Engineering International Conference "UNNES Conservation" 2013 Proceeding
p- ISBN-979-25-2783
January 08, 2013, Semarang, Indonesia

Study of Carrageenan Hydrogel Synthesis of *Euchema cottoni* Using Potassium Hydroxide Extraction and Glutaraldehide Crosslinking

Megawati[1], Astrilia, D[2]
[1,2]*Chemical Engineering, Faculty of Engineering, Semarang State University*
Bldg. E1, Sekaran, Gunungpati, Semarang 50229, Indonesia
[*]*Tel.: +62 24 8508009; Fax: +62 24 8508009; E-mail add.: astriliad@staff.unnes.ac.id*

Abstract— *Seaweed is a type of Indonesia's marine abundant resource that can be extracted to yield several products, one of which is carrageenan which has a high value to produce a hydrogel, a type of gel that can absorb a substance dissolved in a solvent. The hydrogel contains galactose, so that it can adsorb water and dissolve completely in water within a certain time. In this study, the carrageenan was extracted from seaweed with alkali solvent, followed by alcohol precipitation in order to obtain pure carrageenan. And then, the extracted carrageenan was be crosslinked with glutaraldehyde 0.5% v/v followed by curing reaction at various temperatures (80, 90, 100, 110 and 120 ^{o}C). The analysis of carrageenan yield, swelling degree, and molecules structure by FTIR (Fourier Transform Infrared) were conducted to study the effect of crosslinking as well as curing temperature of the carrageenan product. The experimental result shows that the carrageenan yield is about 23.37% w/w of wet seaweed. The swelling degree of carrageenan with crosslinking is relatively good at a temperature of 120 °C with the swelling degree is about 6 w/w water/carrageenan. The FTIR analysis result indicates that the curing temperatures also affect the sulphate and anhydrogalactose contents in the carrageenan. The curing temperature decreases the sulphate content decreases. In addition, the curing temperature decreases the amount of bound water as shown by the number of anhydrogalactose compound increases.*

Keywords — *alkaline extraction, carrageenan, euchema cottoni, glutaraldehyde crosslinking, hydrogel*

I. INTRODUCTION

Eucheuma seaweed chosen in this study is one of the high potential seaweeds to produce carrageenan and includes in red algae class (Rhodophyceae). In addition, carrageenan structure of this seaweed is kappa type. Accordingly, the carrageenan is a natural polymer of (1,3)-D-galactose or (1,4)-3,6-anhydro-D-galactose with sulphate groups at specific positions that can dissolve in hot water (70 °C) and form a strong thermoreversible gel.[1] Because of its ability to form a gel, the carrageenan more often applied to gel formations, including gels for stabilizers, thickeners, emulsifiers for food and non-food industries such as pharmaceuticals and cosmetics.

Recently, Indonesia is one of the carrageenan exporters which was also as importer of carrageenan hydrogel. This is caused by the extracted carrageenan had been not relatively improved in several quality products like carrageenan hydrogel.[2] The hydrogel can be used for pampers, diapers, absorbing toxins and drug storage. Important steps to produce carrageenan hydrogel are extraction of seaweed to yield carrageenan and crosslinking of carrageenan to yield hydrogel. In general, the extraction of seaweed to yield carrageenan is carried out through a series process, i.e. extraction with alkaline solution, alcohol precipitation to separate of carrageenan from alkaline solution, and then drying of carrageenan.[3-7] Theoretically, at alkaline extraction of seaweed, the chemical compound of 3,6-anhidro-D-galactose will be formed from (1,3)-D-galactose-sulphate, so that the extraction is also known as desulfatation. Additionally, the alkaline solutions which can be used in the desulfatation reaction are NaOH, KOH, and $Ca(OH)_2$. Accordingly, the extraction of carrageenan with KOH is better than with NaOH and water.[8] Likewise, the carrageenan hydrogel obtained by potassium hydroxide extraction is stronger than other alkaline solutions.[3,6-8]

