



## Thermal, mechanical and water adsorption properties of corn starch–carboxymethylcellulose/methylcellulose biodegradable films

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### ABSTRACT

The objective of this study was to investigate the effect of the addition of methylcellulose and carboxymethylcellulose on the thermal, mechanical and water adsorption properties of starch-based films plasticized with glycerol or polyethylene glycol (PEG). Mechanical tests showed that as the methylcellulose and carboxymethylcellulose proportion increased, starch films became more resistant to break, resulting in higher TS values. Besides there has been a positive effect on the elasticity of starch films realized by a considerable increase in *E%* values. Depending on the plasticizer type, either single or dual glass transitions were seen in DSC thermograms. One glass transition temperature was observed for films plasticized with glycerol, on the contrary, dual glass transitions were detected for PEG plasticized films. This behavior was attributed to the phase separation of the PEG. In addition, the presence of an endothermic peak in the thermograms of PEG plasticized films was taken as another indicator of the phase separation. As a result, it was suggested that PEG was not as compatible as glycerol with the composite polysaccharide matrix and plasticizer type was the main factor that shaped the thermal profiles of the film samples. Water adsorption isotherm data showed that samples displayed nonlinear sorption profile which is typical for hydrophilic films. In all films tested, equilibrium moisture contents, increased almost linearly up to a  $a_w$  of 0.65–0.85, beyond where a sharp increase was noted. Adsorption data was adequately fitted by BET and GAB models. Eventually, it can be concluded that film forming properties of starch can be improved by incorporation of methylcellulose and carboxymethylcellulose to the polymer matrix.

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### 1. Introduction

The current global consumption of plastics is more than 200 million tones; with an annual grow of approximately 5%, which represents the largest field of application for crude oil. It emphasizes how dependent the plastic industry is on oil and consequently how the increasing of crude oil and natural gas price can have an economical influence on the plastic market. Therefore it has been becoming increasingly important to utilize alternative raw materials. Until now petrochemical-based plastics have been increasingly used as packaging materials because of their large availability at relatively low cost, good mechanical performance, good barrier to oxygen, carbon dioxide, water vapor and aroma compounds, heat sealability, and so on (Siracusa et al., 2008). But the improper disposition of the enormous volume of petroleum-derived plastics in the environment has led to pollution and raised much interest in the biodegradable and renewable resources (Ma

et al., 2008b). In addition, there has been a considerable interest in biodegradable films made from starch (Lawton, 1996). Several studies have been performed to analyze the properties of starch-based biodegradable films (Bertuzzi et al., 2007; Chang et al., 2010; Mali et al., 2005; Parra et al., 2004; Romero-Bastida et al., 2004; Talja et al., 2007; Zhang and Han, 2006a,b, 2008). Starch films generally have good barrier properties to oxygen, carbon dioxide and lipids, however they have limitations in mechanical and water vapor permeability properties (Kester and Fennema, 1986). Three common ways have been used in order to overcome these limitations: genetic modification; such as production of high amylose starch (Ryu et al., 2002), chemical modification (Parra et al., 2004) and blending with appropriate materials. Chemical or genetic modifications are useful methods to get new substances with well-defined properties but they are often time consuming and not seldom costly. On the other side blending is a well-known, efficient way to prepare new materials with improved properties (Vasile et al., 2004). Agar (Wu et al., 2009), chitosan (Bourtoom and Chinnan, 2008; Xu et al., 2005), cellulose fibers (Muller et al., 2009) cellulose crystallites (Ma et al., 2008b), pullulan (Kristo and Biliaderis, 2007), nanoclay (Almasi et al., 2010), nano-SiO<sub>2</sub> (Tang et al., 2009) have been added to enhance film forming

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properties of starch. These studies have demonstrated that mechanical and permeability properties of starch films could be improved in some cases.

In the present article we have reinforced the starch film by mixing with methylcellulose and carboxymethylcellulose. Those cellulose ethers have no harmful effects on human health, and are used as highly effective additive to improve the product and processing properties in various fields of application, from foodstuffs, cosmetics and pharmaceuticals to products for the paper and textile industries (Feller and Wilt, 1990). Methylcellulose has been widely used to prepare edible films and documented in several publications (Debeaufort and Voilley, 1997; Donhowe and Fennema, 1993a,b; Turhan and Sahbaz, 2004). Carboxymethylcellulose is an anionic linear polysaccharide derived from cellulose. It is an important industrial polymer with a wide range of applications (Biswal and Singh, 2004).

Plasticizers are added to polymers to reduce brittleness, since they increase the free volume between polymer chains, decreasing intermolecular forces and thus increasing flexibility and extensibility of polymers (Romero-Bastida et al., 2005). Many researchers studied the effects of various polyols on starch-based films (Yang and Paulson, 2000; Zhang and Han, 2006a,b, 2008). The most preferred polyols were glycerol, sorbitol, and PEG (Mali et al., 2002; Mchugh et al., 1993). In the presented study glycerol and PEG have been used as plasticizers.

