

## Microcomposites of rice starch film reinforced with microcrystalline cellulose from palm pressed fiber

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**Abstract:** Rice starch films reinforced with microcrystalline cellulose from palm pressed fiber (MCPF) were prepared and characterized. The dependence of morphology and properties of rice starch films on MCPF (average length of about  $0.480 \pm 0.023 \mu\text{m}$ ) content in the range of 0 to 40 wt.-percent was characterized by scanning electron microscopy and the measuring of mechanical properties and water barrier property. The results demonstrated that the strong interactions between MCPF and between MCPF and rice starch film matrix play a key role in reinforcing the resulting composites. The rice starch film/MCPF biocomposites increased in tensile strength from 5.16 MPa for pure rice starch film to 44.23 MPa but decreased in elongation at breaking of composites. Additionally, the incorporation of MCPF into rice starch films provided an improvement of the water resistance for the rice starch films. The morphology of the existence of MCPF in the rice starch films can be easily observed in the biocomposite films when more than 15% of MCPF was used concomitant with larger agglomerates was observed.

**Keywords:** rice starch film, microcrystalline cellulose, palm press fiber, mechanical property, water vapor permeability

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### Introduction

Lately, there has been an increased interest in the use of biopolymers. This is possibly due to more environmentally aware consumers, the increased price of crude oil and concern about global warming (Petersson *et al.*, 2007). Biopolymers are based on renewable resources and will degrade to form carbon dioxide, water and biomass. Biopolymers can today be retrieved from, for example, agricultural feedstock, marine fauna and microbial activities. Even though, biodegradable polymer films are not meant to totally replace synthetic packaging films, but to limit moisture, aroma, and lipid migration between food components where traditional packaging cannot function. For instance, biodegradable films can be used for versatile food products to reduce loss of moisture, to restrict absorption of oxygen, to lessen migration of lipids, to improve mechanical handling properties, to provide physical protection, or to offer an alternative to the commercial packaging materials (Murray and Luft, 1973; Kester and Fennema, 1986;

Nelson and Fennema, 1991). Among the many kinds of candidates for use in biopolymers, starch is one of the most promising materials for biodegradable plastics because it is a versatile biopolymer, with immense potential and low price for use in non-food industries (Lu *et al.*, 2005). Rice starch and its major components, amylose and amylopectin, are biopolymers which are attractive raw materials for use as barriers in packaging materials. They have been used to produce biodegradable films to partially or entirely replace plastic polymers because of their low cost and renewability, as well as possessing good mechanical properties (Xu *et al.*, 2005). However, compared to common synthetic polymers, the biodegradable products based on starch, unfortunately, still reveal many disadvantages which are mainly attributed to the highly hydrophilic character of starch polymer. The development of starch composite materials filled with nano/microsized rigid particles has attracted both scientific and industrial interest (Samir *et al.*, 2004). Favier *et al.* (1995) showed that the addition of 3% to 6% of crystalline cellulose in a

copolymer acrylate latex film increased the dynamic modulus more than 3-fold. The effect of fillers on mechanical properties of consistent with the studies in which researchers have shown that the addition of nanosize organo-clay particles to polyamide based composites showed exceptional improvement on mechanical properties compared to their micron size counterparts (Yano *et al.*, 1993; Okada and Usuki, 1995). During the last decade, these nano/micro composites with at least one component in the submicron size have found many applications in the automotive industry and in packaging materials (Ke *et al.*, 1999). In previous work (Bourtoom and Chinnan, 2008) a rice starch edible film was developed. It has been observed that the functional properties, e.g. the film ductility and the barrier properties of rice starch film, are generally poor. Inclusion of cellulose micro fibrils in rice starch films reinforces the starch matrix regardless of the amount of plasticizer used. Despite these promising and attractive properties of packaging microcomposites and cellulose fillers, the effect of microcrystalline cellulose fillers in edible films produced from rice starch has yet to be explored. The goal of this work was to investigate the properties of rice starch films reinforced with microcrystalline cellulose from palm pressed fiber.

