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Contributed Paper

Biopolymer Film Based on Rice Straw Carboxymethyl Cellulose (CMCr) and Chiang Mai University (CMU) Purple Rice Carboxymethyl Flour (CMF)

Anong Jainan [a], Aree Deenu [b] and Suthaphat Kamthai* [c]

[a] Division of Food science and Technology, School of Agro-Industry, Faculty of Agro-Industry, Chiang Mai University, Chaing Mai 50100, Thailand.

[b] Division of Food Engineering, School of Agro-Industry, Faculty of Agro-Industry, Chiang Mai University, Chaing Mai 50100, Thailand.

[c] Division of Packaging Technology, School of Agro-Industry, Faculty of Agro-Industry, Chiang Mai University, Chaing Mai 50100, Thailand.

* Author for correspondence; e-mail: Suthaphat.k@cmu.ac.th; suthaphatk@gmail.com

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ABSTRACT

Carboxymethyl Flour (CMF) is a starchy material with high anthocyanin content, produced from Chiang Mai University (CMU) purple rice by alkalization with sodium hydroxide (NaOH, %w/v) at 10% concentration, and subsequently etherified with monochloroacetic acid. The aim of this study was to develop a biopolymer film based on carboxymethyl cellulose (CMCr) and CMF, and characterize their thermal, physicochemical, mechanical, barrier and morphological properties. In this film production experiment, CMCr was combined with CMF by using 2:1 (% w/v); and glycerol was used as a plasticizer at various concentrations, i.e. 0, 0.25, 0.5 and 1 (%w/v). The results informed that the thermal, physical, chemical, mechanical and barrier properties of plasticized biopolymer film were improved by increasing of glycerol content (without the deterioration of anthocyanin). At 1% (w/v) glycerol addition, CMCr/CMF blended film had the highest film water solubility, elongation at break and water vapor permeability (WVP) (but not tensile strength), which were 83.56%, 61.26% and 7.15×10^{-4} g·m/m²·day·mm·Hg, respectively. In addition, CMF can be used as a raw material for film production, as it contains high anthocyanin, which acts as an antioxidant. It is new alternative modified flour for biopolymer film production or natural additives, which has more anthocyanin than commercial starches.

Keywords: Chiang Mai University (CMU) purple rice, rice straw, carboxymethyl cellulose, carboxymethyl flour

1. INTRODUCTION

Biopolymer has been studied widely in recent years, and there has been an increase in the level of research on the development of new biopolymer packaging materials that could be considered environmentally friendly raw materials in agriculture. Natural polymers have various advantages over synthetic ones due to their low-cost, ready availability and biodegradability [1]. Generally, biopolymer can be produced from renewable raw materials that are biodegradable. A sustainable economy has the advantage of mainly biomass derived raw materials for high-volume applications, such as packaging [2]. Special attention should be paid to barrier properties that are extremely important, especially for bio-based food packaging materials. Moisture resistance with hydrophilic polymers is inadequate in many cases, thus excessive water vapor transmission through packaging dilutes the quality of food, resulting in shorter shelf-life, increased costs and eventually more waste [3].

Moreover, the polysaccharide films are a one kind of biopolymer base film (i.e. starches, cellulose derivatives, chitosan and etc.) that become to increase their role in the field of food packaging materials. Due to polysaccharides film has better film-forming properties and more extensible than proteinaceous film. In particular, the films formed from these hydrophilic compounds provide efficient barriers against oils and lipid [4]. Although starch can produce high gas and oil barrier film but its film water solubility is not quite good. Therefore, many researchers would like to synthesize water soluble starch derivative such as carboxymethyl starch (CMS) from different starch sources (i.e., cassava starch, sago starch, water yam starch, rice starch and so on) having different degree of substitution (DS). [5-8]. CMS is chemically

modified from starch by etherification reaction with monochloroacetic acid (MCA). This anionic starch derivative can be considered as a natural mixture and consequently a suitable raw material for preparing edible or biodegradable film. Moreover, in this work accomplished by the reported that not only starch could synthesize CMS but also Chiang Mai University (CMU) purple rice flour could be modified carboxymethyl flour (CMF) with containing high anthocyanin content (7.67 mg/100g of CMF) [9].

