

Utilization of sugarcane bagasse for synthesis of carboxymethylcellulose and its biodegradable blend films

Supaporn Sophonputtanaphoca^{a,*}, Sehanat Prasongsuk^b, Phussadee Chutong^a, Chalermkhwan Samathayanon^b, Kamonchai Cha-aim^a

^a Division of Biotechnology and Agricultural Products, Faculty of Agricultural Product Innovation and Technology, Srinakharinwirot University, Ongkharak Campus, Nakhon Nayok 26120 Thailand

^b Plant Biomass Utilization Research Unit, Department of Botany, Faculty of Science, Chulalongkorn University, Bangkok 10330 Thailand

*Corresponding author, e-mail: supapornsp@g.swu.ac.th

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ABSTRACT: The objective of this study is to synthesize and extensively characterize carboxymethylcellulose from sugarcane bagasse cellulose (CMC-SC) to evaluate its potential use in blend films. A single step of alkaline hydrogen peroxide pretreatment at a low temperature was used to extract cellulose from sugarcane bagasse. The CMC-SC was extensively characterized with respect to its structure, crystallinity, degree of substitution (DS), average molecular weight (M_w), degree of polymerization (DP), viscosity, thermal property, antioxidant property and morphological structure as compared to a commercial CMC (CMC-COM). CMC-SC displays a DS, average M_w and DP of 0.7, 2×10^6 and 9,204, respectively. The Rapid Visco Analyzer method revealed a relatively low viscosity (65.7 cP) for 4% (w/v) CMC-SC solution at 45 °C. A melting temperature (T_m) close to 250 °C was measured, as was a glass transition temperature (T_g) of 102.4 °C. The DPPH assay indicated that CMC-SC exhibited higher antioxidation activity than CMC-COM. The characterization of the blend films between CMC-SC and polyvinyl alcohol (CMC-SC/PVA) with varying glycerol concentrations showed they had better properties with greater elongation at break than CMC-COM films with or without copolymer blending.

KEYWORDS: biodegradable blend film, carboxymethylcellulose, lignocellulose, alkaline pretreatment, sugarcane bagasse

INTRODUCTION

Sugarcane ranks third among Thailand's major economic crops. From 2015–2020, sugarcane fields accounted for approximately 1.77–1.83 million hectares across 47 provinces [1]. Consequently, sugarcane bagasse, a residue left over from sugar manufacturing in Thailand after extracting juice from sugarcane, is abundant and has the potential to be converted into value-added products. Sugarcane bagasse is a lignocellulosic material composed primarily of cellulose, hemicellulose, and lignin. Thus, it has the potential to serve as a raw material in the production of a wide range of products through various conversion processes. This agro-industrial residue is primarily used as a fuel in the boilers of sugar factories. It has been reported that several products have been made using sugarcane bagasse as a raw material, including fuel for electricity generation, pulp and paper products, fermented products such as enzymes, bioethanol, organic acids, alkaloids, antibiotics, protein-enriched cattle feed, etc [2].

Additionally, sugarcane bagasse can be used to produce biopolymers or polymer derivatives. A valuable cellulose derivative, carboxymethylcellulose (CMC), can be produced from cellulose, which is widely used in a wide range of industries [3]. CMC

is a polyanionic, semi-synthetic polysaccharide formed by partially substituting hydroxyl groups in native cellulose for carboxymethyl groups [4]. As a water-soluble, high viscosity, low toxicity and non-allergenic compound, CMC is an excellent film- and gel-forming compound. CMC is used as a stabilizer, binder, and water-holding compound [5]. Typically, the color of pure CMC is cream or off-white. It is tasteless and odorless [6]. CMC is an ingredient in a great number of commercial products, including foods, toothpastes, eye drops, paints, and cosmetics.

The raw material sources for CMC production are currently wood pulp and cotton due to their high cellulose content. Wood pulp contains 40–50% cellulose by weight, while cotton contains up to 90% cellulose by weight. In addition, these two materials are also used in other industries, such as the paper industry and the textile industry. Thus, several studies have been conducted to look for alternative sources, such as herbaceous plants with high cellulose content which are found in abundant quantities and have low costs. Many agricultural wastes and agro-industrial wastes have been investigated for their potential to be raw materials for CMC production, namely, Cavendish banana pseudostem [6], durian rind [7], cotton by-products [8], rice hulls [5], corn cobs [3], wheat straw and barley straw [5], rice straw [9], etc.

Asl et al [10] reported feasibility of CMC production and properties of CMC films made from sugarcane bagasse. According to Golbaghi et al [11], CMC has been synthesized from sugarcane bagasse using steam explosion pulping and high-molecular-mass hemicellulose was produced as a by-product. However, the methods of cellulose extraction, CMC synthesis and film preparation were different from those used in this study. In this study, cellulose was isolated from sugarcane bagasse using a single-step alkaline hydrogen peroxide pretreatment at a low temperature. NaOH pellets were dissolved in 2.5% H₂O₂ solution to obtain a final concentration of 5% NaOH (w/v). Thus, the alkaline pretreatment and the bleaching step were combined in a single step. According to the literature, alkaline treatment methods and bleaching are usually performed separately [5, 12, 13]. This pretreatment method was effective for 10 varieties of rice straw and resulted in high cellulose yields [9]. To solve the problem of the buffering capacity of plant biomass in alkaline pretreatment, a pretreatment with minimal use of chemical at a low temperature was developed. It is difficult to maintain a constant pH by adding an alkaline solution to plant biomass mixtures since the biomass has a buffering capacity [14]. Chemical compounds in plant biomass, such as carboxylic groups, phenolic groups, and acetyl groups, are hydrolyzed under alkaline conditions, resulting in acid species. The neutralization reaction between these acids and the alkali reduces the hydroxide groups in the solution, thus impairing the effectiveness of the alkali. In addition, more alkali is required to adjust the pH to a desired value [14]. To the best of our knowledge, no report has been published describing the use of this single-step alkaline hydrogen peroxide pretreatment method with sugarcane bagasse. This was therefore the first time that cellulose had been isolated from sugarcane bagasse using a single-step alkaline hydrogen peroxide pretreatment at a low temperature and with minimal use of chemicals. In this study, CMC synthesized from sugarcane bagasse was extensively characterized to determine its physical and chemical properties, including its antioxidant properties, which have not previously been reported.

