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Preparation and Characterization of Carboxymethyl Cellulose Films with Embedded Essential Oils

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Abstract

There is current interest in using biobased materials to produce food packaging that can increase the shelf-lives of fruits and vegetables and minimize food spoilage in supermarkets and at the same time not generating plastic waste that causes long-term disposal problems. A good candidate for such materials is the polysaccharide, such as carboxymethyl cellulose (CMC), which is edible and biodegradable. In this work films were produced from two CMC materials with different degrees of substitution (DS) that encapsulated four different essential oils (eugenol, rosemary oil, coriander oil, and nutmeg oil) that are known to have beneficial properties for food applications. The mechanical properties, opacity, and water vapor permeation were evaluated. In general, the essential oil-embedded CMC with the two DS values behaved rather differently. In particular, the essential oil-embedded CMC with 0.7 DS degree of substitution gave stronger and more flexible films and may be more suited for use in food packaging.

Keywords: active packaging, carboxymethyl cellulose, coriander, essential oil, eugenol, nutmeg, rosemary

1. Introduction

Because of current interest in sustainability, decreased environmental impact, and reduced reliance on petroleum-based raw materials, there are active research and development activities using agro-based materials in polymeric applications (Cheng et al., 2015). One of the promising applications of such materials is food packaging (Mellinas et al., 2015), particularly because they can help minimize the environmental problem of plastic waste (Tullo, 2016). Thus, polysaccharides such as starch (Avella et al., 2005; Glenn et al., 2014), chitosan (Dutta et al., 2009), and carboxymethyl cellulose (Isa & Samsudin, 2017; Shahbazi et al., 2016; Ghanbarzadeh & Almasi, 2011; Sayanjali et al., 2011) can be very helpful because they are edible, biodegradable, renewable, and readily form a continuous matrix. A disadvantage is that the film properties of many polysaccharides may not be optimal, and appropriate modifications and/or formulations may be needed to improve the end-use properties.

In food applications, one of the popular topics today is active packaging. This refers to packaging systems used with foods that help extend shelf life, maintain freshness and quality, improve microbial safety, and enhance convenience (Oliveira et al., 2017; Dainelli et al., 2008). In other words, the packaging material should have active functions beyond the simple containment and physical/barrier protection of food product. A good example of active packaging is to embed an antimicrobial material directly into the packaging film, which can decrease microbial activity and ensure food safety (Oliveira et al., 2017; Otoni et al., 2014; Quintavalla & Vicini, 2002). There have been many reports on the incorporation of antimicrobial substances in packaging films. For example, garlic oil has been incorporated in chitosan films (Pranoto et al., 2005), potassium sorbate in CMC films (Sayanjali et al., 2011), and natural antimicrobial ingredients incorporated in biodegradable films based on cassava starch (Kechichian et al., 2010). This is a very active area of research and has been recently reviewed (Barros-Velazquez, 2016; Irkin & Esmer, 2015).

An essential oil (EO) is an organophilic material obtained from the flowers, fruits, seeds, bark, roots, leaves or other parts of a plant. It is processed commercially for its fragrance and antimicrobial properties (Baser & Buchbauer, 2016; Worwood, 1991). In food applications, the essential oils have been employed extensively as natural antimicrobial additives. For example, Rojas-Grau at al. (2007) reported the antimicrobial activity of several essential oils in alginate apple puree edible films against *E. coli*. The data showed that the antimicrobial activities of the EO's were in the following order: carvacrol > oregano oil > citral > lemongrass oil > cinnamaldehyde > cinnamon oil. Abreu et al. (2012) prepared nanogels based on chitosan and cashew gum and loaded them with *Lippia sidoides* oil. Bioassays showed that larval mortality was related mainly to oil loading, and the nanogels showed more effective larvicide efficacies than the pure *L. sidoides* oil. Espitia et al. (2011) made cellulosic films and paper coated with a cellulosic emulsion incorporated with 20% cinnamon, oregano or lemongrass EO and studied the mechanical properties of the films. Oliveira et al. (2017) investigated cellulose acetate films that incorporated citral. Bastos et al. (2016) made films made from three cellulose esters and embedded three essential oils; the results suggested that the essential oils interacted with the polymers like plasticizers. Biswas et al. (2018) followed up on that work by evaluating the properties of three cellulose ester films that incorporated nine essential oils.

