sulfated galactan extracted from red seaweed (Rhodopyta), such as *Kappaphycus alvarezii* (known as *Eucheuma cottonii* in industry) which is well cultivated in Indonesia. This natural polymers comprise of repeating units of (1,3)-D-galactopyranose and (1,4)-3,6- anhidro-α-D-galactopyranose with sulfate groups in a certain amount and position [2]. The presence of hydroxyl groups in konjac glucomannan and carrageenan structure causes these polysaccharides tend to be hydrophilic. These hydroxyl groups also show that the structure of these polisaccharides may be chemically modified in order to be applied as controlled delivery system.

The swelling ability of material in response to external stimuli as pH, salt, and ionic strength, allows useful in application such as controlled drug delivery, separation, and agriculture [3], [4]. We already reported the preparation of glutaraldehyde cross-linked kappa carrageenan hydrogel using film immersion and followed by thermal curing [5]. In this work, we study the chemically modification of konjac glucomannan and its mixture with kappa carrageenan using glutaraldehyde as the crosslinking agent, in order to get a new material that may be applied as controlled delivery system.

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II. Materials and Methods

A. Material

Seaweeds of *Kappaphycus alvarezii* were harvested from Makassar, South Sulawesi, Indonesia. The seaweeds were washed using tap water to eliminate all impurities such as the salt and sand. After washing, the seaweeds were cut into about 1 cm length, and finally sun dried to constant weight. The 'clean seaweed' sample was kept in a dry state until further processing was done. Konjac bulbs (*Amorphophallus muelleri Blume*) were collected from Madiun, Central Jawa, Indonesia. Konjac bulbs were cleaned, peeled, sliced into chips about 0.5 cm thick and then sun dried. The dried chips were grounded and then sieved. The coarse powder with less than 425 mesh was collected and kept in a dry state until further processing was done. Glutaraldehyde 25 wt% solutions in water (Merck) and all other chemicals were purchased and used without further purification.

B. Carrageenan Preparation

The process of carrageenan recovery from *Kappaphycus alvarezii* followed the previously reported method [5].

C. Konjac Glucomannan Preparation

One hundred gram coarse powder of glucomannan was mixed with 1000 mL technical grade of ethanol (50% w/w). The mixture was stirred using magnetic stirrer in room temperature for 90 minutes. After filtering, the residue was collected and then dried in 40^{o}C to a constant weight. The residue than was named as a glucomannan.

D. Film Preparation

Polymer film 1 was prepared by dissolution the 3.5 gram glucomannan powder in 50 mL distilled water, and the mixture of 3 gram glucomannan and 0.5 gram carrageenan for preparing polymer film 2. The mixture was heated and stirred until a homogeneous solution was obtained. The solution was poured into plastic plate and allowed to solidify and then dried at room temperature to constant weight. The obtained film was cut of 1.5 cm x 1.5 cm and the weight of each piece film was about 0.09-0.15 gram.

E. Film Crosslinking

We prepared control (noncrosslinked) and crosslinked films. GA 4 wt% as the crosslinker was prepared by diluting

GA 25 wt% with distilled water. For preparing the crosslinked film, the both polymer film 1 and 2 were immersed in crosslinker for 2 min. The surface of film were wiped with filter cloth and then cured at 120 ^{O}C in oven for 25 min. The crosslinked film was soaked in water with stirring for 1 min and then in ethanol for 4 h to remove unreacted GA. The wet crosslinked films were dried at room temperature to a constant weight. The initial composition and crosslinking conducted were summarized as displayed in Table I.

TABLE I
THE INITIAL MIXTURE COMPOSITION AND THE TREATMENT

Sample code	Film composition	Treatment
1A	3.5 gram glucomannan	noncrosslinking
1B	3.5 gram glucomannan	crosslinking
2A	3.0 gram glucomannan + 0.5 gram carrageenan	noncrosslinking
2B	3.0 gram glucomannan + 0.5 gram carrageenan	crosslinking