Nevertheless, starch and its modified products exhibit several disadvantages such as a strong water sensitivity and poor mechanical properties compared to conventional synthetic polymers, which make it unsatisfactory for some applications such as packaging [10, 11]. Biocomposite are usually consisting of two or three biopolymers and are prepared by different blending methods or adding some plasticizers for solving the disadvantage of the biopolymer film properties. For instance, the several of CMC addition in modified starch blended film showed better physical and mechanical properties than starch lms at 15-20% w/w CMC blending [12]. This is attributed to CMC has a good inter or intra molecular bonding and compatible with other bio-molecules such as starch and modified starch. Furthermore, CMC can improve the mechanical and barrier properties of starch based film is to be expected due to the chemical similarity of the starch and CMC, which provides good compatibility between them [13].

However, to date, to the best of our knowledge, no research has described the plasticization of CMF from CMU purple rice and rice straw carboxymethyl cellulose (CMCr) blended film for biocomposite film

production. Due to purple rice has high anthocyanin content that have been identified in predominant rice, and mainly consists of cyaniding-3-glucoside [14, 15]. Hence, this research can be able to make a high valued CMCr/CMF blended film with containing anthocyanin and the objective of this work was to study of glycerol concentrations effect on thermal, physical, chemical, mechanical, barrier and morphological properties of CMCr/CMF blended films.

2. MATERIALS AND METHODS

2.1 Materials

Carboxymethyl Flour (CMF) (0.20; Degree of substitution (DS), amylose: 88.11g/100g; amylopectin: 11.89g/100 g; moisture content 7.12%; anthocyanin 7.67 mg/100 g) from CMU purple rice was obtained from the Purple Rice Research Unit (PRRU), Division of Agronomy, Department of Plant and Soil Sciences, Faculty of Agriculture, Chiang Mai University and used as the film-forming component for the continuous biodegradable film matrix [9]. Rice straw carboxymethyl cellulose (CMCr) was synthesized in laboratory (0.68; DS, 80.6%; CMC, 1.25%; NaCl) and used to produce the film. Glycerol (food grade) and distilled water were obtained from local chemical store.

2.2 Film Forming Process

The film forming solution consisted of rice straw carboxymethyl cellulose (CMCr), carboxymethyl flour (CMF) from purple rice and plasticizers (glycerol) (0.125, 0.25, 0.5 and 1% w/v) were added. The film forming solution was prepared by dissolving 2 g of CMCr and 1 g of CMF in 100 ml of distilled water and stirring constantly at 70 °C for 15 min. The film forming solution was added to plasticizers (glycerol) and cast onto acrylic plates. CMF film was obtained

at natural drying temperature overnight, before being dried in an oven at 55 °C. The film could be removed easily from the plate at 24 h of 52% relative humidity (%RH) before being tested.

2.3 Film Characterization

2.3.1 Thermal property analysis

The thermal properties of film samples were examined using differential scanning calorimetry (DSC) (DSC8000, Perkin Elmer Inc., USA). CMF film of about 10 mg suspension of solid sample in water was prepared and sealed in a DSC pan. Samples were allowed to equilibrate for 2 h at room temperature before heating from 30 °C to 180 °C at 10 °C /min. The differential scanning calorimetry analyzer was calibrated using indium as a standard, with an empty DSC pan being used as the reference. Melting temperature (T_m) and enthalpy of melting (ΔH) were calculated automatically [16].

2.4 Physical Properties

2.4.1 Film water solubility

The Solubility of film was determined according to the method described by Colla et al, (2006) [17] with a slight modification. Three film samples of 20×20 mm were prepared, weighed, and immersed in 100 ml of distilled water. The samples were maintained under constant agitation at 175 rpm using an orbital shaker for 24 h at room temperature. The remaining pieces of film were collected by filtration and dried again. The dry mass content of initial and final film was determined by drying the sample at 105 °C for 24 h. The solubility of film was averaged from triplicate and calculated as follows equation (1):

$$\%FS = \left(\frac{W_i - W_f}{W_i} \right) \times 100 \quad (1)$$

Where:

FS is percentage of film water solubility

W_i is the initial dried weight of film (g)

W_f is the final dried weight of film (g)

2.4.2 Contact angle

The contact angle (θ) of water on the film surfaces was measured using a contact angle meter (Drop Shape Analyzer; DSA 30B, Kruss, Germany) with a 10 μ L drop of distilled water on the surface of film with dimensions of 3.0 \times 3.0 cm.

