Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

The Effect of Etherification Agent on the Mechanical Properties of Sodium Carboxymethyl Cellulose-based Bioplastic and Its Application As Fruit Packaging

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Abstract

This study aimed to determine the optimum conditions of sodium chloroacetate (SCA) as an etherification agent, to obtain sodium carboxymethyl cellulose (SCC) bioplastic with a significant mechanical property. In this study, the SCC has been synthesized and concentration of SCA was optimized. SCC was synthesized through etherification reaction using SCA as etherification agent. The SCC synthesis was carried out in a dry system consisting of alkalization and carboxymethylation steps. SCA optimization was determined based on the levels of SCC and DS. The synthesis and characterization of SCC bioplastics has also been carried out.The result obtained were SCC with a level of 88% and a degree of substitution of 1.50. The best mechanical properties of bioplastic were shown at 6% SCA concentration with 9.91 MPa tensile strength and 9% elongation. The degradation test result showed that bioplastic experienced a mass reduction of 17.30% over a period of 21 days. SCC bioplastic application as fruit packaging can reduce the mass of citrus fruits by 10.5% for 10 days of storage.

***Keywords*:** bioplastic, etherification, mechanical properties, sodium carboxymethyl cellulose.

1. Introduction

Sodium carboxymethyl cellulose (SCC) or carboxymethyl cellulose (CMC) is cellulose derivatives modified by cellulose etherification reactions. This biomaterial is widely used as a stabilizer [1] a food thickener [2] and a bioplastic composite crosslinking agent [3]. Sodium carboxymethyl cellulose has the potential to be used as a raw material for bioplastic manufacturing because it is biodegradable, renewable, and has food-grade properties.

Noticeably, despite the plenty of studies on SCC-based bioplastic, they often failed to demonstrate its high mechanical properties for the as-prepared bioplastic. The findings of Almasi and Ghanbarzadeh have reported that SCC-based bioplastic still had low mechanical properties, namely the tensile strength of 2.23 MPa and 89.93% elongation [4]. The mechanical properties of bioplastics are based on hydrogen bonds between molecules in the manufacture of bioplastic films. These bonds can occur inter and intra-molecularly. Therefore, researchers modified cellulose into SCC. This chemical modification causes the addition of new functional groups that will increase hydrogen bonds between monomers for making bioplastics.This causes an increase in film stiffness; thus the tensile strength also increases.One of the parameters that determine the quality of SCC is the etherification agent, namely sodium chloroacetate (SCA). SCA concentration affects the etherification process of cellulose. This is because the quality of SCC will be better when the substitution reaction that occurs in the carboxymethylation process increased [5].

Sodium chloroacetate has a carboxylate group (-COOH) which will attach to the cellulose molecules. The amount of –COOH substituted into cellulose molcules affects the degree of substitution (DS) of SCC. The DS is one of the determinants on the quality of SCC bioplastic, because it is related to the

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Receive Date: 28 June 2021; Revise Date: 30 July 2021; Accept Date: 17 September 2022.

DOI: 10.21608/ejchem.2022.82891.4075.

crosslinking reaction between the constituent polymers. Therefore, this study aimed to determine the optimal SCA concentration on SCC bioplastic production and their application as citrus fruit packaging. The method update carried out by the researchers was that the cellulose used as raw material for the synthesis of SCC was cellulose that has been physically modified, namely cellulose microfibers (CMF). Cellulose with a smaller particle size can increase the homogeneity of the bioplastic film so that it affects its mechanical properties.

SCC bioplastics with excellent mechanical properties can be applied as fruit packaging. The packaging aims to maintain the quality and quantity of fruit from the packaging process until it is purchased by consumers. Several experiments have been carried out on peach [6], fresh-cut papaya [7] and plum [8]. The advantage of packaging fruit with SCC bioplastic is that it is environmentally friendly and food-grade.

2. Materials and Methods

2.1 Materials

The materials used in this study were cellulose microfibers (CMF) (Lab Store, Jakarta, Indonesia), NaOH (Merck), isopropanol (Merck), sodium chloroacetate (SCA) (Lab Store, Jakarta, Indonesia), CH_3COOH (Merck), methanol (Merck), HNO_3 (Merck), chitosan (PT Laborindo Sarana, Jakarta, Indonesia), and sorbitol (C.V Intraco, Makassar, Indonesia).

