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Blended Films of Carboxymethyl Cellulose from Papaya Peel (CMCp) and Corn Starch

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ABSTRACT

Cellulose was extracted from papaya peels by NaOH and then modified by reacting with chloroacetic acid to obtain carboxymenthyl cellulose from the papaya peel (CMCp). Infrared (IR) spectroscopy was used to investigate changes in the functional group of the product obtained at carboxymethylation. A carbonyl peak (C=O) at 1600 cm^{-1}, the $–CH_2$ peak at 1420 cm^{-1} and the ether peak (-O-) at 1060 cm^{-1} on the IR spectra of CMCp increased substantially. The effect of corn starch content on the mechanical properties (tensile strength and %elongation) and water vapor permeability (WVP) of blended films of CMCp and corn starch was investigated. The addition of corn starch in the blended film resulted in an increase in tensile strength but a decrease in %elongation. The weight ratio for CMCp to corn starch of 25:75 gave the maximum tensile strength. This ratio was used to investigate the effect of plasticizer (glycerol) content on the mechanical properties and water vapor permeability (WVP). When glycerol was added to the blended films, the tensile strength decreased, but %elongation and WVP increased.

Key words: papaya peels, carboxymethyl cellulose, cmc, polymer, blend, mechanical properties, permeability

INTRODUCTION

Papaya (*Carica papaya L.*) belongs to the *Caricaceae* family and is grown in Thailand, Australia, Hawaii, the Philippines, Sri Lanka, South Africa, India, Bangladesh, Malaysia and a number of other countries in tropical America (Anuara, *et al.,* 2008). It originated in the lowlands of eastern Central America, from Mexico to Panama, and now can be found in all tropical countries and many sub-tropical regions of the world (Canini *et al.,* 2007). It was widely cultivated for its edible fruits or as a vegetable. In Thailand, raw papaya fruit is used for papaya salad (som tum) or pickled papaya. Thus, papaya peel has become a waste product from restaurants and pickled papaya manufacture. Papaya waste amounts to more than one thousand tons per year. Many researchers have tried to transform this waste into a valuable product. However, very little has been published on the utilization of papaya peel. Tongdeesoontorn and Kanaswat (2004) studied the isolation of hemicellulose from raw papaya peel and determined its constituent sugars. Chaiwut *et al*. (2007) studied the properties and protein components of papaya peel. Rachtanapun *et al.,* (2007a, 2007b and 2008) studied the synthesis of carboxymethyl cellulose from papaya peel and its applications.

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Cellulose is a linear, high molecular weight polymer and a biodegradable material. However, due to its strong inter- and intra-molecular hydrogen bonds, cellulose neither melts nor dissolves readily in common solvents (Hattori *et al.,* 2004). In order to utilize cellulose in the food industry, cellulose must be converted into its derivatives. One of the most common derivatives is carboxymethyl cellulose (CMC). CMC is a linear, long-chain, water-soluble, anionic polysaccharide. Purified CMC is a white- to cream-colored, tasteless, odorless, free-flowing powder (Keller, 1986; Hattori, *et al.,* 2004). Some papers have reported the synthesis of CMC from various agricultural wastes, such as sugar beet pulp (Sun and Hughes, 1998), banana pseudo stem (Hattori *et al.,* 2004), sago waste (Pushpamalar *et al.,* 2007), orange peel (Yasar *et al.,* 2007) and papaya peel (Rachtanapun *et al.,* 2007a and 2007b). CMC has many applications as a constituent in: foodstuffs, drugs, adhesives, lubricants, pesticides, cloth, ceramics, cement, and paper and coating (Boursier *et al.,* 1985; Koyama, 1988; Gayrish *et al.,* 1989; Soper 1991; Lee and Farre Torras 1993; Leupin and Gosselink 1999; S·nchez *et al.,* 1999; Seiichi and Shosuke 2000; Rachtanapun 2008).

In previous work, sun-dried papaya peel was ground to powder. In order to produce the cellulose pulp, papaya peel powder was delignified by a pulping process using NaOH. The cellulose was modified to carboxymethyl cellulose through a substitution reaction using monochloroacetic acid under alkaline conditions (Rachtanapun *et al.*, 2007a; 2007b). Applications of carboxymethyl cellulose from papaya peel (CMCp) include biodegradable film (Rachtanapun *et al.,* 2007a; 2007b) and coating for mango (*Mangifera Indica L.*) (Rachtanapun *et al.,* 2008). However, the mechanical properties of CMCp film from papaya peel were inferior to those of commercial carboxymethyl cellulose (CMCc) film. Some research reported that the addition of corn starch in starch/chitosan blended films could improve the mechanical properties of the films (Xu *et al.*, 2005). Therefore, in this study, the effect of corn starch content on the mechanical properties (tensile strength and elongation) and water vapor permeability (WVP) of blended films of CMCp and corn starch. Moreover, the effect of plasticizer (glycerol) on mechanical properties and water vapor permeability (WVP) of blended films of CMCp and corn starch was also determined.