## Materials and Methods

### Materials

Native rice starch (Thai Flower brand) with 15% amylose was used. It was obtained from Bangkok Starch Industrial Co. Ltd. and had a moisture content of about 14g/100g sample (determined in triplicate by vacuum drying at 70°C and < 1 mmHg pressure for 24 hours, EYELA™, Model VOS-300VD, Japan) and peak viscosity (8 g/100g sample solid) of 500 BU (Brabender unit, Model VISKOGRAF, Germany). Commercial grade sorbitol was obtained from Vidyasom Co. Ltd. (Thailand).

### Preparation of palm pressed fiber microcrystalline cellulose

The cellulose whiskers were extracted from the palm pressed fiber by alkaline treatment (10% NaOH) on dry base of palm pressed fiber) at 100°C for 1 h, and then bleaching the produced pulp using the sodium chloride bleaching method (Browning, 1967). The suspensions of cellulose crystallites were prepared by acid-catalyzed hydrolysis of palm pressed fiber similar to the method described by Lu *et al.* (2005). Briefly, the bleached palm pressed fiber (20 g) was mixed with sulfuric acid (175 ml, 64%) and stirred vigorously at 45°C for 4 h, and then a

dispersion of MCPF was obtained. After sonication of 15 min, the suspension was neutralized with 0.5 N NaOH and then washed by dialysis.

### Particle size analysis

The size distribution of microcrystalline cellulose was determined by a Laser Particle Size Analyzer (Model LS 230, Coulter). After sonication of 15 min, the suspension was neutralized with 0.5 N NaOH and particle size distribution of NCPF in suspension was measured.

### Film preparation

Starch solution with a concentration of 3% (w/v) was prepared by dispersing rice starch in distilled water and heating the mixtures and stirring until it gelatinized (85°C for 5 min), and then cooling to 45±2°C. The solution was filtered through a polyester screen (mesh no. 140 with mesh opening of 106 µm) by vacuum aspiration to remove any small lumps in the solution. Subsequently, the MCPF dispersion was added and stirred for 20 min. After mixing, the mixture was degassed under vacuum and cast onto flat, leveled non-stick trays to set. Once set, the trays were held at 55°C for 10 h undisturbed, and then cooled to ambient temperature before peeling the films off the plates. Film samples were stored in plastic bags and held in desiccators at 60% RH for further testing. All treatments were made in triplicate.

### Film Testing

**Conditioning.** All films were conditioned prior to subjecting them to permeability and mechanical tests according to the Standard method, D618-61 (ASTM, 1993a). Films used for testing water vapor permeability (WVP), tensile strength (TS) and elongation (ε) were conditioned at 60% RH and 27±2°C by placing them in desiccators over a saturated solution of Mg (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O for 72 h or more. For other tests, film samples were transferred to plastic bags after peeling and placed in desiccators.

**Film Thickness.** Thickness of the films was measured with a precision digital micrometer (Digimatic Indicator, Mitutoyo Corporation, Japan) to the nearest 0.0001 (±5%) at five random locations on the film. Mean thickness values for each sample were calculated and used in water vapor permeability (WVP) and tensile strength (TS) calculations.

**Film Solubility.** Film pieces, 20 mm x 20 mm, were dried at 70°C in a vacuum oven for 24 h, and then weighed to the nearest 0.0001 g for the initial dry mass. Films were immersed into 20 ml of distilled water in 50 ml screw cap tubes containing 0.01g/100 g sodium benzoate. The tubes were capped and placed in shaking water bath for 24 h at 25±2°C. A

portion of the solution was removed and set aside for use later in protein solubility tests as described later. The remaining solution and film pieces were poured onto (Whatman #1) quality filter paper, rinsed with 10 ml distilled water, and dried at 70°C in a vacuum oven for 24 h to determine the dry mass of film. Five measurements were taken for each treatment in triplicate. Total soluble matter was calculated from the initial gross mass and final dry mass using the following equation (Jangchud and Chinnan, 1999):

$$\% \text{ FS (db)} = \frac{(\text{film mass before test} - \text{film mass after test}) \times 100}{\text{Film mass before test}}$$