F. Film Characterization

Molecular groups were identified using FTIR spectrometer (Shimadzu IR Prestige-21). The samples were powdered. Infrared spectra were obtained by using KBr pellet method with 10 scans and 16 cm^{-1} resolution. Peak baselines and height were determined in transmittance (T) mode and peak height were converted to absorbance (A). Absorbance was calculated as (1):

$$A= - \log(T) \quad (1)$$

For determining the value of swelling ability, a piece of dry hydrogel film was weighted and then placed in an aqueous medium of 10 mL. The swelling degree was determined in different aqueous media, namely distilled water (pH~7), NaOH 0.1N (pH~13), and HCl 0.1N (pH~1). The swelling degree was evaluated by measuring the weight before soaking (Md) and the weight after soaking (Mw) in solution for 5 hours of soaking time at room temperature. All weight measurements were conducted on a pan balance (Ohaus) having an accuracy up to fourth decimal. Swelling degree (SD) was calculated as (2). Each experiment was done at least one duplicate run and the mean value was used to display the data.

$$SD= ((Mw-Md))/Md \quad (2)$$

III. RESULT AND DISCUSSION

A. FTIR Spectra

Fig. 1 shows the FTIR spectra of glucomannan film (1A) and cross-linked glucomannan film (1B). The study of glucomannan spectra by FTIR spectroscopy shows the presence of very strong absorption band in 805 cm^{-1}and 884 cm^{-1} corresponding to pyran ring and β-D glycosidic bond of glucomannan. Widjanarko et al. [6] reported that mannose and glucose units were assigned from peaks at 808 and 875 cm^{-1}. Xu et al. [7] found that peaks of mannose and glucose units were at 808 and 871 cm^{-1}.

The peak 3367 cm^{-1} was assigned as absorption band of hydroxyl groups (Fig. 1). The peak at 1635 cm^{-1} is the intramolecular hydrogen bonds [7]. The presence of hydroxyl groups in glucomannan chains may cause the glucomannan is possible to be cross-linked with GA.

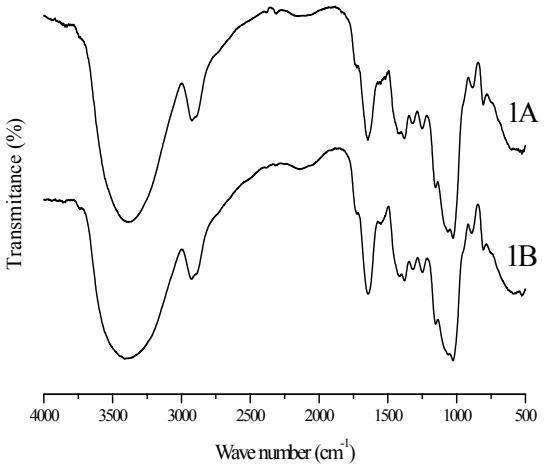

Fig. 1 FTIR spectra of noncrosslinked (1A) and crosslinked glucomannan (1B)

Chemical crosslinking is a direct reaction between linear polymer or branches and at least a bi-functional component, small molecular weight, and called as crosslinking agent or cross linker. This component links the polymer chains with its functional groups [8]. Here, the chemical reaction between hydroxyl groups of glucomannan and GA as the crosslinking agent was confirmed by FTIR measurement. Fig. 1 shows that there is no sharp difference peaks between sample 1A (without crosslinking) and sample 1B (with crosslinking).

The absorbance of peaks attributed to hydroxyls was normalized with respect to that of peak attributed to pyran ring peaks, which remained almost constant. The relative absorbance of the O-H groups was evaluated through the absorbance of ratio of O-H band to pyran ring band. This absorbance ratio serves as semi quantitative index of chemical composition of film. We only observed a slight decrease of the relative absorption bands of hydroxyl group in cross-linked film.

The reduction of this absorbance ratio, namely 2.08 for sample 1A became 1.96 for cross-linked film sample 1B, indicates that reaction glutaraldehyde and glucomannan has occurred. The hydroxyls had been consumed during crosslinking reaction. According to [9]-[11], in the crosslinking reaction, the aldehyde groups from glutaraldehyde reacted with hydroxyl group from polymer under acidic condition, and then formed acetal bridges. One aldehyde group links the polymer chains by reacting with the hydroxyl groups of polymer and produces a hemi-acetal structure [11], [12]. In the present work, the reduction of hydroxyl absorbance of spectra IR indicated that hydrogels based on glutaraldehyde–cross-linked glucomannan were prepared successfully by film immersion and high temperature

curing method without catalyst.