After the alkaline extraction of seaweed to yield carrageenan, the carrageenan obtained is reacted with crosslinking agent, such as glioksal dialdehyde and glutaraldehyde, epichlorohydrin, and genipin in order to produce hydrogel. The crosslinking is followed by heat curing to create a stable structure of the hydrogel formed. According to Rojas et al. (2011) the strength of the hydrogel produced using glutaraldehyde as crosslinking agent is better than glioksal.[9] Moreover, Glutaraldehyde is a chemical compound that readily available in Indonesia and cheaper than other crosslinking agent. The focus of this research is not only potassium hydroxide extraction of seaweed to produce carrageenan but also glutaraldehyde crosslinking of the carrageenan to produce hydrogel. The value of carrageenan yield of Eucheuma seaweed from Semarang was

studied in the extraction step and the effect of curing temperature on the swelling degree as well as the molecular structure of hydrogel is studied in the crosslinking step.

II. RESEARCH METHODOLOGY

This research was conducted into two steps, i.e. potassium hydroxide extraction of seaweed to produce carrageenan and glutaraldehyde crosslinking of carrageenan to produce hydrogel. Before the extraction was done 30 g of seaweed was soaked in distilled water until 15 minutes of time. After soaking, the seaweed was filtered using paper filter, and then the seaweed was cut into small pieces to increase the surface area. In the extraction, the seaweed was reacted with 100 mL of 0.5 mole/L potassium hydroxide at 80 °C in a 100 mL round-bottom flask for 1 hour of time and continued with filtration using filter paper to remove the seaweed residue. After that, the extracted carrageenan was alcohol precipitated (100 mL alcohol) to obtain the pure carrageenan. The carrageenan was then filtered using vacuum filter and dried in oven at 50-60 °C in order to optimally separate from the alcohol-water solution. Since the carrageenan will be used in glutaraldehyde crosslinking step as well as analysis step, so that the dry carrageenan was stored in vacuum plastic bag to keep a sterile condition.

The crosslinking was carried out by dissolving the dried carrageenan with a little water and then formed in a flat gun metal. The carrageenan sheet was then cut with a uniform size (1 x 1 cm). Each 3 pieces of carrageenan sheet was soaked with 10 mL of 0.5% v/v glutaraldehyde at room temperature for 2 min of time. The continue step was the curing reaction in order to stable the molecular structure by heating the carrageenan crosslinked at various temperatures of 80, 90, 100, 110, and 120 °C for 20 min of time. Finally, the swelling degree and molecular structure using FTIR (Fourier Transform Infrared) were conducted in order to study the effect of the glutaraldehyde crosslinking as well as the effect of curing temperature of the swelling and molecular structure of the carrageenan hydrogel. The swelling degree analysis was done by soaking the hydrogel in 10 mL water for 60 min of time. The mathematical formula of swelling degree (SD) used was written as follows:

$$SD = \frac{weight\ of\ water\ in\ hydrogel}{weight\ of\ dryhydrogel}$$

III. RESULTS AND DISCUSSION

The yield of the extracted carrageenan is about 23.67% w/w carrageenan/wet seaweed. The crosslinking results indicate that the swelling degree of the crosslinked carrageenan is relatively better than without crosslinking. Furthermore, the swelling degree of carrageenan with crosslinking is relatively good at a temperature of 120 °C with the swelling degree of 6 w/w water/carrageenan. Before the time of swelling degree analysis (60 min) is reached the crosslinked hydrogel at curing temperatures of 80, 90, 100, and 110 °C was broken. Thus, the FTIR analysis was conducted just for the carrageenan hydrogel produced at curing temperature of 110 and 120 °C and the results was then compared with the carrageenan hydrogel without crosslinking. The comparison of molecular structure between the carragenan without crosslinking and with crosslinking can be seen in Fig. 1, 2, and 3. Based on the literature, the chemical components in the carrageenan are at a wavelength of 805-1260 1/cm (Table 1).[10]

