Morphology and biodegradability of microcrystalline cellulose / chitosan films

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Abstract The microcrystalline cellulose (MCC) chitosan film was produced through solution casting with different composition of chitosan and different plasticizers. Glycerol and polyethylene glycol (PEG) was used as a plasticizer in the MCC/chitosan film. Several testing on the biodegradability were conducted such as scanning electron microscope (SEM), moisture absorption and soil burial test. Results show that addition of plasticizer able to improve the miscibility of chitosan on the MCC film. According to moisture absorption and soil burial test, the addition of plasticizer showed the MCC/chitosan films were better in water resistance due to the plasticizer was able to facilitate the dispersion of chitosan in MCC films. The morphological analysis also found out that better interaction between MCC and chitosan when polyethylene glycol and glycerol was used as plasticizers in the films.

1 Introduction

Environment and sustainability issues have drawn attention from societies, this has giving outstanding improvements in bio-materials via the development of biocomposites in the field of polymer science [1-5]. Advantages of biocomposites which is not possible for synthetic polymer composite to do is able to depose and compose easily without harming the environment. There is a wide range of application for bio- and green composites, which is from structural to biomedical. Cellulose reinforcement and petroleum-based polymers composites are usually referred to as biocomposites, while composites based fully on naturally derived fibres and biopolymers have been named green composite [6]. However, the intrinsic chemical incompatibility between a hydrophobic polymer matrix and hydrophilic cellulose results in weak interfacial bonding between the cellulosic and biopolymer components, especially in the case of thermoplastic biopolymers [7]. There are many applications in natural fibre-reinforced biocomposites such as packaging, automobiles, building industries and aerospace which uses of product is not required high load carrying capacity [8]. The attractive properties of natural fibre compare to traditional counterparts are free formability, fatigue, substantial resistance to corrosion, low self-weight and relatively high specific strength. However, natural fibres are challenging in selection because of their insufficiency characteristics which are highly anisotropic nature.

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and high moisture absorption [9]. There has new interest in chitin and chitosan as a matrix in making of plastic film due to their unique properties such as anti-microbial activity, biocompatibility, economic advantages and biodegradability.

Chitosan is from renewable resource and non-toxic polymer which is derivative of chitin, an abundant by product of seafood processing like crab shell, prawn shell waste and lobster shell. In addition, chitosan is the second most abundant biopolymer after cellulose in the nature [10]. Numerous surveys have been done on the studies of film produced from chitosan, for example, chitosan blend with natural polymer or synthetic polymer and modified chitosan. A research showed plasticized maize starch combined with chitosan so as to enhance mechanical properties, water resistance and provide a barrier to oxygen of starch film which is formed by solution casting. Furthermore, chitosan is a natural polymer which acted as biodegradable additive and give anti-microbial properties to the blend [11].

## 2 Experimental

### 2.1 Materials

Chitosan act as main component in this chitosan MCC film. Chitosan was manufactured at Sigma Aldrich. MCC was obtained from Sigma Aldrich which follow United States Pharmacopeia (USP) Reference Standard (Material number: 1098388; CAS Number 9004-34-6). Glycerol was used as plasticizer in this film. Glycerol was obtained from HmbG Chemicals (Germany; Code: C0347-91552409). Polyethylene glycol (PEG), also sometimes referred to as polyethylene oxide (PEO) was obtained from Sigma Aldrich. Lithium chloride was obtained from Avantor Performace Materials. N,N-Dimethylacetamide is the organic compound which miscible with most other solvents, but it is poorly soluble in aliphatic hydrocarbons. DMAc was obtained from Avantor Performance Materials (Germany; CAS number: 127-19-5).

### 2.2 Preparation of the sample

#### 2.2.1 Preparation of MCC solution

First, the amount of MCC powder, DMAc solution and lithium chloride (dry in oven 24 hours at 110°C) needed was weight. MCC powder was added into DMAc solution and stirred for 15 minutes. Lithium chloride was then added into DMAc solution and stirred for 45 minutes until MCC powder fully dissolved and form colourless solution.