2.4.3 Color measurement

The color characteristic was assessed using a Color Quest XE Spectrocolorimeter (Minolta, model CR-410, Japan) to determine the L^* value (lightness), a^* value (redness) and b^* value (yellowness) of the powder samples. A white standard (tile: $L^* = 93.24$, $a^* = -0.72$ and $b^* = 1.53$) was used to calibrate the colorimeter before each measurement was taken. The sample was measured in triplicate and the values of L^* , a^* and b^* were averaged. The total color difference (ΔE) also was calculated using the equation (2) previously described, and the L^* , a^* and b^* values of the CMU purple rice flour were used as a standard reference.

$$\Delta E = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})} \quad (2)$$

2.5 Chemical Properties

2.5.1 Anthocyanin

Cyanidin-3-glucoside) content

The film was extracted with acidified methanol (1% HCl, v/v) by modifying the method of Chuanguang et al, (2010) [18]. The content of anthocyanin in CMF was quantified using an analytical HPLC system (HP 1200, MSD, Agilent Technologies, Santa Clara, CA). The extracted solution was

injected into a Pursuit XRs 5 C18 column. The mobile phase was a mixture of A (acetonitrile) and B (10% acetic acid, 5% acetonitrile, and 1% phosphoric acid in water) at 1 ml/min with UV detection at 520 nm. The elution gradient was evaluated using the %mobile phase B; 100-80, 80-60 and 60-100 at 5-20, 20-25 and 25-30 min, respectively. The concentration of anthocyanin content in the film extract was calculated based on the Cyanidin-3-glucoside standard curve.

2.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of CMCr/CMF blended film were determined by FTIR using an FTIR spectrometer (Nicolet Nexus 6700, (Thermoscientific, USA). Each spectrum consisted of 32 scans in a 400 to 4,000 cm^{-1} wavenumber range at a resolution of 2 cm^{-1} .

2.6 Mechanical Properties

Tensile strength (TS; MPa) and percentage elongation at break (E; %) were determined using a strong Universal Testing Machine Model 1000 (H1K-S.UK), according to the procedure of ASTM D882-97 (ASTM, 1996). Film was cut to 10 \times 0.5 cm and then conditioned in a humidity chamber with 55 %RH at 25 $^{\circ}$ C for 12 h prior to testing. Samples clamped between tensile and initial grips were set at 50 mm apart with a crosshead speed of 10 mm/min. Ten film specimens were analyzed for each test.

2.7 Barrier Properties

Water vapor permeability (WVP) of the film was determined using the gravimetric modified cup method based on ASTM E96-92 [19, 20]. The test cups were filled with 20 grams of silica gel (desiccant) to produce 0% RH below the film. A sample

was placed in the cup between the ring cover and silicone sealant (high vacuum grease, Lithelin, Hannau, Germany) and held with four screws around the circumference of the cup. The air gap between the film surface and desiccant was approximately 1.5 cm. The water vapour transmission rate (WVTR) of each film was measured at 60 ± 2 % RH and 25 ± 2 °C. The test cups were weighed daily to the nearest 0.0001 g with an electronic scale (Sartorius Corp.). A plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion of this plot represented the steady state amount of water vapor diffusing through the film per unit time (g/h). WVTR was expressed in gram units, per square meter, per day. Steady state over time (slope) yielded a regression coefficient of 0.99 or more. Six pretreated samples were tested. The WVP of film was calculated by multiplying the steady WVTR by the film thickness and dividing that by the difference of water vapor pressure across the film.

2.8 Morphological Properties

Image analysis; the surface characteristic of selected film was shown by a Leica microsystem (Leica Microsystems Ltd, CH-9435 Heerbrugg DFC 295 12V/165mA 365514708).

2.9 Statistical Analysis

The differences between the mean values of the multiple groups were analyzed by one-way analysis of variance (ANOVA) with the Duncan's multiple range test. ANOVA data with a $P < 0.05$ were classified as statistically significant. SPSS 17.0 software and the Microsoft Excel 2010 program were used to analyse and report the data. Mean values from the duplicated experiments were reported.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties

Two characteristic thermal transitions may exist for semi-crystalline polymers such as CMF: a melting transition for the crystalline fraction and a transition due to crystallization. The onset temperature (T_o), melting temperature (T_m) and melting enthalpy (ΔH) of plasticized CMCr/CMF blended films at different levels of glycerol content are reported in Table 1. The results revealed that the melting temperature of CMCr/CMF blended films were decreased from 168.40 to 139.35 °C and it was significantly different with increasing glycerol concentrations. In addition, the ΔH of CMCr/CMF blended film informed that the enthalpies of blended film continue to increase from 4.34 to 7.57 J/g with an increasing of glycerol concentration (0-0.5% w/v) and it was reduced at 1% w/v (6.44 J/g) afterward.