We are interested in CMC films that embed essential oils because all the components are made from agro-based materials and are edible, biodegradable, and eco-friendly. Previously Dashipour et al. (2015) studied the physical, antioxidant and antimicrobial properties of CMC films containing the EO from *Zataria multiflora* Boiss spice plant. Raeisi et al. (2015) looked at the effects of CMC coatings incorporated with *Zataria* EO and grape seed extract on the shelf life of rainbow trout fillets. Dong and Wang (2017) reported the effect of CMC-garlic EO on improving the quality of strawberries. Two other studies reported gelatin/CMC films mixed with bane EO (Ranjibar et al., 2017) and chitosan-CMC films mixed with eucalyptus oil (Pandharipande & Katekhaye, 2017). The purpose of this work was to incorporate four common essential oils into two types of CMC and to determine the physico-mechanical properties of the resulting films. It was anticipated that the data produced in this work may provide guidance as to possible use of these materials for packaging applications.

2. Method

2.1 Materials

Samples of CMC (M_w ~250,000, 0.7 degree of substitution), CMC (M_w ~250,000, 1.2 degree of substitution), Tween™ 80 surfactant, eugenol, and essential oils from coriander, rosemary, and nutmeg were obtained from Sigma Aldrich (Milwaukee, Wisconsin, USA). Glycerol was purchased from EMD Chemicals Inc. (Gibbstown, New Jersey, USA).

2.2. Preparation of Films

For CMC film preparation a modified method of Dashipour et al. (2015) was employed. CMC was dissolved at 1% (w/v) concentration in distilled water with continuous stirring while being heated to 70ºC. Next, 10% glycerol (based on CMC weight) was added and stirred at 70ºC. After 10 minutes, an EO was added at 3% (w/w, relative to CMC) with Tween™ 80 at 0.3% (w/w, relative to CMC) as an emulsifier. This solution was quickly homogenized (IKA T25-Digital Ultra Turrax, Staufen, Germany) at 13,400 rpm for 3 min at 70ºC. The solutions were cast into films on 9" x 13" baking dishes until bubbles were dispersed and solutions were clear. The baking dishes were then put in a forced air oven at 35º C until dry. Five replicates of each of the four EO film formulations were made with each CMC polymer. Films made without the addition of EO were controls. After the films were removed from the dishes, they were conditioned in a temperature- and humidity-controlled room (23 $\pm$ 1 ºC and 50 $\pm$ 5% RH) for at least 40 hours before mechanical testing.

2.3. Mechanical Properties of Films

The tensile strength (MPa), Young's modulus (MPa) and elongation at break (%) of each film were determined via an Instron Model 4201 universal testing machine (Norwood, Massachusetts, USA) using the ASTM method D882-01 (ASTM, 2001). Previously, the films were cut into rectangular strips of 100 mm wide by 160 mm long (Twin blade cutter, model no. 22-34, Testing Machines, Inc., Newcastle, Delaware, USA). Film strips were then conditioned as mentioned in the preparation step. The initial gauge length was set at 125 mm, and the jaws were separated at a speed of 12.5 mm/min, using a 1 kN load cell. Each analysis was performed on five samples cut from each film and the average taken. For the mechanical testing, the thickness of the CMC films was determined by using MiniTest 3100 device from ElektroPhysik (Cologne, Germany). The film was placed on a measuring plate, and the probe imposed a magnetic field through it to determine the thickness.