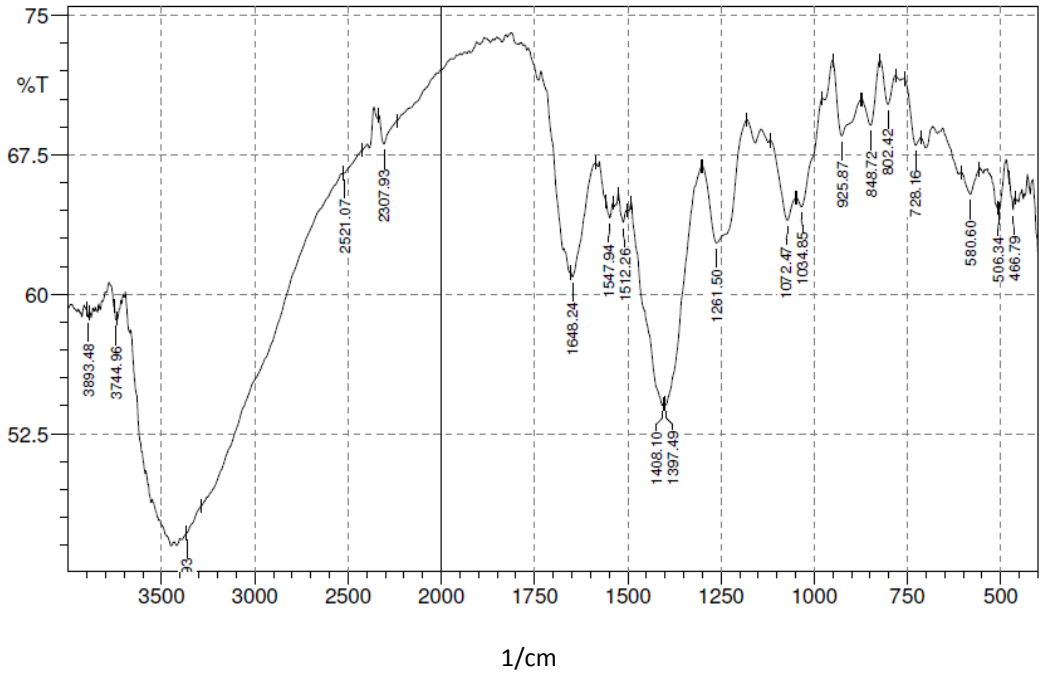

Fig. 1. FTIR analysis result of carrageenan without crosslinking

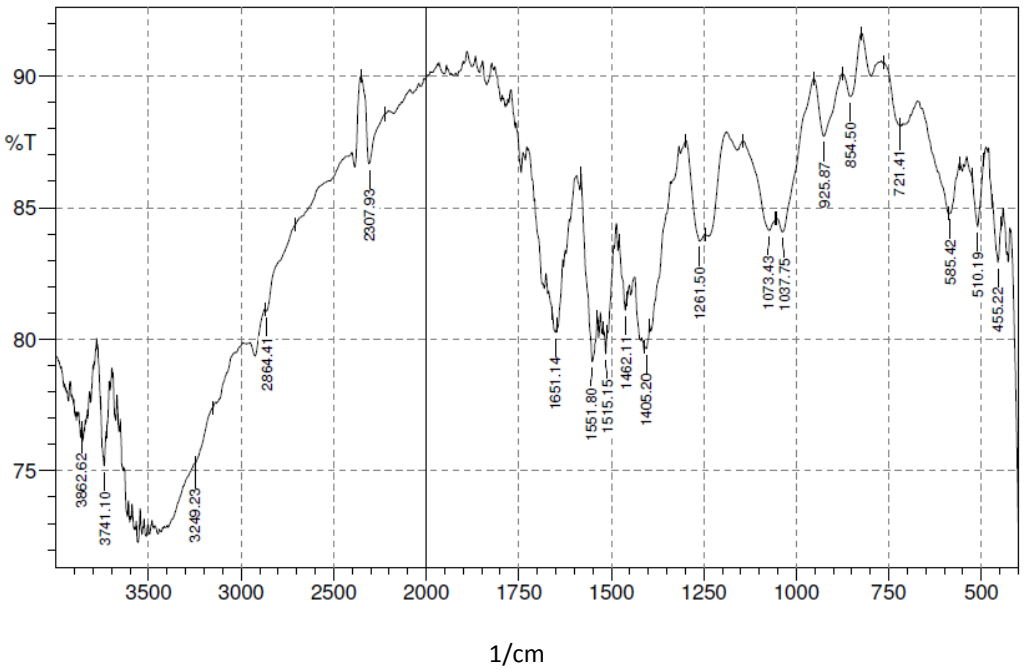

Fig. 2. FTIR analysis result of carrageenan with crosslinking followed curing at 110 ^{o}C