Water Vapor Permeability (WVP). The gravimetric Modified Cup Method based on ASTM E96-92 was used to determine the WVP of films (McHugh *et al.*, 1994). The test cups were filled with 20 g of Silica gel (desiccant) to produce a 0% RH below the film. A sample was placed in between the cup and the ring cover of each cup coated with silicone sealant (high vacuum grease, Lithelin, Hannau, Germany) and held with four screws around the cup's circumference. The air gap was at approximately 1.5 cm between the film surface and desiccant. The water vapor transmission rates (WVTR) of each film was measured at 60±2% RH and 25±2°C. After taking the initial weight of the test cup, it was placed into a growth chamber with an air velocity rate of 450 ft/min (Model KBF115, Contherm Scientific, Lower Hutt, New Zealand). Weight gain measurements were taken by weighing the test cup to the nearest 0.0001g with an electronic scale (Sartorius Corp.) every 3 h for 18 h. 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 greater. Six samples per treatment were tested. The WVP of film was calculated by multiplying the steady WVTR by the film thickness and dividing that by the water vapor pressure difference across the film.

Tensile Strength and Elongation at Break (TS and  $\epsilon$ ). TS was measured with a Universal Testing Machine (LLOYD Instruments, Hampshire, England) as per the ASTM D882-91 Standard Method (ASTM, 1993b). Ten samples, 2.54 cm x 12 cm, were cut from each film. Initial grip separation and crosshead speed were set at 50 mm and 50 mm/min, respectively. Tensile strength was calculated by dividing the maximum force by the initial specimen cross-sectional area, and percent elongation at break was calculated as follows:

$$\epsilon = 100 \times \frac{(d_{\text{after}} - d_{\text{before}})}{d_{\text{before}}}$$

Where  $d$  was the distance between grips holding the specimen before or after the breaking of the specimen.

Color. A CIE colorimeter (Hunter associates laboratory, Inc., VA, USA) was used to determine the film  $L^*$ ,  $a^*$  and  $b^*$  color values ( $L^* = 0$  (black) to 100 (white);  $a^* = -60$  (green) to +60 (red); and  $b^* = -60$  (blue) to +60 (yellow)). The standard plate (calibration CR-A47,  $L^* = 85.45$ ,  $a^* = -0.15$  and  $b^* = 54.55$ ) was used as a standard.

#### Scanning electron microscopy

Film samples were examined for surface characteristics using a JEOL JSM-5800 LV scanning electron microscope (SEM) (JOEL Ltd., Tokyo, Japan) operated at 10 kV. Five samples were mounted on a bronze stub and sputter-coated (Sputter coater SPI-Module, PA, USA) with a layer of gold prior to imaging, allowing surface visualization.

#### Statistical analysis

A completely randomized experimental design was used to characterize the composite films. Analysis of variance (ANOVA) was used to compare mean differences of the samples. If the differences in mean existed, multiple comparisons were performed using Duncan's Multiple Range Test (DMRT).

