

Synthesis of calcium alginate using extracted sodium alginate from Phaeophyceae and evaluating its potential as a substitute for plastics

Lee Le Cheng (4P312)

Chen Yu Jian, Luke (4P302)

Kevin Quah Wei-En (4P311)

Du Bingyuan (4P307)

Group 1-03

Abstract

Wastage of plastics are a pertinent issue faced by almost every country around the world, including Singapore. According to the National Environment Agency, the amount of plastic waste generated yearly has been increasing since 2003, amounting to nearly 950000 tonnes of plastic waste in 2018, with only about 4% being recycled. Locally in Singapore, the key plastic wastes are: polyethylene terephthalate (PET), polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE). This study aims to synthesise calcium alginate and its cation-substituted derivatives from brown seaweed *L. nigrescens*, which will explore the utility of bioplastics made from seaweed. A mixture of sodium hydroxide and sodium sulfite was used for pre-treatment of seaweed for removal of lignin. Sodium alginate was obtained by reacting the treated seaweed with sodium carbonate followed by precipitation with ethanol before centrifugation, and collection of residue. Various metal chlorides were used for the crosslinking of polyanion alginate with aqueous divalent metal cations via precipitation. Due to the limitations of alginate polysaccharides, PET was chosen as the plastic used for comparison. The alginates synthesised were comparable with commercial PET plastic in different categories such as flexibility and tensile strength. Hence, alginates were successfully synthesised from *L.nigrescens* and are useful for consideration of next-generation bioplastics.

1. Introduction

Plastic is the largest component accounting for 50-80% of debris that contaminates marine habitat at global scale (Fotopoulou & Karapanagioti, 2017). Examples of such plastics include polyethylene, polypropylene and polyethylene terephthalate(PET). These plastics are being generated and disposed of at an alarming rate, of which persist in the environment. Therefore,

there is a need for biodegradable sources of plastics so that such adverse effects can be negated. Alginates are natural polymers consisting of linear copolymers of β -(1–4) linked d-mannuronic acid and β -(1–4)-linked l-guluronic acid units which exist widely in brown seaweeds (Alihosseini, 2016).

Objectives:

1. To find a successful substitute for plastics in order to combat the excessive usage of the above-mentioned.
2. To extract sodium alginate from *L. nigrescens* and crosslink it with calcium chloride to obtain calcium alginate.
3. To investigate the properties of calcium alginate, namely tensile strength, solubility, specific heat capacity and electrical conductivity.
4. To explore different utility of different metal chlorides for crosslinking and using various property tests to determine if the characteristics of synthesised alginates can be better than that of calcium alginate.

Type of plastic used for comparison: PET (Polyethylene terephthalate)

Hypothesis: The synthesised calcium alginate will exhibit useful properties such as high tensile strength, water insolubility, be electrically insulative and have a high heat capacity, hence being a successful substitute for PET plastic.

Materials and Methods

Preparation of dried seaweed:

Dried brown seaweed *L. nigrescens* was obtained from Qingdao Bright-Moon Company. The seaweed were then washed thoroughly with deionised water to remove dust and impurities on the surface. Thereafter, they were dried to constant mass in the oven at 60°C.

Extraction of alginate:

6 grams of *L. nigrescens* was washed with deionised water and a mixture of 2M sodium hydroxide and 0.4M sodium sulfite was added to the algae before being set aside for 12 hours. Thereafter, the supernatant was decanted away and 2%(w/v) sodium carbonate added to the resulting residue and left for 5 hours for extraction by agitation. The viscous mixture was filtered multiple times through a sieve to collect the filtrate. 70%(w/v) ethanol was then added to the

mixture. The mixture was poured into 50ml centrifuge tubes and centrifuged at 10000 rpm for 10 minutes. The supernatant obtained after centrifugation was eliminated by decanting. The residue was dried overnight and weighed subsequently.

