STARCH - CELLULOSE ETHER FILMS: MICROSTRUCTURE AND WATER RESISTANCE

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Abstract–In this study, composite films of corn starch, methylcellulose and carboxymethylcellulose plasticized by glycerol or polyethylene glycol (PEG) were prepared and the effects of blending level as well as the plasticizer type on the microstructure, water vapour permeability (WVP), opacity and solubility properties were investigated. SEM observations showed homogeneous matrix of glycerol plasticized films and it was taken as an indicator of structural integrity. PEG plasticized films exhibited discontinuous surface, and this was attributed to phase separation.

Keywords: *Biodegradable film; Starch; Methylcellulose; Carboxymethylcellulose; Water vapour permeability*

1. INTRODUCTION

For the last decade, there has been a considerable interest in biodegradable and edible films made from renewable and natural polymers such as starch [1]. Starch films have good barrier properties to oxygen, carbon dioxide and lipids, however they have limited water vapour resistance [2]. Three common ways are generally used in order to overcome this limitation: genetic modification; such as production of high amylose starch, chemical modification and blending with appropriate materials. Blending is an easy, efficient way to prepare new materials with improved properties [3]. Carboxymethylcellulose and methylcellulose are well-known cellulose ethers and have good film forming properties. Besides they 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. Therefore, they may be considered as promising materials as reinforcing agents for starch based films. In the present article we have supported starch film by blending with methylcellulose and carboxymethylcellulose.

The object of the present work was to study the microstructural and physical properties of composite films produced from corn starch and carboxymethylcellulose or methylcellulose. The films were characterized in terms of water vapor permeability, water solubility, opacity and scanning electron microscopy images.

2. EXPERIMENTAL

2.1. Film preparation and casting

Film-forming solutions were prepared as previously described with different blending levels of carboxymethylcellulose/corn starch (CMC/CS) and methylcellulose/corn starch (MC/CS) in order to study the roles of these components

2.2. Water vapor permeability (WVP)

WVP of films was determined gravimetrically at 25±1°C using a modified ASTM E96-80 [4] procedure as described elsewhere [5]. WVP was calculated from the following equation:

$$WVP = C/ [x/A\Delta P)] \quad (1)$$

Where WVP is in g/m s Pa, x is the film thickness (m), A is area of the exposed film (m^2), ΔP is the water vapor pressure differential across the film (Pa), and C is the slope of the weight gain of the dish, to the nearest 0.0001 g, versus time. Slopes were calculated by linear regression and correlation coefficient (R^2) for all reported data were 0.99 or greater. At least three replicates of each film type were tested for WVP.

2.3. Scanning electron microscopy

Small film strips (4x4 mm) were coated with gold using a sputter coater (EMS 550X, Pennsylvania, USA). After gold coating, film surfaces were observed using scanning electron microscopy (JEOL JSM 5400LV, Tokyo, Japan) and imaging was

conducted at an accelerating electron beam voltage of 15kV.

2.4. Opacity

Film opacity was determined using the described procedure by the other authors [6].

3. RESULTS AND DISCUSSION

3.1. Microstructure observations

Scanning electron micrographs (SEM) of film samples were given in Fig. 1. CMC / starch / glycerol composite films showed the most smooth and homogenous surfaces (Fig 1.c). This might be due to the miscibility and/or compatibility between CMC and starch in the presence of glycerol. Interestingly, for their PEG containing counterparts this compatibility was decreased significantly and discontinuous surface and sponge-like appearance occurred (Fig 1d). This might be due to the phase separation of the plasticizer. Similar result was obtained in our previous study [7], where a phase separation behaviour of PEG and a better plasticization effect of glycerol were reported. Besides, it was reported that glycerol had more hydrogen bond formation capability and was a more compatible plasticizer than PEG (Arık Kibar, et al., 2013). Methylcellulose films were exhibited a homogenous and smooth surface without any phase separation which confirmed a dense structure (Fig 1 a-b). Unfortunately, when the starch content was increased up to 60-80% (w/w), surface homogeneity was no longer preserved in those films. This might be due to the compatibility of starch and MC was declined when an appropriate starch/MC ratio was exceeded.