MATERIALS AND METHODS

Cellulose extraction from papaya peel

Papaya peel was sun-dried for 2 d. Dried papaya peel was ground with a hammer mill (Armfield, England) to screen powder with a size below 1 mm. One hundred and fifty gram of papaya powder (88.3%dryness) was cooked with 0.5 M NaOH (3 liters) for 3 h. The black slurry obtained was filtrated and washed with cold water. The residue was dried overnight in an oven at 55° C. The percent yield of cellulose pulp from papaya powder delignified with NaOH solution was 19.14%. The cellulose was ground to pass through 70 mesh sieves and kept in polyethylene bags until used for modification of CMC in the next process (Rachtanapun *et al.,* 2007a).

Synthesis of carboxymethyl cellulose from papaya pulp

Cellulose pulp powder from papaya peel (15 g) was dispersed in 450 mL of isopropyl alcohol (IPA) and then stirred. Next, 50 mL of 40% NaOH was added into the mixture and further stirred for 30 min prior to adding chloroacetic acid (18 g) and stirring for 30 min. The mixture was covered with aluminium foil and placed in a hot air oven at 55°C for 3.5 h. The liquid phase was removed and the solid phase was washed with 100 mL of absolute methanol, neutralized with acetic acid (90% v/v) and then filtered using a Buchner funnel. The final product was washed five times

by soaking in 300 mL of ethanol (70% v/v) for 10 min to remove undesirable byproducts, before being washed again with 300 mL of absolute methanol. The CMC obtained from papaya peel (CMCp) was dried at room temperature overnight (Rachtanapun *et al.,* 2007a). The yield of CMCp was calculated using Equation 1:

$$\%yield\ CMCp = \frac{Weight\ of\ obtained\ CMC\ (g)}{Weight\ of\ dried\ cellulose\ (g)} \times 100 \quad (1)$$

The yield of CMCp obtained was 126.454%.

Film casting

Film-forming solutions of CMCp to corn starch (100:0, 75:25, 50:50, 25:75 and 0:100 w/w) were stirred at 90-95°C for 10 min. The temperature of the film-forming solutions was cooled down to 20-25°C (Rachtanapun *et al.*, 2007c) and the mixture solution was then cast with a tape casting machine at 10 rpm. An optimum weight ratio of CMCp/corn starch blends was added with glycerol (1 mL (3.33% v/w), 2 mL (6.66% v/w) and 3 mL (10.00% v/w)) and was cast as discussed previously. Film thickness was measured with a micrometer. Measurements were taken at five different locations on each sample and the average value was used to calculate the strength and water vapor transmission rate (WVTR) and water vapor permeability (WVP).

Mechanical properties and water vapor permeability of CMCp/corn starch blend films

Blended films of CMCp and corn starch were preconditioned at 27±2°C with 65±2% relative humidity for 24 h. Tensile strength (TS) and percentage of elongation at break (EB) were measured using an Instron Universal Testing Machine Model 1000 (H1K-S, UK) according to ASTM method (ASTM D882-80a, 1995a). Ten film samples were tested. The WVTR and WVP of the films were determined using the ASTM method (ASTM E96-93, 1993). Film samples were performed with three replicates. WVTR and WVP were calculated from Equations 2 and 3, respectively.

$$WVTR = \frac{slope}{film\ area} \quad (2)$$

where, slope is the slope of the graph of storage time against weight gain of blended films of CMCp and corn starch and the film area was 28.27 cm^2.

$$WVP = \frac{WVTR \bullet L}{\Delta P} \quad (3)$$

where, L is the mean film thickness (mm); ΔP is the partial water vapor pressure difference (mmHg) across the two sides of the film specimen (the vapor pressure of pure water at 25°C = 23.73 mmHg).

Infrared spectroscopy (IR)

The functional groups of samples were investigated using infrared spectroscopy (Bruker, Tensor 27, Germany) (Rachtanapun *et al.,* 2007a; 2007c).

Statistical analysis

The statistical significance of the data was determined by a one-tailed analysis of variance (ANOVA) using STATISTIX 7.0 software ($p<0.05$). Data points were compared to confirm their statistical significance.

