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The Effect of Plasticizer on the Development of Chitosan-Based Bioplastic

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Abstract. Bioplastics are plastics derived from materials that can be decomposed by nature. A series of bioplastics based on chitosan and modified chitosan have been produced, namely chitosan thin film (C) citric acid cross-linked chitosan (CCA), chitosan-carrageenan/PVA (CKP), chitosan-carrageenan/PVA/Glycerol (CKPG), CCA-Carrageenan/PVA (CCA KP), and CCA-carrageenan/PVA/Glycerol (CCA KPG). The results of the functional group characterization showed that the cross-link modification reaction of citric acid and glycerol plasticizer had been successfully carried out on chitosan to produce CCA, CCA KP, CCA KPG and CKPG thin films. The addition of citric acid as a crosslinker and glycerol as plasticizer affects the physicochemical properties of bioplastic thin films, the addition of these two materials causes an increase in the value of thickness and weight, porosity, water vapor absorption, swelling, pH resistance and thin film biodegradability, but decreases the contact angle value. hydrophilicity). The optimal composition of the best bioplastics was obtained from CKPG thin films with test results of weight 0.042 grams, thickness 0.00076 mm, porosity 57.4%, contact angle (hydrophilicity) 38.1°, water vapor absorption 110.5%, swelling 134 %, resistant to pH range 5-11 and the ability to be degraded for 98 days in the soil.

Keywords: *bioplastic, chitosan, crosslinker, plasticizer, physicochemical*

INTRODUCTION

Great attention is paid to biodegradable films made from renewable and natural polymers. Environmental pollution due to the disposal of plastic waste from materials that cannot be decomposed naturally has encouraged research and development of biodegradable materials with characteristics that allow them to resemble plastic in general.

Bioplastics are environmentally friendly plastics made from biopolymers, such as cellulose, chitin, chitosan and starch contained in plants, as well as several other polymers in plant and animal cells [1]. The availability of this material is very abundant and is non-toxic. In addition, this natural polymer is easily decomposed by microbes in nature (biodegradable) so it is quite potential to be used as a bioplastic material. The character and morphology of bioplastics are strongly influenced by the main constituent components, such as hydrocolloids (proteins or polysaccharides), lipids and composites.

Chitosan is an interesting natural polysaccharide to be developed because it is non-toxic, reactive, abundant, regenerative, and easy to make thin films. However, chitosan thin films have limited mechanical properties when stretched and when exposed to high relative humidity [2]. Carrageenan is a red seaweed extract which is still included in the galactose polysaccharide group. Carrageenan consists of esters of potassium, sodium, magnesium and potassium sulfate with galactose 3,6 anhydrogalactose copolymer. Carrageenan is hydrophilic and is formed from repeating polymers of disaccharide units. Carrageenan is widely used as an emulsifier, stabilizer, and thickener. In addition, it is also used as a coating (marbling) in the paper industry, sizing in the textile industry and as a thickener in the cosmetic industry.

The combination of chitosan with cellulose will result in interactions in the form of hydrogen bonds that can fill the voids in the cellulose and make bioplastics stronger but less elastic [3]. The addition of a synthetic polymer

Polyvinyl Alcohol (PVA) in chitosan makes the resulting film more elastic [4]. The modification of functional groups to chitosan and the addition of PVA could increase the flexibility and mechanical strength of the resulting thin films. Another study said, which studied the effect of adding graphene and glycerol to the manufacture of bioplastics based on sweet potato starch and PVA [5]. It was found that the addition of glycerol increased the flexibility, biodegradation, and water uptake, but decreased the mechanical strength and refined the morphology of the bioplastic along with the addition of glycerol [1].

Glycerol is quite effective in increasing the plastic properties of the film because it has a small molecular weight, besides that it can increase the permeability of the film to water vapor, gases and solutes, so glycerol is commonly used as a plasticizer [6]. The flexibility of the plasticizer can reduce the intermolecular forces on the thin film, so that the value of the tensile strength of the thin film decreases as well. This reduction in tensile value causes the thin film structure to become smoother and more flexible. The use of glycerol as a plasticizer is better than sorbitol, because the biodegradable plastic produced is more flexible and not easily brittle and has mechanical properties and appearance that does not change during the storage period. The use of glycerol is more effective in improving the mechanical properties of the resulting biodegradable plastic [7].