In terms of blend films, polyvinyl alcohol (PVA) and CMC have been widely developed for biodegradable packaging. There are multifunctional groups on the macromolecular chains of both PVA and CMC, making them miscible and compatible biopolymers. Thus, blend films of these polymers can be used to produce biodegradable materials with properties suitable for use in bio-based packaging [15]. The use of suitable and eco-friendly plasticizers is essential to prevent the brittleness of biodegradable blend films. Natural-based plasticizers such as glycerol are widely used in several types of films [16]. The aim of this study is to determine the optimal glycerol concentration for good

film properties. This study hypothesizes that CMC from sugarcane bagasse (CMC-SC) and its blend films possess better properties than commercial CMC (CMC-COM). To demonstrate the validity of this hypothesis, cellulose extraction was performed in a single step followed by the synthesis of CMC. Additionally, blend films of CMC-SC and PVA (CMC-SC/PVA) with varying ratios of glycerol as a plasticizer were prepared and both the CMC and its films were evaluated for potential use as food packaging.

MATERIALS AND METHODS

Raw material

Sugarcane bagasse (cultivar; Khon Kaen 3) was kindly provided by Korat Industry Co., Ltd., located in Phimai City, Nakhon Ratchasima Province, Thailand. After air drying, the bagasse was cut into small pieces (approximately 2.5 cm in length) and then dried in a hot-air oven at 40 °C for 24 h. Particles of the dried biomass were reduced in size using a cutting mill (Retsch, Haan, Germany). The milled biomass was sieved to pass through a 20-mesh sieve and was kept in an airtight lid jar with a screw cap lid at room temperature for all experiments.

Chemicals

All chemicals were reagent grade and HPLC grade purchased from Sigma-Aldrich (St. Louis, MO, USA), UNIVAR and LABCHEM (Ajax Finechem, Australia), EMPLURA and EMSURE (Merck Millipore, Germany). Commercial carboxymethylcellulose (product no.419303, M_w ~250,000, degree of substitution = 0.9) was purchased from Sigma-Aldrich.

Determination of chemical composition of native sugarcane bagasse

All analysis for the determination of sugarcane bagasse composition followed the Laboratory Analytical Procedures (LAP) issued by the National Renewable Energy Laboratory (NREL, Golden, CO, USA). The moisture content and total solids content were determined by drying approximately 0.5 g (weighed to the nearest 0.1 mg) of the sample at 105 °C until a constant weight was achieved [17]. The ash content was determined by ashing 0.1 g (weighed to the nearest 0.1 mg) of the sample in a furnace at 575 °C for 24 h [18]. The structural carbohydrates and lignin were determined using extractive-free biomass. The extractive-free bagasse was prepared by exhaustive extraction of the native biomass using a Soxhlet apparatus with water extraction for 24 h, followed by 95% ethanol for 24 h [19]. Water and ethanol were removed from the extracts using a rotary evaporator, followed by a vacuum oven drying process to obtain the dried extractives. The extractive-free biomass was air-dried and stored in an airtight screw cap bottle. The moisture content of the extractive-free biomass was determined as described

above. The extractive-free biomass was subjected to a two-step acid hydrolysis to determine the structural carbohydrate content by measuring the sugars of the neutralized hydrolyzate using high-performance liquid chromatography (HPLC). Acid-soluble lignin (ASL) and acid-insoluble lignin (AIL) were determined using the spectrophotometry method by measuring the absorbance at 320 nm and the gravimetric method, respectively [20]. The experiments were conducted in triplicate.

HPLC analysis

The hydrolyzate samples were filtered through 0.2 μm syringe filter prior to HPLC analysis. An Alltech (Rockland, ON, Canada) HPLC system was equipped with an evaporative light scattering detector (Model 200ES), a column heater (Model 630) and a pump (Model 626). A Rezex RPM Monosaccharide Pb^{2+} column (300 \times 7.8 mm, Phenomenex; Torrance, CA, USA) equipped with a guard column (Phenomenex) was used to separate the monosaccharides in the samples. The separation conditions were as follows: 50 μl sample injection, HPLC-grade water as the mobile phase, 0.6 ml/min flow rate, 60 $^{\circ}\text{C}$ column temperature and 25–30 min retention time. A calibration curve was established using standard sugars (glucose, xylose, galactose, arabinose, and mannose) at various concentrations (0.1–1.0 mg/ml). Amounts of the monomeric sugars were converted to their polymeric forms by multiplying with the correction factors (0.9 for C6 sugars and 0.88 for C5 sugars). The polymeric form of glucose was identified as cellulose, whereas the combination of other polymeric sugars was identified as hemicellulose. The analysis was done in triplicate.

Isolation of cellulose

Cellulose was isolated from the native biomass using a single-step alkaline hydrogen peroxide pretreatment (5% w/v NaOH in 2.5% (w/v) H_2O_2) with 3% (w/v) solid loading at a low temperature (35 $^{\circ}\text{C}$, 24 h) as described by Soponputtanaphoca et al [9]. Approximately 0.3 g dry weight of the biomass was placed into a 20-ml scintillation vial and 10 ml of 5% NaOH in 2.5% H_2O_2 was added before closing the vial with a screw cap. The sample was placed on a rotator located in an incubator with a rotation speed of 25 rpm. The treatment was carried out at 35 $^{\circ}\text{C}$ for 24 h. To separate the solid from the liquid phases, the slurry was filtered through a Gooch crucible (pore size = 10–12 μm). The solid phase in the crucible was washed with 50 ml distilled water, followed by 10 ml 0.01 mM HCl and then rinsed with 50 ml distilled water. The washed solid was dried in a vacuum oven at 40 $^{\circ}\text{C}$ for 24 h. Dried-solid was referred to as cellulose. The experiment was conducted in triplicate. The cellulose content was determined using the two-step acid hydrolysis by the

NREL method as described above. The HPLC analysis was used to determine the content of cellulose in the dried-solid.

Synthesis of carboxymethylcellulose (CMC)

CMC was synthesized from the extracted cellulose [9]. To initiate the alkalization process, 20 ml isopropanol and 5 ml NaOH (6 M) were mixed with 1 g dry weight of the extracted cellulose. The suspension was set aside overnight at room temperature. A methylation process was carried out by slowly adding 1.08 g sodium monochloroacetate to the suspension within 30 min. The reaction mixture was then incubated at 50 $^{\circ}\text{C}$ for 3 h. After cooling to room temperature, the reaction mixture was filtered through a filter paper (Whatman No.1) to obtain the solid phase (CMC). CMC was purified by suspending it in 70% ethanol and neutralized by adding glacial acetic acid. After that, it was washed with 70% ethanol, 80% methanol, and 95% ethanol, respectively. The purified CMC was dried overnight in a vacuum oven at 70 $^{\circ}\text{C}$ to obtain the powder form. The experiment was conducted in triplicate. The CMC yield was calculated using Eq. (1).

$$\text{Yield of CMC}(\%) = \frac{\text{Weight of CMC (g)}}{\text{Weight of cellulose (g)}} \times 100 \quad (1)$$

Characterization of CMC

Fourier-transform infrared (FTIR) analysis

FTIR analysis was used to determine the functional groups in sugarcane bagasse, extracted cellulose, and CMC-SC. The analysis was performed as described by Haleem et al [8].

