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Swelling Behaviour of Kappa Carrageenan Hydrogel in Neutral Salt Solution

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Abstract**—**Hydrogel films were prepared from kappa carrageenan by crosslinking with glutaraldehyde. Carrageenan films extracted from *Kappaphycus alvarezii* seaweed were immersed in glutaraldehyde solution for 2 min and then cured at 110 °C for 25 min. The obtained crosslinked films were washed with ethanol to remove the unreacted glutaraldehyde and then air dried to constant weights. The aim of this research was to study the swelling degree behaviour of the hydrogel film to neutral salts solution, namely NaCl, KCl, and $CaCl_2$. The results showed that swelling degree of crosslinked films varied non-monotonically with salinity of NaCl. Swelling degree decreased with the increasing of KCl concentration. Swelling degree of crosslinked film in $CaCl_2$ solution was lower than that in NaCl and in KCl solutions.

Keywords**—**Hydrogel, carrageenan, glutaraldehyde, swelling, salt.

I. Introduction

OUR research is related to the development of hydrogels based on natural polysaccharides. Kappa carrageenans as a source of natural polysaccharides were extracted from *Kappaphycus alvarezii* seaweed from Indonesia. Kappa carrageenans are linear polysaccharides sulfated galactan extracted from Rhodophyta seaweed. This natural polymers comprise of repeating units of (1,3)-D-galactopyranose and (1,4)-3,6-anhydro-alfa-D-galactopyranose with sulfate group in a certain amount and position. Kappa carrageenans have ability to form reversible gel [1]. The presence of hydroxyl groups in carrageenan structure causes these polymers tend to be hydrophilic and may be chemically crosslinked to increase their stability in aqueous.

We already reported the preparation of glutaraldehyde crosslinked kappa carrageenan hydrogel using film immersion and followed by thermal curing method [2]. The influence of extraction procedure of *Kappaphycus alvarezii* on the properties of obtained glutaraldehyde crosslinked kappa carrageenan has been studied [3].

Hydrogels are three-dimensional networks of hydrophilic polymers which are able to swell in water. The study of swelling behaviors of hydrogels as a function of their ionic environment should allow for a better understanding of the potential of these crosslinked kappa carrageenan hydrogels as smart release delivery systems. Hydrogel ability to swell in response to external stimuli as pH, ionic strength, temperature, electric fields depends on the nature of polymer chains and allows hydrogels useful in application such as controlled drug delivery, separation process or agricultural application [4], [5]. Hydrogels responding to the external stimuli are often referred to as smart polymers.

In this work, we studied the swelling properties of glutaraldehyde crosslinked kappa carrageenan at neutral salt solution for evaluating the suitability of hydrogel application. The aim of this research was to investigate the salt responsiveness properties of obtained hydrogel film to neutral salts, namely NaCl, KCl, and $CaCl_2$. The responsiveness was evaluated by using swelling degree measurements in solutions with various ionic strength and cation radius.

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II. Materials and Methods

A. Material

Seaweeds of *Kappaphycus alvarezii* were harvested from Makasar, South Sulawesi, Indonesia. The seaweeds were soaked in water for 2 h, and then washed by using tap water several times to eliminate all impurities such as 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. Technical grade of potassium hydroxide (purity 88%) was used as alkali treatment before extraction process. Glutaraldehyde (25 wt.% solution in water (Merck)) and all other chemicals were purchased and used without further purification.

B. Carrageenan Preparation

The procedure of carrageenan recovery from *Kappaphycus alvarezii* followed the previously reported method [6] with minor modification. The clean seaweed was treated using KOH solution before being extracted. Thirty gram of seaweed was soaked in KOH 0.3 N overnight and then heated at 60 °C for 30 min. After alkali treatment, the seaweed was washed with tap water and neutralized with HCl 0.1 N. A specified amount of distilled water was heated in a beaker as an extractor. After the temperature of the water reached 80 °C, the seaweed was then added into solvent, and the time of extraction started to be counted. A constant ratio of seaweed weight to solvent volume (1:50 g/mL) was maintained by adding hot water. After 1 h extraction, the filtrate was separated from residue and immediately poured into 4.5 L of cold (5 °C) ethanol (90 wt.%) which caused precipitation of polysaccharides. The precipitation was allowed for 30 min while a gentle stirring was done. The precipitated carrageenans were collected.

C. Film Preparation

Carrageenan films were prepared by dissolution of the precipitated carrageenan in distilled water. The mixtures were heated and stirred until homogeneous solutions were obtained. The solutions were poured into plastic plate and allowed to solidify and then dried at room temperature to constant weights. The obtained films were cut into 1.5 cm x 1.5 cm pieces and the weight of each piece film was about 0.03-0.04 g.

