Investigation Of the Biodegradable Plastic and The Application by Cornstarch and Kappa-Carrageenan

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Abstract. By comparing the manufacturing of conventional plastic with biodegradable plastic, a brief investigation of plastic and future developing trend was done. It is essential to investigate a biodegradable polymer which is produced with low cost and recyclable resources. An experiment was carried with cornstarch and kappa-carrageenan, which aim to produce a natural polymer can be biodegradable and has similar properties to conventional plastic. This experiment focuses on the mechanical properties and solubility of different amount ratio of the dry components to find out whether it has any functions that can be use in daily life. The results show the membrane with higher ratio carrageenan represents lower solubility, better mechanical properties and water resistance, but these properties become weaker in dry environment. The results provide a theoretical basis of the application of this polymer in medical region and food packaging.

Keywords: Cornstarch; kappa-carrageenan; marine; actual use.

1. Introduction

After the foundation of plastic, humans' life has become more convenient and more flexible. By the help of its extraordinary properties, people can be able to use them as the protection of fresh food, packaging goods with lower price and the main material of daily supplies. Global annual plastic production increased from 1.5 million tons in the 1950s to 359 million tons in 2018. Micro plastic, a newly found harmful thing, was mainly created by the separation of the plastic products. After soaking in water, or buried in the earth, will cause the micro plastic to goes into underground water and will transport through food chain. According to latest research of a Chinese group, 98% of the micro plastics come from human activities and only 2% from sea creatures [1]. Through all the sources causing this problem, fiber and debris are the main forms of microplastics in water environment. The main types of microplastics in freshwater are polyethylene (PE) and polypropylene (PP) while polystyrene (PS) in seawater [2].

Ocean, which has covered over 70%of the surface of earth, has influenced the most from the conventional plastic waste. According to estimates by American scholars, the weight of plastic waste entering the ocean worldwide in 2010 was as high as 4.8 to 12.7 million tons [3]. In July 2011, the China National Oceanic Administration discovered through monitoring the pollution situation in China's offshore waters in 2010 that there was a large amount of plastic waste in floating debris, seabed debris, and beach debris, especially in the seabed garbage, which accounted for 83%. Moreover, due to the inherent characteristics of plastics, they are not easily decomposed and decomposed after disposal, which has seriously affected the marine ecological environment [4]. These pollutions will not only threat the health and life of sea creatures, but also need 250 million dollars to 700 million dollars to catch and deal with these plastics.

To avoid these serious risks, there are several solutions, including proclaim of plastic ban to rise the tax of conventional plastic or develop a biodegradable plastic with low cost. The previous way has been executed in most of the countries, while the development is more time consuming and cost spending. Biodegradable plastic, a newly invented plastic which can be degrade with the help of light, water or microorganisms, is a solution to plastic pollution. Under certain conditions, biodegradable plastics can be decomposed into carbon dioxide, water and other inorganic organisms in a short period

of time. Since the conventional plastic is mainly made from petroleum, the material for biodegradable plastic should be cheaper and can be more recycled.

Starch is a widely used raw material for biodegradable plastic, mainly because of its highly amount in most crops and other plants. Meanwhile, starch-based materials, have the characteristics of low cost, good gas resistance, high solubility and good degradation, and are currently the research hotspot in the field of natural polymer for food packaging [5]. However, the starch membrane has some defects in mechanical properties, including poor physical strength and brittle texture. Therefore, it is necessary to add plasticizers to improve the flexibility of the membrane. Glycerol, as a commonly used plasticizer, is widely used on natural polymer packaging materials. Besides, glycerol could improve the flexibility and thermal stability of the membrane [6].

Carrageenan is another main component to produce the membrane. Carrageenan, as a natural polysaccharide mainly derived from Marine algae, which is often used in food gelling, emulsification and thickening [7]. Carrageenan molecule is composed of β-(1-3)-D-galactose-4-sulfate and α-(1-4)-3,6-lactose-D-galactose. The alternating copolymer formed has excellent thermal reversible gel property, non-toxic, hydrophilic, stable dispersion and good membrane forming property [8].

