สมบัติของฟิล์มคาร์บอกซีเมทิลเซลลูโลสจากเปลือกทุเรียน โดยการทรีตด้วยโซเดียมไฮดรอกไซด์ที่ความเข้มข้นต่าง ๆ

The properties of carboxymethyl cellulose films from durian rind with treatment of different sodium hydroxide concentrations

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บทคัดย่อ

คาร์บอกซีเมทิลเซลลูโลสจากเปลือกทุเรียน (CMC_d) ถูกสังเคราะห์ขึ้นภายใต้สภาวะเบสโดยใช้กรดมอโนคลอโรแอซีติก (MCA) เป็นตัวให้หมู่คาร์บอกซีเมทิล ในตัวกลางไอโซโพรพานอล (IPA) โดยใช้โซเดียมไฮดรอกไซด์ในปริมาณที่แตกต่างกัน (20, 30, 40, 50, and 60 %NaOH) ในการทำปฏิกิริยา ฟิล์ม CMC_d ที่เตรียมขึ้นมา ถูกนำมาทดสอบสมบัติเชิงกล (แรงดึงขาด (TS) และร้อยละการยืดขาด (EB)) การซึมผ่านไอน้ำ (WVTR) และซอพชันไอโซเทอม แนวโน้มของค่า TS เพิ่มขึ้นเมื่อความเข้มข้นของ NaOH ในการทำปฏิกิริยาเพิ่มขึ้น (20-40%) แต่ค่า TS กลับลดลงเมื่อความเข้มข้นของ NaOH เพิ่มมากกว่า 40% ส่วนค่า EB ของฟิล์มแต่ละสภาวะมีค่าไม่แตกต่างกัน ฟิล์ม CMC_d จากการสังเคราะห์โดย 30% NaOH ให้ค่า WVTR มากที่สุด ในขณะที่ฟิล์มสภาวะอื่นๆ แสดงผลที่ไม่แตกต่างกัน (20, 40, 50, และ 60%) ฟิล์ม CMC_d ให้สมบัติของซอพชันไอโซเทอม เป็น ซิกมอยด์-เซพ ชนิดที่ 2

ABSTRACT

Carboxymethyl cellulose from durian rind (CMC_d) was synthesized under alkaline condition using monochloroacetic acid (MCA) as carboxymethylating agent. Isopropanol (IPA) was employed as a medium. The reaction was preformed with various amount of sodium hydroxide (20, 30, 40, 50, and 60 %NaOH). The CMC_d films were prepared and investigated on mechanical properties (tensile strength (TS) and percent elongation at break (EB)), water vapor transmittion rate (WVTR), and sorption isotherm. The trend of TS of CMC_d films was increased with increase of NaOH concentration (20-40%) but it decreased after 40%NaOH. The results of EB were not different in each CMC_d film. The highest WVTR value was provided from the film cast from CMC_d synthesized with 30% NaOH. The CMC_d films cast from

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CMC_d synthesized with other amount of NaOH (20, 40, 50, and 60%) were not different in WVTR value. The CMC_d films gave the characteristic of sorption isotherm as sigmoid-shaped type II isotherm.

Keywords Carboxymethyl cellulose, durian rind, eidble film, tensile and barrier properties, sorption isotherm, sodium hydroxide

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INTRODUCTION

The conversion of agricultural waste materials into useful products would alleviate a variety of socio-economic problems. Agricultural wastes comprise of celluloses which are amenable to both chemical and biochemical modifications. Carboxymethyl cellulose (CMC) is another important artificial-nature polymer derived from cellulose.

CMC is a copolymer of two units: ß–D–glucose and ß–D–glucopyranose 2–O–(carboxymethyl)–monosodium salt, not randomly distributed along the macromolecule, which are linked via ß–1,4–glycosidic bonds. The substitution of the hydroxyl groups by the carboxymethyl group is slightly preponderant at C–2 of the glucose (Charpentier et al., 1997). CMC is obtained by activation of the cellulose with aqueous NaOH in slurry of an aqueous organic solvent following reacting the cellulose with monochloroacetic acid. CMC is widely applied in a lot of industrial sectors including food, paper making, paints, pharmaceutics, mineral processing and cosmetics (Barbucci et al., 2000) due to it is simply and low cost to process. In addition, it is used in other applications such as fruit coating (Rachtanapun et al., 2008), film (Rachtanapun et al., 2007a; Rachtanapun et al., 2007b) and polymer blend (Rachtanapun, 2009; Cheng et al., 2008; Go'mez-Burgaz et al., 2008). Many researchers reported the preparation and properties of CMC from agricultural waste as cellulose sources such as sago waste (Pushpamalar et al. 2006), orange peel (Ya**ş**ar, et al. 2003), sugar beet pulp cellulose (To**ğ**rul et al. 2003), sugarcane bagasse waste (Cerqueira, et al. 2009), papaya peel (Rachtanapun et al. 2007a), waste of mulberry paper (Rachtanapun et al., 2007c), However, very little work has been done on CMC film from agricultural wastes.