D. Film Crosslinking

We prepared crosslinked films. GA 4 wt.% as the crosslinker was prepared by diluting GA 25 wt.% with distilled water. For preparing the crosslinked film, the carrageenan films were immersed in crosslinker for 2 min. The surface of film was wiped with filter cloth and then cured at 110 $^{\circ}$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 hydrogels were dried at room temperature to a constant weight.

E. Hydrogel Characterization

For determining the value of swelling ability, a piece of hydrogel film was weighted and then placed in distilled water of 10 mL. The equilibrium swelling degree was evaluated by measuring the weight before soaking (Md) and the weight after soaking (Mw) in solution for 24 hours at room temperature. All weight measurements were conducted on a pan balance (Ohaus) having an accuracy up to fourth decimal. Equilibrium swelling degree (SD) was calculated as (1). Each experiment was done at least one duplicate run and the mean value was used to display the data.

$$SD = (Mw - Md) / Md \quad (1)$$

To study the responsiveness of obtained hydrogels to neutral salt, the swelling tests were conducted in water (pH~7), aqueous NaCl 0.001 M – 0.35 M, KCl 0.01 M – 0.15 M, and $CaCl_2$ 0.15 M (pH~7).

III. Result and Discussion

Swelling degree in salt solutions is of prime significance in many practicals such as personal hygiene products and water release systems in agriculture. In this research, to investigate the effect of ion strength, the equilibrium swelling degree was measured in sodium chloride solutions at neutral pH with various concentrations. The higher of salt concentration indicates the higher ionic strength also. Fig. 1 shows the effect of sodium chloride concentration on the equilibrium swelling degree of obtained hydrogel. At low concentration of NaCl, 0.0001-0.001 M, the value of swelling degree was similar with that in distilled water.

As shown in Fig. 1, at neutral pH the swelling degree first increased with increasing ionic strength up to 0.15 M, however, above this value it decreased with further increases in ionic strength. The swelling degree reached it maximal point at 0.15 M. This trend indicated that glutaraldehyde-crosslinked kappa carrageenan hydrogels exhibited the salt responsive properties.

Stimuli responsive hydrogels are produced by adding acidic or basic functional groups to the polymers structure. These functional groups either accept or release protons in response to appropriate pH and ionic strength changes in aqueous media. The network porosity of these hydrogels will change with electrostatic repulsion. The dominant driving force for swelling in charged hydrogel is the inherent electrostatic repulsion between gel charges.

Kappa carrageenan based hydrogels are composed of polymer chains containing charged groups, namely sulfate groups. Sulfate groups are ionizable groups that will be deprotonated at pH neutral system resulting ionic groups – OSO_3- in hydrogel structure. These same negatively charged groups are repelled by each other. The negatively charged sulfate groups on different chains induce the electrostatic repulsion, as a result the distance between the chains increase. The space of network becomes larger, so that the network becomes more permeable to large molecules and much water can penetrate into the network, leading to the higher swelling degree. Therefore, the driving force for swelling in this hydrogels is electrostatic repulsion between gel charges. As a result, the swelling degree of carrageenan hydrogels can be induced through such stimuli as changes in pH and salinity [7]. The maximal swelling degree was found to increase with the sub chain length, the length of chains between crosslinks.

Fig. 1 shows that swelling degree of hydrogel as a function of salt depended on the level of salt in the surrounding environment. It is showed that swelling degree values varied in a non-monotonic way, first increasing and then decreasing with salt concentration. These phenomena are due to the fact that the degree of dissociation saturated at a finite salt concentration, above which the salt screening effect dominates [8]. Regarding the effect ionic strength, the dissociation of sulphate groups in hydrogel may be enhanced as the ionic strength increases up to a fixed value, but with ionic strength continuously increasing, the anionic groups in hydrogel are screened by Na+ ions. As a result, the anionic groups in hydrogel changes from an expanded to a more compact matrix, so that the swelling degree drops with increasing ionic strength [7].

The same trends of non-monotonic behavior in the present research were also found in hydrogels of polymethacrylic acid-graft-ethylene glycol [8], chitosan-carbomethylchitosan [9], and carboxy methyl dextran [7].

The effect of ionic strength on swelling behavior is also confirmed using KCl solution. Fig. 2 shows effect of KCl concentration on value of equilibrium swelling degree. At concentration of KCl from 0.01 M to 0.15 M, the swelling degree increased with decreasing salt concentration. Compared with NaCl, the value of swelling degree on KCl solution was lower than in NaCl solution. This indicates that cation type strongly determines the electrostatic repulsion between the gel charges.