At present, there are few reports about the best membrane forming process of cornstarch, carrageenan and glycerol both domestic and international. Therefore, this study took carrageenan as the substrate, cornstarch and glycerol as the plasticizer, and determined the best membrane forming ratio of the membrane with mechanical properties and solubility.

2. Methodology

2.1. Materials

Cornstarch, carrageenan and glycerol are used as thickening agent. Ethanol, hydrochloric acid and sodium hydroxide solution are used to test the solubility of membrane. Deionized water is used throughout the experiment.

2.2. Procedure of Producing Membrane

5 g of the total amount of cornstarch and carrageenan with 100 ml of water to obtain 5 % of the weight of the dry components. There were 5 groups of dry components: 0.5 g of cornstarch and 4.5 g of carrageenan (1: 9), 0.25 g of cornstarch and 4.75 g of carrageenan (1: 19), 0.2 g of cornstarch and 4.8g of carrageenan (1: 29), 0.1 g of cornstarch and 4.9 g and carrageenan (1: 49), and 0.05 g of cornstarch and 4.95 g of carrageen (1: 99). The concentration for glycerol solution was 4% w/v. The amount of 4% w/v glycerol solution was 2 g each, which should be mixed with the water to avoid the dry powder to clump together while stirring. Table 1 shows the data of the weight of each group.

Table 1 The weight of the components of each group.

Group	Amount of cornstarch/g	Amount of carrageenan/g	Amount of glycerol/g	Amount of water/ml
1	0.5	4.5	2	100
2	0.25	4.75		
3	0.2	4.8		
4	0.1	4.9		
5	0.05	4.95		

After all dry components and wet components were prepared, mix all the materials into a beaker with the volume of 100ml to make the final mixture more spontaneous after stirring (20 s, 30 s, 40 s, 50 s, 60 s). Then pour the mixture into a petri dish. Noticed that the mixture was recommended to have a thickness with over 3mm to ensure the mixture are fully stick onto the bottom of the petri dish. Then stewing for 3-4hours to ensure that the solid mixture can precipitate and sink to the bottom of the petri dish. The lighter fluid was carefully poured off after precipitation. Put 5 petri dish into the

drying equipment to accelerate the rate of evaporation. Wait for 12 hours to make sure all the membrane were dried, and they should look like the white part in Fig. 1.

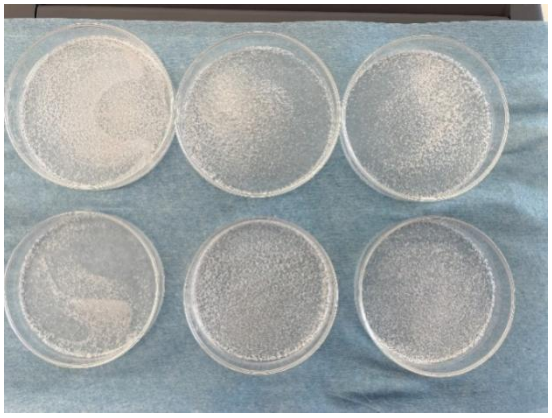


Fig. 1 The appearance of the dried mixture. (Picture credit: Original)

After the membrane had completely dried, the membrane should drip water along the edge of Petri dish to rinse the side part of the membrane which was too hard and brittle to be taken off. Place the petri dishes for a few minutes to make sure that the whole membrane had been rinse that can be taken off. Carefully peel the membrane by a tweezer. Repeat the same operation with other membrane. These 5 membranes will be tested their mechanical properties through hanging various weight to record the maximum and their solubility by adding ethanol, HCl and NaOH. To make sure the size and weight would not affect too much on the final results, the membrane had been separated into 8 equally sized parts. The way to separate the membrane looks like the way in Fig. 2. 2 pieces of the membrane sample were dropped with some water on the smooth side. Place the wet side up to accelerate the rate of evaporation. Wait for 10 minutes and test the mechanical properties to compare with the totally dried membrane.