#### 2.2.2 Preparation of MCC chitosan films with glycerol and polyethylene glycol

Glycerol as plasticizer was added into MCC chitosan solution and then stirred for 15 minutes to get homogeneous solution. Similar steps were used for polyethylene glycol as plasticizer. Then, the solution was casted to the glass plate (50 ml). Finally, took out the film when it fully dried. The formulation of MCC chitosan films were shown in Table 1.
Table 1. Formulation of MCC chitosan film.

| Sample name       | MCC: Chitosan ratio | Glycerol (%) | Polyethylene glycol (%) |
|-------------------|--------------------|--------------|-------------------------|
| MCC film          | 100:0              | 0            | 0                       |
| MCC/chitosan (95/5) film | 95:5              | 0            | 0                       |
| MCC/chitosan (90/10) film | 90:10             | 0            | 0                       |
| MCC/chitosan (85/15) film | 85:15             | 0            | 0                       |
| MCC/chitosan (80/20) film | 80:20             | 0            | 0                       |
| MCC film          | 100:0              | 3            | 0                       |
| MCC/chitosan (95/5) film | 95:5              | 3            | 0                       |
| MCC/chitosan (90/10) film | 90:10             | 3            | 0                       |
| MCC/chitosan (85/15) film | 85:15             | 3            | 0                       |
| MCC/chitosan (80/20) film | 80:20             | 3            | 0                       |

3 Characterization and Testings

Morphology of the MCC/chitosan films were observed under the SEM model JEOL JSM 6460LA. Crystalline structure and chemical composition of specimen can be determined. The specimens were prepared by mounted it on the aluminum stubs and coat it with the palladium. Specimen need to coat in order to make it conductive so that the electron can react with the specimen to get the morphology needed. Moisture absorption test was used to test the moisture absorption ability of the film. This test was conducted by weight specimens before and after dried in the oven at 45°C for 2 hours. The weight of dry finish product was cut into 4cm x 2cm x 1cm size and test according to ASTM D-570. The specimens were cooled down in the desiccator. Weighed were taken for all the specimens for every 5 days interval in the room temperature.

MCC chitosan film was cut into dimension of 3 cm × 3 cm. Containers with few tiny holes at bottom of container were prepared. Moist soil was filled into the container. Specimens were buried from the soil surface with the depth of 5 cm. The specimens were taken out and weighted for first 10 days and followed by 5 days interval after 10 days.

4 DISCUSSION

4.1 SEM morphology

Fig. 1 shows the SEM image of MCC chitosan films. The fracture surface of MCC film was smooth compare with the fracture surface of MCC with addition of plasticizer which was glycerol and polyethylene glycol (PEG). There were more resistant to break was observed due to effect of plasticizer [12,13]. From Fig. 1, the beard formation after tensile test, the surface of MCC with glycerol was prominent as compared to the fracture surface of MCC with PEG. It shows the resistant of the films to break after addition of glycerol.
as plasticizer. The darker region in the Fig. was chitosan filler which embedded fitly into MCC matrix. This was because chitosan has high compatibility with MCC. Plasticizer only exhibit its effect on MCC matrix and not to the interaction between chitosan and MCC [14]. Hence, there is little different to the MCC chitosan film’s fracture surface which due to the plasticizer effect only on MCC matrix. From the SEM image shown in Fig. 1, the fracture surface of MCC chitosan film is rougher compared to MCC film. This due to the addition of chitosan into MCC film which make the void exist in the MCC film filled with chitosan make the film stronger resist to external force. Hence, the tensile strength and break elongation is higher when chitosan added into MCC film.

![Fig. 1. Image of Scanning Electron Microscope for MCC chitosan films with x2000 magnification.](image)

A) MCC film. B) MCC with glycerol. C) MCC with polyethylene glycol (PEG). D) MCC with 10% of chitosan. E) MCC with 10% of chitosan and glycerol. F) MCC with 10% of chitosan and polyethylene glycol (PEG).

4.2 Moisture absorption

Moisture absorption test is carried up to measure the moisture intake by the film after expose to the surrounding in room temperature for days. There were three stages in moisture absorption curve as shown in Fig. 2. The moisture absorption of MCC chitosan
for the first stage was increase steeply. This was due to void present between the polymer phases. Water molecules hence fill up the void in the film results in increase weight of the film. However, the moisture absorption of MCC chitosan film were increased moderately on second stage. The water molecules was attach to hydroxyl group of the MCC and chitosan. At last, the moisture absorption curve of MCC chitosan film shown in Fig. 2 almost constant at third stage. This was due to void and hydroxyl group of MCC chitosan film almost fully filled and multiple layer of water absorption take place on the surface of the film form at third stage. MCC was very sensitive to moisture absorption. The cellulose crystals with their surface hydroxyls also contribute to moisture uptake. In other words, the density of the hydroxyl groups on the film surface increases with the MCC content in the film [15].

However, this can be improved by adding chitosan as filler. Due to high compatibility of MCC and chitosan, chitosan able to embed well into void of MCC. With the reducing void in the MCC chitosan film, the water molecules which filled up the voids exist in the film will be reduced. The incorporation of chitosan into cellulose film has made cellulose film less water permeable because chitosan could form hydrogen bond with cellulose molecules, thus decreasing water absorbency. Furthermore, the dimension of chitosan formed a rough and compact film structure, and therefore, decreasing water absorbency of cellulose films [16]. Therefore, MCC with 10% chitosan film has 14.56% at day 30 lower moisture absorption compared to that of MCC film which 15.15% at day 30.

