

Synthesis Of Bio-Degradable Copolymers from Sodium Alginate and Konjac Glucomannan Via Dehydration and Ca²⁺ Cross-Linking

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Abstract. The study aimed to develop bio-degradable, grafted copolymers using sodium alginate and Konjac-glucomannan. Sodium alginate, extracted from seaweed, and Konjac-glucomannan, derived from the Konjac plant, form a brown, viscous paste in pH 4.0-7.0 liquids. Sodium alginate is known for its solubility, stability, and viscosity. The research involved mixing different ratios of sodium alginate and Konjac-glucomannan with water and glycerol as a compatibilizer. These combinations were used to create various colloid-polymer pastes, and their properties were assessed. Glycerol played a vital role in enhancing performance and compatibility. Two processing methods were employed. The first method involved immersing the pastes in a calcium chloride solution, enabling cross-linking through Ca²⁺ ions. This formed films with distinct properties, including strength, brittleness, elasticity, and solubility. The second method involved dehydration, drying the pastes to form films with different properties than the cross-linked films. The resulting films exhibited diverse characteristics depending on the ratios of sodium alginate and Konjac-glucomannan. Cross-linked films demonstrated varying levels of strength, brittleness, elasticity, and solubility due to the network structure formed during cross-linking. Dehydrated films, obtained by removing water molecules, exhibited unique properties. This study contributes to the field of bio-degradable copolymers by successfully developing grafted copolymers using sodium alginate and Konjac-glucomannan. These natural polymers hold promise for sustainable materials in applications like packaging, drug delivery, and biomedical engineering. Further research is necessary to optimize copolymer compositions and processing techniques in order to fully harness their potential. Understanding the structure-property relationships will enable the customization of copolymers for specific applications, advancing the development of eco-friendly materials for a greener future.

Keywords: Bio-degradable; solubility; heat sealing ability; cross-linking.

1. Introduction

From the 1970s to the 1990s, plastic waste generation more than tripled, reflected by similar boost in the production of plastic. Single-use plastic products have become an integral part of our everyday lives. And of these conventional, single-use plastics, approximately 36 per cent of all plastics produced are used in packaging, and of which approximately 85 per cent ends up in landfills or as unregulated waste. The level of greenhouse gas emissions associated with the production, use and disposal of conventional fossil fuel-based plastics is estimated to grow to 19 per cent of the global carbon budget by 2040 [1]. However, on the optimistic side of reality, as we saw a rapid increase in the public awareness of environmental protection, the industry for bio-degradable plastics and polymers have expanded rapidly in size over the past two decades. The exploration for bio plastics of higher durability, degradability, elasticity, barrier properties and lower costs have continued to this day. In this project, we explored the correlations between different film forming methods (dehydration and cross-linking), as well as different konjac- Sodium Alginate ratios of the pastes, and the properties of the film.

Konjac- glucomannan (KGM) comprises 40% by dry weight of the roots, or corm, of the plant *Amorphophallus konjac Konnyaku* (presented within konjac powder, as used in our investigation) [2].

Its degradation product is konjac oligo-glucomannan (KOG), a saccharide polymer which contains a *small* number (typically three to ten) of monosaccharides [3]. The term Glucomannan refers to a mostly straight-chain polymer with small amounts of branching. When applied to liquids of pH 4.0-7.0, Konjac- glucomannan forms a brownish, viscous paste [4]. Konjac- Glucomannan and their derivatives bears several importance in the multiple research fields such as nutrition, biotechnology and fine chemistry. In recent years, konjac glucomannan has attracted attention from many research organizations due to its relatively safe and non-toxic properties, good biocompatibility, biodegradability [5]. Konjac- glucomannan was chosen for the synthesis of the membranes since membranes formed by polysaccharides such as glucomannan and galactomannan could effectively prevent the diffusion of oxygen and lipids across the membrane, and possesses good mechanical properties and high solubility in water [6].