In our previous studies, properties of CMC film from agricultural wastes as cellulose sources were invewstigated. We studied the production of CMC films from papaya peel and their mechanical properties (Rachtanapun et al. 2007a). The effect of blend CMC from papaya peel/corn flour films on mechanical properties and water vapor permeability was also studied (Rachtanapun, 2009). In addition, the effect of sodium hydroxide concentration on mechanical properties of carboxymethylcellulose films from waste of mulberry paper was presented (Rachtanapun et al., 2007c). Furturemore, study on hydrogen bonds of carboxymethyl cellulose sodium film with two-dimensional correlation infrared spectroscopy was studied by Li et al. (2009). In this study, the effect of NaOH concentrations of CMC_d on mechanical properties

[tensile strength (TS) and elongation at break (EB)], water vapor transmittion rate (WVTR) and sorption isotherm of CMC film were studied.

EXPERIMENTAL

Materials

Durian rind was obtained from Taladthai (Bangkok, Thailand). All chemicals used in the preparation and analysis of CMC were AR grade or equivalent. Sodium hydroxide was purchased from Lab-scan (Bangkok, Thailand); isopropanol, ethanol and methanol from Union science Co., Ltd. (Chiangmai, Thailand). Monochloroacetic acid was purchased from Sigma-aldrich (Steinhiem, Germany).

Extraction of cellulose

Cellulose was extracted from durian rind according to the method described by Rachtanapun et al. (2011) and Rachtanapun et al. (2007c). First, durian rind was cleaned, sun-dried and grounded. The grounded product was cooked with NaOH ,and then black slurry was obtained. The slurry was filtered and washed with water sevaral times and dried. Then, it was bleached with H_2O_2 and grounded into powder with size below 70 mesh and stored in polyethylene (PE) bag.

Synthesis of carboxymethyl cellulose from cellulose of durian rind (CMC_d)

CMC_d was synthesized according to the procedure described by Rachtanapun et al. (2007a), Rachatnapun and Rattanapanone (2009) and Rachtanapun et al. (2011). Cellulose powder, various amount of NaOH (20, 30, 40, 50 and 60% w/v) and isopropanol were mixed in the beaker for 30 min. Monochloroacetic acid was added to start the carboxymethylation including the mixture was continuously stirred at 55°C for 1.5 h. Then the mixture was placed in an oven at 55°C for 3.5 h. The mixture was filtered, suspended in methanol, and neutralized. Then, it was filtered and washed for several times with ethanol and with methanol for the final time. The final product, CMC_d, was dried and kept in dry place.

CMC_d film preparation

The 3.0 g of CMC_d was dissolved in 100 ml of distilled water at 80 °C for 10 min to prepare the film-forming solution. The solution was cooled down to 25°C and cast on to cellulose acetate plate (30 cm × 15 cm). Thickness of film was controlled by the amount of solution (70 ml) in each plate. The plate was left and dried at room temperature for 36 h, and then CMC_d film was obtained. The films were peeled, kept in PE bag and placed in desiccator to control the moisture content of the films. The film was cut for property testing before test. Mechanical properties testing (tensile strength and elongation at break) required the specimen of 1.5 cm × 14 cm rectangular strips (ASTM, D828-80a, 1995a). Circular specimen of 7 cm diameter was used for WVTR testing. Thickness of the films was measured using a micrometer model GT-

313-A (Gotech testing machine Inc., JAPAN). The average of thickness values was used in calculation of tensile strength.

Mechanical properties

Tensile strength (TS) and percentage elongation at break (EB) were determined using Instron Universal Testing Machine Model 1000 (H1K-S, UK). CMC_d films were preconditioned before testing. The precondition was described in detail elsewhere (Rachatanapun et al., 2007a). Initial grip separation and cross-head speed was set at 100 mm and 20 mm/min, respectively. The TS value was calculated by dividing the maximum load with the initial cross-sectional area of the specimen. The EB value was calculated as the percentage of change of the initial gauge length of a specimen (100 mm) at the point of a sample failure (ASTM, D828-80a, 1995a).