B. Swelling Behavior

Beside IR spectra measurement, the cross-linked film was also tested with regard to their swelling in aqueous solution. Figs. 2 and 3 show the comparison of that value of swelling degree of non-cross-linked film and cross-linked film with different polymer composition at various medium, measured at room temperature.

In general, there is a trend that with crosslinking treatment the swelling degree decreased. The decreasing of swelling degree indicates that there is a denser crosslinked structure. More crosslinked structure causes the smaller space in molecules, as the result the less water can be absorbed. It shows that crosslinked structure increases with crosslinking. The reduction of swelling degree value indicates that crosslinking occurred.

Crosslinking procedure by film immersion followed by high temperature curing could drive the reaction between hydroxyl groups of glucomannan and aldehydes of glutaraldehyde to form crosslink structures. Although it is difficult to exactly determine the conversion of polymer, the physical characteristics of crosslinked polymer, especially swelling behavior, indirectly demonstrated the success of crosslinking reaction. The crosslinking way also be expressed by stability of crosslinked film in aqueous solution as characterized by a significant decrease of swelling degree.

The swelling degree expressed a gram of water uptake per gram of polymer film. The decreasing of swelling degree of crosslinked film indicated the presence of crosslink structure as described in Figs. 2 and 3.

The effect of polymer composition on swelling degree can be seen by comparing Figs. 2 and 3. It was known that glucomannan polymers consist of a linear chain of β 1-4 linked glucose and mannose units with a glucose mannose [1], besides the carrageenan polymers comprise of repeating units of (1,3)-D-galactopyranose and (1,4)-3,6-anhydro-α-D-galactopyranose with sulfate groups [2].

In the lower pH media, cross-linked glucomannan hydrogels were stable. Comparing to the previous paper [5] which the glutaraldehyde cross-linked kappa carrageenan could not stable at pH 1.2, the glutaraldehyde cross-linked glucomannan-carrageenan did not disintegrate in HCL media (pH~1.2) for 5 hours swelling. The strength of beta chain in glycosidic linkage of glucomannan may cause this stability network in low pH media. This data showed that glucomannan may enhance the swelling stability in lower pH media.

The value of swelling degree of sample 2B at NaOH media (pH~11.0) was higher than that of sample 1B. This indicated that different group chain in polymer mixture affected the properties of swelling ability. The carrageenan contributed sulfate groups in hydrogel. The presence of sulfate groups from carrageenan structure tends to increase the hydrophilic chain in polymer film. Sulfate groups are charged groups. This ionic groups of $–OSO_3H$ will be ionized in higher pH media resulting higher swelling degree. The noncrosslinked and crosslinked films show the pH sensitive properties as seen in Figs 2 and 3. The presence of hydroxyl and sulfate groups makes this polymer are pH sensitive. The obtained crosslinked film shows to be potential for controlled release delivery system.

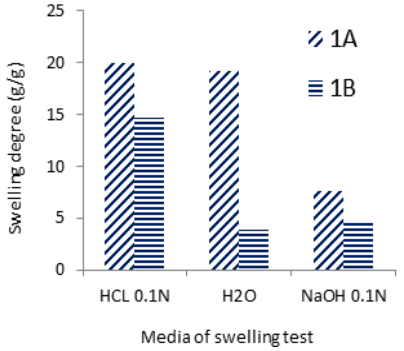

Fig. 2 Swelling degree of non-cross-linked (1A) and cross-linked glucomannan (1B) at various media

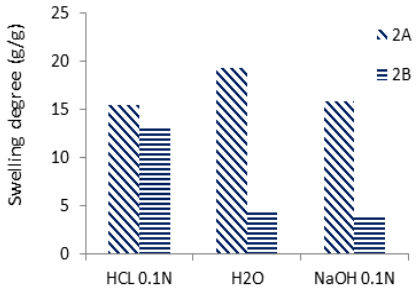

Fig. 3 Swelling degree of non-cross-linked (2A) and cross-linked glucomannan-carrageenan (2B) at various media

IV. Conclusion

Crosslinked glucomannan and kappa carrageenan film have been successfully prepared by crosslinking with glutaraldehyde using film immersion and followed by thermal curing. The prepared crosslinked film showed responsive to the change of pH Indicating may be developed as controlled release delivery system.

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