This phenomenon has been suggested by illustrated that the addition of plasticizer could induce the starch polymer matrix became less dense and the mobility of polymer chains raised [16]. Moreover, the addition of glycerol in CMCr/CMF blended films motivates high hydrophilic hydroxyl groups as active sites which can be bonded with water molecules. Thus, films with higher glycerol represented higher moisture content and it is well implied that it has high water molecules in a polymer matrix, resulting in reducing of film thermal properties. Because water molecules have a plasticizing effect and could be considered as a polymer inter-chain mobility enhancer [21]. For this reason, the movement of polymer chain is not only effect on thermal properties and it can improve the physical, mechanical and barrier properties of CMCr/CMF blended films as well.

Table 1. Thermal properties of plasticized CMCr/CMF blended films at different glycerol concentrations.

Glycerol concentration (% w/v)	T _o (°C)	T _m (°C)	ΔH (J/g)
0	167.77±1.29 ^a	168.40±0.89 ^a	4.34±0.06 ^d
0.125	153.98±0.02 ^b	154.34±0.03 ^b	5.56±0.16 ^c
0.25	152.90±1.17 ^b	153.64±1.77 ^b	5.19±0.02 ^c
0.5	146.17±2.50 ^c	146.53±2.62 ^c	7.57±0.12 ^a
1	138.98±0.05 ^d	139.35±0.00 ^d	6.44±0.59 ^b

Mean a, b, c and d with the same letter are not significantly different at 5%, LSD. Mean ± standard deviation. T_o and T_m represent onset and melting temperature, ΔH represents melting enthalpy.

3.2 Physical Properties

3.2.1 Film water solubility and contact angle

The relationship between film solubility and contact angle when the concentration of glycerol is increased shown in Table 2. Addition of glycerol, in all concentrations, increased the water solubility of CMCr/CMF blended films and reduce contact angle, which increased from 60.21 to 83.56% and dropped from 91.03 to 40.31°, respectively (Table 2). This is in accordance with the report of according to reveals that glycerol showed more solubility this is due the higher hygroscopic behaviour of glycerol, which strongly interacts with water and is easily incorporated into the chains of hydrogen bonds [22]. Consequently, the high solubility of the film with high glycerol concentration is because of glycerol has a strong affinity for water molecules, as well as low molecular weight facilitates the entry of glycerol between polymer chains, thereby increasing the free space volume between the polymer chain [16].

The effectiveness of glycerol in increasing the water solubility of CMCr/CMF blended films was most likely due to its lower molecular weight, which allows it to be more readily inserted between the polymer chains.

In addition, the application of CMCr as a main bio-composite film composition combines with CMF, which could be occupied by water molecules due to CMC is water-soluble cellulose derivatives and its hydrophilic nature can induce the water solubility of CMCr/CMF blended films.

The contact angle (θ) of the film is another indicator for direct determination of the hydrophilicity of films. In contrast with synthetic polymer films, the contact angles of the natural material films decreased rapidly with contact time. The photographs were taken for each sample after water was dropped on the surfaces of the films. Figure 1 shows the contact angles of plasticized CMCr/CMF blended films had a relatively high contact angle, and plasticization with glycerol decreased the contact angle. The results presented at 1% w/v glycerol addition that had lowest contact angle of CMCr/CMF blended film and it was an average angles of 40.31, greater the wettability. Thus, it can be suggested that the presence of glycerol contributes to higher hydrophilicity and moisture sensitivity of the blended films which cause affect the barrier properties of CMCr/CMF blended film, afterward.