X-ray diffraction (XRD) analysis

Crystallinity of CMC-SC was compared to that of the extracted cellulose using XRD analysis. The method was carried out as described by Rachtanapun et al [7] and Haleem et al [8]. The samples were dried at 105 $^{\circ}\text{C}$ for 3 h before the testing. The scattering angle was 2θ between 1 $^{\circ}$ and 80 $^{\circ}$ at a scanning rate of 5 $^{\circ}$ /min.

Degree of substitution (DS)

A titration method was used to determine the DS of CMC-SC [8]. The sample was treated with ethanol and nitric acid before being filtered to obtain the solid phase. After washing the solid phase with ethanol and methanol, the solvent was removed and the solid phase was dried. The titration was performed using phenolphthalein as an indicator by mixing the dried solid with NaOH solution and titrating with HCl. The end point of the titration was observed when the color of the mixture changed from light pink to colorless. The experiment was done in triplicate. The DS was calculated using Eqs. (2) and (3).

$$A = \frac{(BC - DE)}{F} \quad (2)$$

$$DS = \frac{(0.162 \times A)}{(1 - 0.0058 \times A)} \quad (3)$$

where A = milli-equivalents of acid used per 1 g of sample, B = volume of NaOH used, C = concentration of NaOH, D = volume of HCl used, E = concentration of HCl, F = weight of sample (g), 162 = molecular weight of anhydrous glucose, 58 = net molecular weight increases in anhydrous glucose due to the substitution with each carboxymethyl group.

Average molecular weight (M_w)

An average M_w of CMC-SC was determined using gel permeation chromatography (GPC, Shimadzu, LC-10 ADvp). An aliquot of 10 ml of 0.2% (w/v) CMC-SC solution was prepared by dissolving CMC-SC in a 20-ml scintillation vial containing 50 °C distilled water. The solution was incubated in a rotator located in an incubator at 50 °C for 1 h. After the solution cooled to room temperature, it was injected into a Shudex-SB-804 HQ column using distilled water as a mobile phase. The flow rate of the mobile phase was set at 1 ml/min. A series of CMC solutions with different molecular weights were used to prepare the CMC standards. The M_w of CMC-SC was compared to the standards and expressed as an average M_w . The experiment was done in triplicate.

Degree of polymerization (DP)

Based on the DS and the average M_w results, the DP of CMC-SC was calculated using the CMC Book issued by CP Kelco company (USA) as shown in Eq. (4).

$$DP = \frac{M_w}{162 + (80 \times DS)} \quad (4)$$

Viscosity

Rapid Visco Analyzer was used to measure the viscosity of a CMC-SC solution [7]. Briefly, CMC-SC powder was dissolved in distilled water to prepare a 4% (w/v) solution. The viscosity was measured in two steps. First, the solution was stirred at 960 rpm for 10 s at 45 °C. Second, the speed was adjusted to 160 rpm for 10 min at 45 °C. For comparison, the viscosity of CMC-COM was tested under the same condition. The final viscosity values of CMC-SC and CMC-COM were recorded. The experiment was done in triplicate.

Thermal properties

According to modified methods of Siqueira et al [21], thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods were used to investigate the thermal properties of CMC-SC and CMC-COM. The TGA was carried out using a TG analyzer (TGA Q50 V6.7 Build 203) in the presence of nitrogen gas at temperatures between 30 and 700 °C. Approximately 5 mg of the sample was heated in an aluminum pan at a heating rate of 10 °C/min.

DSC analysis of CMC-SC and CMC-COM was performed using a DSC analyzer (NETZSCH DSC 204F1 Phoenix 240-12-0322-L) under the nitrogen condition at a flow rate of 50 ml/min. Approximately 9 mg of the sample was tested at –90 °C to 120 °C with a heating rate of 5 °C/min. Two consecutive scans were performed on each sample. In the first scan, the temperature ranged from –90 °C to 120 °C, and in the second scan, the temperature ranged from –90 °C to 300 °C. Between the scans, an isothermal step at 120 °C for 10 min was applied. All experiments were done in triplicate.

Antioxidant properties

DPPH assay modified from Erkan et al [22] was used to investigate the antioxidant properties of CMC-SC. The sample was dissolved to obtain a solution at a final concentration of 0.1, 1.0, and 10 mg/ml, respectively. An aliquot of 100 µl of the sample was mixed with 100 µl of 100 µM DPPH standard solution. The mixture was kept in a dark chamber for 30 min. The absorbance of the sample was then measured using a spectrophotometer at 517 nm and was used to calculate an antioxidant activity as shown in Eq. (5).

$$\% \text{Antioxidant activity} = \frac{(A_c - A_t)}{A_c} \times 100 \quad (5)$$

where A_c = absorbance at 517 nm of DPPH standard solution, A_t = absorbance at 517 nm of DPPH standard solution and the sample.

An antioxidant property of CMC-COM was used as a reference. In addition, the antioxidant activity of the sample was reported as IC_{50} (a concentration of the sample that has the potential to reduce the concentration of free radicals by 50%). The experiment was done in triplicate.

Scanning electron microscope (SEM) analysis

The surface morphology of CMC-SC was examined by using SEM analysis. A comparative analysis was conducted on the surface of the extracted cellulose. The sample was coated with gold and photographed at magnifications of 100, 300, 500 and 1000.

Preparation of CMC blend films

Blend films were prepared using a casting method modified from Sothornvit et al [23]. CMC-SC (2% w/w) and PVA (1% w/w) solutions were mixed with various concentrations of glycerol, i.e., 0.3, 0.5, 0.7 and 1.0% (w/w). Distilled water was used as a solvent and glycerol was applied as a plasticizer. The mixture was constantly stirred using a magnetic stirrer until it was thoroughly mixed. Air bubbles were removed by centrifugation at 5000 rpm for 5 min. The polymer mixture was cast onto a mold film and dried at 60 °C for 24 h to evaporate the solvent. The film was collected and removed from the mold. CMC-COM/PVA films

Table 1 Chemical composition of native sugarcane bagasse. Data represent average \pm SD.