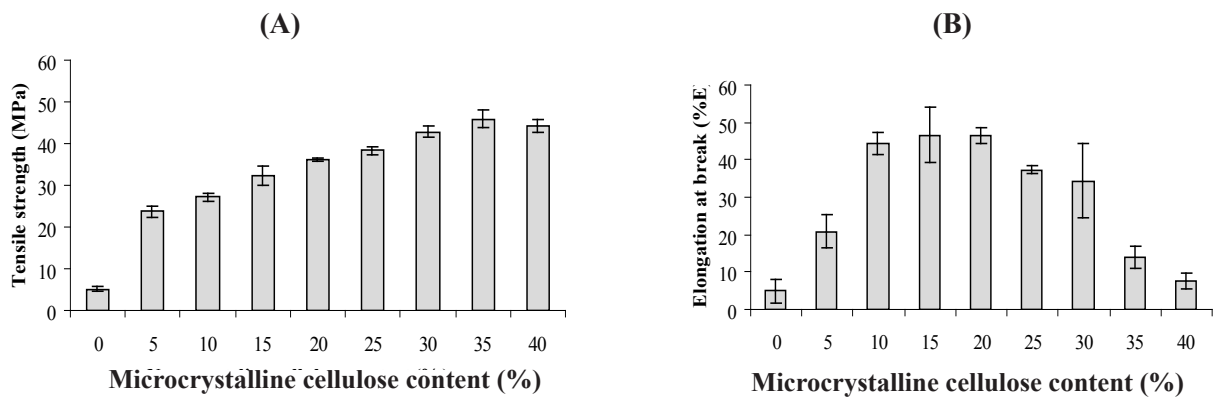
## Results and Discussion

#### Particle size distribution

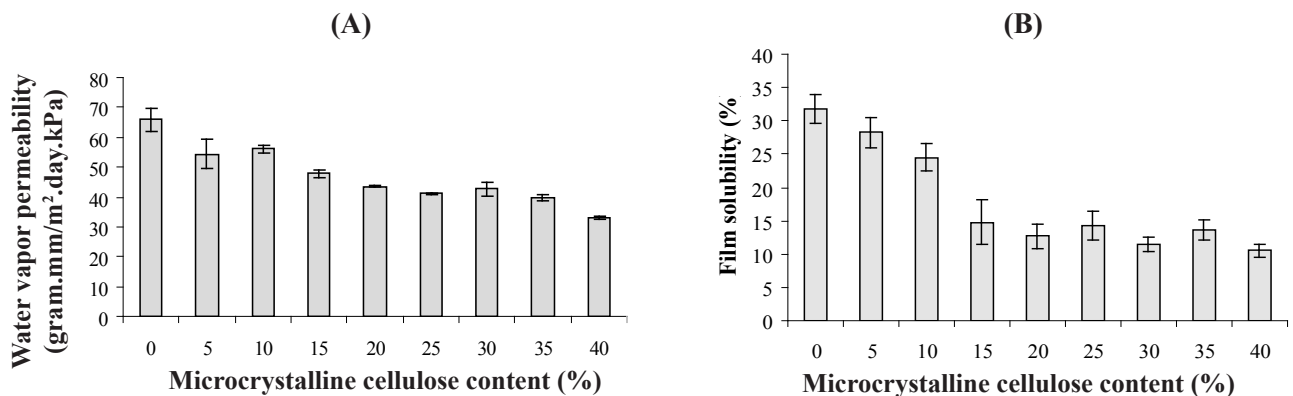
Cellulose whiskers for this study were prepared by acid hydrolysis of palm pressed fiber and analyzed by Laser Particle Size Analyzer. The results showed that the most presence (60-70%) of particle size distribution in the micrometer scale (0.480±0.023  $\mu\text{m}$ ) (data not shown).

#### Tensile strength and elongation at break

A biodegradable composite film must withstand the normal stress encountered during its application and the subsequent shipping and handling of the food to maintain its integrity and barrier properties. Tensile strength is the maximum tensile stress sustained by the sample during the tension test. If maximum tensile stress occurs at either the yield point or the breaking point, it is designated tensile strength at yield or at break, respectively (ASTM, 1991). High tensile strength is generally required, but deformation values must be adjusted according to the intended application of the films. That is, whether it is undeformable material to provide