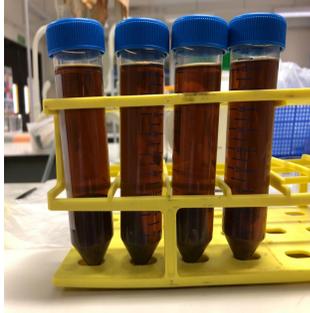


Figure 1: Residue obtained after centrifuging

Yield of sodium alginate extracted :

The process of the extraction of sodium alginate was repeated using different temperatures on the heat stir, at room temperature, 50 °C and 75 °C ,The respective yields of sodium alginate is weighed and calculated. The independent variable is the extraction temperature, while the dependent variable is the yield of sodium alginate, and the constants are the type of algae used and the particle size of the algae.

The process of the extraction of sodium alginate was repeated using different particle sizes of algae, of an average length of 3cm, 1cm and lastly, blended into powder. The respective yields of sodium alginate is weighed and calculated. The independent variable is the particle size of the algae, while the dependent variable is the yield of sodium alginate, and the constants were the type of algae used and the extraction temperature, which is fixed at 75 °C.



Figure 2: *L. nigrescens* powdered in a blender

Qualitative analysis tests to determine purity of sodium alginate:

To a 0.5% solution of the sample in sodium hydroxide TS, one-fifth of its volume of a 2.5% solution of calcium chloride was added. A voluminous, gelatinous precipitate was formed.

To a 0.5% solution of the sample in sodium hydroxide TS, one-half of its volume of a saturated solution of ammonium sulfate was added. No precipitate was formed.

Characterisation of sodium alginate:

Powdered sodium alginate was characterised using Fourier-Transform Infrared Spectroscopy. Hydroxyl groups at around 3400cm^{-1} indicated the hydrogen bonds present. Stretching at $1600\text{-}1400\text{cm}^{-1}$ concluded that the carboxylate ion was present, confirming the identity of sodium alginate.

Crosslinking of alginates:

4% sodium alginate solution was prepared and using a pipette, it was pipetted into a 2cm layer of 2% calcium chloride solution in a petri dish. The mixture is then allowed to sit overnight to complete the cross-linking process. Excess 2% calcium chloride in the petri-dish was decanted away and the calcium alginate obtained was soaked in a saturated oxalic acid solution for chelation of excess metal ions overnight. It was finally removed from the solution and washed before being dried in oven. Dried calcium alginate was obtained.

Exploring different cross-linking agents:

Following the same procedure, the precipitation process was repeated 7 more times with 7 more metal salts. This was to explore different cross-linking agents and investigating their potential to exhibit properties more favourable to PET plastic as compared to calcium alginate.

Property tests:

Four property tests were conducted on various alginates to compare their properties and identify the most suitable substitute for PET plastic.

Solubility:

Each sample of alginate was first weighed on a weighing scale and their mass was recorded. They were each placed into a beaker of deionised water and stirred continuously for 30 seconds. The samples were then taken out of the beaker, placed into an oven to dry, and then their mass was measured using an electronic balance. A loss in weight would conclude that the alginate sample is soluble in water.

Tensile strength:

To each sample of alginate, a hole of diameter 0.1cm is created in the centre of the sample. Using the hole, the sample was hung by a string on the retort stand and another string connected the alginate sample to the weights. Through increments of 5g, weights were added onto the string until the alginate is observed to be cracked. The maximum pressure the alginate can withstand was then calculated by F/A , where A denotes diameter of string.



Figure 3: Hanging of weights from our synthesised polymer

Heat insulation property:

1.5 grams of each sample of alginate was placed in a beaker of deionised water and was heated in an oven to 90°C. The temperature of the water after heating was measured using a thermometer and was recorded as the initial temperature of the sample. Another beaker was filled with 20ml of deionised water at room temperature of 24.5 °C, and wrapped in paper towels to minimise heat loss by conduction. After 2 minutes, the alginate was removed from the hot water of 90 °C and was placed into the second beaker. A thermometer was used to record the temperature change of the water in the beaker containing room temperature water and the highest temperature achieved was recorded. The change in temperature in the room

temperature water was recorded. Using $(M_w)(C_w)(\theta_w) = (M_a)(C_a)(\theta_a)$, the specific heat capacity of the alginates was calculated.



