PREPARATION AND PROPERTIES OF MODIFIED CARBOXYLMETHYL CELLULOSE WITH CASSAVA STARCH

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Abstract: In this work is focused on the preparation and properties of the carboxymethyl cellulose (CMC)/cassava starch (St)/natural rubber (NR) biopolymer blend films and crosslinked with CaCl\textsubscript{2} were prepared by casting method. The effects of CMC content, cassava starch content and blend ratio were investigated. The swelling ratio of the polymer blend film decreased with increasing NR contents and CaCl\textsubscript{2}. But the swelling ratio of the polymer enhanced with increasing amount of CMC in sample increased. After adding NR, the immiscible blend between NR and CMC/starch blend was observed by SEM. The best condition of the preparing biopolymer blend was 1.0:5.0:5.0 by weight, respectively and crosslinked with 2% w/w CaCl\textsubscript{2}. This is because NR can save the shape of sample and decrease of swelling ratio.

Introduction: Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups bound to some of the hydroxyl groups of the glucopyranose monomers that obtain from the cellulose backbone.\textsuperscript{1,2,3} It is a hydrophilic white powder in pure form and dissolves in water, forming a clear viscous solution or gel. It is sold under a variety of trade names and is used as a thickener and emulsifier in various food and cosmetic products and also as a treatment of constipation. The properties of CMC depend on the degree of substitution of the cellulose structure (i.e., how many of the hydroxyl groups have taken part in the substitution reaction), as well as the chain length of the cellulose backbone structure and the degree of clustering of the carboxymethyl substituents.\textsuperscript{4,5} Because of its polymeric structure and high molecular weight, it is capable to use as a filler in biocomposite films production. Unfortunately, the drawbacks of CMC present such as low degradation temperatures, which make them difficult to process, poor mechanical properties and high water susceptibility. CMC is able to improve the mechanical and barrier properties of the starch-based films. This aim of this work is to develop the properties of CMC by blending with starch and natural rubber (NR) latex and followed crosslinking with CaCl\textsubscript{2} as shown in Figure 1.

\[ \text{CMC} + \text{CaCl}_2 \rightarrow \text{CMC-Ca}^2+ + 2\text{Cl}^- \]

\[ \text{St} + \text{NR} \rightarrow \text{St-NR} \]

\[ \text{St-NR} + \text{CaCl}_2 \rightarrow \text{St-NR-Ca}^2+ + 2\text{Cl}^- \]

Figure 1: Structure of CMC cross linked by CaCl\textsubscript{2}
**Materials and Methodology:** Carboxymethyl cellulose (CMC) with an average molecular weight of 41,000 g/mol (practical grade) was purchased from Fluka company. Calcium chloride was provided from commercial grade, Thailand. Cassava starch was provided from General starch company (Bangkok, Thailand). The NR latex having 60 % dry rubber content (DRC) was manufactured by Thai Rubber Latex (Thailand). The 2 % (w/w) CMC was solubilized in 98 ml of water at 60 °C for 20 min. In case of starch, the gelatinization was performed by stirring 5 g of cassava starch in distilled water at 75 °C for 2 h. After cooling, the gelatinized cassava starch was mixed with 2% w/w CMC solution, stirred at 60°C for 30 min. The desired amount of CaCl₂ (0.5 1.0 3.0 and 5.0 g) was mixed with polymer blend. In addition, the desired amount of NR latex (0.5 1.0 3.0 and 5.0 g) was mixed with polymer blend. When prepared CMC, St, CaCl₂ solution and NR take it was mixed by stirrer at room temperature, when the solution is homogeneous casting in plate glass. Left at room temperature for 24 hours and then baked in an oven at 50 °C for 24 hours.