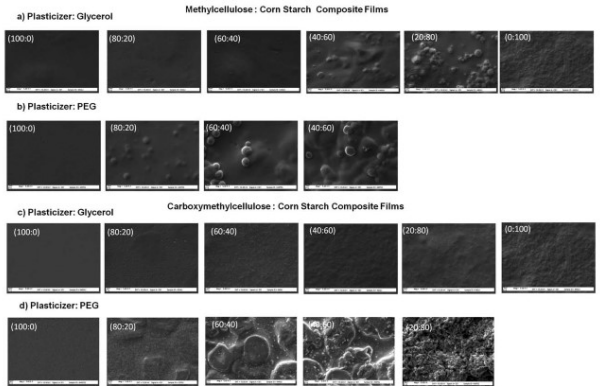

Figure 1. SEM micrographs of film samples

3.2. Water vapor permeability (WVP)

The WVP of films was determined to be 1.5x10^{-11} - 13.3x10^{-11} g.s-1.m-1.Pa-1 depending on the film composition (Table 1). Although CMC and MC are more hydrophilic materials than starch [7], their WVPs were lower than starch film, probably due to their three-dimensional dense structures. Thus, we obtained 6.1, 1.7 and 1.5 times lower WVP values for starch film than for CMC film with glycerol, CMC film with PEG and MC film respectively. This could be attributed to the strong inter-molecular interaction between cellulose ether chains which minimized the free volume and the inter-molecular distance in the films. Consequently, water molecules diffused more difficultly in the compact network and resulted in lower WVP values. Incorporation of CMC and MC into starch matrix generally decreased WVP values of composite films, as expected (Table 1). Similar results were given in the literature and was explained by the dispersion of cellulosic material blocked the water vapour and which probably introduced a tortuous path for water molecule to pass through.

Table 1. Water vapor permeability (WVP)values of CMC, MC, starch and composite film samples.

	WVP × 10^{11} (g/s/m/Pa)			
Blending ratio	Methylcellulose: corn starch Plasticizer: glycerol	Methylcellulose: corn starch Plasticizer: PEG	Carboxymethylcellulose: corn starch Plasticizer: glycerol	Carboxymethylcellulose: corn starch Plasticizer: PEG
100:0	5.9 ± 0.2^{f}	5.4 ± 0.1^{fg}	1.5 ± 0.2^{h}	5.9 ± 0.1^{f}
80:20	7.3 ± 0.6^{e}	6.0 ± 0.1^{f}	1.7 ± 0.3^{h}	9.2 ± 0.2^{d}
60:40	6.2 ± 0.2^{ef}	9.4 ± 0.6^{d}	2.1 ± 0.3^{h}	10.4 ± 0.3^{cd}
40:60	7.3 ± 0.2^{e}	13.3 ± 0.7^{a}	2.5 ± 0.4^{h}	11.6 ± 0.2^{bc}
20:80	7.1 ± 1.0^{ef}	–	4.2 ± 0.5^{g}	12.5 ± 0.2^{ab}
0:100	9.1 ± 0.6^{d}	–	9.1 ± 0.6^{d}	–

Note: All values shown are means ± standard deviations. Data with the same letter (a–h) within a column are not statistically different at a ($P < 0.05$) level.

WVP was accepted as an important property that greatly affects the utility of the film in food systems. Since the main function of an edible or biodegradable film was often to hinder moisture transfer between the food and surrounding atmosphere, WVP should be as low as possible. But one of the major problems found in the applications of starch films was the high permeability due to the hydrophilic character. Therefore addition of CMC and MC could be promising reinforcing materials in order to improve starch film's water vapour resistance in edible film applications.

When WVP values were compared in terms of plasticizer type, it was obvious that, PEG containing films showed lower resistance to water vapour than their glycerol containing counterparts. Differences in permeability could be attributed to the alterations in film microstructures which were revealed previously by SEM micrographs. As already mentioned, PEG containing films exhibited discontinuous surface which accompanied by a phase separation. This could lead to lack of structural integrity and presence of sponge-like structure that induced the higher water permeability.

The WVP values measured in the current study were similar to other MC/starch/glycerol films and cellophane reported in literature. In addition, they were substantially lower than the potato starch and cellulose acetate films. So it was obvious from the results that it was possible to improve water resistance of starch films by incorporation of cellulose ethers to the matrix. However the aforementioned values were significantly higher than many of the synthetic films, such as LDPE, HDPE Therefore, it was not reasonable to consider them as a complete substitute for those synthetic materials.

