



Effect of Relative Humidity on Mechanical Properties of Blended Chitosan-Methylcellulose Film

Pornchai Rachtanapun* and Panchat Wongchaiya

Division of Packaging Technology, Faculty of Agro-Industry, Chiang Mai University, Thailand.

* Author for Correspondence: E-mail: p.rachta@chiangmai.ac.th

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ABSTRACT

The effects of relative humidity (RH) on the mechanical properties of polymer films obtained by blending of chitosan-methylcellulose were investigated. The film samples were conditioned at various % RH for at least 48 h and then the mechanical properties were analyzed. The blended film achieved an optimum tensile strength (20.86 mPa) at 45.9% RH and elongation at break (52.4%) at 76.2% RH. Thermal properties and morphologies of the blended films were also studied. Melting points of the chitosan and methylcellulose films as examined by differential scanning calorimetry (DSC) were 115°C and 118°C, respectively. After blending of chitosan and methylcellulose the melting point of the blended film was lower than that of the individual film and the blended film had only one peak at 110°C. This phenomenon shows that the blended chitosan-methylcellulose film forms a homogeneous mixture. Scanning electron microscopy (SEM) was used to characterize the morphology of the films. SEM images confirmed the homogeneous nature of the blended films.

Keywords: biopolymer, chitosan, methylcellulose, blended polymer film, relative humidity.

1. INTRODUCTION

Biodegradable polymers are materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics [1]. Biodegradable polymers are polysaccharide, proteins, lipid and others. The most important biodegradable film is polysaccharide including starch, cellulose derivatives, chitin and chitosan, alginate, carrageenan and pectin because they have a good film-forming property and can be used for preparation of edible films and coatings [2]. However, biodegradable films are often sensitive to relative humidity since they are hygroscopic and have limited mechanical resistance [1]. One strategy to overcome this drawback is to associate biodegradable polymer with a moisture-resistant polymer. These polysaccharide films are

blended to synthetic polymer such as thermoplastic starch/synthetic polymer. The polysaccharide films are also blended with each other such as carboxymethylcellulose/ corn starch [3]. In some cases, these formulas can improve the mechanical and moisture barrier properties of the edible films depending on the interactions between components.

The National Innovation Agency (NIA) of Thailand reported that demand for biodegradable plastic is rapidly growing. In Europe and the United States of America, market demand for biodegradable plastic is 40,000-50,000 and 70,000-80,000 tons/year and has expanded 20 and 16% per year, respectively. This is due to growing solid waste disposal, resulting in shortage of landfill availability and the need for environmentally responsible use of resources together with

CO₂ neutrality [4]. To address these problems, biodegradable plastics are preferred to synthetic plastics.

Methylcellulose (MC) is a water soluble cellulose derivative that exhibits thermal gelation [5]. It has excellent film forming properties and provides an effective barrier to lipid but non-effective barrier to oxygen and water vapor. To improve the barrier properties to water vapor, oxygen and carbon dioxide, mixtures of MC with polysaccharides [6] have been made.

Chitosan (CHI) derived by the deacetylation of chitin to the d-N-acetylated form is biocompatible and biodegradable, nontoxic and edible material. Moreover, chitosan can form transparent film with good oxygen and carbon dioxide permeability but it is also sensitive to moisture. Chitosan has been employed in a variety of applications such as food, medicine, cosmetics and wastewater treatment and it is commercially available.

However, individual CHI and MC films have poor mechanical properties. CHI film is hard and brittle while MC film is soft and flexible. In order to overcome these poor mechanical properties of film, chitosan and methylcellulose were blended. The blended film may improve mechanical properties since these two types of polysaccharides have compatible structure [7-8].

The objective of this work is to investigate the effects of relative humidity (RH) on the mechanical and thermal properties of the 1:1 chitosan-methylcellulose blended films and to examine the morphology and compatibility between these two polysaccharides.

2. MATERIALS AND METHODS

2.1 Materials

Chitosan (90% deacetylation and purity 99.75%) was purchased from Bannawach Bioline Co., Ltd (Samuthsakorn, Thailand), methylcellulose from Gammaco (Bangkok, Thailand). Acetic acid and ethanol were purchased from MERCK (Darmstadt, Germany). Glycerol was purchased from Ajax Finechem (NSW, Australia).