To study the effect of cation radius on swelling behaviors, the equilibrium swelling degree was measured in 0.15 M

chloride salt solutions of Na^+ and K^+. The effect of cation charge on swelling was measured in 0.15 chloride salt solution of Na^+ and Ca^{2+} and can be concluded from Fig. 3. With increasing radius and charge of cation, the degree of swelling is decreased.

The swelling degree of obtained hydrogel is in the order NaCl>KCl>CaCl2. This well-known swelling loss is often attributed to a charge screening effect of the additional cations, causing a nonperfect anion-anion electrostatic repulsion [10]. Moreover, in salt solution, the osmotic pressure resulting from the difference in the mobile ion concentration between gel and aqueous phases is decreased and consequently the water diffusion is low. A stronger interaction between sulphate groups and large cation may cause the swelling degree in KCl solution is lower than in NaCl solution.

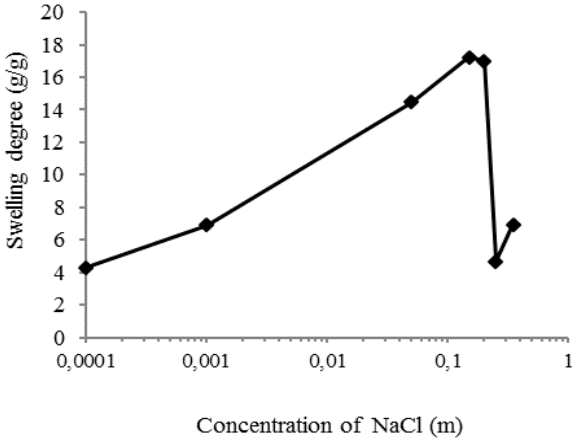

Fig. 1 Swelling degree of the hydrogel in sodium chloride with various concentrations

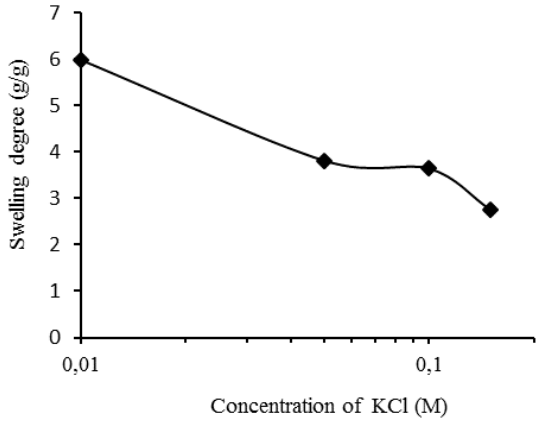

Fig. 2 Swelling degree of the hydrogel in potassium chloride with various concentrations

The process of gelation of kappa carrageenan occurs as a result of coil to helix conformational transition. The presence of suitable cation is an absolute requirement for gelation to proceed. Kappa carrageenan with Li+, Na+ forms no gel, but with K+, Rb+ or Cs+ forms clear elastic gel, and with Ca2+ forms brittle gel [1], [11]. The kappa carrageenan with heavier metal ions revealed to form gel by aggregation of double helices.

According to the dependence of swelling behavior from kappa carrageenan based hydrogels on the type of counter ions, it suggested that some of counterions condensed to sulfate groups in carrageenan chains by electrostatic interaction. In addition, with the increasing charge of cation in the case of salt solutions, ionic crosslinking at the surface of hydrogel causes an appreciable in swelling degree.

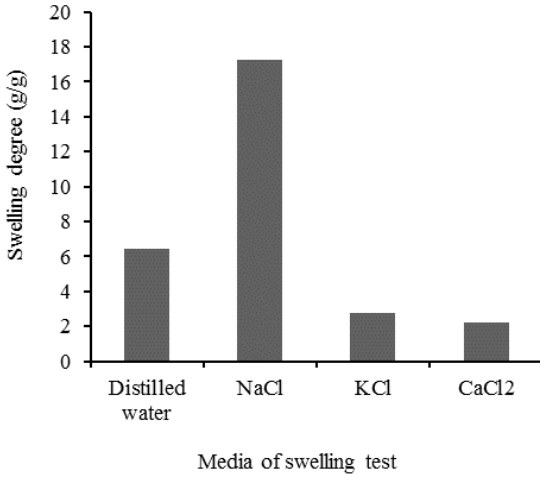

Fig. 3 Swelling degree of the hydrogel in different chloride salt solutions (0.15 M)

IV. Conclusion

The prepared glutaraldehyde crosslinked kappa carrageenan exhibited salt responsive hydrogel properties. The swelling degree varies nonmonotonically with solution NaCl concentration, first increasing and then decreasing with salinity. The swelling loss in salt solutions can be attributed to the charge screening effect and ionic crosslinking for mono and multi valent cation. The swelling degree in $CaCl_2$ is much lower than that in NaCl solution.

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