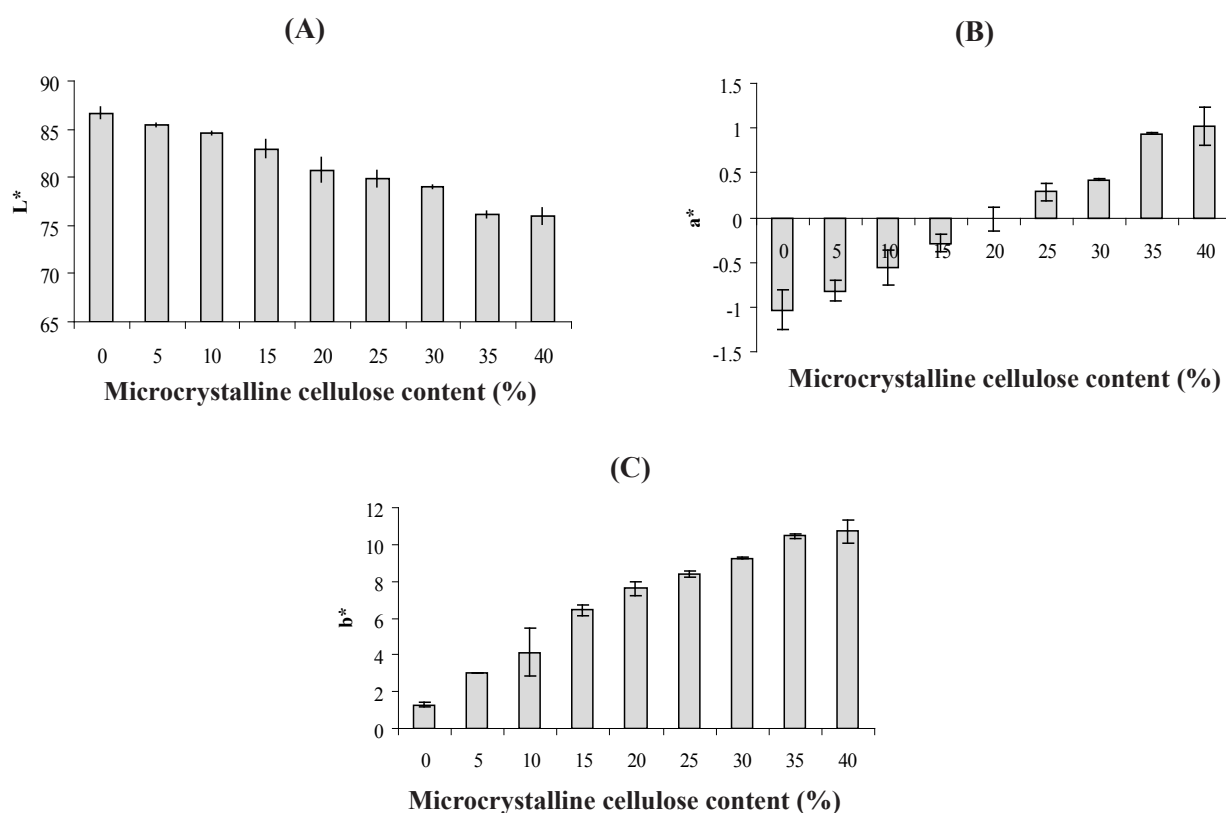
**Figure 1.** The mechanical properties of tensile strength (A) and elongation at break (B) of rice starch films as a function of MCPF content



**Figure 2.** The water vapor permeability (A) and film solubility (B) of rice starch films as a function of MCPF content

structural integrity or reinforce structure of the food (Gontard *et al.*, 1992). Elongation at break is an indication of films flexibility and stretch ability (extensibility), which is determined at point when the film breaks under tensile testing and is expressed as the percentage of change of the original length of the specimen between the grips of a film to stretch (extend). The tensile strength (TS) and elongation at break ( $\epsilon$ ) of the rice starch (RS) films reinforced with microcrystalline cellulose from palm pressed fiber (MCPF) or RS/MCPF biocomposite films is depicted in Figure 1. This figure clearly demonstrates the reinforcing effect of MCPF fillers. The TS of the biocomposite films increased from 5.16 MPa to 44.23 MPa when increasing the MCPF fillers content from 0 to 40% (Figure 1A) and this indicated that a high compatibility occurs between starch matrix and MCPF fillers and the performances (e.g., mechanical properties) due to 3D hydrogen bonds network

formed between different component (Lu *et al.*, 2005). Regarding the  $\epsilon$ , results showed that increases in MCPF fillers from 0 to 15 or 20% provided an increase in  $\epsilon$  from 8.5% to 48.32%. However, addition of MCPF fillers higher than 25% resulted in decreased elongation at break (Figure 1B). It is possibly due to the presence of high content of MCPF fillers might contribute to retarding the intermolecular interaction of the starch films. This induces the development of a heterogeneous film structure, featuring discontinuities, resulting in the decrease in  $\epsilon$  of the films. In addition, MCPF fillers could not fully homogeneous and form small aggregates when 25-40% of MCPF fillers were filled. The results showed that addition of MCPF fillers provided the better mechanical properties of biocomposite films in this work and they are similar to those of biocomposites of plasticized starch reinforced with cellulose crystallines from cottonseed linter (Lu *et al.*, 2005).