Sodium Alginate ($\text{NaC}_6\text{H}_7\text{O}_6$) has been investigated in drug delivery and cell encapsulation due to its biocompatible and biodegradable nature [7]. Furthermore, Sodium alginate is also the linear polysaccharide derivative of alginic acid comprised of 1,4- β -d-mannuronic (M) and α -l-guluronic (G) acids. Known for its high solubility, stability and viscosity, it is used as a stabilizer and gelling agent for ice cream and other dairy products such as yoghurt and cheese. Sodium alginate was chosen for the synthesis of the membranes in the investigation as the biggest advantage for alginates in general in the forming of membranes is its liquid–gel behavior in aqueous solutions. When monovalent ions from an aqueous alginate (e.g., sodium in sodium alginate) are exchanged for divalent ions (especially calcium, as in a calcium chloride solution), the reaction proceeds almost immediately, changing the alginate- containing solution from a low viscosity solution to a highly viscous paste with a gel structure [8].

Fig. 1 is the skeletal formula for sodium alginate and konjac glucomannan [9]. According to the two diagrams, sodium alginate bears multiple carboxyl groups, hydroxyl groups and ether groups. Similarly, Konjac- Glucomannan also bears multiple hydroxyl groups and ether groups in its structure. In terms of the microscopic phenomenon, when the two substances bond with each other, the carboxyl groups of the have higher probabilities of connecting with the hydroxyl groups to form ester links. Therefore, the new copolymer formed is theorized to possess a grafted structure, as the ester groups in the copolymer are regarded as ‘hydroneutral’ groups [10].

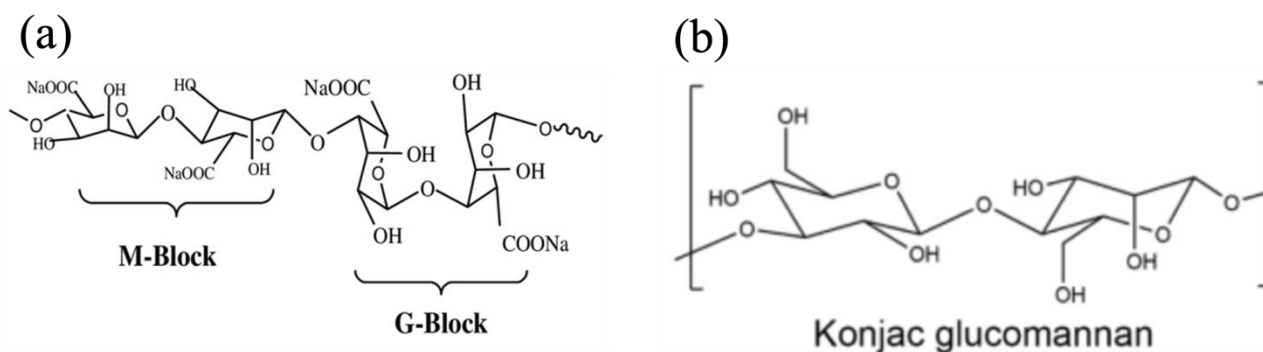


Fig. 1 The chemical structure of (a) sodium alginate and (b) Konjac Glucomannan.

https://www.researchgate.net/figure/Molecular-structure-of-sodium-alginate_fig1_282208702.

<https://www.mdpi.com/1420-3049/13/3/490/htm>

This article discussed the synthesis of a bio-degradable plastic with konjac and sodium alginate. Analysis the properties which is forming the paste, forming the membrane, solubility and heat-sealing ability. This article looks forward to finding pollution by conventional plastics.

2. Methodology

2.1. Materials

Throughout the study, the stirring is completed by the magnetic stirrer (M-CL.) was purchased from Hangzhou Qiwei instrument Co., LTD. As for the drying process, the dehydrator (TS-9688-3(L-01D)) is used. For the heat-sealing test, a closed electric furnace (JZFL-1) is used, which was purchased from the Hebi Jingzhong Technology Co., Ltd.

2.2. Preparation of paste

Firstly, konjac and sodium alginate were mixed at the ratio of 1:1, 2:3, 3:2, 4:1, 6:1, and 9:1 to form the solution A. The total weight of konjac and sodium alginate is 5g. Then, 1g of the glycerol and 100ml of distilled water was pour into the solution A by the magnetic stirrer. Finally, let is rest until any air bubbles have dissipated.