2.2 Film Preparation and Film Thickness Measurement

Methylcellulose (MC) film was prepared by dissolving 1.5 g of methylcellulose in 100 ml of 50% ethanol and then 0.5% (v/v) glycerol was added as plasticizer. The solution was then heated at 75°C for 10 minutes [6]. The chitosan (CHI) film was prepared by dissolving 1.5 g in 100 ml of 1% acetic acid (v/v). The solution was then heated at 72°C for 60 min. These film-forming solutions were then mixed, continuously stirred, filtered, degassed, and cast using a tape casting machine with a speed of 5 rpm and 2 mm thickness gage. Then, the film was allowed to dry at 40°C for 24 h in a hot air oven. Dried films were peeled off and conditioned at 25±2°C, 50±5% RH for at least 48 h before testing [8]. Film Thickness was measured using a gage micrometer (GT-313-A, Mitutoyo Co. Ltd, Japan) with an accuracy of 0.01 mm at 5 different locations on each film (~52-54 micrometers). The mean thickness value of each sample was used in calculation of tensile strength.

2.3 Mechanical Properties

Films specimens used for testing the tensile strength and percent elongation at break were conditioned over saturated salt solutions having the desired relative humidity (15.6, 35.5, 45.9, 67.5, 76.2 and 92.7 %RH) at 25 ± 2°C for at least 48 h.

The tensile strength (TS) and percent elongation at break (%EB) were measured according to ASTM D 882-80 [9] using an Instron Universal Testing Machine (Model 1000, H1K-S, England). Test specimens were cut into rectangular strips with dimensions 140×15 mm. The initial grip separation and crosshead speed were 100 mm and 20 mm/min, respectively. The TS was calculated by dividing the maximum load by cross-sectional area of the specimen. %EB was calculated as the percentage of change of the initial gage length of a specimen at moment of rupture.

Data were analyzed using Duncan's Multiple Range Test ($P \leq 0.05$) within the SPSS software program.

2.4 Thermal Properties

The thermal property of the films was

determined using differential scanning calorimetry (DSC) model DSCQ100 (TA Instrument, UK). Aluminum pans containing approximately 10 mg of films were used for the DSC measurement. The heating rate was 10°C/min from -50 to 350°C under N₂ gas at a flow rate of 50 ml/min. The DSC thermograms were used to determine the melting point of the films.

2.5 Scanning Electron Microscopy (SEM)

Sample morphology was investigated through a scanning electron microscope SEM (JSM-5910LV (JEOL, Tokyo, Japan) at acceleration voltages of 15 kV. Each film was mounted on a bronze stub and coated with gold, then observed and photographed.

3. RESULTS AND DISCUSSION

3.1 Film Appearance

The obtained chitosan film was yellowish, brittle and homogeneous. The MC film was colorless, flexible and homogeneous. The chitosan-methylcellulose (CHI-MC) films had a slightly yellowish appearance and were also flexible and homogeneous.

3.2 Effect of Percent Relative Humidity on Mechanical Property of the Biodegradable Film

The effect of polymer blending on tensile strength and percent elongation of MC film, CHI film and blended CHI-MC films are shown in Figure 1 and 2. The CHI-MC film had a higher tensile strength than the MC film but was lower than the CHI film (Figure 1) because CHI contributes a stronger film and reduction in flexibility of composite films [7]. The MC film had the highest %elongation at break compared with CHI and CHI-MC films as expected. These differences correspond to the glass transition of the polymer, which affects the elongation more than the tensile strength. Depending on the stress-strain curves, MC-based films were classified as pseudoductile. Increases in %elongation at break mainly occur when films become rubbery, i.e., when structure changes from ductile to elastic [10].

The effect of percent relative humidity on tensile strength of these films is shown

in Figure 1. The tensile strength of the CHI films decreased as RH increased. The tensile strength of the MC films slightly increased as RH increased below 67.5 %RH and then tensile strength dramatically decreased as RH increased. For blended CHI-MC films, the tensile strength increased from 15.6 to 45.9 %RH after that tensile strength decreased as %RH increased. The results indicated that film deformation due to moisture occurred after 45.9 %RH. Addition or removal of water may cause phase transitions in the macromolecular structure [10]. The results correspond to other types of polymer blend at low and moderate relative humidity. However, at high relative humidity the studied film was deformed since the mechanical properties were decreased. This variation is acceptable for the application when used in low and moderate relative humidity atmosphere but unsuitable for high relative humidity.

Figure 2 presents the effect of relative humidity on %elongation at break of the tested films. The trend of %elongation at break increased with increasing relative humidity. The relative humidity did not affect on the %elongation of CHI film. The percent elongation of MC film slightly increased as relative humidity increased. The percent elongation of the blended CHI-MC film increased with increasing of relative humidity and had a slight decrease at high 93 %RH. Gennadios et al. [11] reported that films with higher elongation values usually required a lower load to cause film breakage. These results could be related to structural modification of film by water which causes a greater flexibility in polymer structure. This result indicates that the mechanical properties of blended CHI-MC films were between the CHI and MC films; moreover, relative humidity affected on both the tensile strength and %elongation at break of the tested films. This incident is acceptable because it is typical behavior of hydrophilic nature of studied and other polysaccharide films [12]. This result agreed with effect of carboxymethyl cellulose concentration on physical properties of biodegradable cassava starch-based films [13]. The influence of relative humidity on the mechanical