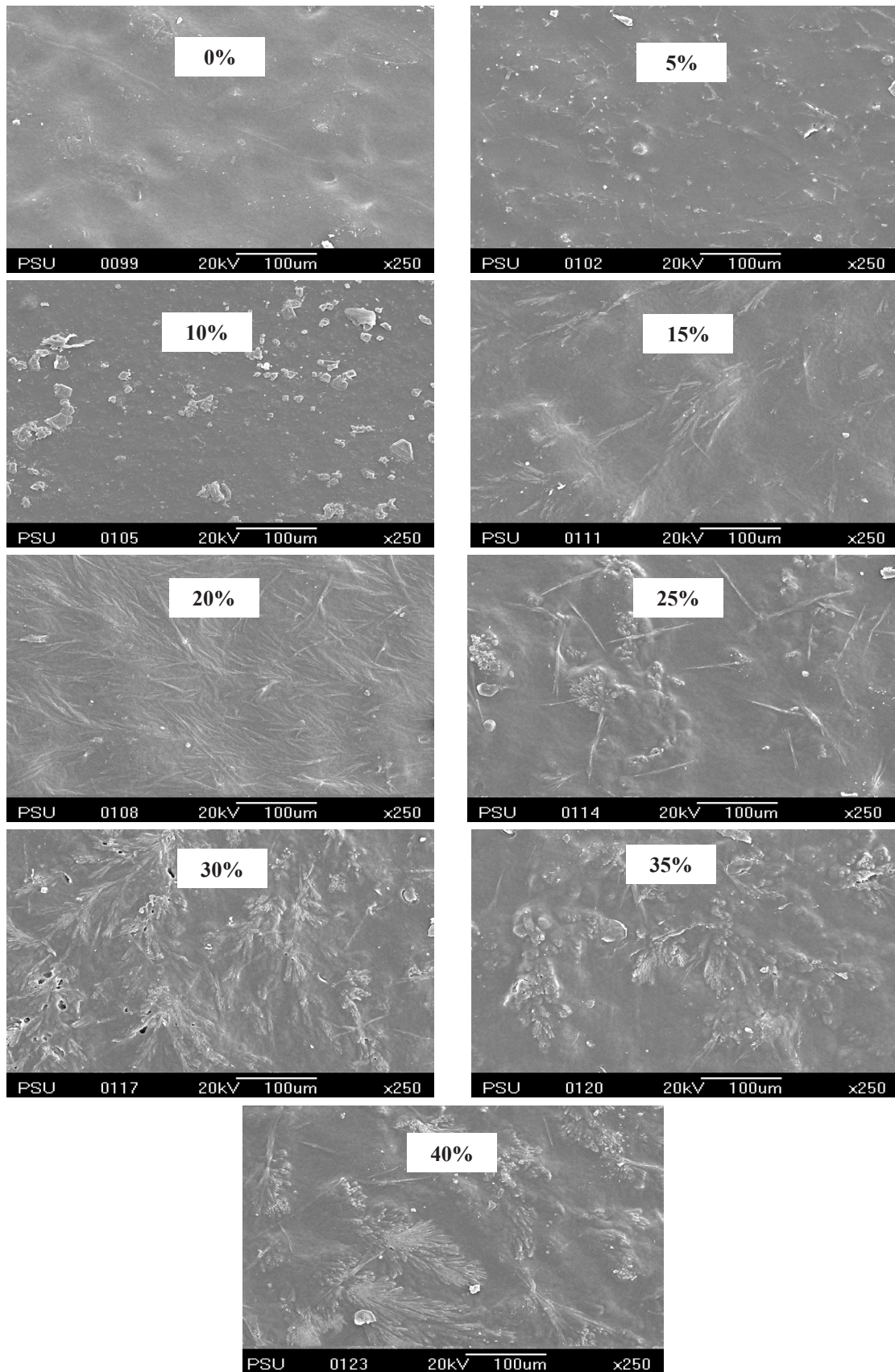


**Figure 3.** The color of L\* value (A); a\* value (B) and b\* value (C) of rice starch films as a function of MCPF content