2.3. Forming the membrane

2.3.1 By drying

15g of the paste is added into a 9cm petri dish (or lid) to a depth of 2 mm. Then, the sample is placed into the dehydrator and heated for 3 hours (the temperature of the dehydrator is 70 Celsius) or let the paste dry in the petri dish at the room temperature overnight. Finally, use a spatula or tweezers remove the membrane from the petri dish (rehydrate slightly if necessary)

2.3.2 By calcium ion cross-linking

15g of the paste is added into a 9cm petri dish (or lid) to a depth of 1 mm. Immerse the petri dish in a bath of 10% w/v aqueous calcium chloride for 15 minutes. Then, rinse by immersion in a water bath and dry the membrane with paper towel. Finally, use a spatula or tweezers remove the membrane from the petri dish.

2.4. Performance test

2.4.1 Strain test

The tensile strain of the films could be calculated through the equation (1). The membrane that after drying or forming through calcium ion cross-linking is cut into a diamond (ruler is needed to let side length of the diamond is 2cm and 3.5cm). Then, the diamond's one side is pressed, and another side is stretched till the sample is broken. Finally, the change of the sample's length is recorded to calculate the strain of the sample.

$$strain = \frac{\Delta L}{L} \quad (1)$$

where, ΔL is the change in length of the membrane and L is the initial length of the membrane.

2.4.2 Solubility

The membrane that after drying or forming through calcium ion cross-linking was sliced into a rectangular chip (the side length of the chip is also 2cm and 3.5cm). Then, the chip is added into 100ml distilled water or 100ml alcohol and stirred until it was completely dissolved, and any air bubbles have dissipated.

2.4.3 Heat-sealing ability

The membrane formed after drying or calcium ion cross-linking is cut into a rectangular chip (the side length of the chip is also 2cm and 5.5cm). The sample is then folded in half and place onto a closed electric furnace (the temperature of the electric furnace is 80 to 100 Celsius) until the upper and lower part of the chip can stick together.

3. Results and discussion

3.1. Solubility

The result of the solubility is concluded in Table 1. When conducting the solubility test, it was observed that the films synthesized through cross linking would react with the ethanol solution, resulting in a stiff, white solid. It was then theorized that the Hydroxyl group from ethanol reacted with the calcium ion chains within the films, hence, forming calcium peroxide ($\text{Ca}(\text{OH})_2$), a white solid which coats the film.

From the results, all of the membranes do not dissolve in water completely within 1 hour, which could be attributed to the copolymer structure. The whole structure formed is considered as a grafting copolymer. Since the ester groups in the copolymer are regarded as ‘hydroneutral’ groups, they do not dissolve easily in water. To test the solubility of the samples, a Konjac-Sodium Alginate sample of 4:1 ratio is used to carry out a comparison between the results of the films formed by cross linking and those formed by dehydration. The result displays a negligible difference. However, after more comparisons of samples with varying ratios (e.g: between 1:1 and 4:1), the data show that the solubility of samples with a higher sodium alginate percentage is much higher than samples with the lower amount of sodium alginate. This indicates that the samples with a higher sodium alginate to konjac ratio could be more soluble. In order to decrease the solubility of the membrane, the amount of sodium alginate should be reduced. One of the possible reasons for this is that the carboxyl groups from sodium alginate is hydrophilic and can form hydrogen bonds with water molecules. In addition, regardless of whether the membranes are formed through calcium ion cross-linking or dried by dehydrator, the method of synthesis did not influence the solubility of membranes in any way. Additionally, when the membrane formed by calcium ion cross-linking placed into ethanol. A stiff, white solid forms and coats the film. One of the probable reasons for this is that calcium ion connects with hydroxide so that the white solid substance is calcium hydroxide.

Table 1. The solubility of samples in water or ethanol.