In addition, to increase the elasticity of the plastic, the researchers added carrageenan. A seaweed-derived biopolymer that adds elasticity and functions as an adhesive between thin film bodies. In addition to being strong, elastic and flexible, plastic materials must also have good mechanical strength. The use of a mixture of PVA and chitosan resulted in better mechanical characteristics due to the presence of intermolecular bonds between the mixture of PVA and chitosan. PVA has good chemical stability, biodegradability, and mechanical properties [4,8].

This study aims to find the composition of chitosan-based bioplastic material modified using carrageenan, PVA and glycerol. This formulation is expected to produce bioplastic thin films that have good chemical, physical and mechanical properties and are easily degraded in the soil.

RESEARCH PROCEDURE

Tools and Materials

The tools used are standard glassware (Herma and Pyrex), petri dishes (Sterilpan), magnetic stirrer (Biomega and Jenway), digital analytical balance (OHAUS), a set of thin film printing equipment, hotplate, ultrasonic homogenizer, oven, ruler, pH meter (Hanna), thicknessmeter (Mitutoyo), Ostwald viscometer, stopwatch, tensile strength analyzer (Zwick/Z0.5), FTIR spectrophotometer (Perkin Elmer), SEM Instrument (JEOL JSM-6510LA).

The materials : chitosan (BM = 161 g/mol), carrageenan (BM = 386 g/mol) obtained from www.oil-atsiri.com, PVA (BM = 44 g/mol), glycerol (BM = 92.09 g/mol), citric acid pa (BM = 210.14 g/mol) (Merck), distilled water, NaOH (BM = 40 g/mol), acetic acid pa (BM = 60,052 g/mol) (Merck).

Chitosan solution, 1.5 g of chitosan was dissolved in 100 mL of 1% acetic acid then stirred using a stirrer until homogeneous for ± 24 hours to obtain a 1.5% chitosan solution. *Carrageenan solution*, 1 gram of carrageenan is dissolved in 100 mL of distilled water, then stirred and heated using a stirrer for 30 minutes at a temperature of 50-60°C to obtain a 1% carrageenan solution. *PVA solution*, 1.5 g of PVA was dissolved in 100 mL of warm water and then stirred using a stirrer until homogeneous for ± 2 hours to obtain a 1.5% concentration of PVA solution.

Preparation of chitosan-citric acid compounds

A total of 1.5 g of chitosan was dissolved in 90 mL of 1% acetic acid and stirred for ± 24 hours. A total of 1,986 g of citric acid was dissolved in 10 mL of 1% acetic acid. Furthermore, the citric acid solution was added dropwise into the chitosan solution while continuously stirring for ± 4 hours at a temperature of 60°C, and a crosslinked solution of chitosan-citric acid (CSCA) was obtained.

Thin Film Synthesis

The manufacture of thin films begins with mixing a solution of each ingredient into a two-neck flask gradually, with the composition of each ingredient shown in Table 1. After that, each ingredient is heated at 45 °C for 45 minutes, and the dope solution is filtered, and stored as standard solution. Then the dope is poured to be printed into a thin film and characterized physicochemically.

TABLE 1. Thin Film Composition

Membrane code	Ratio of material (%)				
	Chitosan	CSCA	Carragenan	Glycerol	PVA
C	100	-	-	-	-
CCA	-	100	-	-	-
CKP	40	-	40	-	10
CKPG	40	-	40	1	9
CCA KP	-	40	40	-	10
CCA KPG	-	40	40	1	9

Thin Film Characterization

The physicochemical characterization of thin films included testing of thin film functional groups using FTIR, porosity, hydrophilicity, water vapor absorption, mechanical strength, biodegradability and pH resistant.

RESULTS AND DISCUSSION

The synthesized thin film has a physical appearance of clear to yellowish color, thin, elastic, not easily torn and not brittle, in a dry state it resembles plastic.