Component	% by dry weight of native biomass
Cellulose	26.7 \pm 2.0
Xylan	8.6 \pm 1.0
Galactan	2.8 \pm 0.8
Arabinan+Mannan	3.6 \pm 2.0
Acid-soluble lignin	1.1 \pm 0.2
Acid-insoluble lignin	17.1 \pm 1.0
Water extractives	20.0 \pm 1.4
Ethanol extractives	2.5 \pm 0.3
Ash	11.6 \pm 1.4
Mass closure	94.0

were prepared as control films. The blend films were stored in a desiccator for further analysis.

Characterization of blend films properties

Thickness

The thickness of the CMC-SC/PVA and the CMC-COM/PVA films was measured with a thickness gauge. The measurement was conducted by randomly measuring three positions on a 12 \times 50 mm testing film. An average thickness value was calculated.

Mechanical properties

CMC-SC/PVA blend films were cut into strips (12 \times 50 mm) and used as test specimens. Tensile strength and elongation at break of CMC-SC/PVA blend films were measured using a Universal Testing Machine (Tinius Olsen TMC, PA, USA) equipped with a 500 N load cell in accordance with ASTM D882-02. The crosshead speed was set at 10 mm/min with a gauge length of 5 cm. Comparative testing was conducted on the mechanical properties of CMC-COM/PVA blend films. The measurement was done in triplicate.

Statistical analysis

Averages and standard deviations (SD) of the data were calculated using Excel (Microsoft; Redmond, WA, USA). Statistical analysis was performed using IBM's SPSS program, version 22 statistical package (Microsoft; Chicago, IL, USA, license number ICN:793700) with a one-way ANOVA test and Duncan's multiple range test (DMRT) at 95% confidence.

RESULTS AND DISCUSSION

Chemical composition of native sugarcane bagasse

The native sugarcane bagasse sample contained 91.1 \pm 1.4% total solids. Table 1 shows chemical components determined in the native biomass. Cellulose (26.7%) was the major constituent found in the sample. Hemicellulose (xylan, galactan, arabinan and mannan), the other source of structural carbohydrates, accounted for \approx 15% of the sample. Total lignin

(ASL + AIL) was responsible for 18.2% by dry weight of the native biomass. Water extractives contained hydrophilic compounds such as inorganic materials, non-structural sugars, and nitrogenous materials while ethanol extractives contained hydrophobic compounds such as waxes and chlorophylls [16]. Minerals were detected as ash content. A study reported that sugarcane bagasse contained 40–50% cellulose, 25–35% hemicellulose, 15–20% lignin and lesser amounts of mineral, wax, and other compounds [24]. Other studies revealed that sugarcane bagasse contained 42–55% cellulose, 19–27% hemicellulose and 20–21% lignin. [25, 26]. Our sample contained lower amounts of cellulose and hemicellulose than those reported in the literature. However, the amount of lignin was comparable. The differences in the chemical composition may have resulted from the differences in the sugarcane cultivar and environments. These factors affect plant cell wall composition [27]. The chemical composition of the sugarcane bagasse used in this study was analyzed using the NREL method. Three separate determinations (with three replicates each time) were carried out. The results were in close ranges as shown in Table 1 with a mass closure of 94.0%. Some factors including high extractives, high ash and relatively high lignin affected the holocellulose content of the sample. Planting environments influence these factors.

It is worth noting that amounts of arabinan and mannan were reported as the combination of both compounds. The HPLC column was unable to completely resolve the arabinose and mannose peaks under the tested condition (data not shown). The identity of both compounds was confirmed by the standard solution of both sugars.

Total solid recovery and cellulose content after extraction

The total solid recovery after the alkaline hydrogen peroxide pretreatment was 35.5 \pm 0.8% by dry weight of the native biomass. The solid recovered from the pretreatment was subjected to cellulose determination. The amount of cellulose in the recovered solid was 66.5 \pm 2.7% by dry weight of the pretreated biomass. The results revealed that cellulose was the major component in the pretreated solid. In comparison to the cellulose content in the native biomass, as shown in Table 1, the amount of cellulose in the pretreated solid was equivalent to 23.6 \pm 0.9% by dry weight of the native biomass. This suggests that 88.4 \pm 3.6% of the cellulose in bagasse was recovered after the alkaline hydrogen peroxide pretreatment.

A study revealed that using solely NaOH in the pretreatment caused significant removal of lignin (67–87%) when applied 5% (w/v) NaOH to rice straw at relatively mild conditions (50–100 $^{\circ}$ C, 1–5 h, 3% solid loading) [28]. Delignification occurs due to the mechanism of solvation and saponification of intermolec-

ular ester bonds between lignin, hemicellulose, and cellulose. In contrast, cellulose was preserved in the pretreated solid due to its low reactivity with alkali and its high crystallinity [29]. Another study showed that combining NaOH with H_2O_2 at a lower temperature enhanced the effectiveness of cellulose isolation. More than 60% of recovered solids from rice straw were cellulose [9]. This agrees with the results obtained from this present study. The combination of alkali and H_2O_2 enhances effectiveness in removing components other than cellulose. H_2O_2 is degraded to form a hydroxyl radical ($HO\cdot$) which reacts rapidly with lignin. This reaction generates low molecular weight and water-soluble products from lignin leading to delignification of lignocellulose [30]. In this study, the pretreated biomass with high cellulose content served as a good quality raw material for CMC synthesis.

Yield of CMC

CMC-SC was synthesized through the alkalization reaction of cellulose with NaOH solution (final concentration $\approx 5\%$, w/v) in the presence of isopropanol, followed by carboxymethylation with sodium monochloroacetate. The carboxymethylation process occurs immediately under the alkaline condition. Firstly, cellulose chains are swollen by NaOH, and the accessibility of the cellulose chain is increased to allow substitution of the hydroxyl groups with carboxymethyl groups at C2, C3 and C6. The feasibility of the substitution is affected by the crystallinity and regularity of the cellulose structure. There is a higher chance of substitution when the cellulose has a more amorphous region [10]. The appearance of CMC-SC powder was off-white in color and odorless. It was partially soluble in water ($56.2 \pm 0.5\%$ CMC-SC was soluble in water at $50^\circ C$). The yield of CMC-SC obtained in the present study was $95.8 \pm 1.3\%$ and it was comparable to those obtained from 10 cultivars of rice straw [9]. One study revealed that higher NaOH concentrations (20–30%, w/v) during the alkalization process of cellulose derived from sugarcane bagasse favored the formation of CMC, with yields of 120–180 g/100 g reported (relative yields to 100 g of cellulose). However, above 30% (w/v) NaOH, the CMC yield decreased due to an undesired reaction that favored the formation of sodium glycolate more than CMC [10]. The increase in NaOH concentrations to a certain value during the synthesis corresponded to the increase in CMC yield [7]. However, in the present work, the NaOH concentration was constant during the synthesis. It is worth noting that the NaOH concentration used in the synthesis process was significantly lower compared to that found in the literature. However, a high yield of CMC-SC was still attained.