Ratio (Konjac: Sodium alginate)	Preparation methods	The solubility in water	The solubility in ethanol
1:1	Drying	Completely dissolved at 7 minutes	N/A
4:1	Drying	Insoluble at 1 hour	Insoluble at 1 hour
4:1	Cross-linking	Insoluble at 1 hour	Insoluble at 1 hour (white solid substance formed)
6:1	Cross-linking	Insoluble at 1 hour (white solid substance formed and coats the film)	Insoluble at 1 hour (white solid substance formed)
6:1	Drying	Insoluble at 1 hour	Insoluble at 1 hour
9:1	Drying	Partially at 1 hour	Insoluble at 1 hour

3.2. Strain

The result of the strain is concluded in Table 2. In terms of strain, testing on the samples with a Konjac- sodium alginate ratio of 4:1 and prepared with either cross linking or dehydration, shows that the elongation of the samples synthesized by calcium ion cross-linking is less than the samples made by dehydration. This indicates that the calcium ion can make the sample less elastic yet stronger. For the samples with a Konjac- sodium alginate ratio of 9:1 and 1:1, a comparison of the results of samples with these two ratios show that the elongation of the sample with the higher amount of konjac is less than the sample with lower amount of konjac. This suggests that konjac had made the membrane stronger yet less elastic. One of the possible reasons for this is that when the sodium alginate is dissolved in the water, the COONa function group will disassemble into COO^- and Na^+ ions. The

COO⁻ ion will connect with the calcium ion to form an ionic bond, which can be described as ‘egg-box model’, and the sodium ions would combine with the chlorine ions. Therefore, the film will become significantly stronger (electrostatic force).

Table 2. The strain of each sample.

Ratio (Konjac: Sodium alginate)	Preparation method	Initial length (L/mm)	Change in length ($\Delta L/mm$)	Strain ($\Delta L/L$)
1:1	Drying	35	35	35
4:1	Drying	35	4	0.114
4:1	Cross-linking	35	3	0.0875
7:3	Drying	35	5	0.143
9:1	Drying	35	2	0.0571
6:1	Cross-linking	35	2	0.0571

3.3. Heat-sealing ability

The result of the heat-sealing ability is concluded in Table 3. In terms of the heat-sealing ability, testing on the samples with a Konjac- sodium alginate ratio of 4:1 and prepared with either cross linking or dehydration, shows that the heat-sealing ability of samples formed through calcium ion cross-linking is better than the sample which are treated with a dehydrator. This meant that the presence of calcium ions can improve the scalability of the films. In order to make the membrane more sealable, the synthesizing method of films using calcium ion cross-linking should be utilized. A suggested reason for this result is that these samples which are treated by a dehydrator has a greater percentage of polymerisation. Therefore, the membranes would appear to be more stable.

Table 3. The ratio of each sample.

Ratio (Konjac: Sodium alginate)	Preparation methods	Heat-sealing ability at 150° C
4:1	Drying	Un-sealable
4:1	Cross-linking	Sealed at 3min 20s
6:1	Drying	Un-sealable
6:1	Cross-linking	Sealed at 3min 22s
7:3	Drying	Un-sealable
7:3	Cross-linking	Sealed at 3min 20s

4. Conclusion

In terms of the solubility, when the amount of the sodium alginate is higher the solubility of the membrane is higher. And regardless of whether the membrane is heated to dryness by a dehydrator or formed through calcium ion cross-linking, the methods of synthesis did not pose a significant influence on the solubility of the membrane. In terms of the strain, when the amount of sodium alginate is higher in the membrane, the membrane would possess a higher strain. Additionally, the membranes formed through calcium ion cross-linking possesses a lower strain than the membranes synthesized by the dehydrator. In terms of the heat-sealing ability, the samples which are formed through calcium ion cross-linking demonstrates better heat-sealing abilities than membranes that are prepared with the dehydrator. Samples with a Konjac- Sodium alginate weight ratio of 4:1 and formed through calcium ion cross-linking has the best general performance in all three tests. The result of this investigation could be applied to multiple fields in real life. All membranes synthesized in this investigation is non-harmful and non- toxic for the human body and could be used for food packaging and containers. However, the odor of the membrane should be coped with if it is used to be food packaging or single-use food containers. Additionally, due to the poor solubility of our membranes in general, it would be unadvisable to apply the membranes to fields such as encapsulation and organ-specific drug delivery.

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