Functional Group Spectra

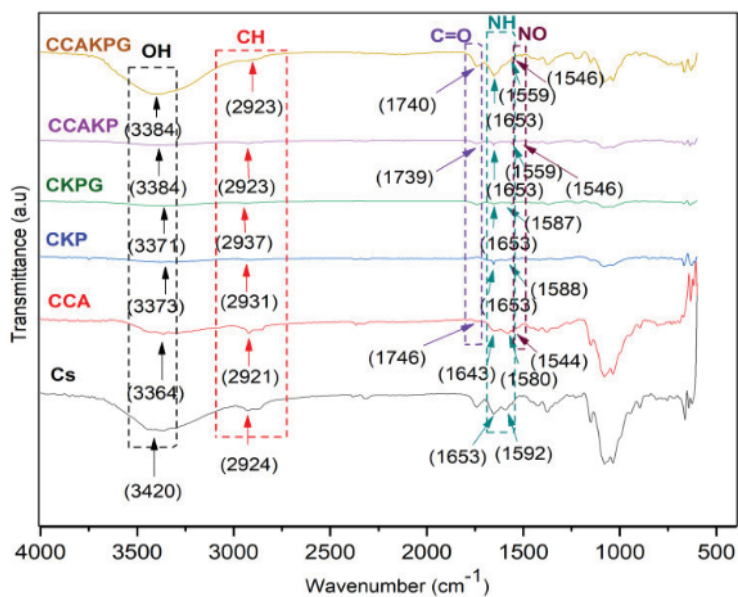


FIGURE 1. Results of functional group of films Chitosan (C), Carragenan (K), Chitosan-Citri Acid (CCA), Chitosan-Carragenan_PVA (CKP), Chitosan-Carragenan-PVA_Gliserol (CKPG).

The results of the functional group spectra from the reaction between the materials can be seen in Fig. 1. The specific spectra of carrageenan (K) were indicated by the strong absorption in the 1247 cm^{-1} region which was the absorption of sulfate esters ($\text{O}=\text{S}=\text{O}$), the absorption in the 1028 cm^{-1} region which was a glycosidic bond ($\text{C}-\text{O}-\text{C}$) and absorption in the 845 cm^{-1} region indicates the presence of galactose-4 sulfate bonds. Specific PVA spectra were indicated by absorption in the 3330 cm^{-1} region which was the $\text{O}-\text{H}$ strain, the absorption in the 2944 cm^{-1} region was the $\text{C}-\text{H}$ strain and the absorption at wave numbers 1435 and 1091 cm^{-1} which was the $-\text{CO}$ group absorption. The success of the cross-linking reaction between chitosan and citric acid can be proven where, twin bending in the wave

number region of 1592 cm^{-1} and 1653 cm^{-1} which shows the primary N-H group of chitosan, turns into a secondary amine that undergoes a shift and forms a peak at 1746 cm^{-1} wave which is the absorption of the C=O group. This change indicates that the cross-linking reaction of chitosan with citric acid has been successfully carried out on the -NH₂ group in chitosan with the -COO group in citric acid. These results are in accordance with the research of [9].

In the CKP and CKPG bioplastic thin films, the effect of adding glycerol causes a wider increase in the intensity of the -OH group at 3370 cm^{-1} area than the bioplastic thin film without glycerol. Based on the spectra it can be seen that the CCAKP and CCAKPG bioplastic thin films show the effect of adding citric acid and glycerol which causes an increase in the -OH functional group. Accordance with research of [9,10], where the addition of citric acid causes a widening of -OH in the 3380 cm^{-1} area and glycerol in bioplastic thin films gives a wider increase in intensity in the -OH group than bioplastic thin films. without glycerol.

Thin Film Porosity

Thin film porosity measurement aims to determine the amount of empty space in the thin film. The results of the porosity measurements can be shown in Fig. 2. Based on Fig. 2, it can be seen that the percentage of modified chitosan thin film porosity increased compared to pure chitosan thin film. The increase in the value of the porosity test was related to the inclusion of carboxylic groups of citric acid and glycerol hydroxyl groups into the thin film composition. The carboxylate and hydroxyl groups in the thin film structure cause the thin film to be more hydrophilic, because the thin film interacts with water molecules through hydrogen bonds, thereby increasing the porosity value.

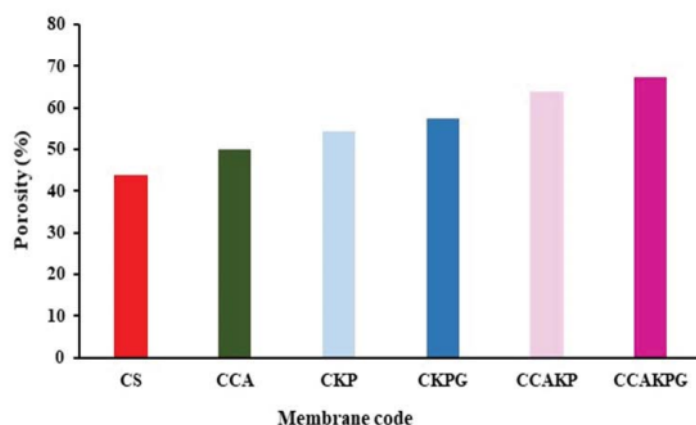


FIGURE 2. Porosity of various membranes: Chitosan (C), Carragenan (K), Chitosan-Citric Acid (CCA), Chitosan-Carragenan-Pva (CKP), Chitosan-Carragenan-Pva-Gliserol (CKPG), Chitosan-Citric Acid-Carragenan-Pva (CAKP), Chitosan-Citric Acid-Carragenan-Pva-Glyserol (CAKPG).