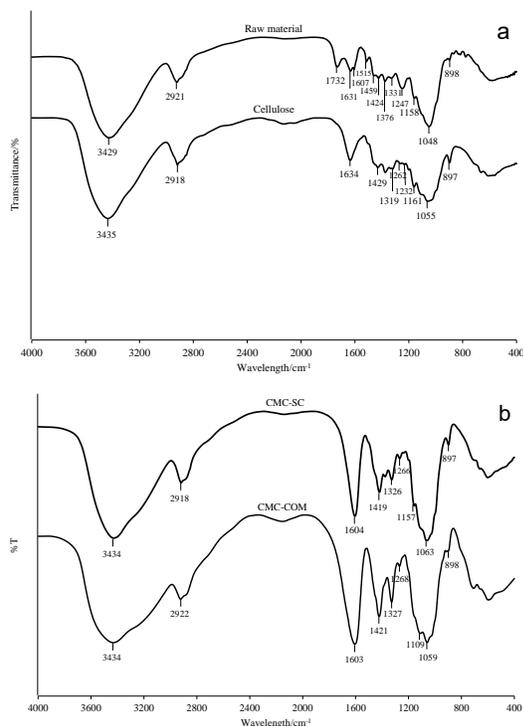


Fig. 1 Comparison of FTIR spectra: (a) raw material (sugarcane bagasse) and extracted cellulose; (b) CMC-COM and CMC-SC.

Characterization of CMC-SC

FTIR analysis

FTIR spectra of the sugarcane bagasse sample (raw material) and extracted cellulose are shown in Fig. 1a. A comparison of the FTIR spectra of CMC-SC and CMC-COM are shown in Fig. 1b. The FTIR spectra of all samples have the same absorption bands at 3600–2800 cm^{-1} in FTIR for the stretching vibrations of CH and OH [31]. The peaks at 877–898 cm^{-1} of all samples are related to C–O–C stretching at the β -(1,4)-glycosidic linkage of cellulose [31, 32]. Some other peaks indicate chemical changes in the polymer structures of the raw material, extracted cellulose and CMC-SC.

In the raw material, the peak at 1732 cm^{-1} refers to the C=O stretching band of hemicellulose [31]. The peak at 1048 cm^{-1} typically indicates xylan as a dominant constituent of hemicelluloses [33, 34], which concurs with the findings of the chemical composition of native sugarcane bagasse as shown in Table 1. The peak at 1607 cm^{-1} is related to the aromatic skeleton vibrations of lignin. The C–H deformations and aromatic ring vibrations of lignin and the HCH and OCH in-plane bending vibrations of lignin appear at 1459 cm^{-1} and 1424 cm^{-1} , respectively [31]. The peak at 1515 cm^{-1} is related to C=C stretching of

lignin [11, 32]. The stretching of the C=O group of the syringyl ring at 1331 cm^{-1} indicates phenolic compounds [33]. These peaks (1732 cm^{-1} , 1048 cm^{-1} , 1607 cm^{-1} , 1515 cm^{-1} and 1331 cm^{-1}), which are associated with hemicelluloses and lignin, are absent in the cellulose extract and CMC-SC.

The peaks at 1631 cm^{-1} and 1634 cm^{-1} found in the FTIR spectra of the raw material and the extracted cellulose, respectively, are related to the O–H bond of cellulose structure [11]. The peak at 1319 cm^{-1} in the extracted cellulose is related to a CH_2 wagging vibration in cellulose [35]. The peaks at 1158 cm^{-1} , 1161 cm^{-1} found in the raw material and extracted cellulose are related to anti-symmetric bridge stretching of C–O–C groups in cellulose [35], which is also present in the CMC-SC structure (the peak at 1157 cm^{-1}). The intensity of the peak at 1634 cm^{-1} in the extracted cellulose indicates higher purity of cellulose compared to the raw material. However, some contamination of lignin in the extracted cellulose was detected by the presence of a peak at 1232 cm^{-1} in the spectra, which refers to the acetyl group of lignin [11, 35]. Nevertheless, a substantial amount of lignin was removed from the extracted cellulose. This phenomenon is represented by the disappearance of the peaks at 1607 cm^{-1} and 1515 cm^{-1} that are related to the aromatic skeleton vibration of lignin [30]. Singh and Singh [3] assigned the absorption band at 1249 cm^{-1} to C–O stretching of ether linkage in lignin. In addition, Golbaghi et al [11] reported that the peak at 1252 cm^{-1} was related to the stretching bond of the aryl group of lignin. Besides these two important peaks, the absence of the peak at 1247 cm^{-1} (corresponding to the peaks reported in the literature) also confirmed that most of the lignin had been removed.

In terms of CMC-SC, the difference in the intensity of the peaks at 1604 cm^{-1} and 1419 cm^{-1} compared to those of the extracted cellulose indicates a C=O bond of carboxymethyl group substitution [11]. This result agrees with the literature that used the same method of CMC synthesis but a different substrate [9]. These two peaks confirmed the success of CMC synthesis from sugarcane bagasse cellulose with no contamination of hemicellulose and lignin in CMC-SC, which could be observed from the absence of the peaks related to hemicellulose and lignin as discussed above. A similarity between the FTIR spectra of CMC-SC and those of CMC-COM was found, which was the DS of 0.9 (Fig. 1b). The characteristics of the peaks at 1604 cm^{-1} and 1419 cm^{-1} of the CMC-SC spectra and the peaks at 1603 cm^{-1} and 1421 cm^{-1} of the CMC-COM spectra shared the common characteristics of carboxymethyl substitution.