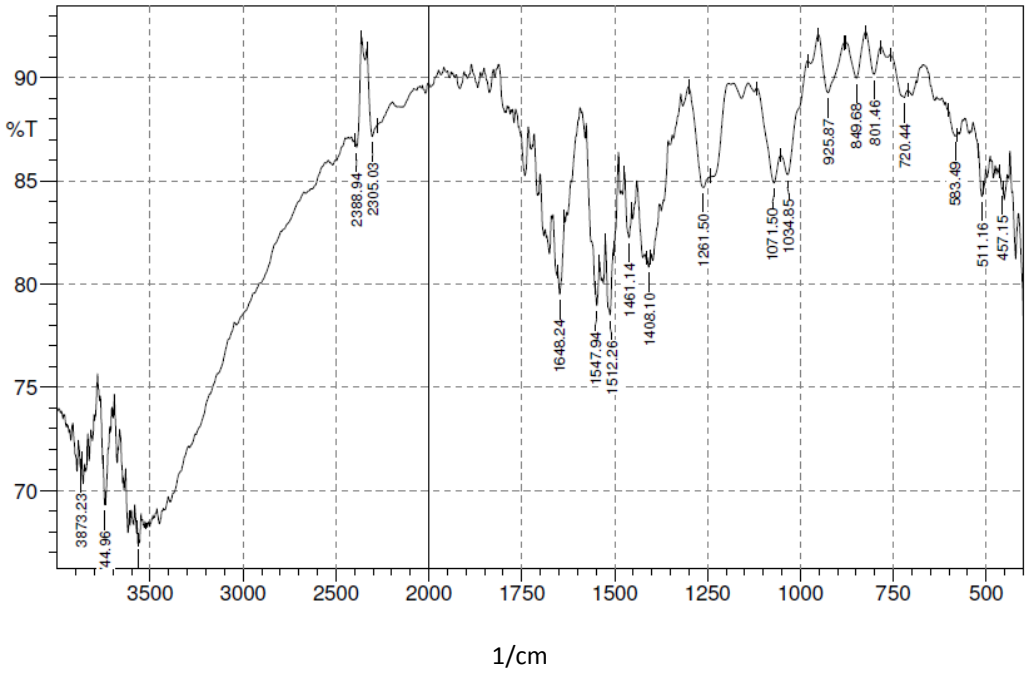

Fig. 3. FTIR analysis result of carrageenan with crosslinking followed curing at 120 ^{o}C

Table 1. Identification of chemical group in carrageenan by infrared spectroscopy

Wavenumbers (cm^{-1})	Bond(s)/group(s)
1240–1260	S═O of sulphate esters
1070	C–O of 3,6-anhydrogalactose
970–975	Galactose
930	C–O of 3,6-anhydrogalactose
905	C–O–SO_3 on C2 of 3,6-anhydrogalactose
890–900	Unsulphated β-D-galactose
867	C–O–SO_3 on C6 of galactose
845	C–O–SO_3 on C4 of galactose
825–830	C–O–SO_3 on C2 of galactose
815–820	C–O–SO_3 on C6 of galactose
805	C–O–SO_3 on C2 of 3,6-anhydrogalactose

Fig. 1 presents that the carrageenan without crosslinking contains chemical groups of anhydrogalactose-sulphate, galactose-sulphate, anhydrogalactose, and sulphate as indicated by the wavelength of 801, 849, 925, 1071, and 1261 1/cm respectively. On other hand, the chemical group composition of the carrageenan hydrogel with crosslinking using glutaraldehyde followed by curing at temperature of 110 ^{o}C is galactose-sulphate, anhydrogalactose, and sulphate (see Fig. 2). Similarly, at curing temperature of 120 ^{o}C, the chemical group composition of the carrageenan hydrogel is anhydrogalactose-sulphate (801 1/cm), galactose-sulphate (850 1/cm), anhydrogalactose (930 1/cm), and sulphate 1261 1/cm). As a result, the sulphate group content of carrageenan with crosslinking is lower than without crosslinking as indicated by the peak area of sulphate group.