2.4. Water Vapor Permeability (WVP) Measurements

The WVP was determined gravimetrically at 25 ºC, based on the ASTM E96-00 method (ASTM, 2000). The films were cut (discs with a diameter of 50 mm), placed at the top of a permeation cell containing distilled water. The cells were then placed in a desiccator containing dried silica at 24 °C and 47% RH. The cells were weighed eight times over a 24-h period in intervals of at least 1 h. The calculations were carried out according to the ASTM method.

2.5. Opacity

The opacity of the films was determined with a Minolta colorimeter (Model Cr 410, Minolta, Japan). Opacity of a material is an indication of how much light passes through it: the higher the opacity, the lower the amount of light that passes through the material. Generally, the opacity is calculated from reflectance measurements. In this work, the opacity of the samples was determined according to the Hunter lab method, as the relationship between the opacity of each sample on a black standard (Y_b) and the opacity of each sample on a white standard (Y_w): Opacity = 100 * Y_b/Y_w. The measurements were repeated three times for each film.

For opacity measurements, the film thickness was determined with a manual digital micrometer (No. 293–140, Mitutoyo, Japan) with a sensitivity of 0.001 mm. For each sample, eight measurements of thickness were made, and the mean and the standard deviation were reported.

2.6. Scanning Electron Microscopy

Scanning electron microscopy (SEM) of samples was examined on a JEOL 6400V scanning electron microscope (JEOL, Peabody, MA) with an accelerating voltage of 10 kV, after gold coating with an SPI (West Chester, PA) sputter coater. Photomicrographs were taken of representative fields of view.

3. Results and Discussion

Four essential oils were studied in this work. For future reference, the compositions of the essential oils are given in the Table A1 (Appendix). Eugenol is a member of the phenylpropanoid class of chemical compounds. It is a colorless-to-pale yellow, aromatic oily liquid extracted from clove oil, cinnamon, basil and bay leaf. Rosemary oil contains a large number of terpenoid components, the major ones (over 10%) being camphor, α-pinene, and 1,8-cineole. Coriander oil contains linolool and geranyl acetate as its main components. Nutmeg oil comprises many components, of which the major ones (over 10%) are sabinene, terpinen-4-ol, myristicin, and α-pinene. Some of these structures are shown in Figure A1 (Appendix). All four essential oils are known to have antimicrobial properties (Marchese et al., 2017; Takikawa et al., 2002; Inouye et al., 2001).

3.1 Mechanical Properties

Each of these EO's (at 3%) was incorporated into CMC films, together with 10% (w/w) glycerol and 0.3% (w/w) Tween™ 80 surfactant (polyoxyethylene sorbitan monooleate); all weights were expressed relative to the weight of CMC. The mechanical properties for the CMC films at two degrees of substitution (DS) with and without the EO's were then measured (Table 1). In the data, the largest difference was observed for CMC at different DS values. For CMC with 0.7 DS, all the mechanical property values were higher; the Young's modulus (YM) was about 2300 – 2600 MPa, the tensile strength (TS) about 46-51 MPa, and elongation at break (EAB) about 10-18%. For CMC with 1.2 DS, the YM was about 1400 – 2100 MPa, the TS about 34-43 MPa, and EAB about 10-16%.

As for the effect of different EO's, in general the values of YM and TS for different CMC and EO combination followed a linear relationship, although the correlation showed quite a bit of scatter (Figure 1). Furthermore, from the values in Table 1, the addition of an EO in general increased the EAB, although one exception (rosemary oil in CMC 1.2 DS) was noted. As for TS, the addition of EO either slightly increased it or kept it the same relative to the control for CMC 0.7 DS, but decreased it for all CMC 1.2 DS films. Another way to view the data is to plot the YM versus EAB (Figure 2). Separate inverse relationships between YM and EAB were observed for CMC DS 0.7 and for CMC DS 1.2, although some scatter was present in the latter case. Thus, the EO's serve like plasticizers for CMC; they all increase the flexibility of CMC films.

