Synthesis and properties of new hydrogel from cross-linked galactomannan boric

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Abstract: A new hydrogel of crosslinked galactomannan boric has been synthesis from galactomannan Arenga pinnata seed (GAP) with boric acid. Galactomannan was isolated from immature Arenga pinnata seed through centrifugation and extracted using ethanol. Cross-linking GAP with boric acid was conducted in the various ratio of GAP and boric acid of 1:0.05 (CGB 1), 1:0.10 (CGB 2), 1:0.20 (CGB 3), 1:0.30 (CGB 4) and 1:0.40 (CGB 5). The product was determined using spectrophotometer infrared which showed the appearance of stretching vibration of B-O at 800 – 1100 cm⁻¹ and the decreasing absorbance at 3394 – 3417 cm⁻¹ which correspondence to stretching vibration of OH group in the increasing of boric acid used. The image of scanning electron microscopic (SEM) of GIB 4 showed the roughness and bumped of the surface morphology of hydrogel compared to the SEM image of GAP. The thickness of the crosslinked films is in the range of 1.42 – 1.98 mm. The maximum swelling value of the hydrogel in aquadest and buffer phosphate solution was obtained in CGB, and the swelling value in 0.9% sodium chloride solution was increased in the increasing of boric acid while all the hydrogel was dissolved in HCl 0.1 N solution.

1. Introduction

Commonly hydrogel is formed by a hydrophilic polymeric molecule which interacts together through chemical bond or cohesion force such as hydrogen bond, ionic or hydrophobic interaction [1]. Hydrogel has been applied in medicinal industry as a medium matrix for storage and releasing active compound of drugs and cell. In tissue engineering, the hydrogel was used for repairing and regenerating human cell and organs [2]. The hydrogel can be obtained from the synthetic or natural polymer. A synthetic polymer such as polyhydroxyethyl methacrylate (pHEMA), polyacrylamide and polyvinyl alcohol are derivates of fossil fuel which make the hydrogel product is difficult to unravel naturally [3]. World consumption of hydrogel is more than 1 million tonnes per year [4]. Due to depletion of fossil fuel, the price of a hydrogel made from synthetic polymer has increased recently. Therefore the study to find natural polymer for hydrogel production have to conduct to reduce the utilization of synthetic polymer.

Hydrogel from natural polymer has some advantages such as environmentally friendly, biodegradable, nontoxic, naturally abundant and cheap price [3]. Alginate, carrageenan, tragacanth, pectin, xanthan gum, gellan gum and guar gum are carbohydrate polymer which is abundantly in nature can be used as the source for hydrogel production [1]. The polysaccharide is a natural biopolymer. Galactomannan is a polysaccharide which usually found in nuts [5]. Galactomannan consists of two monomers such as mannose and galactose. Mannones is the main compound of...
galactomannan. The amount of galactose in polysaccharide usually lower than mannose [5]. One of galactomannan source is *Arenga pinnata* seed which is an immature endosperm of *Arenga pinnata*.

After processing the seed will become soft, chewy and have white appearance [6]. The molecular weight of galactomannan containing in *Arenga pinnata* seed is in the range of 6,000 – 17,000 kDa [7]. Galactomannan is isolated from *Arenga pinnata* seed using aquadest and is separated by centrifugation to produce 4.58% of galactomannan [8]. Pezron et al. have studied the interaction occurred in the formation of a reversible gel which affected by ion boric complex with galactomannan guaran [9]. Another researcher has demonstrated the production of hydrogel and studied the effect of cross-linked between gum and boric acid [10]. Burrano et al. have successfully synthesis cross-linked guar gum with boric acid which containing mucin compound with have similar concentration as in cervical mucus [11].

Based on that, this present study explores the formation of hydrogel galactomannan *Arenga pinnata* which have cross-linked with the boric compound. The formation of hydrogel was determined using spectrophotometer infrared while scanning electron microscopy was used to study the surface morphology. The physicochemical properties of the hydrogel such as swelling property and the thickness also presented in this study.

2. Materials and Methods

2.1 Materials

*Arena pinnata* seed was obtained from a local market in Medan, North Sumatera, Indonesia. All chemicals used in this experiment were obtained from Sigma Aldrich and were used without further purification. The boric acid solutions with different concentrations were prepared with the variation of boric acid weight 0.05; 0.1; 0.2, 0.3; and 0.4 gram in 20 ml of aquadest.