2.2 Instruments

The instruments of this study were glassware, Universal Testing Machine (UTM) Hydraulic, Fourier Transform Infra Red (FTIR) Shimadzu, shaker waterbath Recipocating type, and oven GenLab.

2.3 Methods

2.3.1. Sodium carboxymethyl cellulose synthesis.

Cellulose microfibers 8% were mixed with NaOH 8%-isopropanol 83% solution . The mixture was put into a waterbath shaker for 1 hour at a speed of 150 rpm and temperature of 30°C. After 1 hour, the mixture was added to different concentration of SCA (4%, 6%, 8%, 10%, and 12%). Thereafter, mixture was re-immersed into the waterbath shaker for 3 hours at 56°C. Then, the cellulose slurry was washed with 90% CH_3COOH and methanol. Finally, the residue was dried in an oven at 60°C [9, 10].

2.3.2. The degree of substitution for the SCC products.

Determination of DS was based on American Standard Testing and Material (ASTM) D1439-61T. The DS was calculated according to equation (1).

$$DS = \frac{0.162 \times nCOOH}{1-(0.058 \times nCOOH} \qquad (1)$$

$$nCOOH = \frac{(VNaOH \times CNaOH) - (VHCl \times CHCl)}{weight}$$

Where:

C_{NaOH} = NaOH concentration (M)
V_{HCl} = HCl Volume (L)
C_{HCl} = HCl concentration (M)

2.2.3 Bioplastic sodium carboxymethyl cellulose (BSCC).

The SCC powder produced from the method mentioned in Section 2.3.1 was settled in 5 different beakers. After that, 0.012% chitosan solution (w/v in 1% CH_3COOH) was added to each of these beakers. The mixture was stirred until homogeneous and 1 mL sorbitol was added. The mixture was casting on a glass plate and dried in an oven at 60°C [11].

2.2.4 Bioplastic degradation test.

The degradation test was carried out on the optimum SCC bioplastic which referred to ASTM D 5988-12. Bioplastic film degradation can be observed from the morphology and weight loss of bioplastics after being buried in soil media. The Determination of the percentage of mass loss degradability rate, and complete degradation time were calculated using the following equations (2), (3), and (4).

$$Weight\ loss\ (\%) = \frac{W_0 - W_1}{W_0} \times 100 \qquad (2)$$

$$Degradation\ rate = \frac{W_0 - W_1}{t} \qquad (3)$$

$$Complete\ degradation\ time = \frac{100\%}{weight\ loss} \times t \qquad (4)$$

Where:

W_0 = Initial weight (g)
W_1 = Final weight (g)
t = Test time (days)

3. Results and Discussion

3.1 The effect of SCA Concentration on DS SCC

Sodium chloroacetate is an etherification agent that determines the SCC levels and DS. Based on Table 1, levels and DS of SCC were directly proportional to the concentration of SCA. This was occured because of hydroxyl groups of cellulose from SCA were replaced by more carboxymethyl groups [12]. The highest degree of substitution was shown at the SCA 12%, but based on Indonesian National Standard (SNI) 8762 (2019), the DS CMC requirements were 0.60-1.50. Therefore, the optimum concentration of SCA in this study was 8%.

Table 1. The effect of SCA concentration on SCC levels and DS.

Material	SCC levels (%)	Degree of substitution (DS)
CMF/SCA 4%	87	1.28
CMF/SCA 6%	87	1.34
CMF/SCA 8%	88	1.50
CMF/SCA 10%	88	1.66
CMF/SCA 12%	90	1.80

3.2 FTIR analysis

Chemical modification causes a shift in wavenumber at the O-H vibrational peak, from 3350 cm-1 (cellulose) to 3441 cm-1 (SCC). The similar thing was also showed at the C-H peak which experienced a shift to a larger wavenumber. These changes can be associated with the disarrangement of intra- and intermolecular hydrogen bonds [13]. In Figure 2 (b), the vibration peak of –CH2- appeared in the region of 1462 cm-1. Absorption in the area of 1000-1200 cm-1 indicated the presence of ether group(-O-) [14].