Figure 4: Calculation of specific heat capacity of alginate using thermometer

Electrical conductivity:

Each sample of alginate was connected to an electrical circuit with a 4V battery, 0A - 1.0A ammeter, switch and a 2.2V light bulb with an operating current of 250mA. A 1.0V - 3.0V voltmeter was connected parallel to the light bulb to detect any voltage across the light bulb.

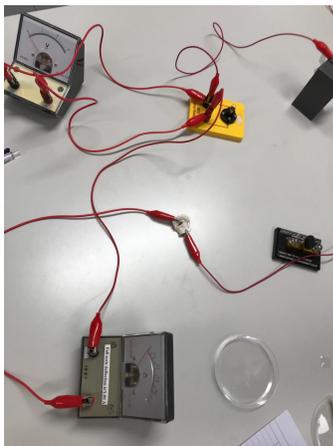
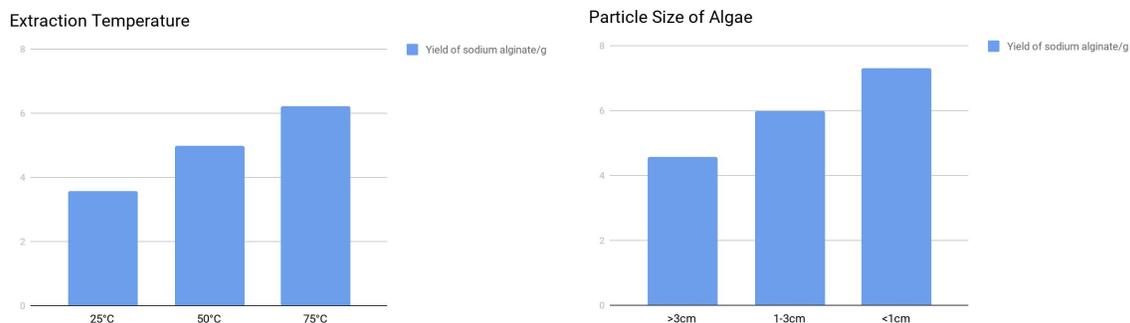


Figure 5: Determining electrical conductivity of alginates using a voltmeter in circuit

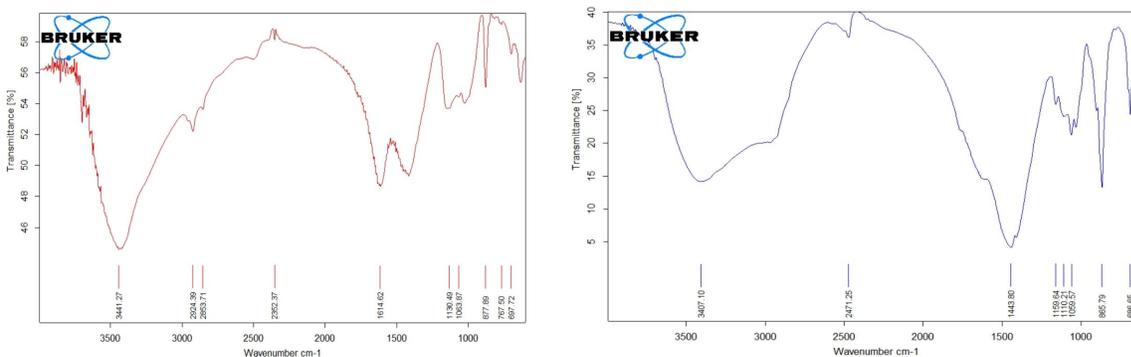
Results and Discussion

Yield of sodium alginate



Comparing the temperature used during the extraction procedure, it was found that within limits, higher temperatures suggest a higher yield of sodium alginate. For particle size of brown algae used, it was found that a smaller particle size generally produced a higher yield of sodium alginate.