RESULTS AND DISCISSION

Infrared spectroscopy (IR) analysis

Infrared spectroscopy spectra of cellulose and synthesized CMCp are shown in Figure 1. Cellulose and CMCp had the same functional groups, such as an hydroxyl group (–OH stretching) at 3400 cm^{-1}, a hydrocarbon group (C-H stretching) at 2950 cm^{-1}, a carbonyl group (C=O stretching) at 1600 cm^{-1}, a $–CH_2$ scissoring around 1420 cm^{-1}, an –OH bending vibration around 1320 cm^{-1}, and ether groups (-O- stretching) at 1060 cm^{-1} (Kondo, 1997; Rachtanapun *et al.,* 2007a; 2007c). Celluose from

papaya peel was not bleached; therefore, it may have had some impurities, which could be observed from a small carbonyl peak in the IR spectra of cellulose. However, a carbonyl peak (C=O) at 1600 cm^{-1}, a $–CH_2$ peak at 1420 cm^{-1} and an ether peak (-O-) at 1060 cm^{-1} on the IR spectra of CMCp increased substantially. All these peaks confirmed the introduction of a $–OCH_2COO-$ group into the cellulose molecule. The reaction of cellulose hydroxyl and sodium monochloroacetate (NaMCA) to produce CMC is shown in Equation (4).

$$Cell–OH + ClCH_2COONa \rightarrow Cell –O–CH_2COO^-Na^+ + NaCl + H_2O \quad (4)$$

Similar observations have been reported previously by Adinugraha *et al*. (2005) and Rachtanapun *et al*. (2007a; 2007c).

Effect of corn starch content on mechanical properties of blended films of CMCp and corn starch

The effect of corn starch content on the mechanical properties (tensile strength and %elongation) of blended films of CMCp and corn starch without plasticizer was investigated. Tensile strength increased as the amount of corn starch increased (Figure 2a). This result was similar to the case of chitosan-starch composite film as

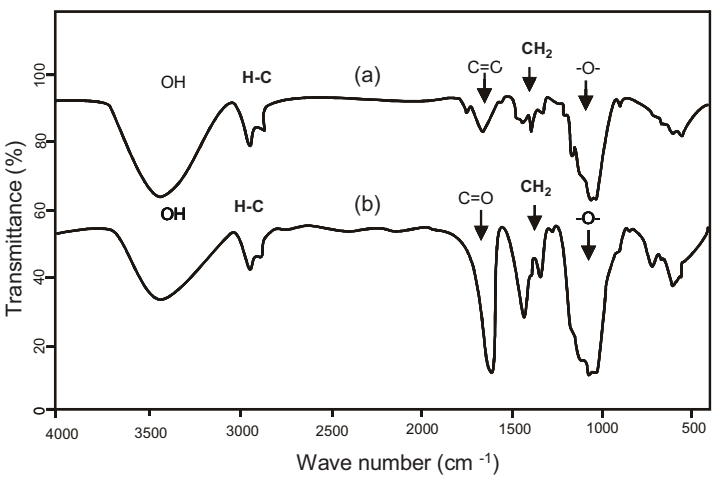

Figure 1 IR spectra of (a) cellulose and (b) CMC from papaya peel.

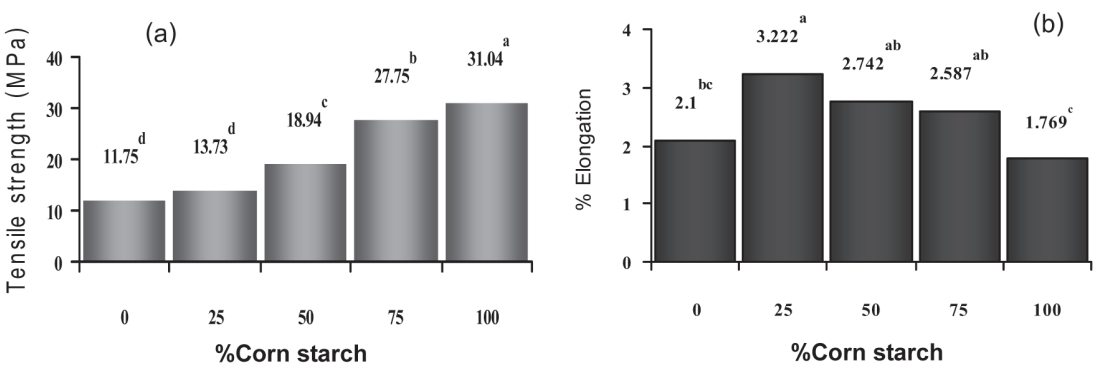

Figure 2 Effect of corn starch content on: (a) tensile strength; and (b) %elongation of blended films of CMCp and corn starch without plasticizer.

reported previously. When the starch content in the chitosan-starch composite film increased, the tensile strength increased (Xu *et al*., 2005). The addition of 25% corn starch increased %elongation, but %elongation decreased as the amount of corn starch increased in blended films.