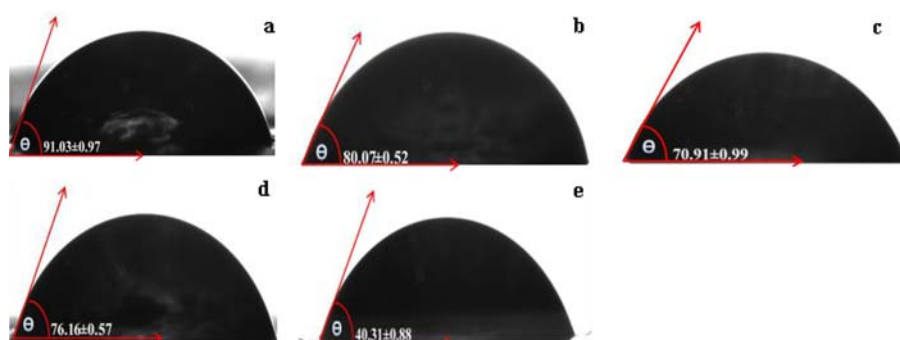


Figure 1. Contact angles of plasticized CMCr/CMF blended films at different glycerol concentrations (a) 0%, (b) 0.125%, (c) 0.25%, (d) 0.5% and (e) 1%, w/v.

3.2.2 Color measurement

Color is an important property of edible films because it could affect consumer acceptance of both edible and inedible films. The L^* , a^* and b^* Hunter Lab color values, and total color difference (ΔE) of the blended films are shown in Table 2. The main differences in color values among the CMCr/CMF blended films at different glycerol concentration were increased the L^* , b^* values and decreased a^* values of blended film. This shows that CMCr/CMF produces dark purple color films. L^* values of the film increased significantly by increasing the glycerol content ($P < 0.05$). Conversely,

a^* values decreased by increasing glycerol content in the CMCr/CMF blended films. Therefore, addition of glycerol to CMCr/CMF blended films can improve film properties and reduce ΔE , which indicates the degree of total color difference from the standard color plate. In general, edible or biodegradable films should be as close to colorless as possible to simulate the appearance of common polymeric films [12]. However, the appearance properties as film color are according to film application and its specific properties such as antioxidant film, antimicrobial film and so on.

Table 2. Physical properties of plasticized CMCr/CMF blended films at different glycerol concentrations.

Plasticizer concentration (%w/v)	Solubility (%)	Contact angle (θ)	L^*	a^*	b^*	Color (ΔE)
0	60.21±0.78 ^a	91.03±0.97 ^c	54.45±0.59 ^a	7.55±0.34 ^c	16.40±0.37 ^a	23.38±0.40 ^c
0.125	65.91±0.05 ^b	80.07±0.52 ^d	57.90±0.54 ^b	10.44±0.79 ^d	19.90±0.28 ^b	20.42±0.40 ^b
0.25	77.52±0.27 ^c	70.91±0.99 ^c	64.26±0.78 ^c	8.27±0.06 ^c	21.69±0.12 ^c	20.75±0.23 ^b
0.5	78.62±0.09 ^d	76.16±0.57 ^b	71.63±0.39 ^d	6.50±0.10 ^b	21.46±0.01 ^c	18.26±0.04 ^a
1	83.56±0.27 ^e	40.31±0.88 ^a	74.66±0.65 ^e	5.44±0.14 ^a	20.42±0.130 ^c	18.09±0.08 ^a

Mean a, b, c, d and e with the same letter are not significantly different at 5%, LSD. Mean \pm standard deviation.

3.3 Chemical Properties

3.3.1 Anthocyanin (cyanidin-3-glucoside) Content

The anthocyanin content of CMCr/CMF blended films at different glycerol concentrations was no significant ($P > 0.05$) differences in values among the film. Anthocyanins are generally accepted as the largest and most important group of water soluble pigments in nature [23]. In the present study, anthocyanins were extracted from CMCr/CMF blended films, using acidified methanol (Soxhlet). The result of blended film informed that the concentration of glycerol had no significant effect on anthocyanin content and it was approximately 0.20 mg/100g blended film. Therefore, it can be discussed the role of glycerol in the film forming process is a good plasticizer or disperser to distribute color pigment in a polymer matrix and without anthocyanin deterioration. Moreover, it is well known that pigmented rice or black rice has been reported to have a very high content of total anthocyanins mainly cyanidin-3-glucoside and peonidin-3-glucoside [24]. Hence, the remaining pigmented in CMCr/CMF blended films from CMU purple rice, which is known for its had high antioxidant activity also high phenolic content, can be apply to use as an antioxidant packaging films.