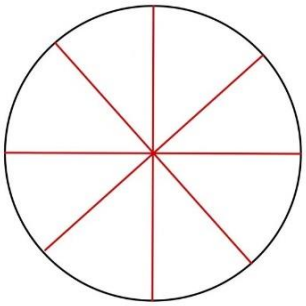


Fig. 2 The diagrammatic sketch of the way of separation. (Picture credit: Original)

2.3. Procedure of Measuring the Solubility of Membrane

Although the best method to test the solubility was immersing the whole membrane into the solvent, the membranes in this experiment were separated into small pieces due to the time limitation. Therefore, dropping the solvent on one sample of each group's membrane becomes an appropriate way. Put one piece of membrane of each group on a 300mm*300mm aluminum foil to prevent the solvent contaminate surface of table. Then drop 2 drops of the solvent on each sample. Record the transmittance of each sample through the photometer. Then a glass rod is used to test thew texture and state of the mixture.

2.4. Procedure of Measuring the Mechanical Properties of Membrane

The procedure of measuring and recording the mechanical properties had reference MU method, which separate the membrane into small pieces and test the property separately [9]. For each group, there are 2 pieces of membrane to have the same experiment. One is for testing and the other is for

repeating. To make the mechanical properties more visualized, both tensile strength and the rate of elongation. Tensile strength was shown in formula (1).

$$Ts=\frac{F}{S} \quad (1)$$

where, Ts represents the tensile strength, with Mpa as its unit; F represents the force acting on the membrane before it broke, with N as its unit; S represents the cross-section area of the sample, with mm^2 as its unit.

Rate of elongation was shown in formula (2).

$$EB=\frac{l_1-l_0}{l_0}*100\% \quad (2)$$

where, EB represents the rate of elongation until it broke, with % as its unit; l_1 represents the final length of the sample, with mm as its unit; l_0 represents the initial length of the sample, with mm as its unit.

3. Results and Discussion

3.1. Membrane Formation

Because the pure Carrageenan membrane has a large swelling ratio, the single material Carrageenan membrane is easy to absorb water and break in the air. As the starch content increases, the tensile strength of the blend membrane increases. This may be due to the sufficient physical crosslinking and hydrogen bonding between molecular chains after Carrageenan and starch are mixed in proper proportion (both Carrageenan and starch molecules contain -OH), so that the mixture has sufficient strength and cross-linking degree, thus forming a membrane [10].

3.2. Solubility of Membrane

Table 2 shows the appearance of the sample of each group after adding different solutions. According to this table, the group of 1: 9 and 1: 19 has higher solubility under water conditions. For the rest of the groups, the structure is stronger and has lower solubility. These data indicates that there is a thickening effect between hydrophilic colloids and starch; Carrageenan and starch molecules intertwine to form a stable hydrogen bond, thus increasing the peak viscosity of the blend system. The blend system of hydrophilic colloids and starch can be regarded as starch particles dispersed in a hydrophilic colloidal solution, with starch particles as the dispersed phase and the colloidal solution as the continuous phase; During the gelatinization process, starch absorbs water from the colloidal solution, resulting in a relative increase in the concentration and viscosity of hydrophilic colloids in the continuous phase, resulting in an overall increase in the viscosity of the blend system [11].

Table 2 The appearance of each sample

Group	Deionized water	Ethanol (99%)	HCl (0.1M)	NaOH (1.9M)
1	D	X	D	D
2	D	X	PD	PD
3	WS	X	X	JS
4	WS	X	X	JS
5	WS	X	X	JS

Note: D means it directly dissolved. PD means it partially dissolved. WS means it structure become weaker. JS means it forms a jelly-like structure. X means no clear appearance.