Hydrophilicity

The test uses the sessile drops method by dripping liquid water on the surface of the thin film, then the contact angle is measured on the surface of the thin film. The results of the measurement of the contact angle can be seen in Fig. 3. It can be seen that the increase in the hydrophilicity value is directly proportional to the increase in the porosity of the thin film. The results of the data from the hydrophilicity test showed that the inclusion of carboxyl and hydroxyl groups caused a decrease in the value of the contact angle. The decrease in the contact angle correlates with the increase in the hydrophilicity of the membrane. Accordance with research of [9], where the presence of carboxylic groups in hydrophilic citric acid interacts highly with the presence of water molecules and causes the modified citric acid membrane to absorb more water when compared to pure chitosan membranes. In addition, the effect of the presence of the carboxylate group (-OH) of glycerol that enters the membrane composition which of course causes the bioplastic membrane to easily absorb water (hydrophilic), so this result is still far from the conventional SNI standard plastic which has a hydrophobicity level of 99 %.

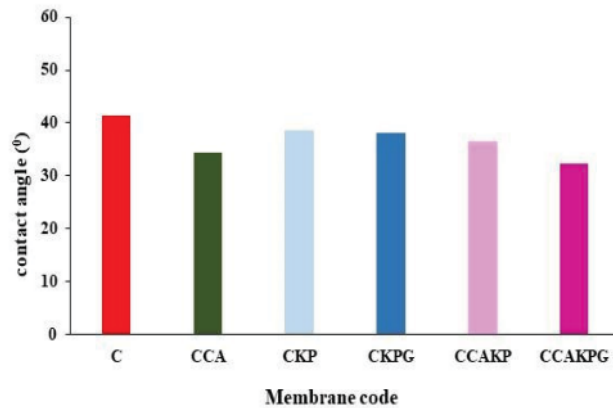


FIGURE 3. Hydrophilicity of various membranes: Chitosan (C), Carragenan (K), Chitosan-Citric Acid (CCA), Chitosan-Carragenan-PVA (CKP), Chitosan-Carragenan-PVA-Gliserol (CKPG), Chitosan-Citric Acid-carragenan-PVA (CCAKP), Chitosan-Citric Acid-carragenan-PVA-Glyserol (CCAKPG)

Water Vapor Absorption

Bioplastics can be said to be good if they have the ability to absorb less water vapor where the value of water vapor resistance produced is smaller. This is because the lower the absorption of water vapor in bioplastics, the shelf life of bioplastics will be longer. The results of the porosity measurements can be seen in Fig. 4.

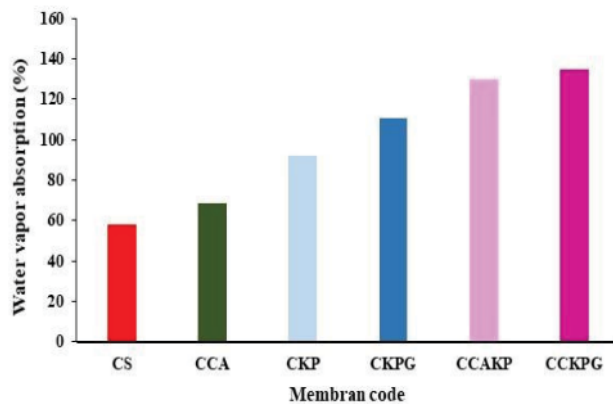


FIGURE 4. Absorption of water vapor membranes : Chitosan (C), Carragenan (K), Chitosan-Citric Acid (CCA), Chitosan-Carragenan-PVA (CKP), Chitosan-Carragenan-PVA-Gliserol (CKPG), Chitosan-Citric Acid-carragenan-PVA (CCAKP), Chitosan-Citric Acid-carragenan-PVA-Glyserol (CCAKPG)

From Fig. 4 it can be seen that the modified membrane has a higher water vapor absorption value than the unmodified membrane. According of [1], glycerol has the ability to bind water vapor because it has a hydroxyl group (OH-) so it is hydrophilic. If the value of the water vapor absorption test of all membranes is compared with conventional plastic (polypropylene) which has a water vapor absorption value of 0.01%. So, this test shows that the membrane resistance to water vapor is still low when compared to conventional plastics.