3.3.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of CMCr/CMF blended films at different glycerol concentrations is shown in Figure 2. It results manifested that all films showed absorption peaks in the same regions that stronger hydrogen bonds were formed between CMCr/CMF and glycerol mixing but the peaks shifted to lower wave numbers with increasing glycerol content. In FTIR analysis, the specific chemical groups present

in the various glycerol concentrations was also characterized (0-1% w/v). The result reported that the FTIR spectra of CMCr/CMF blended films showed an absorption band at 3260 to 3289 cm^{-1} are attributed to the hydrogen bonds formed by the interaction of -OH groups at the end of polymer chains of glycerol and in the CMCr/CMF blended films. Such a decrease in -OH stretching frequency by adding 1% (w/v) of glycerol is associated hydroxyls, connected with other hydroxyls by hydrogen bonds of CMCr or CMF, to form a stronger hydrogen bond network [25].

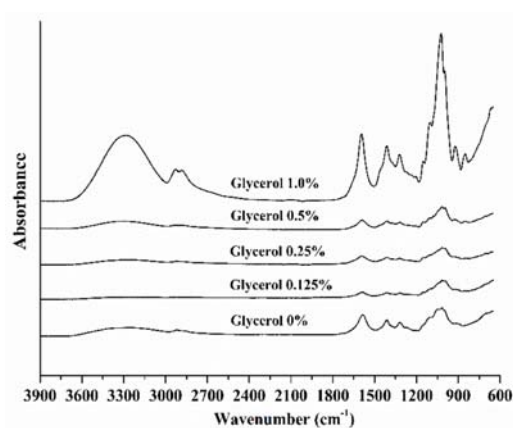


Figure 2. The FTIR of CMCr/CMF blended films at different glycerol concentrations.

While, the increase in IR absorbance intensity area of 1% (w/v) was more dramatic than the intensity area of other glycerol concentrations, which is due to the extinction coefficient of associated hydroxyls is high, resulting more intermolecular bonding with glycerol [26] and consequently larger the hydrogen bond network (more free volume). The absorbance over the region from 2920 to 3078 cm^{-1} , attributed to the -CH stretch vibration, also confirmed the molecular structure of anthocyanin compounds such as cyanidin-3-glucoside and peonidin-3-glucoside in CMF [9]. The characteristic peaks at 1015 and 1023

cm^{-1} were attributed to C-O bond stretching of the C-O-C group in the anhydro-glucose ring of CMF [27, 30].

3.4 Mechanical Properties

Mechanical properties data tensile strength (TS; MPa) and elongation at break (E;%) of CMCr/CMF blended films are shown in Table 3. Films containing glycerol exhibited negative depends on the plasticizer

concentration for TS, although the increasing plasticizer concentration increased elongation at break of blended films with glycerol significantly. The TS and E% of plasticized CMCr/CMF blended films notably decreased from 14.76 to 1.66 MPa and increased from 6.93 to 61.26% as glycerol concentration increased from 0.125% to 1% (w/v), respectively.

Table 3. Mechanical and barrier properties of plasticized CMCr/CMF blended films at different glycerol concentrations.

Plasticized concentration (%w/v)	Tensile strength (MPa)	Elongation at break (%)	WVTR ($\text{g}/\text{m}^2/\text{day}$)	WVP ($\text{g}\cdot\text{m}/\text{m}^2\cdot\text{day}\cdot\text{mm}\cdot\text{Hg}\times 10^{-4}$)
0	5.25 ± 0.43^b	8.46 ± 0.40^b	1.56 ± 0.13^a	$0.20\pm 1.71\times 10^{-5a}$
0.125	14.76 ± 0.14^c	6.93 ± 0.76^a	2.92 ± 0.05^a	$0.30\pm 5.71\times 10^{-5a}$
0.25	7.30 ± 0.09^d	13.45 ± 0.38^c	6.96 ± 0.04^b	$0.70\pm 48.3\times 10^{-4b}$
0.5	6.09 ± 0.09^c	25.79 ± 0.77^d	13.48 ± 0.16^c	$1.45\pm 0.12\times 10^{-4c}$
1	1.66 ± 0.12^a	61.26 ± 0.27^e	56.08 ± 1.44^d	$7.15\pm 0.02\times 10^{-4d}$

Mean a, b, c, d and e with the same letter are not significantly different at 5%, LSD. Mean \pm standard deviation.