A camera is set under the petri dishes to measure the transmittance of each sample. The luminosity indoor is 260 lux, which is the maximum value. Then measure each sample and therefore get these final results. The detail data of each sample shows by Fig. 3. As the starch content decreases, the

transmittance gradually increases. This is due to the high crystallinity of starch, which refracts and reflects light at the grain boundaries when it passes through its crystal region (it cannot directly pass through). Therefore, for blend membranes with low starch content, their transmittance shows an upward trend [12].

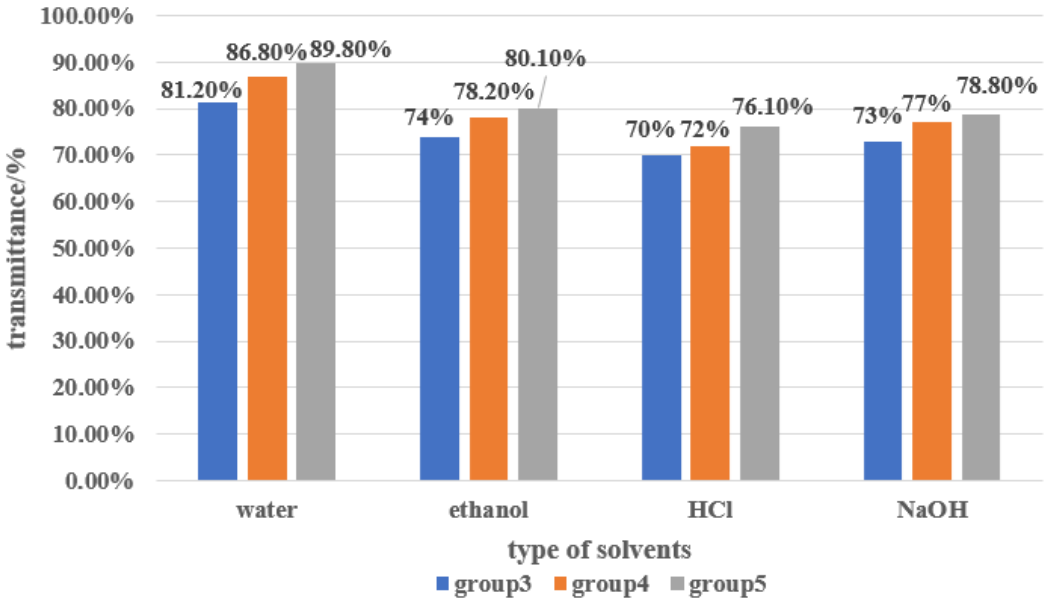


Fig. 3 The transmittance of each type of solvents. (Picture credit: Original)

3.3. Mechanical Properties of Membrane

In this period, each sample is repeated with the same experiments twice to get the average value of the tensile strength and rate of elongation. Fig. 4 shows the average results for the dry membrane samples. The tensile strength has a rising trend while the rate of elongation shows the opposite. With the increase of the addition of Carrageenan, the tensile strength of the membrane gradually increases, indicating that Carrageenan and starch have good compatibility within a certain range. The combination of Carrageenan molecules and starch molecules has a good synergistic effect, making the original spatial structure more compact. However, Carrageenan interacts with starch, and the close connection between molecules hinders the activity of molecules, reducing the activity of molecular chains, resulting in lower toughness and lower elongation at break [13].