Characterization of extracted sodium alginate using Fourier-Transform Infrared Spectroscopy (FTIR)



Sample 1	Sample 2	Assignments
Broad band centered at 3441.27 cm-1	Broad band centered at 3407.10 cm-1	Stretching vibration of O-H (hydrogen bonded)
Weak signal at 2924.39 cm-1	Very weak signal around 2900 cm-1	Stretching vibration of C-H

Strong bands at 1614.62 cm ⁻¹	-	Asymmetric stretching vibration of carboxylate O-C-O
Strong bands around 1400 cm ⁻¹	Strong band at 1443.80 cm ⁻¹	Symmetric stretching vibration of carboxylate O-C-O

Property test results:

Tensile strength test:

Sample	Tensile strength (Pa)
PET	10 ⁶
Calcium alginate	82.7*10 ³
Aluminium alginate	0.80*10 ³
Iron (II) alginate	133*10 ³
Iron (III) alginate	-
Barium alginate	11.3*10 ³
Manganese (II) alginate	73.3*10 ³
Copper (II) alginate	150*10 ³
Zinc alginate	45.0*10 ³

Solubility test:

Insoluble	Soluble
-----------	---------

PET, calcium alginate, aluminium alginate, iron (II) alginate, manganese (II) alginate, zinc alginate	Barium alginate, copper (II) alginate
---	---------------------------------------

Heat insulation test:

Sample	Specific heat capacity (J/g°C)
PET	1.00
Ca ²⁺	0.87
Al ³⁺	2.21
Fe ²⁺	1.31
Ba ²⁺	1.31
Mn ²⁺	0.43
Cu ²⁺	1.76
Zn ²⁺	2.21

Electrical conductivity test:

Sample	Ammeter reading (A)	Voltmeter reading (V)
PET plastic	0	0
Conductor (switch)	1.75	4.00

All the alginate samples showed readings of 0A and 0V, as they are all electrically insulative due to their giant ionic lattice structure which results in the absence of any mobile ions to conduct electricity.

Conclusion

Of the various crosslinked alginates tested, iron (II) alginate proved to be superior over the other alginate samples in terms of tensile strength and thermal insulation. Although copper (II) alginate has a higher tensile strength as compared to iron (II) alginate, it failed the solubility test as it was soluble, which is the most critical test for comparing plastic properties. Calcium

alginate, the original cross-linking agent, had a lower heat capacity and tensile strength as compared to iron (II) alginate.

Future work

As future work, the method of adding sodium alginate dropwise from the centre of the petri dish can be adopted to help create a more uniform alginate structure. Plasticizers or mixed ions can be used to further increase the tensile strength and heat capacities of the alginate samples.

References

Alihosseini, F. (2016). Plant-based compounds for antimicrobial textiles. *Antimicrobial Textiles*, 155-195. doi:10.1016/b978-0-08-100576-7.00010-9

Fotopoulou, K. N., & Karapanagioti, H. K. (2017). Degradation of Various Plastics in the Environment. *The Handbook of Environmental Chemistry Hazardous Chemicals Associated with Plastics in the Marine Environment*, 71-92. doi:10.1007/698_2017_11

Urbanek, A. K., Rymowicz, W., & Mirończuk, A. M. (2018). Degradation of plastics and plastic-degrading bacteria in cold marine habitats. *Applied Microbiology and Biotechnology*, 102(18), 7669-7678. doi:10.1007/s00253-018-9195-y

Fertah, M., Belfkira, A., Dahmane, E. M., Taourirte, M., & Brouillette, F. (2017). Extraction and characterization of sodium alginate from Moroccan *Laminaria digitata* brown seaweed. *Arabian Journal of Chemistry*, 10, S3707-S3714. doi:10.1016/j.arabjc.2014.05.003