#### *Water vapor permeability and film solubility*

Water vapor permeability is proportionality constant assumed to be independent of the water vapor pressure gradient applied across the films. However, hydrophilic (edible or nonedible) materials, such as protein films, derivative from this ideal behavior due to interactions of permeating water molecules with polar groups in the films structure (Hagenmaier and Shaw, 1990). Deviation from the ideal behavior can also be induced by temperature effects on materials (Myers *et al.*, 1962). Since a main function of an edible films or coatings are often to impede moisture transfer between food and the surrounding atmosphere, or between two components of a heterogeneous food products, water vapor permeability should be low as possible. The WVP of rice starch composite films with different MCPF were examined at a vapor pressure difference of 0/60% across films. The effect of content of MCPF fillers on water vapor permeability (WVP) of the rice starch films is shown in Figure 2. The WVP of rice starch films decreased as the content of MCPF fillers increased. For example, the WVP of the films decreased from 67.2 g.mm/m<sup>2</sup>.day.kPa to 32.51 g.mm/m<sup>2</sup>.day.kPa when increasing the MCPF fillers content from 0 to 40% (Figure 2A). The improvement of the WVP of the films can

be attributed to the formation of a rigid hydrogen-bonded network of cellulose in the composite that is governed by percolation mechanism (Pu *et al.*, 2007). These considerations and the importance of the MCPF fillers aspect ratio are undoubtedly contributing factors to the mechanical and physical properties of the RS/MCPF biocomposite films reported in this study. Film solubility (FS) is advantageous in situations when the films will be consumed with a product that is heated prior to consumption and may also be an important factor that determines the biodegradability of films when used as a packaging wrap. Biocomposite film pieces produced from RS/MCPF maintain their integrity (i.e., did not dissolve or break apart) even after 24 h of incubation with a gentle motion. This indicates that the rice starch and MCPF had intermolecular networks that remained intact and only the monomers were soluble (Stuchell and Krochta, 1994). The FS of the rice starch films as a function of MCPF in the film forming solutions are shown in Figure 2B. The results demonstrated that the FS of rice starch films decreased with the addition of MCPF. These results could arise from the fact that higher content of MCPF induced a rice starch and MCPF interaction and resulted in a decrease in the FS.



**Figure 4.** The SEM imaging of rice starch film and rice starch/MCPF biocomposite films of 0 to 40% of MCPF

### Films Color

Figure 3A-3B shows the results from the effect of content of MCPF fillers on color ( $L^*$ ,  $a^*$  and  $b^*$ ) of rice starch films. These results show that the amount of MCPF fillers can have significant effect on the color of RS films. Rice starch films became darker as evidenced by the decrease  $L^*$  value as the content MCPF filled Rice starch increased from 0 to 40% concomitant with decreased in  $a^*$  and  $b^*$  values (Figure 3B and 3C). This indicated the decreasing lightness ( $L^*$  value) of the film, possibly due to the original dark color of the MCPF.

### Morphology of the films

The morphology of the rice starch/MCPF biocomposite films was identified by Scanning electron microscopy (SEM). Figure 4 shows the surface of unfilled MCPF fillers (0%) and biocomposite films reinforced with 5 to 40% of MCPF fillers. The rice starch film shows a relative smooth morphology. Compared with rice starch film, the surface morphology of the existence of the MCPF in the rice starch matrix can be easily observed in the composite films. However, it is difficult to distinguish the individual MCPF filler dispersion due to its small size. Some MCPF fillers appear as white domains at the surface of the sample (Figure 4). This should correspond to the MCPF filler in the perpendicular plane of the biocomposite film. By comparing the distribution of MCPF fillers in to the rice starch films as affected by the MCPF content, the results showed that addition of MCPF fillers are more or less evenly distributed within the rice starch films. However some MCPF fillers are not fully individualized and form small aggregates (15 to 40% of MCPF).

### Conclusions

A suspension of microcrystalline cellulose from palm pressed fiber (MCPF), having an average length about  $0.480 \pm 0.023 \mu\text{m}$ , was prepared by acid hydrolysis and used as a reinforcing agent for RS film to obtained RS/MCPF biocomposite films. The rice starch film/ MCPF biocomposite films increased in TS from 5.16 MPa for pure rice starch film to 44.23 MPa but decreased in elongation at the break of composites. The incorporation of MCPF into rice starch films provided an improvement of water resistance for the rice starch films. The improvement properties of the films can be attributed to the formation of rigid hydrogen-bonded network of cellulose in the composite that is governed by the percolation mechanism. The morphology of the existence of MCPF in the rice starch film can be

easily observed in the composite films when more than 15% of MCPF was used, and was concomitant with larger agglomerates.

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