Besides, plasticizer PEG and glycerol can replace water in low concentration in order to form interaction PEG or glycerol with MCC. This can be proved by the result where the MCC chitosan film has low moisture absorption when adding plasticizer. During day 30, the moisture absorption for MCC film with PEG and glycerol were 13.86% and 12.36% respectively compared to that of without plasticizer which 15.15%. Plasticizer make MCC chains tightly hold together and make the chain flexible. However, volatility of PEG was higher than glycerol [17]. For example, results shows during day 30, moisture absorption for 10% of chitosan in MCC chitosan film with PEG was 12.86% while 10% of chitosan in MCC film with glycerol only 12.15%. This was because PEG has two hydroxyl group while glycerol only has one hydroxyl group. There was why the moisture absorption of MCC chitosan with PEG is higher compared to MCC chitosan with glycerol. Since the plasticizer volatility may influence film properties and stability, the less volatility plasticizer is better for use.

![Fig. 2. Moisture absorption of MCC chitosan film in 30 days.](image-url)
4.3. Soil burial test

Soil burial test is used to measure the degree of film degrade after being expose to the decomposition condition. MCC chitosan film was a biodegradable product that have the degradation properties. Thus, soil burial test was applied to the film in order to know the degree of degradation of the film. Fig. 3 has shown the weight change during the degradation of MCC chitosan film. The weight of MCC chitosan film were initially increase until day 5. This is because the film were absorb water from soil. However, there was different water uptake by the film which due to the function of filler, chitosan and plasticizer. The different water uptake by films from soil were explained in the moisture absorption test. The slower degradation rate in the MCC chitosan film was due to the resistance in water uptake and diffusion through the composite compared to pure MCC, which readily takes up water[ 18]. After day 5, MCC chitosan films starting experience weight loss over time. 10phr of chitosan in MCC chitosan film having lowest weight loss compared to others. This was because the function of plasticizer and filler, chitosan mostly filled all the voids in the MCC film, thus, the reaction between the film and soil lesser.

On the other hand, pure MCC film was experienced huge weight loss due to the substitution of OH group in MCC with soil and there was many void inside the MCC chains compared to others. From the result, MCC film which adding chitosan as plasticizer having low degree of degradation compared to pure MCC film. This was because chitosan has antimicrobial properties which prevented the microbial attack. Therefore, MCC chitosan film has low weight loss compared to that of pure MCC film. There was degradation mechanism taken place from day 5 on the surface of the film. However, starting from day 10, MCC chitosan film experienced degradation inside the film and begin to break the chains. MCC chitosan film were then having huge weight loss due to chain break and the degradation were faster [19]. After day 15, the MCC film were fully degrade while MCC chitosan film left some residues. Fig. 4 shows the MCC chitosan film condition before and after 5 days. From the Fig. 4 (A), it can be seen clearly that there was some parts of MCC chitosan film started to degrade after 5 days. This results of significant weight loses in MCC chitosan film. There were microbial attack by the microbial colonies on the MCC chitosan film. This can be seen from all MCC chitosan film where yellow colour spot was the microbial colonies. The microbial attack causes the discolouration on the surface of MCC chitosan film. Microbial colonies were microorganisms that will generate the enzymes to causes the breakage of the MCC and chitosan backbone chain [20]. Hence, the film will degrade fully after a certain period. From Fig. 5, MCC film with 3% glycerol was degraded faster as compared to MCC chitosan film after 5 days.
Fig. 3. Weight change of MCC chitosan film (%).

Fig. 4. MCC/chitosan film with 3% polyethylene glycol images from optical microscope before and after 5 days of soil burial.

Fig. 4. MCC/chitosan film with 3% polyethylene glycol images from optical microscope before and after 5 days of soil burial.
5 Conclusions

In the optimum composition of chitosan in MCC/chitosan film, the weight loss in soil burial test is the lowest due to the chitosan antimicrobial properties. Besides, moisture absorption of MCC chitosan lesser when compared to control film counterparts. This was due to high compatibility of MCC and chitosan which has been proven in Scanning Electron Microscopy images which MCC was embeded well into of chitosan phase. It was then reduced the water molecules filled up the voids exist in the film. From SEM, It was clearly shown that plasticizer enhances the interaction between MCC chains which result in the formation of beards on the surface which resist the external force applied. Besides, the addition of plasticizer has improved the properties of MCC chitosan films.

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