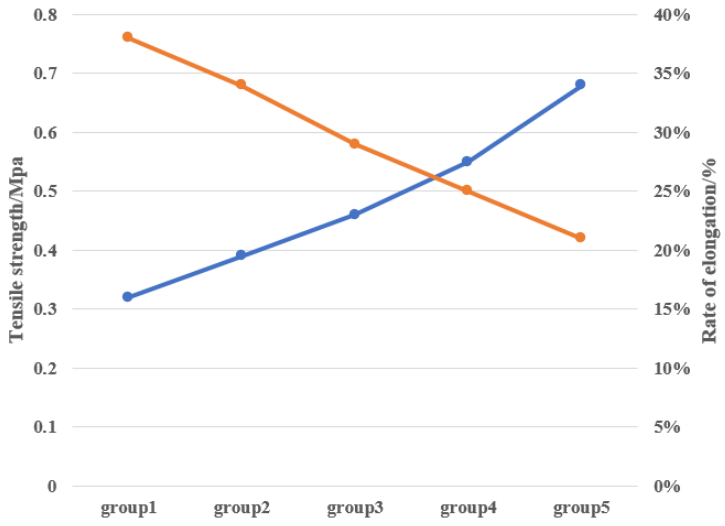


Fig. 4 The mechanical properties for dry sample. (Picture credit: Original)

Instead, the membrane retouch with water represents much better mechanical properties. Fig. 5 shows the average results for the moist membrane samples and the data proves that the membrane produced by carrageenan and cornstarch under both conditions does not have very strong structure like conventional plastic, while the wet sample shows a much better property than dry one. This may because of the -OH group of water can further combine with the mixture and therefore increase the amount of hydrogen bond to form a stronger structure and product.

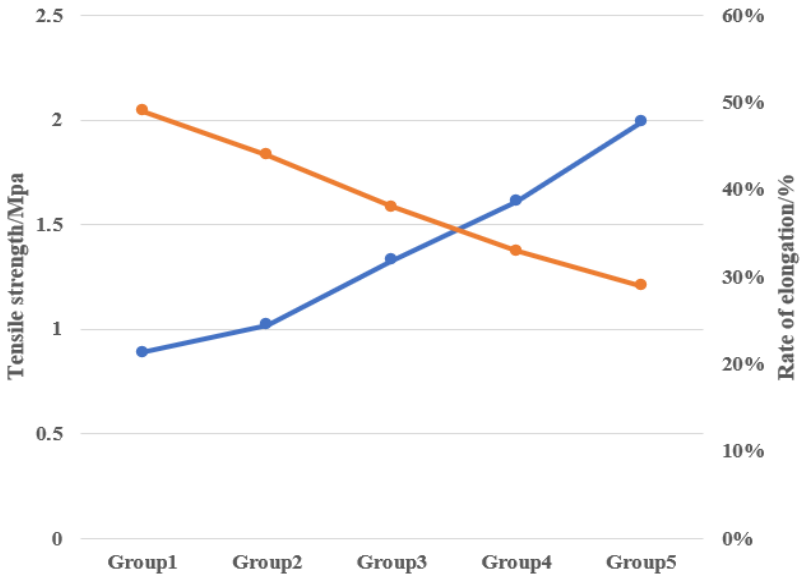


Fig. 5 The mechanical properties for wet sample (Picture credit: Original)

3.4. Heat-sealing Ability of Membrane

Two pieces of sample were put from the same group folded together on the heater, and record the time until the sample below change its color and release unpleasant smell. After the whole process, the polymer does not have the ability of heat-sealing. There is a guess that it may because of the further evaporate of water makes the membrane become very dry and brittle, and thus does not show any properties of a gel. Meanwhile, the water loss of carrageenan will break its chemical structure, and the property of water retention will loss as well. Therefore, further water will release to cause worse damage. In addition, this kind of membrane does not show the property of water retention under high temperature.

3.5. Water Resistance of Membrane

For each sample, 1 ml of deionized water was dropped on it, and immediately take a photo of the state of the water drop on the membrane [8]. Since the sample has already run out, therefore this process is repeated to produce membrane with the ratio 1: 19, 1: 29 and 1: 49. Fig. 6 shows three states of the water drop on the membrane. For each drop, the height and the contact angle between water drop the petri dish has been measured and recorded in Fig. 7. Both the table and the pictures show the height of the water drop with more carrageenan is higher. There is a deduce that higher amount of carrageenan makes the membrane denser and tighter, therefore water is harder to go through it, and the water above the membrane will remain higher.