3.3. Optical properties

Opacity or transparency of a packaging material was an important factor in terms of general appearance and consumer acceptance because it had a direct impact on the product appearance [8]. The opacity values of the presented films were evaluated through their absorption of the visible-light and given in Fig 2. It was obvious from opacity values that plasticizer type was the main factor that affected the transparency of the films (Fig 2). PEG containing films were significantly more opaque than their glycerol containing counterparts. This could be related with their surface morphology because surface homogeneity played an important role on the specular reflectance characteristics at the air-film interface; the higher the surface homogeneity, the lower the opacity. As previously reported in the SEM results, PEG decreased the compatibility between the constituents in the polymer matrix and caused formation of discontinuous surface and sponge-like appearance.

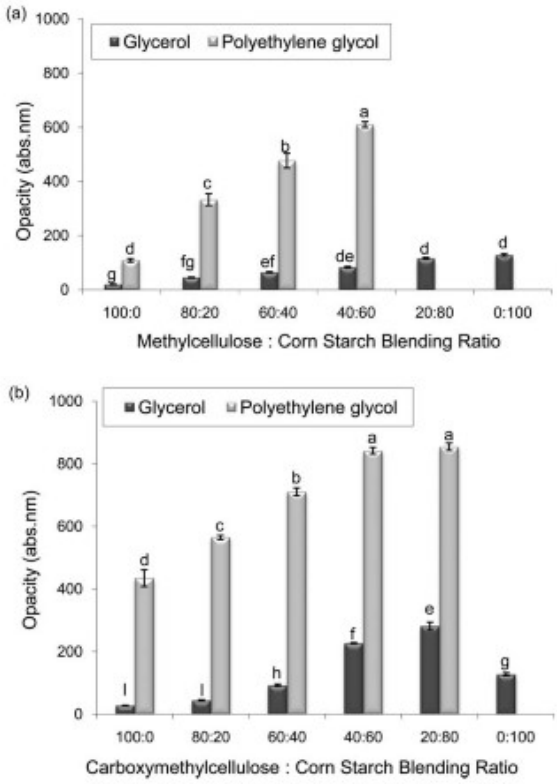

Figure 2. Opacity values of (a) methylcellulose-corn starch and (b) carboxymethylcellulose-corn starch films.

The cellulose ether and starch ratio of the films also had an impact on the opacity of the films. Starch film was more opaque than CMC and MC films; thereby improvement of transparency of the starch films by incorporation of the cellulose ethers would be expected. In the composite film samples, increase in the starch ratio increased the opacity significantly. This could be related with their internal structure developed during film formation. The opacity of the polymers was generally related with their degree of crystallinity and presence and dimensions of crystallites, lamellar structures and spherulites [9]. It was reported in the literature that the increase in crystalline zone decreased the absorbance and increased the film transparency [10]. In our previous study we have revealed the presence of ordered crystalline structure and

spherulites in the glycerol plasticized MC and CMC films and PEG plasticized MC film (more transparent samples) [7]. However starch film and PEG plasticized CMC film exhibited amorphous structure (more opaque samples). Therefore, it could be concluded that differences in crystalline structure affected the opacity of the films and the transparency of the starch films could be improved by incorporation cellulose ether and appropriate plasticizer in the film matrix.

4. CONCLUSIONS

Incorporation of CMC and MC into starch matrix generally decreased WVP values of composite films; therefore they could be promising materials in order to reinforce starch film's water vapour resistance. However WVP values were significantly higher than many of the synthetic films, as a result, one of the potential applications for presented films might be utility as a hydrophilic polymer layer in active food packaging applications.

The plasticizer type and the cellulose ether /starch ratio affected the surface homogeneity significantly and thereby structural integrity. Besides PEG decreased the compatibility of film matrix which lead to lack of structural integrity and presence of sponge-like structure that induced the higher water permeability.

Cellulose ether and starch ratio of the films also had an impact on the opacity of the films. Starch film was more opaque than CMC and MC films; thereby transparency of the starch films was improved by incorporation of the cellulose ethers.

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