2.2 Extraction of galactomannan from Arenga pinnata seed

Galactomannan was extracted from *Arenga pinnata* based on the method used in our previous research with a slight modification [12]. A 20 gram of *Arenga pinnata* seed was crushed in a blender with 200 ml of aquadest and stored in a cold room for 24 hours. Next, the blended seed was centrifuged at 9500 rpm for 15 min to obtain supernatant 1. The residue was added next with 75 ml of water followed by centrifuge in similar conditions to obtain supernatant 2. The supernatant 1 and 2 were mixed and added with 96% ethanol in the range of 1:2 and stored in a cold room. After 24 hours storage, the precipitate was separated using a filter bag, and the residue was soaked in 100 ml ethanol 96% for 24 hours, followed by separating and soaking again in 100 ml of ethanol for the next 24 hours. The residue obtained after separation was dried in a desiccator.

2.3 Preparation of hydrogel film crosslinked galactomannan boric (CGB)

A 1.0 gram of galactomannan was dissolved in 80 ml of aquadest in beaker glass and was added with 2 M NaOH until pH of 9. Next, the boric acid solution was added drop by drop and the solution was stirred for 15 min at 1000 rpm and poured to glass plate size 13x13 cm. The glass plate was dried in oven blower at 40°C for 12 h, and the hydrogel was stored in a desiccator. After 96 hours, the hydrogel was released from the glass plate and stored before use. Following similar procedure the hydrogel from galactomannan and boric acid with ratio of 1:0.1 (CGB 1), 1:0.2 (CGB 2), 1:0.3 (CGB 3) and 1:0.4 (CGB 4) were prepared. The thickness of all the hydrogel films was determined using micrometer screw gauge in five different positions. The properties of hydrogel film were determined using infrared and SEM.

2.4 Determination of swelling property in simulated gastric and simulated intestinal fluid

The swelling property of CGB was determined in aquadest, simulated gastric fluid (SGF) and simulated intestinal fluid (SIF). Hydrogel film of CGB was cut to 3x3 cm and weighed. The film was added with 10 ml aquadest and the time was counted until hydrogel swelling. The wet hydrogel was weighed, and the swelling value was calculated. A similar procedure was applied using SIG and SGF.
3. Results and Discussion

A white galactomannan powder of 0.8554 gram was obtained from 20 gram *Arenga pinnata* seed using extraction method with aquadest. This result is similar to the previous researcher which extracted galactomannan from canned *Arenga pinnata* in base condition [7]. Our previous research also extracted 4.58% galactomannan in neutral condition [8]. Galactomannan extraction in neutral condition offers some advantages such as simple method, no further purification, without using an organic solvent that can be harmful and produce pure galactomannan that can consume directly [13]. Commonly galactomannan was used in the pharmaceutical and cosmetical industry without any purification [14].

Boric acid is a Lewis acid which could form a complex boric ion in crosslinked reaction with galactomannan at pH 9. The crosslinking of a boric ion with galactomannan occurred in the cis position of –OH group at carbon atom number 4 and 6 of galactopyranose unit. The hydrogel obtained as a crosslinking product [9]. Figure 1 shows the reaction scheme of crosslinking boric ion with galactomannan.

![Figure 1](image_url)

**Figure 1.** the crosslinking reaction scheme of galactomannan and boric ion.

The preparation of crosslinked hydrogel galactomannan boric was confirmed using FT-IR with absorbance recorded in the wavelength range from 4000 – 400 cm\(^{-1}\) as shown in figure 2 and 3. The FT-IR spectrum of galactomannan showed a peak at 3433 and 1631 cm\(^{-1}\) which represent the –OH stretching vibration. The peak at a wavelength of 2819 cm\(^{-1}\) shows a stretching vibration of –CH\(_2\) group which supported by the appearance of a peak at 1376 cm\(^{-1}\) [15]. A widen peak at 900 – 1200 cm\(^{-1}\) represents the stretching vibration of –C-C-O, C-OH, and C-O-C- of the polymer while a peak at 1138 cm\(^{-1}\) showed the stretching vibration of C-O of pyranose ring. A peak at 870 cm\(^{-1}\) is identical to β-D-mannopyranose bond in the polysaccharide, and a peak at 811 cm\(^{-1}\) represent a ring of α-D-galactopyranose [16]. FT-IR spectra of CGB showed a widen peak at a wavelength of 3394 – 3417 cm\(^{-1}\) which represent a stretching vibration of –OH groups. The appearance of a peak at 1643 cm\(^{-1}\) showed that CGB had been bonded with water. A peak at a wavelength of 800 – 1100 cm\(^{-1}\) is a stretching vibration of B-O. Interestingly the absorbance of –OH group tend to decrease in the increasing of the amount of boric acid added which presumably due to rising of crosslinking bond. The formation of CGB was determined by SEM and swelling property.
**Figure 2** the spectrum FT-IR of galactomannan from *Arenga pinnata*.  