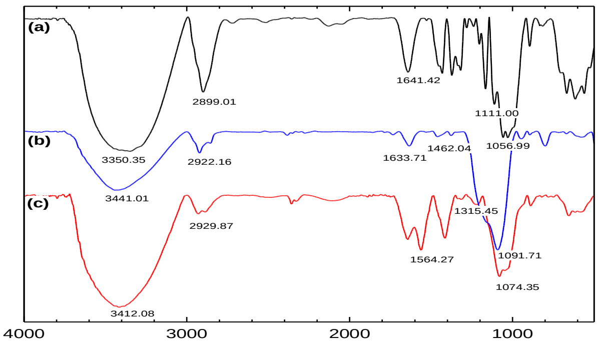

Fig 1. FTIR spectrum of (a) cellulose, (b) SCC, and (c) bioplastic

The difference between the cellulose spectrum (Figure 1a), SCC (Figure 1b), and bioplastic (Figure 1c) was due to the presence of a new functional group derived from the chitosan molecule. In the 3500-3100 cm-1 area, the O-H peak may overlap with the NH2 stretching vibration of the cellulose molecule. These peaks are reinforced by N-H bending and CN peaks in the 1564 and 1315 cm-1 regions. At peak 2 are the C-H strain, the bending and stretching of the N-H amide and the C-O stretch of the acetyl group [15].

3.3 The mechanical properties of SCC bioplastic

As can be seen in figures 2 and 3, that at a concentration of SCA 4-6% the tensile strength value increased by 30%. This was because the increase in the concentration of SCA causes an increase in the carboxymethyl group, which was substituted into the cellulose molecule. The presence of these groups must be crosslinked with chitosan and sorbitol in order to increase the tensile strength of bioplastics. However, at higher SCA concentrations, the tensile strength of bioplastics decreased. This was because the increase in the carboxymethyl group of cellulose was not coexisted by an increase in the concentration of the supporting polymer, hence the carboxymethyl group did not bind. The compatibility of the mixture was reduced, therefore a weakening of the adhesion force between SCC and other polymers occurred. This situation will cause the bioplastic film to become brittle and its elasticity decreases [14]. The values obtained were better than the previous studies (Table 2.). In Figure 3, it can also be observed that the value of tensile strength is inversely proportional to the elongation, because film stiffness reduces flexibility.

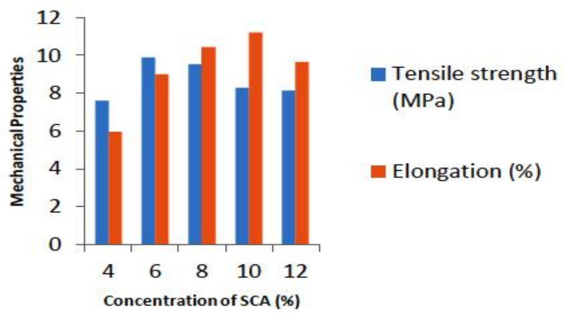

Fig 2. The effect of SCA concentration on the tensile strength and elongation of SCC bioplastics.

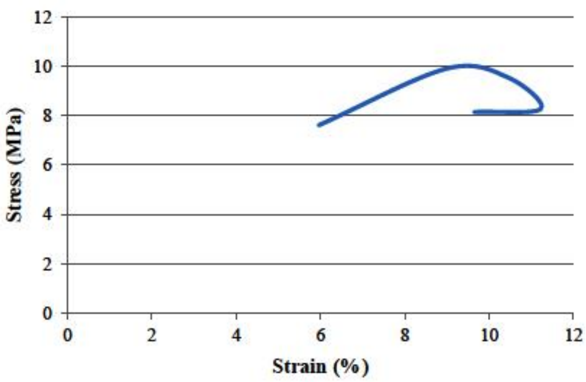

Fig 3. Stress vs strain curve for SCC bioplastic.

Table 2 shown the bioplastics that based on unmodified cellulose (CU) had the lowest tensile strength [11]. Bioplastic synthesized from microcrystalline cellulose (MCC) (physical modification) [16] and SCC (1 g) (chemical modification) [4] has a higher tensile strength than CU. The combination between physical and chemical modifications carried out in this study showed better results compared to similar with previous studies.

Table 2. Differences in the mechanical properties of several types of cellulose bioplastics.

