Mechanical Properties and Biodegradability of Starch-based Biocomposite Films Reinforced with Microcrystalline Cellulose from Rice Embryo

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Abstract. In this research, glycerol-plasticized cassava starch/San Pa Tong sticky rice embryo plant microcrystalline cellulose (SPT-MCC) biocomposite films were prepared by solvent casting technique. SPT-MCC were extracted from sticky rice embryo plant by alkaline delignification process, bleached with hydrogen peroxide and hydrolysis with sulfuric acid, respectively. Effect of SPT-MCC content (0-60% wt% based on starch content) on thermal properties, mechanical properties and biodegradability of the biocomposite films were studied. Biodegradation of biocomposite films were investigated by soil burial test methods for 8 days. The biodegradability test results were compared with the degradation of three types commercial plastic bags. The result showed that thermal stability of biocomposite films decreased with the increasing of SPT-MCC addition while the tensile strength and Young’s Modulus of biocomposite films increased with the increment of SPT-MCC content. Starch-based biocomposite films reinforced with 10-40% wt% of SPT-MCC completely decomposed within 3 day, while the 50-60% wt% of SPT-MCC biocomposite films entirely degrade within 8 day.

1. Introduction
Plastic materials are an important material used worldwide but it is very resistant to micro-organism and difficult to be naturally decomposed. This will be led to environmental problem and solid waste management. There has been a widespread interest in films made from renewable and natural polymers, biopolymer films have been regarded as potential replacements for synthetic films in food packaging applications in response to a strong marketing trend towards more environmentally friendly materials. Among all biopolymers, starch is a biopolymer of wide availability, low-cost, renewable, and biodegradable agro-polymer that is being investigated as a potential material for biodegradable films. However, compared to the common thermoplastic polymers, starch films have disadvantaged including poor mechanical properties and high-water sensitivity. To improve mechanical strength, many previous studies have determined that natural fibers like cellulose have ability to reinforce and improve the mechanical properties of film in the starch matrix [1-4]. Microcrystalline cellulose (MCC) are the crystalline domains of cellulose fibers, isolated by means of acid hydrolysis, chemical treatments with acids or bases promote hydrolysis and improve the yield of glucose from cellulose by removing hemicellulose or lignin during pretreatment. The preparation of MCC from several agricultural lignocellulosic waste such as wheat and cereal straws, rice straw, soybean husk, bagasse and corn cob, rice husk, banana plant wastes, sugar cane bagasse has been studied [5-7]. Since cellulose from different sources differs in properties, different properties of MCC obtained from different cellulose sources are
expected. In this research, microcrystalline cellulose that extracted from San Pa Tong sticky rice embryo plant was used as reinforcing filler in cassava starch films. San Pa Tong sticky rice embryo plants that used to prepared MCC was the waste from the phytochemical active compound extraction in Maejo University research laboratory, Thailand. The effect of San Pa Tong sticky rice microcrystalline cellulose (SPT-MCC) content on mechanical properties and biodegradability of the starch-based biocomposite films have been investigated.

2. Experimental Procedure

2.1. Microcrystalline Cellulose Extraction
In this work, raw material for microcrystalline cellulose production was the residue of San Pa Tong sticky rice embryo plants. San Pa Tong seed was soaked in 25 mg/L fish protein hydrolysates for 24 hrs. After air dried for 12 hrs, the seeds were placed in coco coir as substrate. Nine days old seedling was harvested to extract phytochemical with distilled water for spray dying. After squeezing and extraction of active compound, San Pa Tong sticky rice embryo plants residue was dry. Then, dried residue San Pa Tong sticky rice embryo plants was soaked in boiling distilled water for 1 hr and delignification with 0.5 M NaOH at 60°C for 4 hrs (1 g : 30 ml). San Pa Tong sticky rice plants pulp was then bleached with 5%(v/v) H2O2 in 0.5 M NaOH 60°C for 4 hrs (1 g : 30 ml). After that, bleached pulp was hydrolyzed with 60%v/v H2SO4 at 55°C for 30 mins to obtained microcrystalline cellulose. The SPT-MCC was received after dialysis and freeze-drying process.

2.2. Biocomposite Films Preparation
The biocomposite films were prepared using the solution casting method. The cassava starch was mixed with distilled water (1 g cassava starch: 14 ml distilled water) and continuous stirring at 80°C for 30 mins until the gelatinization of the cassava starch occurred. The slurry was then mixed with glycerol and SPT-MCC were added and the mixture was stirred for another 20 mins at 80°C. The SPT-MCC content was varying from 0-60 wt% based on cassava starch content. Subsequently, the mixture was degassed by setting the mixture at room temperature. The gel was poured and spread thoroughly on the Petri dish mold. The film was left dried at ambient temperature for 48 hrs., after which the obtained films were stored under dry conditions until testing. The final thickness of cast films was about 0.5 mm, which was controlled by calculating the quantity of suspension poured onto the Petri dish plate. The actual film thickness was measured by micrometer (μm).