**Figure 3** the spectrum FT-IR of crosslinked galactomannan boric.

**Figure 4** presents the SEM images of galactomannan and CGB. As can be seen, the surface morphology of galactomannan and CGB is different. The surface morphology was changed from the smooth surface in galactomannan film (fig 4A) became rough and regularly bumped into CGB film (fig 4B). The appearance of shipshape pattern like a flower indicates that boric ion binding 2 –OH groups in anhydroglucose.
The swelling properties and the thickness of the hydrogel film are presented in Table 1. The swelling percentage was calculated based on the equation 1.

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\text{Swelling percentage} = \frac{W_1 - W_0}{W_1} 	imes 100\% 
\]

As shown in Table 1, CGB 5 hydrogel film has the biggest thickness of 1.98 mm while the thinness film is CGB 1 at 1.42 mm. Therefore it can be concluded that in the increasing of boric ion added to galactomannan the thickness of the hydrogel film was increased. This was due to the increasing volume of solution which rendering is increasing the film thickness.

### Table 1 The thickness value and swelling percentage of hydrogel CGB

| Parameter                  | CGB 1 | CGB 2 | CGB 3 | CGB 4 | CGB 5 |
|----------------------------|-------|-------|-------|-------|-------|
| Thickness (mm)             | 1.42  | 1.50  | 1.78  | 1.82  | 1.98  |
| Swelling in aquadest (%)   | 8.89  | 11.76 | 10.77 | 9.26  | 8.77  |
| Swelling in NaCl 0.9 % (%) | 4.69  | 6.52  | 8.62  | 8.75  | 9.68  |
| Swelling in buffer phosphate pH 7.4 (%) | 11.54 | 13.16 | 10.14 | 8.96  | 6.90  |
| Swelling in HCl 0.1 N (%)  | Dissolve | Dissolve | Dissolve | Dissolve | Dissolve |

The swelling property of CGB was determined by monitoring the weight changes before and after soaking in aquadest, NaCl 0.9% solution, buffer phosphate pH 7.4 solution and HCl 0.1N solution. It has been demonstrated that in the increasing the amount of boric acid added to the aquadest and buffer phosphate pH 7.4, the swelling property was decreased for all the solution used. The results can be explained by the fact that more hydroxyl groups have bent with boric ion rendering decreasing the amount of hydroxyl group to form a hydrogen bond with water. However, contrary result was obtained when using NaCl 0.9% solution. The swelling property of CGB in NaCl solution was increased in the increasing boric ion added. This phenomenon can be explained that there is an ionic interaction between NaCl with a boric ion which increases interaction of water molecule with hydroxyl groups in...
galactomannan [17]. The interesting result obtained when using HCl solution that all the CGB hydrogel was dissolved in 10 min due to reversible reaction boric ion with acid rendering the dissolution of crosslinked [9].

![Graph of Swelling Level of CGB Hydrogel](image)

**Figure 5** the graph of the swelling level of CGB hydrogel.

**Conclusion**

The percentage galactomannan extracted from *Arenga pinnata* seed is 4.27% and the thickness of CGB hydrogel in the range of 1.42 – 1.98 mm. The formation of CGB was confirmed using FT-IR which showed a peak at a wavelength of 800 – 1100 cm⁻¹ representing stretching vibration of B-O. The increasing of boric acid added to CGB was decreased the absorbance of stretching vibration of –OH group at a wavelength of 3394 – 3417 cm⁻¹. SEM image of CGB showed a rough and regularly bumped pattern which due to crosslinking of the boric ion to galactomannan. The swelling level of hydrogel CGB occurred in aquadest, and buffer phosphate at pH 7.4 was decreased while it was increased when using NaCl 0.9% solution and it dissolved in HCl 0.1 N.

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