Materials	Tensile strength (MPa)	Elongation (%)
CU	0.089	15.90
MCC	2.740	3.16
CMC	2.230	89.93
CMF-SCC	9.910	9.00

3.4 SCC bioplastic degradation

Biodegradation is one of the parameters that determine whether bioplastics are biodegradable or not. The degradation process consists of 2 stages, namely chemical and biological processes. Chemical degradation will cause a molecular oxidation process that produces low molecular weight polymers [17]. Then biologically, degradation is based on the activity of microorganisms and the work of enzymes. Degradation testing was carried out in soil media through quantitative and qualitative observations. Quantitatively, observations were made based on a decrease in mass with changes as shown in Table 3. Observations were stopped at week 3 because the condition of the sample had been torn apart and most of it had mixed with the soil, making it difficult to observe.

Table 3. The effect of burial time on the weight and morphology of SCC bioplastic

Weeks	Weight (g)	Morphology
0	0.185	
1	0.181	
2	0.153	
3	Not determined	

Table 4 was the result of calculating the degradation rate and the time of complete degradation of SCC bioplastic. The degradation time obtained was higher than ASTM D-6002 which was 60 days. Visually, SCC bioplastic degradation was characterized by the damage of the bioplastic film structure (Table 4). This damage can be caused by the absorption of water from the soil and the activity of microorganisms [18].

Table 4. Result of Calculation and Complete Degradation of SCC Bioplastic

Parameters	The values
Weight loss (%)	17.30
Degradation rate (g/day)	0.0015
Complete degradation time (days)	121

3.5 Application of Bioplastics as Fruit Packaging

One of the most common uses of plastic is fruit packaging. The plastic is in the form of clip wrap which can protect the fruit from contamination with the outside environment, so that the fruit has a longer shelf time. The bioplastics that have been successfully synthesized in this study were applied as packaging for citrus fruits and stored in a refrigerator at a temperature of 5°C. The first parameter was a change in the weight of oranges which can be seen in Figure 4.

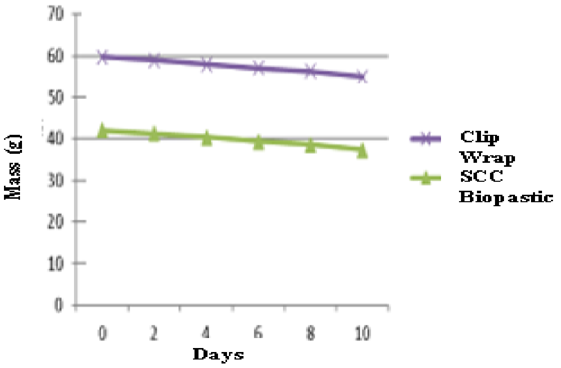

Fig 4. Effect of storage period on mass changes in citrus fruit packaging with SCC bioplastic

Based on Figure 4, the weight of oranges was reduced in all bioplastic samples. The weight reduction may be caused by two things, first one is a decrease in surface water vapor permeability thereby limiting water transfer. The second factor is the low respiration rate because the molecular film layer reduces the availability of O_2 and CO_2 on the surface, thereby reducing the metabolism of citrus fruits [19, 20].

Citrus fruit packed with SCC bioplastic and clip wrap. The percentages of citrus fruits were 10.5% and 0.4%, respectively [21]. The results obtained are in line with the mechanical properties of bioplastics, the value is still higher than those reported by Almenar, et al, 2010 which is 1% for PLA bioplastics and 13% for PET (14 days shelf life). The same thing also happened to CMC bioplastics, where the percentage reduction in mass obtained in this study was much larger than that reported by Ansorena, et al (2011) which only experienced a decrease in weight of 0.3% [22].

4. Conclusion

In this study, sodium carboxymethyl cellulose was obtained with an optimum sodium chloroacetate concentration of 8% with levels of 88% and DS 1.50. Etherification agents influenced the mechanical properties of SCC bioplastic. Optimum mechanical properties were obtained at a SCA 6% with a tensile strength of 9.91 MPa and 9% elongation. Bioplastic SCC showed symptoms of degradation biosensors. The application of SCC bioplastic as fruit packaging still has weaknesses in terms of maintaining the weight of citrus fruits.

5. Conflicts of interest

There are no conflicts of interest to declare.

6. Research Funding Sources

This research was funded by The Doctoral Dissertation Research (PDD) Grant for first year with Contract No. 761/UN4.22/PT.01.03/2021, from the Ministry of Research and Technology of the Directorate General of Higher Education of Indonesia.

7. Acknowledgments

The authors thank for head of the National Research and Innovation Agency (BRIN) Prof. Bambang Permadi Soemantri Brodjonegoro, Ph.D for their help and cooperation during our study.

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