IV. CONCLUSION

Eucheuma seaweed can be extracted using potassium hydroxide to yield carrageenan and the carrageenan can be converted using glutaraldehyde crosslinking to produce hydrogel. The extraction of carrageenan yields about 23.67% w/w carrageenan/wet seaweed. The crosslinking result indicates that the

carrageenan hydrogel quality with crosslinking is relatively better than without crosslinking. More ever, the swelling degree of carrageenan with crosslinking is relatively good at curing temperature of 120 °C with the swelling degree of 6 w/w water/carrageenan. Furthermore, the carrageenan contains chemical groups of anhydrogalactose-sulphate, galactose-sulphate, anhydrogalactose, and sulphate. Finally, the sulphate group content of carrageenan with crosslinking is lower than without crosslinking.

REFERENCES

[1] Campo, V.L., Kawano, D.F., Silva Júnior, D.B., Carvalho, I., 2009, "Carrageenans: biological properties, chemical modifications and structural analysis", Carbohydrate Polymers, 77, 167-180.

[2] Distantina, S., Wiratni, Fahrurrozi, M., dan Rochmadi, 2011, "Desulfation and Oversulfation of Carrageenan from Eucheuma cottonii", Journal of Science and Technology, 49 (5A), 240-246.

[3] Pelegrin, Y.F., Robledo, D., and Azamar, J.A., 2006, "Carraggeenan of Eucheuma isiforme (Solieriaceae, Rhodophyta) from Yucatan Mexico. I. Effect of Extraction Conditions", Botanica Marina, 49, 65-71.

[4] Ciancia, M., Noseda, M.D., Matulewicz, M.C., and Cerezo, A.S., 1993, "Alkali-modification of carrageenans: Mechanism and Kinetics in the kappa/iota-, mu/nu- and lambda-series", Carbohydrate Polymers 20, 95-98.

[5] Ciancia, M.,. Matulewicz, M.C. and. Cerezo, A.S., 1997, "Alkaline modification of carrageenans. Part III. Use of mild alkaline media and high ionic strengths", Carbohydrate Polymers, 32, 293-295.

[6] Uy, F.S., Easteal, A.J., and Fard, M.M., 2005, "Seaweed Processing Using Industrial Single-mode Cavity microwave heating : a preliminary investigation", Carbohydrate Research, 340, 1357-1364.

[7] Hilliou, L., Larotonda, F.D.S, Abreu, P, Ramos A.M., Sereno, A.M. and Gonc¸alves, M.P., 2006, "Effect of extraction parameters on the chemical structure and gel properties of k/i-hybrid carrageenans obtained from Mastocarpus stellatus", Biomolecular Engineering, 23, 201–208.

[8] Tuvikene, R., Truus, K., Vaher, M., Kailas, T., Martin, G., and Kersen P., 2006, "Extraction and Quantification of Hybrid Carrageenans from the Biomass of the Red AlgaeFlcellarian lumbricalis and Cocotylus truncatus", Proc. Estonian Acad. Sci. Chem., 55, 1, 40-53.

[9] Rojas, J. and Azevedo, E., "2011, Functionalization and Crosslingking of microcrystalline Cellulose in Aqueous Media: A Safe and Economic Approach", Int'l J. Pharmaceutical Sciences and Research, Vol. 8, 28-36.

[10] Pereira, L., Amado, A. M., Critchley, A. T., van de Velde, F., and Ribeiro-Claro, P. J. A., 2009, "Identification of selected seaweed polysaccharides (phycocolloids) by vibrational spectroscopy (FTIR-ATR and FT-Raman)", Food Hydrocolloids, Vol. 23, 1903-1909, Elsevier.Odian, G. 1981. Principles of Polymerization. 2nd ed., Canada: John Wiley & Sons, Inc.