The possible reason for the higher tensile strength at low plasticizer concentration is due to the domination of strong hydrogen bonds produced by CMCr and CMF intermolecular interaction. However, the elongation at break of blended film is increased due to the glycerol addition can reduce the intra and intermolecular bonds between CMCr and amylose-amylopectin of the CMF and thus, replace them with hydrogen bonds. After that, plasticizer bonded with CMCr or CMF molecules and motivated the molecular chain mobility, which informed that the elongation of polymeric materials depends on the mobility of their molecular chains [28]. In addition, the disruption and reconstruction chains decrease the rigidity and promote flexibility of blended films by allowing more chain

mobility. In work accomplished by Mellan (1965) reported that glycerol could be bound with flour molecules after that the cohesive tension of the molecules became weakened in attached polymer chains, and the resulting structure was more flexible [29]

3.5 Barrier Properties

Barrier Properties data WVTR ($\text{g}/\text{m}^2/\text{day}$) WVP ($\text{g}\cdot\text{m}/\text{m}^2\cdot\text{day}\cdot\text{mm}\cdot\text{Hg}\times 10^{-4}$) of plasticized CMCr/CMF blended films showed significantly ($P > 0.05$). They were found to be from 2.92 to 56.08 $\text{g}/\text{m}^2/\text{day}$ and 0.30 to 7.15 $\text{g}\cdot\text{m}/\text{m}^2\cdot\text{day}\cdot\text{mm}\cdot\text{Hg}\times 10^{-4}$, respectively (Table 3). The barrier properties of blended films illustrates that WVTR tends to rise with an increasing of WVP. This could be related to the CMCr and CMF molecule interactions, which are dominant at lower

plasticizer concentrations, resulting in a dense and more compact hydrogen network and structure, resulting in the lower the WVTR and WVP values. Moreover, glycerol is a relatively small hydrophilic molecule and may be inserted easily between CMCr and CMF molecules, to establish hydrogen bonds with hydroxyl groups of CMCr and amylose or amylopectin in CMF. This observation can be attributed to the hydrophilic nature of glycerol reduced internal hydrogen bonding while increasing intermolecular spacing with decreasing brittleness and increasing permeability of the film materials [30].

3.6 Morphological Properties

The photograph surfaces and fractures of CMF/CMCr blended films are presented in Figure 3. The appearance of plasticized CMCr/CMF blended films was essentially clear and more uniform than the control film after drying. Non-plasticized CMCr/CMF blended film gave a rough surface appearance; whereas glycerol plasticized CMF/CMCr blended film was relatively smooth. Therefore, the addition of glycerol can be incorporated homogeneously within a dispersion of particles and hydrogen bond between CMCr and CMF so that the surface of blended films becomes transparent and their texture is more flexible and soft.

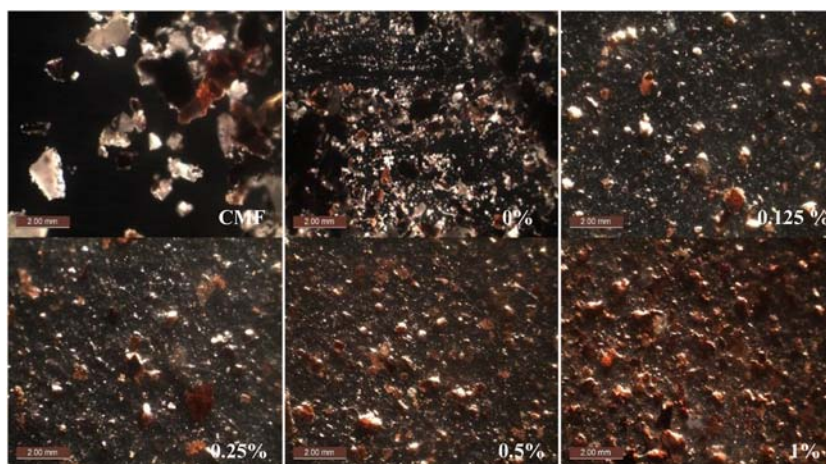


Figure 3. Photograph at (80X) of plasticized CMCr/CMF blended films.

4. CONCLUSIONS

The various addition of glycerol concentrations had more effect on the bio-composite film properties, which were produced from CMCr and CMF (2:1) blending. In this work, physical and mechanical properties of CMCr/CMF blended film were highly dependent on the glycerol concentration. It is while increasing glycerol concentrations tend to increase the water solubility, elongation at break, WVP

and WVTR of film but decrease the T_m and tensile strength of the blend films. In particular, this current research can be promoted the application of rice straw and CMU purple rice for producing the bio-composite films based on CMCr and CMF. It has become a very attractive function as an antioxidant film. This production of modified flour can apply to use as edible film or biodegradable plastic, which is gradually obtained considerable concern in Thailand.

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