Biodegradability

This test uses the Soil Burial Test method, namely by burying the membrane into the soil. The results of the membrane biodegradability test can be seen in Table 2. It can be seen that the rate of membrane degradation with the

addition of citric acid crosslinker and glycerol plasticizer causes the membrane to become more hydrophilic so that it is easier to bind water molecules in the soil. The increased absorption of bioplastics in water causes water in the soil to interact with the membrane so that bioplastic degradation runs faster. According of [3] the rate of bioplastic degradation of the international standard bioplastic ASTM D-6002, this regulation explains that bioplastics can be 100% degraded within 60 days. The duration of the degradation ability resulting from this study was 63 - 112 days for all types of bioplastic membranes. Therefore, this degradation ability does not meet the standards used by biodegradable plastics.

TABLE 2. Microbial Degradation Time

Film code	Degradation (days)
CS	77
CCA	63
CKP	112
CKPG	98
CCAKP	91
CCAKPG	77

Resistance to pH

The stability of the membrane over a wide pH range indicates the better chemical resistance of the membrane. In other words, the membrane can be utilized in various pH conditions. The pH resistance test was carried out on solutions of pH 5, 7, 9 and 11. A significant decrease in the mass of the membrane indicated the instability of the membrane at certain pH conditions which could be caused by the decomposition of the components of the membrane under acidic or alkaline conditions. The results of the measurement of membrane resistance to various pH conditions can be seen in Table 3.

TABLE 3. Film Weight Loss Percent

Film code	Weight loss (%)			
	pH 5	pH 7	pH 9	pH 11
C	11	0	0	0
CCA	2.8	0	0	0
CKP	0	0	0	0
CKPG	0	0	0	0
CCAKP	0	0	0	0
CCAKPG	0	0	0	0

Mechanical properties

Tensile strength and elongation test aims to determine the mechanical properties of the membrane. The mechanical properties of the membrane are very important to maintain the structural consistency and physical integrity of the membrane during use. Tensile strength is the maximum tensile force that a film can withstand until it breaks. The percentage of elongation is the change in maximum length before the membrane breaks. The results of the measurement of tensile strength and percentage of elongation can be seen in Fig. 5.

Tests of tensile strength and elongation of chitosan and citric acid crosslinked chitosan membranes showed that the modification by the crosslinked method caused an increase in the membrane strain value but decreased the tensile strength of the membrane when compared to pure chitosan [10]. This is due to the cross-linked membrane structure, which contains more hydrophilic groups and causes the membrane to bind more easily to water molecules and swell.

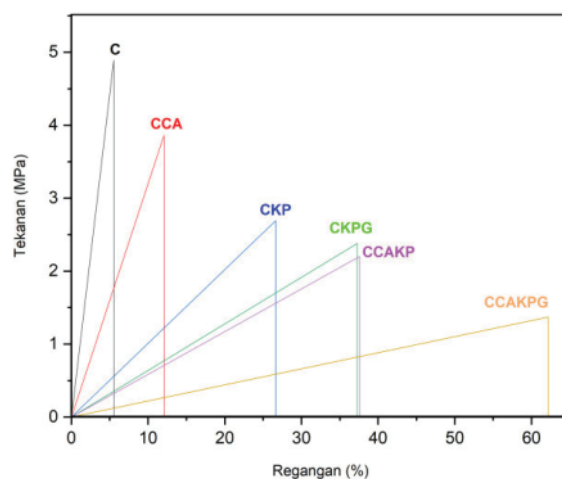


FIGURE 5. Tensile Strength and Elongation of membranes : Chitosan (C), Carragenan (K), Chitosan-Citric Acid (CCA), Chitosan-Carragenan-PVA (CKP), Chitosan-Carragenan-PVA-Glycerol (CKPG), Chitosan-Citric Acid-carragenan-PVA (CAKPG), Chitosan-Citric Acid-carragenan-PVA-Glycerol (CAKP)

CONCLUSION

The combination of chitosan, carrageenan and PVA produces a film that has a transparent, translucent and caterpillar appearance. The addition of citric acid crosslinker and glycerol plasticizer affects the physicochemical properties of bioplastic membranes, the addition of these two materials causes an increase in the value of thickness and weight, porosity, water vapor absorption, swelling, pH resistance and membrane biodegradability, but decreases the contact angle value (hydrophilicity).

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