Water vapor transmission rate (WVTR)

WVTR was investigated by using the ASTM method (ASTM, E96-93, 1993). The cups containing ten grams of dried silica gel was covered with the specimens and sealed with paraffin wax. Sealed cups were weighed and kept at 25°C in a desiccator with saturated solution of sodium chloride (NaCl) to provide 75% RH. Then, the cups were re-weighed daily for 14 days. Water vapor transmission rate (WVTR) of films was measured from weight gain of the cups and calculated following by Equation 1:

$$WVTR = \frac{slope}{film\ area} \quad (1)$$

Where slope is the slope of linear equation of time (y-axis) versus weight gain (x-axis)

Moisture sorption isotherm

CMC_d film was cut into the size of 30 x 30 mm as a specimen, dried in an oven at 105°C for 3 h, and then placed in desicators containing silica gel for 2 days at 25±2°C. The specimens were then placed in several desiccators containing saturated salt solutions having known relative humidity of 16.1, 34.8, 55.0, 75.9 and 99.0%. In the desiccators containing salt solution of high relative humidity, a cotton wool bathed of 95% ethanol was used as a fungi static agent. The specimens were weighed daily until equilibrium was attained. ‘‘Equilibrium” was achieved when the change in weight did not exceed 0.1% for three consecutive weighings. Percent of equilibrium moisture content was calculated by Equation 2.

$$\%EMC = \{\frac{We}{Wi}(Mi + 1) - 1\} x100 \quad (2)$$

When We is the equilibrium weight of film specimen (g). Wi is the initial weight of film specimen (g) and Mi is the initial moisture content of film specimen (g/g). (Rachtanapun and Suriyatem, 2010; Rachtanapun and Thondeesuoontorn, 2008; Rachtanapun and Thondeesuoontorn, 2009a; Thondeesuoontorn et al., 2009).

Statistical Analysis

Data were analyzed by one-way analysis of variance (ANOVA) and Duncan's multiple range test ($p \leq 0.05$) using statistica software version 11.

RESULTS AND DISCUSSION

The researches related with film normally focused on the properties of the film as the mechanical properties such as tensile strength and elongation at break (Rachtanapun et al., 2007a, b, c). In this study, mechanical properties (tensile strength and elongation at break) of CMC_d films from several NaOH concentrations (20, 30, 40, 50 and 60%w/v) were determined. The results of tensile strength and elongation at break are shown in Figure 1 and 2, respectively. This is obvious that higher tensile strength of CMC_d film was achieved from higher NaOH concentration at initial (20 to 30%). However, at higher than 30% NaOH, decrease tensile strength of film was occurred. The result was related to many results in term of previous study such as DS and viscosity of CMC_d (Rachtanapun et al., 2011). We found the highest value of tensile strength was presented at CMC_d synthesized with 30% NaOH which also provide the highest yield, DS and viscosity value. This result was also similar with that of CMC from cellulose of *Mimosa pigra* peel (Rachtanapun and Ratanapanon, 2009) in previous study. In term of elongation at break of CMC_d film, they were not significant different between CMC_d in each condition.

The effect of NaOH concentration in alkalization on water vapor transmision rate (WVTR) of CMC_d was investigated. The weight gain of CMC_d film increased with increase of experiment time (data not shown). Table 1 lists water vapor transmission rate (WVTR) for CMC_d films synthesized with different of NaOH concentrations. The WVTR of CMC_d films were slightly different in each condition, while the film from 30% NaOH showed the highest value of WVTR. This is interestingly that the trend of WVTR was related with DS value which agee with our previous study (Rachtanapun et al., 2011). We found that when NaOH in carboxymethylation synthesis increased up to 30%, DS and WVTR increased. However, DS and WVTR would decreased as NaOH beyond 30%. This result could be explained by higher hydrophilic groups of CMC_d after substitued by carboxymethyl groups on cellulose structure. Some researches persented agreement such as cassava starch-CMC-gelatin blend film (Tongdeesoontorn et al., 2009), rice starch-chitosan blend film (Bourtoom and Chinnan, 2008) and chitosan-whey protein film (Ferreira et al., 2009). They presented that water vapor permeability (WVP) of film increased with increase of hydrophilic content in the film.

The curve of sorption isotherm for CMC_d films from different of NaOH concentrations in synthesis are shown in Figure 3. The sorption isotherm of all films gave the characteristic sigmoid-shaped type II isotherm (Cho and Rhee, 2002; Rachtanapun and Thongdeesoontorn, 2009; Tongdeesoontorn et al.,

2009; Rachtanapun and Suriyatem, 2010. This nonlinear sorption curves was occurred due to their hydrophilic property. At the same NaOH concentration, the increasing of percent relative humidity resulted in increasing the equilibrium moisture content (EMC) of CMC_d films. At each % relative humidity when NaOH concentration increased, EMC of CMC_d films increased as well. The highest EMC was 30% NaOH concentration which gave the highest DS value (DS = 0.87). The cause was the substitution of carboxymethyl, when DS value increased, hydrophilic also increased. Therefore, CMC_d films could absorb more water and EMC increased. Conversely, at 40% NaOH concentration, EMC decreased because DS value decreased (DS = 0.78) (Rachtanapun et al., 2011), so film adsorbed less water. This pnenomenon similar to previous literatures such as carboxymethyl cellulose films from carboxymethyl rice starch (Rachtanapun et al., 2009). It should be noted that the samples at 99%RH had water droppets on the surface and the %EMC of samples were above 200%. Therefore, the data at this point were omitted.