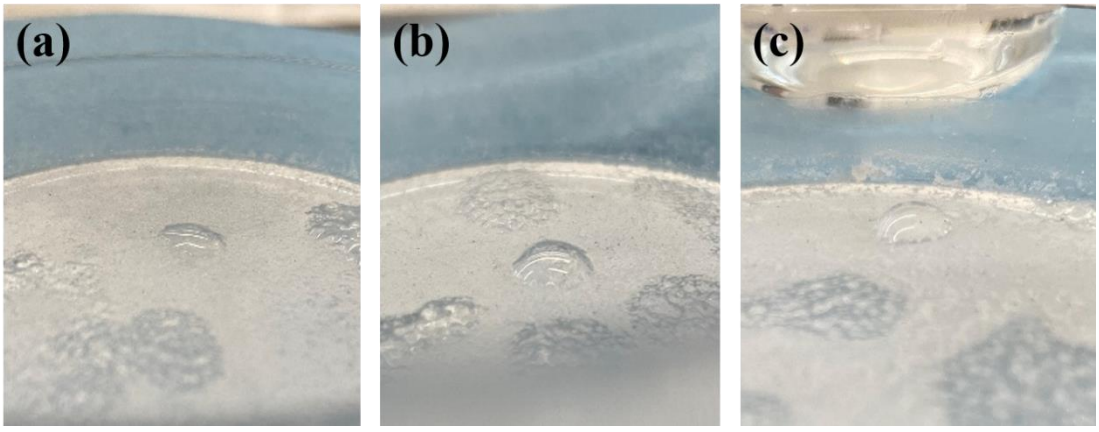


Fig. 6 The appearance of water drops on (a) 1:19, (b) 1:29, (c) 1:49 membrane (Picture credit: Original)

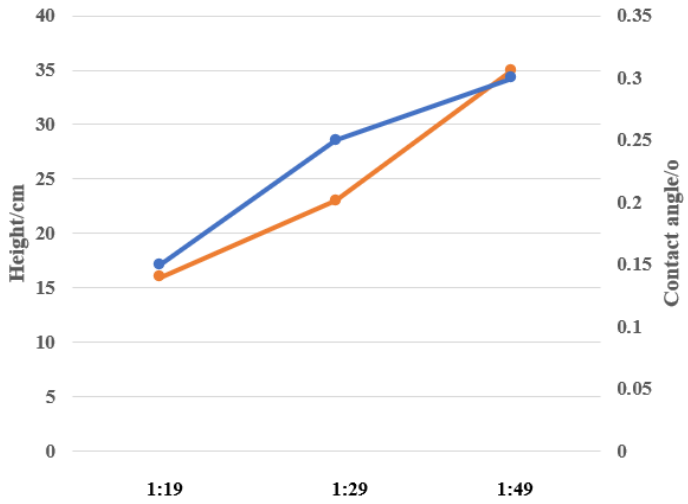


Fig. 7 Water resistance of each sample. (Picture credit: Original)

4. Conclusion

This paper has tested the biodegradable membrane with different amount ratio of dry components. This paper also shows how the solubility, transmittance, mechanical strength, heat-sealing ability and water resistance of each ratio. Meanwhile, the experiment has tested the property of the membrane under dry and wet conditions. From the data above, there is a discovery that under the same condition, membrane with higher ratio of carrageenan represents better solubility, tensile strength and water resistance, while the membrane with more cornstarch have lower properties and weaker structure to form membrane. If the amount of starch is too high it will even stop forming a membrane, and all the components will sink at the bottom of the beaker. From the evidence above, there is an indication that this kind of polymer may be used as the capsule shell, which can be transported under dry condition and dissolved after it was swallowed, so it may have medical developing potential. But this experiment still has lots of deficiency such as the acidic resistance. Therefore, further research of this field is expected.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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