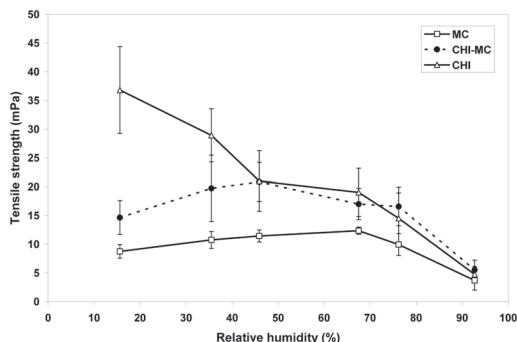


Figure 1. Tensile strength of films at different relative humidity.

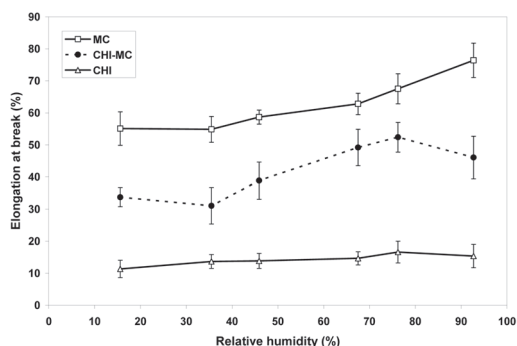


Figure 2. %Elongation at break of films at different relative humidity.

properties can be explained by its plasticizing effect since water loosens the interaction with the chain links in the film [14]. The obtained results are in agreement with other films [6, 14]. The good points of studied film are improved functionality to edible films for food applications. Blending the CHI with MC improves tensile strength and flexibility. Furthermore, the blend film showed advancement in mechanical properties compared to original CHI and MC.

3.3 Differential Scanning Colorimetry (DSC)

Figure 3 shows the DSC thermograms of MC, CHI and blended CHI-MC films. Thermograms of blended film exhibited a single sharp endothermic peak, which indicated homogeneity of films and miscibility among the major components. This result agreed with DSC thermograms of other blended cassava starch-carboxymethylcellulose films [13].

The melting point of MC, CHI and blended CHI-MC films were 118, 115 and 110°C, respectively. The endothermic peak of the blended film shifted to a temperature 8°C and 5°C lower than MC and CHI films. The melting point of blended film shifted due to the interaction of two biopolymers, the interaction between CHI and MC molecules interrupted the rearrangement of polymer chain [8]. This incident can be described in terms of intermolecular forces. In crystalline molecules of original CHI were packed in a way that their interactions are strongest. When the CHI is blended it stretches the crystal lattice, molecules are not in optimal positions and their interactions are weaker, thus less energy is required to break them apart.

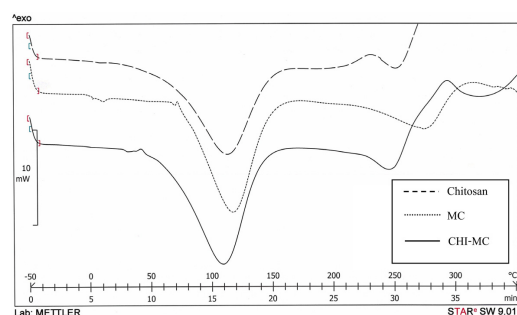


Figure 3. DSC thermogram of different films.

3.4 Scanning Electron Microscopy (SEM)

SEM analysis was used to characterize the morphology of the films. Scanning electron micrographs of both original and blended film (data not shown). All samples presented smooth and homogeneous surface where no straps, pores and interface layer are seen. In addition, the blended films exhibit flat smooth surface in general indicating uniform hydrogen bonding throughout the films. The formation of homogeneous blends of CHI and MC was mostly caused by the interactions of hydrogen bonds between the functional groups of the blended component. Thus, we can conclude that the blends of CHI and MC are miscibility. The micrographs and result were similar to the surface morphology of cassava starch-carboxymethylcellulose blended film [14].

4. CONCLUSIONS

Relative humidity affected on mechanical properties of chitosan, methylcellulose and blended chitosan-methylcellulose film. The mechanical properties of the blended films were between those of the chitosan and methylcellulose films. The DSC thermogram of blended film confirmed chemical interaction of CHI and MC. The homogeneity of blended film was represented as a single melting peak. The melting point of the blended film was lower than the original one. The SEM micrographs also confirmed the homogeneous structure of blended film. Thus, it was observed that the blending of CHI and MC films show better mechanical properties than original one, as aspect. These blended films have potential to use as biodegradable and edible films for low and moderate moisture products.

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