XRD analysis

The XRD analysis revealed the crystallographic structure, chemical composition, and physical properties of

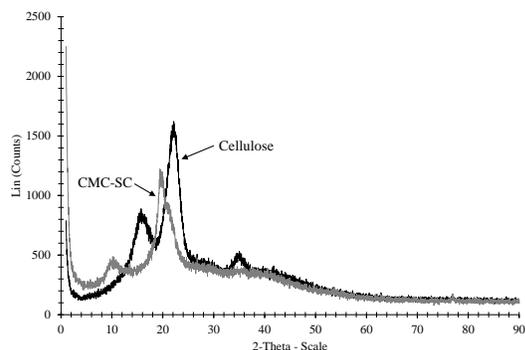


Fig. 2 Comparison of XRD chromatograms between extracted cellulose and CMC-SC.

the material [8]. The XRD patterns of the extracted cellulose and CMC-SC are illustrated in Fig. 2. The two sharp peaks which appeared in the XRD pattern of the cellulose were typical characteristics found in cellulose [8]. The height of the peak indicates the crystallinity level of the sample. In comparison, the peak height of CMC-SC was lower than that of the cellulose. This suggests that CMC-SC had lower crystallinity compared to its starting material (cellulose). It is clear that the alkalization process during the CMC synthesis had an effect on the crystallinity of the final product by reducing its crystallinity since the crystallinity of the cellulose is associated with intermolecular and intramolecular hydrogen bonds of cellulose. Thus, this reduction resulted from the cleavage of hydrogen bonds when the cellulose was treated with NaOH during the alkalization [3]. This result agrees with the literature [9].

Degree of substitution (DS)

Degree of substitution refers to the average number of carboxymethyl groups per monomer unit [4]. The substitution by carboxymethyl groups occurs at positions C2, C3 and C6 of the cellulose structure. If no substitution occurs, the DS value is 0 (cellulose). In theory, fully substituted cellulose would have the highest possible attained DS ($\text{DS} = 3$) [10]. The DS of the CMC-SC obtained in this study was 0.7. The DS is the most important factor because industrial applications of CMC depend on the DS [3] since the DS affects the average M_w and DP of CMC as well as solubility and viscosity. Thus, usage in CMC applications such as stabilizing agents and moisture absorbents is determined by the DS of CMC. Typically, the DS range of commercial CMC is between 0.5 and 1.4 [36]. The roles of DS, average M_w , DP and viscosity are discussed below.

Average M_w and DP

The average M_w and DP of CMC-SC were 2.0×10^6 and 9,024, respectively. The carboxymethyl substitution at

the hydroxyl group position increases the molecular weight of the synthesized CMC to one higher than that of cellulose. This means that the higher the DS, the higher the M_w . In addition, DP is a function of molecular weight and DS as displayed in Eq. (4). A higher DS yields a lower DP. In comparison, the CMC-COM used in this study had a higher DS value (0.9) but had a lower M_w ($\sim 250,000$) than those of CMC-SC. If these two values are used in Eq. (4), the calculated DP of CMC-COM is 1,068. This illustrates the relationship between DS and DP according to the equation, i.e., the higher DS of CMC-COM resulted in a lower DP when compared to CMC-SC. In contrast, the higher average M_w and the lower DS of CMC-SC compared to those of CMC-COM did not support the substitution theory. However, the theory and the relationship between these parameters might be applicable when comparing with the CMC synthesized from the same raw material. In this case, the sources of the raw materials of CMC-SC and CMC-COM were different. The complexity and molecular arrangement of cell wall architecture varies depending on plant species [25]. The other explanation is that the NaOH concentration during CMC synthesis influences the DS value. At a higher NaOH concentration, polymer chain degradation occurs [10]. CMC-SC was synthesized using a relatively low NaOH concentration (final concentration $\approx 5\%$, w/v). This might be the main effect that led to the high DP value.

Viscosity

Viscosity is a measurement of a solution's resistance to gradual deformation by shear stress [10]. For comparison, the viscosity of a CMC-COM (DS = 0.9; $M_w \sim 250,000$) solution and a CMC-SC solution with the same concentration (4% w/v) was tested under the same condition. The result revealed that the viscosity of CMC-COM (703 ± 34.3 cP) was approximately 10 times higher than that of the CMC-SC (65.7 ± 8.6 cP). In theory, many factors influence the viscosity value of CMC including CMC concentration, sodium monochloroacetate concentration [6], NaOH concentration, temperature, DS [10] and M_w [37]. As reported in the literature, CMC viscosity increased as DS increased since carboxymethyl groups (hydrophilic groups) in CMC have a high ability to be soluble in water [7, 10]. In this study, CMC-COM had a higher DS than CMC-SC. However, the average M_w and DP of CMC-SC were substantially higher than those of CMC-COM. As stated above, the solubility of CMC affects the viscosity of the CMC solution. Hence, further study was conducted to reveal the solubility of CMC-SC. In total, 2 g (dry weight) of CMC-SC was extracted using Soxhlet apparatus with 250-ml of distilled water for 2 h. The dry weight of the residues of CMC were determined after they had been dried. The result showed that only $56.2 \pm 0.5\%$ of CMC-SC was soluble while CMC-COM was completely soluble. This suggests that

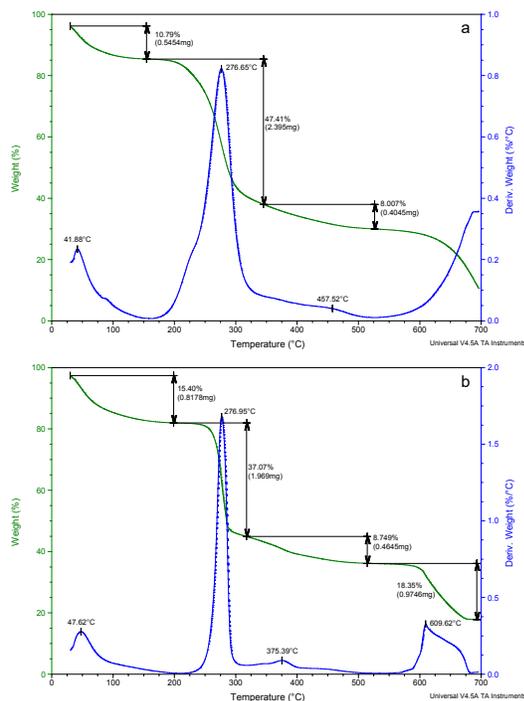


Fig. 3 Thermal degradation profiles of CMC obtained by TGA: (a) CMC-SC and (b) CMC-COM.

solubility of the CMC solution plays an important role in its viscosity.