CONCLUSIONS

The cellulose was successfully extracted from durian rind. Then, the cellulose was converted to CMC by carboxymethylation with various NaOH concentrations. The CMC_d film was prepared and the effect of NaOH concentrations on mechanical properties, WVTR and sorption isotherm of the film were studied. The WVTR, tensile strengh and sorption isotherm were strongly related to DS. The highest tensile strenght, WVTR and EMC(%) were obtained from the film of CMC_d synthesized with 30% NaOH but the elongation at break is not different for varoius NaOH concentration.

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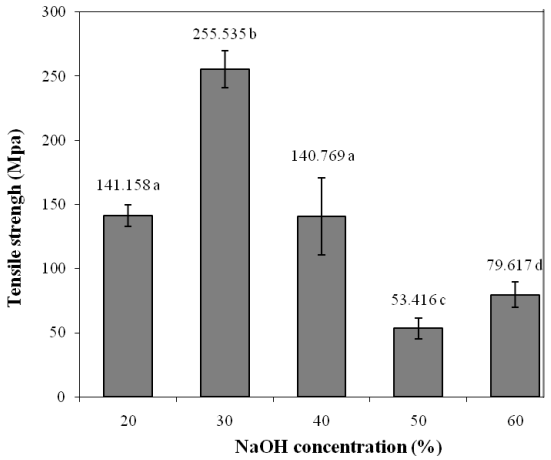

Figure 1. Tensile strength of CMC_d films synthesized with various NaOH concentrations.

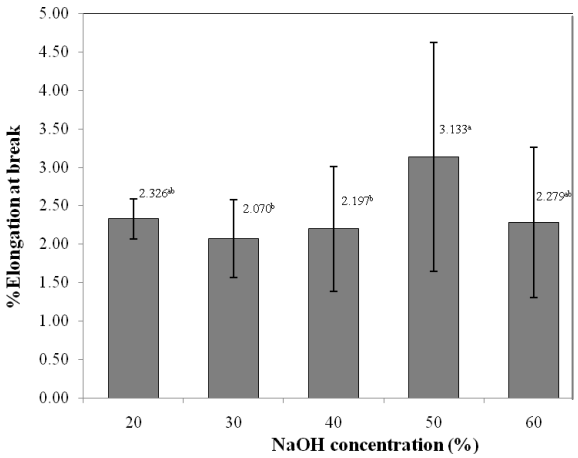

Figure 2. Percent elongation at break of CMC_d films synthesized with several NaOH concentrations

Table 1

Water vapor transmission rate and water vapor permeability for CMC films synthesized with various NaOH concentrations at 25°C, 75% RH.

Type of films	Water vapor transmission rate (WVTR) ($g/day.m^2$)
20%NaOH-CMC_d	205.518 ± 4.599 a
30%NaOH-CMC_d	220.847 ± 4.130 c
40%NaOH-CMC_d	211.060 ± 4.220 ab
50%NaOH-CMC_d	217.309 ± 1.081 bc
60%NaOH-CMC_d	204.575 ± 1.745 a

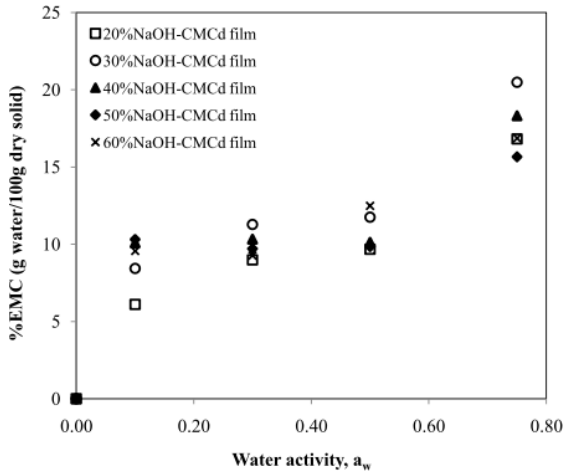

Figure 3. Sorption isotherm of CMC films synthesized with various NaOH concentrations (20, 30, 40, 50 and 60% w/v)

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