**Characterization of polymer blend:** The chemical structure of modified NR was analyzed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Bruker EQUINOK 55 measuring in the range of 4000–500 cm⁻¹. The samples were placed in distilled water at room temperature (ASTM D2765). Each sample was weighed periodically until no weight change was observed. Equilibrium swelling ratio was determined as the weight of final (equilibrium) water uptake divided by the weight of dry polymer. The degree of swelling ratio was estimated from equation (1).

\[
\text{Swelling ratio} = \frac{W_2 - W_1}{W_1} \quad \text{.........(1)}
\]

Where \( W_1 \) is the weights of dry sample and \( W_2 \) is the weight of swollen sample after immersion for 24 hours. The morphology of the polymer blend was confirmed by scanning electron microscopy (JMS-5800 LV, JEOL).

**Results, Discussion and Conclusions:** The ATR-FTIR spectra of cassava starch, CMC, cassava starch/CMC and cassava starch/CMC/NR are presented in Figure 2. It is clear that the carboxyl group was observed at 1732 cm⁻¹ due to the carbonyl (–CO) stretching of the protonated carboxylic acid group (–COOH) (Figure 2 (b)). This is accompanied by the appearance of both the peak at 1583 cm⁻¹ due to the –COO– asymmetric stretch and the peak at 1418 cm⁻¹ due to the –COO– symmetric stretch. The broad band at 3328 cm⁻¹ for starch (Figure 1(a)) is due to the stretching mode of O–H groups. The adsorption band at 1648 cm⁻¹ is attributed to an intramolecular H-band carboxyl group. The bands at 1155 and 2931 cm⁻¹ are assigned to C–H and C–O stretching, respectively. Strong band at 1079 cm⁻¹ was attributed to CH₂–O–CH₂ stretching vibration. Compared to the FTIR spectra of CMC and starch, CMC-starch recorded the new peak at about 1010 cm⁻¹, which was attributed to –C-O-C- from CMC/starch blend as shown in Figure 2(c).
Figure 2: ATR-FTIR Spectra of (a) cassava starch (b) CMC (c) cassava starch/CMC blend and (d) cassava starch/CMC/NR blend

Figure 3 shows the effect of polymer blend ratio on the swelling ratio of CMC/St blend. At low amount of St, the polymer blend shows poor water resistance of polymer blend in water due to less interaction between them. But when the St content in blend increased from 2 to 3 or 5 g the polymer blend displays a good water resistance. This is due to hydrogen bonding formation in polymer blend.

Figure 3: Swelling ratio of CMC/St blend at (1) 1:0.5, (2) 1:1, (3) 1:2, (4) 1:3 and (5) 1:5 in water

Figure 4 shows the effect of CaCl$_2$ on the swelling ratio of CMC/St blend. It was found that when CaCl$_2$ increased in system, the swelling ratio of polymer blend decreased since carboxyl group from CMC was cross linked with CaCl$_2$ as shown in Figure 1.
In addition, the water resistance of the polymer blend was improved by addition of NR and result is displayed in Figure 5 and Figure 6. The dimensional stability of the polymer blend increased as a function of NR in sample because NR as a hydrophobic polymer shows the barrier for water attack. The lowest swelling ratio was observed in sample in presence of 5% NR.

**Figure 4**: Influence of CaCl$_2$ on the swelling ratio of CMC/St blend

**Figure 5**: Swelling ratio of preparing polymer blend between CMC/St/NR blend content at (1) 1:0.5:1, (2) 1:0.5:3 and (3) 1:0.5:5 in water
Figure 6: Influence of NR on the swelling ratio of CMC/St

Figure 7 represent the morphology of the polymer blends. It was clear that the morphology of polymer blend containing 5% NR (a) was roughness than that without NR (b) due to its immiscible blend between NR and CMC/starch.

(a)                                                                    (b)

Figure 7: Morphology of CMC/St blend in the presence of NR (a) 5% and (b) 0%

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References:

Keywords: Polymer blending, Natural rubber (NR), Carboxymethyl cellulose (CMC), Cassava starch and Calcium chloride (CaCl2)