Thermal properties

TGA is a technique used to determine the thermal stability of materials through the measurement of weight change with temperature [11]. Thermal degradation profiles of CMC-SC and CMC-COM analyzed by TGA are shown in Fig. 3a and 3b, respectively. Both samples show a three-step degradation under N_2 flow rate. Initial weight losses of 10.79% for CMC-SC and 15.40% for CMC-COM between 30 and 180 °C were observed due to the removal of moisture and some unknown volatile organics with smaller molecular weights [11, 21, 38]. The decomposition of CMC-SC started at 180 °C while the decomposition of CMC-COM started at 225 °C. The differences in the starting degradation temperatures implied that CMC-SC had a lower thermal stability than that of CMC-COM. The decomposition of CMC-SC had a sharp mass loss at 300 °C. This phenomenon was also found in CMC-COM. These results were in accordance with those reported by Ge and Li [38], who revealed that sodium carboxymethylcellulose from sugarcane bagasse had the same thermal degradation behavior. The second weight loss for CMC-SC occurred in the 200–400 °C range and was a result of the decarboxylation of COO-groups in CMC and the loss of CO_2 [11]. The final

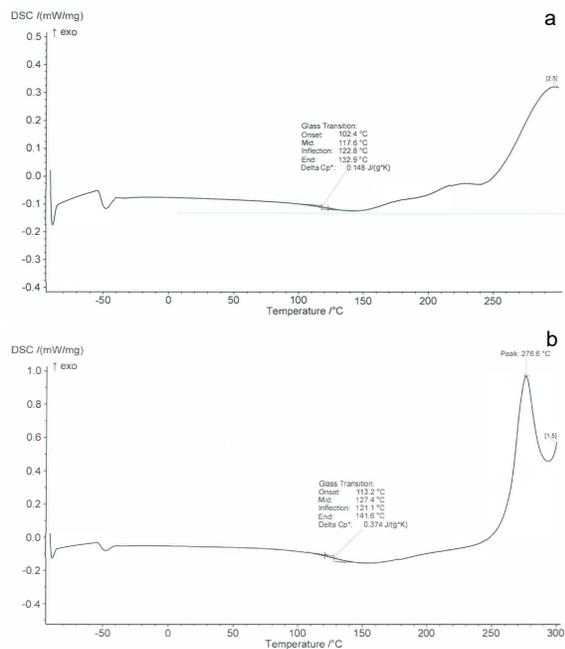


Fig. 4 DSC thermograms of CMC samples: (a) CMC-SC and (b) CMC-COM.

step at 600–700 °C was a result of the degradation of residual organic fractions [21]. The final weight of the remaining CMC-SC at 700 °C was about 10% of its original weight.

CMC-SC and CMC-COM samples were investigated by DSC analysis and the thermograms obtained (heat flow vs. temperature) revealed similar tracings (Fig. 4a and 4b). The main thermal transitions observed were: (i) an endothermic transition during the first scan attributed to water evaporation; (ii) an endothermic transition during the second scan close to 250 °C, which was associated with the melting temperature (T_m) of the crystalline regions of the CMC; and (iii) an exothermic transition between 250 to 300 °C attributed to the thermal degradation of the CMC structure. These results corresponded to those reported in the literature [21]. The glass transition temperature (T_g) of CMC-SC was 102.4 °C and T_g of CMC-COM was 113.2 °C. These T_g values were considerably higher than those reported in the literature [39, 40], where the T_g value of sodium carboxymethylcellulose (NaCMC) was about 55 °C. NaCl did not affect thermal transition values close to T_m . However, it influenced T_g , and the thermal and mechanical properties close to T_g [21].

Antioxidant properties

DPPH radical scavenging activity was tested to determine the antioxidant property of CMC-SC. The antioxidant activity of the sample was evaluated by the inhi-

Table 2 Antioxidant properties of CMC-SC and CMC-COM. Data represent average \pm SD.

CMC concentration (mg/ml)	% Antioxidant activity*	
	CMC-COM	CMC-SC
0.1	20.9 \pm 0.0 ^{CB}	34.8 \pm 0.0 ^{CA}
1.0	22.7 \pm 0.1 ^{BB}	35.8 \pm 0.0 ^{BA}
10.0	24.7 \pm 0.0 ^{AB}	40.7 \pm 0.0 ^{AA}

* Different lower-case letters within one column are significantly different ($p < 0.05$). Different upper-case letters within one row are significantly different ($p < 0.05$).

bition percentage of DPPH. The antioxidant activities of different concentrations of CMC-SC (0.1, 1.0 and 10 mg/ml) were tested and compared to those of CMC-COM with the same concentrations. The results are shown in Table 2. All CMC-SC samples had higher antioxidant activities compared to those of CMC-COM. The antioxidant activities ranged from ca. 34% to 40% depending upon the CMC concentration. As the CMC concentrations increased, the antioxidant activities increased. The antioxidant activities were converted into IC_{50} . The results confirmed that CMC-SC had a higher antioxidant property compared to CMC-COM. The IC_{50} value of CMC-SC (25.8 mg/ml) was approximately 3.5-fold lower than that of CMC-COM (88.3 mg/ml). This suggests that a lower concentration of CMC-SC was required to quench the oxidation reaction in order to reduce the radical concentration by 50%. Fan et al [41] reported that NaCMC had 11.5% scavenging activity on DPPH. CMC-SC in this present work had a better antioxidant property compared to that reported in the literature. When CMC-SC was compared to CMC-COM, CMC-SC has better antioxidant property which may be due to residual lignin. CMC-SC may have the residual lignin remaining from the cellulose extraction that contains phenolic groups. The amount of the residual lignin might be too low to be detected by the FTIR analysis. The purity of CMC-SC may be lower compared to that of CMC-COM. Phenolic groups have an antioxidant property since they react with the free radical DPPH. Thus, they contribute to the better antioxidant property of CMC-SC compared to that of CMC-COM.

SEM analysis

Morphological structures of the extracted cellulose and CMC-SC were analyzed by using the SEM method with different magnifications (Fig. 5). The external surface of CMC-SC was smoother than that of the extracted cellulose. The smooth surface of CMC-SC suggests that the cellulose fiber was intensely carboxymethylated [8]. In addition, the morphological structure of CMC-SC was less compact and less ordered compared to that of the cellulose fibers. The carboxymethylation creates a steric effect between the cellulose chains and

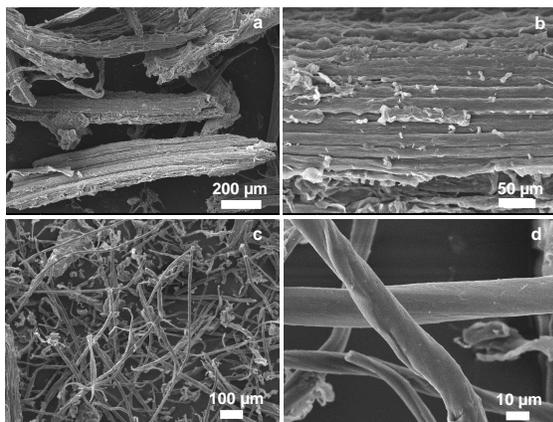


Fig. 5 SEM images for comparison of morphological structures of extracted cellulose (a = 100 × ; b = 1000 × magnification) and CMC-SC (c = 100 × ; d = 1000 × magnification).

electrostatic repulsion between fibers. Thus, it reduces the structural crystallinity of the CMC [42]. The latter effect was confirmed by the XRD results.