2.3. Characterization and Testing
Thermogravimetric analysis (TGA) was performed at a heating rate of 10°C/min from 25°C to 600°C under nitrogen atmosphere. The tensile stress at maximum load, tensile modulus, and percent elongation at break of the starch-based biocomposite films were measured by Universal Testing Machine (Model LLOYD LR 100K). The film samples in the size of 100 mm x 10 mm were carried out according to the ASTM D 882 standard method, with initial grip separation or gauge length of 50 mm, crosshead speed of 5 mm min⁻¹, and load cell of 100 N. Five specimens of each sample were tested and averaged to obtain a mean value. Biodegradability test of films was followed during soil burial test for 8 days. The samples in the form of thin films were cut into the size of 1 cm x 5 cm. Soil was placed into plastic box (32 x 39.5 x 14 cm) with tiny holes at the bottom and on each side of the box to increase air and water circulation. Soil was kept moist with water and stored outside the room at ambient humidity (44-55%) and temperature (25-30°C). Samples were buried in soil at a depth of 7 cm. The biodegradability of starch-based biocomposite films were evaluate by observation the physical appearance of films every day.
3. Results and Discussions

3.1. Chemical Composition and % Conversion of San Pa Tong sticky rice embryo plants

The chemical composition of lignocellulosics is inherent according to the particular needs of the plants. Cellulose, hemicellulose and lignin are the three main constituents of any lignocellulosic source. Table 1. present the chemical composition of San Pa Tong sticky rice embryo plants.

| Testing                     | % weight of dry sample |
|-----------------------------|------------------------|
| Alcohol benzene soluble     | 8.86                   |
| α-Cellulose                 | 39.70                  |
| β-Cellulose                 | 5.71                   |
| γ-Cellulose                 | 7.27                   |
| Lignin                      | 7.86                   |
| Hemicellulose               | 13                     |
| Ash                         | 10.50                  |

Table 1. Chemical composition of San Pa Tong sticky rice embryo plants

Determination of the percentage of conversion of SPT-MCC after delignification, bleaching and hydrolysis process was calculated as equation (1) and the % conversion of SPT-MCC was 12.95%.

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\text{% conversion} = \frac{\text{weight of SPT-MCC (g)}}{\text{weight of dry SPT sticky rice embryo plant (g)}} \times 100
\]  

(1)

3.2. Physical Appearance of Biocomposite Films

Figure 1 present the physical appearance of native cassava starch film compared with biocomposite films reinforced with different contents of SPT-MCC. Starch films were apparently transparent. However, the transparency of starch-based film was decreased after the increment of microcrystalline cellulose content due to the formation of two phases in the system. The biocomposite films became opaque and turned to yellow color with the increasing the amount of SPT-MCC.

Figure 1. Physical appearance of cassava starch film and biocomposite films reinforced with different contents of SPT-MCC.
3.3. Thermogravimetric Analysis (TGA)
The thermal stability of starch-based biocomposite films was studied by TGA. The decomposed temperature reported in this work was the temperature at maximum rate of mass loss (Td_{max}). TGA curves of cassava starch film plasticized with glycerol, SPT-MCC and biocomposite films are presented in Figure 2. The TGA curve of SPT-MCC present three decomposition stages. The first one around 90-100°C with about 8% of the total weight loss is due to the absorbed water in cellulose structure. The second stage appearing at higher temperature around 220°C is due to the decomposition of hemicellulose that remained in the structure with the 34% of total weight loss. The third stage around 320°C is due to cellulose decomposition. In the cassava starch film plasticized with glycerol, it shows two events of decomposition. The first event (260°C) refers to degradation of glycerol and the second event (310°C) relates to the degradation of starch. The degradation of starch-based films reinforced with 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt% and 60 wt% SPT-MCC tool place at 294, 306, 308, 304, 321 and 276°C, respectively. By addition of SPT-MCC, the result revealed that, the thermal stability of biocomposite film had tendency to decrease with the addition of SPT-MCC reinforcement.

Figure 2. TGA curve of cassava starch plasticized glycerol film, SPT-MCC and starch-based films reinforced with different contents of SPT-MCC.

3.4. Tensile Testing
Cassava starch film and biocomposite films were prepared by casting method and the thickness of the films sample was approximately 0.4-0.9 mm. Figure 3 illustrates the effect of SPT-MCC content on tensile strength (a), Young’s modulus (b) and %elongation at break (c) of the films.

Figure 3. Tensile strength (a), Young’s modulus (b) and %elongation at break (c) of starch-based biocomposite film at various SPT-MCC content.

As clearly seen in Figure 3, the films with higher ratio of SPT-MCC had better tensile strength and Young’s modulus but they show poorer flexibility. The tensile strength and Young’s modulus of the films increase significantly from 1.93 to 8.49 MPa and from about 0.22 to 5.32 MPa with increasing
SPT-MCC content from 0 to 60 wt%, whereas the elongation at break decreases from 59.80% to 3.85%. This behavior is in agreement with the results reported in the literature about starch films reinforced with different kinds of cellulose fibers [8-9]. The reinforcement mechanism by the addition of rigid particles acted as reinforcement agents into a matrix is well known and the SPT-MCC act similarly. In addition, this significant increasing of films rigidity has been attributed to the similarity between the chemical structures and strong interactions by hydrogen bonding between cellulose and starch, result in efficient stress transfer from the matrix to the fillers [10].

3.5. Biodegradability

Figure 4 display the physical appearance of cassava starch film and biocomposite films after soil burial test for 0-8 days. It can be seen that starch-based biocomposite films reinforced with 10-40% wt% of SPT-MCC completely decomposed within 3 day, whereas the 50-60 wt% of SPT-MCC biocomposite films entirely degrade within 8 day. For all three types of commercial plastic bags, no degradation occurred within the testing period.
Figure 4. The physical appearance of cassava starch film and biocomposite films after soil burial test for 0-8 days.

4. Conclusion
Thermal stability of biocomposite films decreased with the addition of SPT-MCC. The tensile strength and Young´s Modulus of biocomposite films increased with the increment of MCC content while the %elongation at break decreased with the increasing of MCC. Starch-based biocomposite films reinforced with 10-40% wt% of MCC completely decomposed within 3 day, while the 50-60% wt% of MCC biocomposite films entirely degrade within 8 day.

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