There are some studies about the carboxymethylcellulose and/or methylcellulose starch composite films in the literature. Peressini et al. (2003) have investigated the rheological properties of starch–methylcellulose blends and exhibited the compatibility of two polysaccharides in the film forming dispersions. In their subsequent work, starch–methylcellulose–lipid film has been developed and the influence of deposition process of film-forming dispersion on the shelf-life of dry bakery food has been examined (Bravin et al., 2006). Ma et al. (2008a) have studied the thermo-plastic starch/cellulose derivatives as potential biodegradable packaging materials. They have proposed that the introduction of carboxymethylcellulose and methylcellulose increased the glass transition temperature and improved the tensile stress and elongation at break, as well as the barrier property against water vapor. In a recent study of Tongdeesontorn et al. (2011) mechanical properties of CMC reinforced cassava starch films have been investigated. They have reported that addition of CMC to the cassava starch films has increased tensile strength and reduced elongation at break (Tongdeesontorn et al., 2011). However, there is negligible data available about the physicochemical properties of corn starch–carboxymethylcellulose and corn starch–methylcellulose based films. Thus the objective of this study is to determine the effect of blending level and plasticizer type on the physicochemical properties of carboxymethylcellulose and methylcellulose–corn starch composite films and investigate the potential usage as biodegradable packaging material.

## 2. Materials and methods

### 2.1. Materials

Normal corn starch (Unmodified regular corn starch containing approximately 73% amylopectin and 27% amylose) and methylcellulose (Molecular weight of 41,000 and degree of substitution of 1.5–1.9) were purchased from Sigma Chemical CO. (St. Luis, Missouri, USA). Carboxymethylcellulose, with a molecular weight of 90,000 and degree of substitution of 0.7 was purchased from Acros Organics (Geel, Belgium). Analytical grade glycerol (GLI; Merck; Darmstadt, Germany) and polyethylene glycol 400 (PEG; Merck; Hohenbrunn, Germany) were used as plasticizer.

### 2.2. Film preparation and casting

Film-forming solutions were prepared with different blending levels of carboxymethylcellulose/corn starch (CMC/CS) and methylcellulose/corn starch (MC/CS) to study the roles of these components on the physical properties of the composite films. The blends of CMC/CS and MC/CS (0:100; 20:80; 40:60; 60:40; 80:20; 100:0) and the plasticizer content (50% w/w on dry basis) were established according to the preliminary tests. In each formulation, the weight of dry matter was maintained at a constant value of 1.5 g per 100 mL water. Film-forming dispersions were obtained by the dispersion and solubilization of CMC and MC in 50 mL of water at room temperature and at 95 °C, respectively. CS was gelatinized in 50 mL of water at 95 °C for 45 min in the presence of the plasticizer. When the CS/plasticizer solution temperature was around 50 °C, solution was added to the CMC or MC solution. Then the mixture was homogenized using an Ultra Turrax T25 (Ika Labor-technik, Staufen, Germany) for 2 min at 13,000 rpm, followed by 2 min at 11,000 rpm. In order to remove air bubbles, the solutions were placed in an ultrasonic water bath (Elma LC 30 H, Singen, Germany) for 30 min and finally, solutions were allowed to stabilize at room temperature overnight. Films were cast by pouring 30 mL of solution onto the 85 mm internal diameter Petri dishes and dried in a climatic room with controlled conditions (25 °C and 45% RH) for at least 3 days. Thickness of films was determined using a digital micrometer (Mitutoyo, Manufacturing Co. Ltd., Japan, 0.001 mm accuracy). Reported thickness values were the mean value of five measurements for each film sample.

### 2.3. Differential scanning calorimetry (DSC) analysis

DSC experiments were carried out using TA Q20 model DSC apparatus (TA Instruments, USA). The calorimeter was calibrated with indium (melting point = 156.6 °C,  $\Delta H = 28.5$  J/g). The DSC runs were operated under nitrogen gas atmosphere (30 mL/min) and an empty pan was used as the reference. The film samples, approximately 3 mg, were hermetically sealed in aluminum pans after equilibration over P<sub>2</sub>O<sub>5</sub> for 10 days. The pans were heated from –90 °C to 100 °C at the scanning rate of 10 °C/min. The DSC thermograms were evaluated to characterize the onset, peak and end temperatures and the enthalpy changes of the phase transitions. The glass transition temperature was determined by taking the first derivative of the thermograms. Glass transition was analyzed for the onset, mid, end points and the midpoint temperatures were reported as glass transition temperatures of the samples.

### 2.4. Mechanical properties

A TA Plus Texture Analyzer (Lloyd Instruments, West Sussex, England) was used to determine the tensile strength and percentage of elongation at break. Film specimens were tested as suggested by ASTM D683M (ASTM, 1993). All film strips were equilibrated for ten days to 52 ± 2% RH in a cabinet using saturated magnesium nitrate solution at room temperature (25 ± 1 °C). At least 10 replications of each test sample were run. Tensile strength (MPa) was calculated by dividing maximum load by cross-sectional area of the film. Per cent elongation at break was expressed as percentage of change of the original length of a specimen between grips at break.

### 2.5. Moisture adsorption isotherm

Moisture adsorption isotherm of films was determined at 25 °C for  $a_w$  varying from 0.11 to 0.92 using saturated salt solutions (Merck; Darmstadt, Germany) in desiccators [LiCl,  $a_w$  0.11; CH<sub>3</sub>-COOK,  $a_w$  0.22; MgCl<sub>2</sub>,  $a_w$  0.33; K<sub>2</sub>CO<sub>3</sub>,  $a_w$  0.43; Mg(NO<sub>3</sub>)<sub>2</sub>,  $a_w$

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