Blend films properties

Mechanical properties

Blend films of CMC-SC (2% w/w) and PVA (1% w/w) were prepared using a solution casting method, and the effect of glycerol at concentrations ranging from 0.3–1.0% (w/w) was evaluated. Table 3 shows the comparison of film tensile strength and elongation at break of CMC-SC/PVA, CMC-COM/PVA and CMC-COM blend films. All films tested had a thickness of 0.10 mm. This thickness is suitable for use as a plastic film since the standards for the thickness of a food packaging film range from 0.010–0.100 mm (TIS.1027-2553). The tensile strength values of the CMC-COM films and CMC-COM/PVA films were significantly higher than those of the CMC-SC/PVA films. It seemed that the high level of carboxymethyl substitution on the commercial CMC (DS: 0.9) provided more intermolecular interaction among the polymer chains, thus it increased the film tensile strength [7]. Contrary to the pattern of tensile strength, elongation at break of all prepared films was significantly enhanced after increasing glycerol concentration. As a plasticizer, glycerol has been reported to be capable of reducing the strength of interaction between polymer chains improving mobility [43]. The elongation at break values of all CMC-SC/PVA films were statistically higher than those of the CMC-COM films and the CMC-COM/PVA films except the CMC-COM/PVA film with 0.5% glycerol.

The increase or decrease in the values of tensile strength and elongation at break varied due to the change in glycerol concentrations. A study found that

increasing glycerol concentrations (10–30%, w/w) reduced tensile strength but increased elongation at break of CMC films obtained from rice stubble [44]. Thus, glycerol concentrations substantially modified the mechanical properties of the films. The hydrophilicity of glycerol attracts water into the polymer matrix. This enhances the free volume of the polymer resulting in higher film extensibility and lower mechanical strength of the films. All CMC-SC/PVA blend films prepared with different concentrations of glycerol had better properties compared to those of CMC-COM films without copolymer blending. The structures of the cross-linked based CMC/PVA films and glycerol contain more hydroxyl groups that reduce the steric hindrance between the chains resulting in higher film extensibility. We stated that the hydroxyl groups in glycerol successfully worked as cross-linkers between CMC-SC and PVA chains, reducing the steric hindrance and enhancing film extensibility. At a glycerol concentration of 0.5%, the elongation at break value of both CMC-COM film (13.3%) and CMC-SC/PVA film (14.7%) was comparable with an oil palm empty fruit bunch (EFB) CMC film (13.8%), as previously reported [45]. Since CMC is non-toxic and biodegradable, it could be stated that the use of CMC-SC was promising for use in PVA blend film which could potentially be used in food packaging applications. CMC-SC/PVA films had high elongation at break values, especially with 1.0% glycerol. A strength property such as high elongation at break enhances the film stretching capacity, which is suitable for food packaging applications. Besides, CMC-SC powder had high antioxidant activity, which is useful for making food packaging. This antioxidant property is essential for extending food shelf-life.

CONCLUSION

In this study, sugarcane bagasse biomass contained cellulose as a major component. Cellulose was extracted from the sample using the alkaline hydrogen peroxide pretreatment at a low temperature. CMC-SC was successfully synthesized from the extracted cellulose. The yield of the CMC obtained implied that 1 ton of sugarcane bagasse (dry weight) can be used to produce approximately 255 kg of CMC. The distinguishing characteristics of CMC-SC included its high average M_w , high DP , and antioxidant property. Residual lignin containing phenolic groups may enhance the antioxidant property of CMC-SC. The thermal property of CMC-SC was determined to elucidate its degradation profile. CMC-SC had a lower thermal stability than that of CMC-COM. Blend films of CMC-SC/PVA showed better mechanical properties (tensile strength and elongation at break) than the CMC-COM films with no copolymer crosslink. With a copolymer crosslink, CMC-SC/PVA films had higher elongation at break compared to CMC-COM/PVA films. A higher

Table 3 Tensile strength and elongation at break of blends films of CMC-SC/PVA with different concentrations of glycerol as a plasticizer. Data represent average \pm SD.

Glycerol (%, w/w)	Mechanical Properties*					
	Tensile strength (MPa)			Elongation at break (%)		
	CMC-COM	CMC-COM/PVA	CMC-SC/PVA	CMC-COM	CMC-COM/PVA	CMC-SC/PVA
0.3	20.3 \pm 1.1 ^{ab}	24.7 \pm 2.4 ^{aA}	8.7 \pm 0.1 ^{aC}	6.4 \pm 0.1 ^{dC}	9.9 \pm 1.6 ^{cb}	13.8 \pm 0.2 ^{ca}
0.5	10.9 \pm 0.5 ^{ba}	12.9 \pm 1.6 ^{ba}	6.5 \pm 0.2 ^{bb}	13.3 \pm 0.4 ^{cb}	17.7 \pm 1.7 ^{ba}	14.7 \pm 0.2 ^{cb}
0.7	8.7 \pm 0.3 ^{cb}	11.5 \pm 0.8 ^{ba}	4.1 \pm 0.1 ^{cc}	19.2 \pm 0.5 ^{bb}	18.2 \pm 1.8 ^{bb}	29.6 \pm 1.0 ^{ba}
1.0	5.4 \pm 0.2 ^{da}	6.5 \pm 1.2 ^{ca}	3.6 \pm 0.2 ^{db}	28.7 \pm 1.0 ^{ac}	33.3 \pm 2.1 ^{ab}	39.2 \pm 2.0 ^{aa}

* Different lower-case letters within one column are significantly different ($p < 0.05$). Different upper-case letters within one row are significantly different ($p < 0.05$).

concentration of glycerol, a plasticizer, yielded better mechanical properties of the films. Based on the obtained results, CMC-SC and CMC-SC/PVA films can be candidates for use in the food industry as food additives and food packaging, respectively.

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