Effect of plasticizer content on mechanical properties of CMCp/corn starch blend films

The tensile strength and %elongation of blended films of CMCp and corn starch with various plasticizer (glycerol) contents are shown in Figure 3. ANOVA indicated that the addition of glycerol caused significant differences in both tensile strength and elongation of blended films of CMCp and corn starch ($p<0.05$). An increase in concentration of glycerol (0-10 %v/w) yielded a decrease in tensile strength. Tensile strength decreased from 27.25 to 21.10 MPa (Figure 3a), while %elongation increased from 2.5 to 3.5% (Figure 3b). The change in tensile strength and %elongation was characterized by glycerol weakening the intermolecular forces between the chains of adjacent molecules, increasing the free volume and causing a reduction of mechanical resistance (Sobral *et al.,* 2001; Shaw *et al.,* 2002; Selke *et al*., 2004; Mali *et al.,* 2005; Rachtanapun *et al.,* 2007c; Bourtoom, 2008). This was in agreement with Park *et al*. (1993), Donhowe and Fennema (1993), McHugh and Krochta (1994), Laohakunjit and Noomhorm (2004), Bourtoom (2008).

Effect of corn starch and plasticizer content on water vapor transmission rate (WVTR) and water vapor permeability (WVP) of blended films of CMCp and corn starch

The effect of corn starch and plasticizer content on the water vapor transmission rate (WVTR) and water vapor permeability (WVP) of blended films of CMCp and corn starch was also investigated. WVTR and WVP significantly increased as the amount of corn starch increased. This result was in agreement with Mali *et al*. (2005), who stated that WVTR in yam starch films increased with the presence of glycerol. Bourtoom (2008) also reported that the polymer network might have become less dense because the mobility of the polymeric chains and the free volume of the film increased. Moreover, the increase in WVP might have been related to the hydrophillicity of glycerol, which promoted the diffusion of water molecules (Gennadios *et al*., 1993; Laohakunjit and Noomhorm, 2004; Bourtoom, 2008).

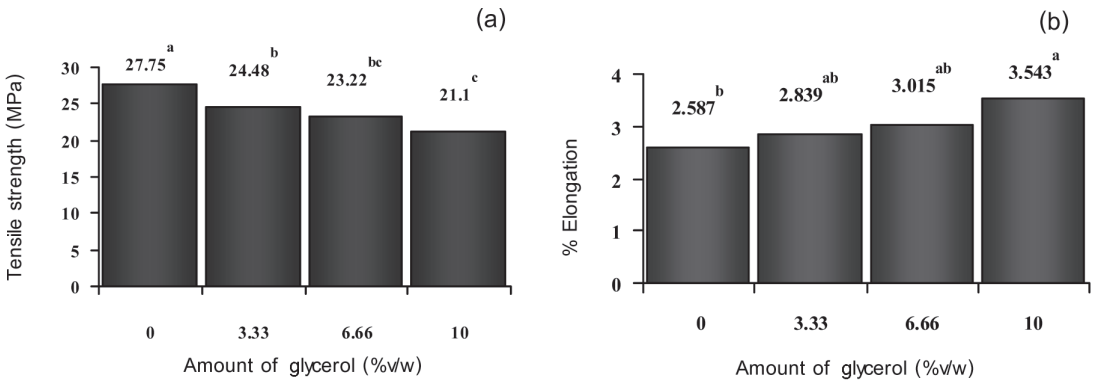

Figure 3 Effect of plasticizer content on (a) tensile strength and (b) %elongation of blended films of CMCp and corn starch.

Table 1 Effect of corn starch and plasticizer on water vapor transmission rate (WVTR) and water vapor permeability (WVP) of blended films of CMCp and corn starch.

Sample	WVTR ($g/m^2.day$)	WVP ($g.m/m^2.mmHg.day$)
CMCp/Corn starch 100 : 0	87.68^{f}	$1.391 \times 10^{-4\ f}$
CMCp/Corn starch 75 : 25	88.28^{e}	$1.401 \times 10^{-4\ e}$
CMCp/Corn starch 50 : 50	89.62^{d}	$1.422 \times 10^{-4\ d}$
CMCp/Corn starch 25 : 75	90.61^{c}	$1.438 \times 10^{-4\ c}$
CMCp/Corn starch 0 : 100	119.54^{a}	$1.897 \times 10^{-4\ a}$
CMCp/Corn starch 25 : 75 with glycerol 3.33% (v/w)	90.79^{b}	$1.440 \times 10^{-4\ b}$

a,b,c,d,e,f = values with different letters are significantly different ($p \leq 0.05$).

CONCLUSIONS

The IR spectrum confirmed the change of cellulose to CMCp by dramatically increasing the area under the peak C=O at 1600 cm^{-1}, the peak $–CH_2$ at 1420 cm^{-1} and the peak -O- at 1060 cm^{-1}. The tensile strength of blended films increased, but the %elongation decreased as the amount of corn starch increased. A weight ratio of CMCp to corn starch of 25:75 gave the maximum tensile strength. Addition of plasticizer (glycerol) into blended films increased the %elongation and WVP, but lowered the tensile strength.

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