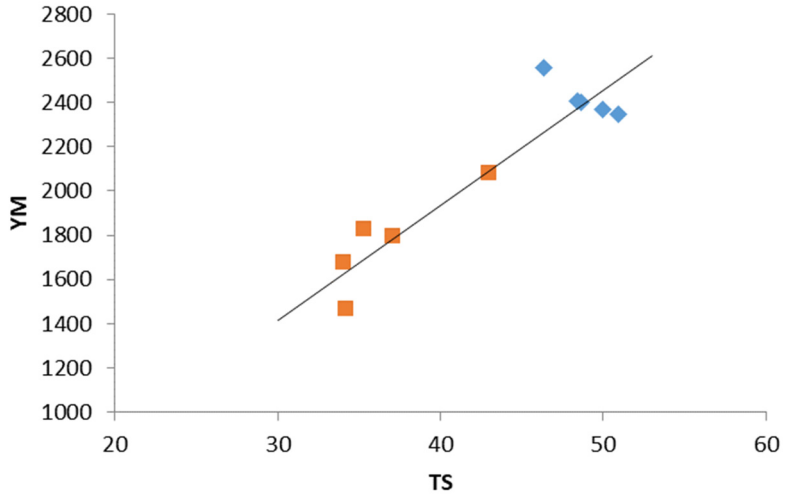

Figure 1. The correlation of Young's modulus (YM, in MPa) and tensile strength (TS in MPa) for EO-embedded CMC films. CMC DS 0.7 data are in blue diamonds, CMC DS 1.2 data in red squares

Table 1. Young's modulus (YM), tensile strength (TS), and elongation at break (EAB) for CMC films embedded with different EO's

DS of CMC	EO	Thickness (mm)	YM (MPa)	TS (MPa)	EAB (%)
0.7	Control	0.111±0.016	2559±174	46±2	10±2
	eugenol	0.112±0.011	2408±73	48±3	17±5
	rosemary	0.110±0.005	2370±163	50±4	16±1
	coriander	0.105±0.020	2401±190	49±3	18±4
	nutmeg	0.092±0.010	2347±131	51±4	18±1
	average	*0.106*	*2417*	*49*	*16*
1.2	Control	0.105±0.022	2081±461	43±9	13±4
	eugenol	0.102±0.019	1799±99	37±1	13±2
	rosemary	0.101±0.005	1828±71	35±1	10±2
	coriander	0.116±0.014	1677±233	34±2	13±3
	nutmeg	0.109±0.010	1469±147	34±1	16±3
	average	*0.107*	*1771*	*37*	*13*

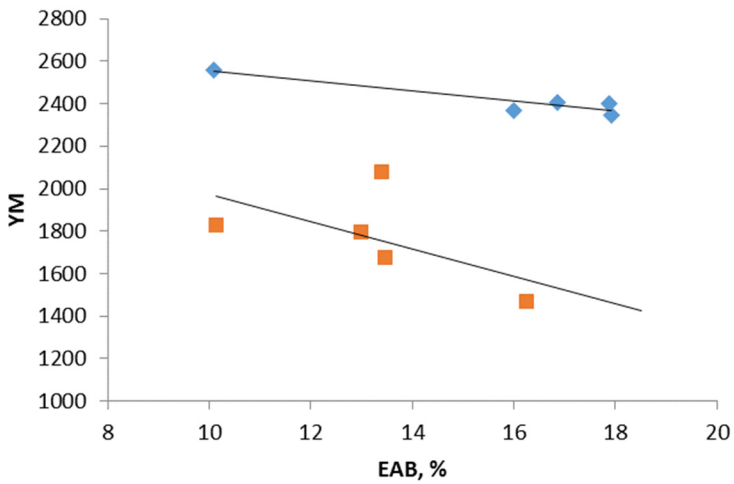

Figure 2. The correlation of Young's modulus (YM, in MPa) with elongation at break (EAB, in %) for EO-embedded CMC films. CMC DS 0.7 data are in blue diamonds, CMC DS 1.2 data in red squares

There is a fair amount of data in the literature on the mechanical properties of EO-embedded water-soluble polymers, e.g., *Zataria multiflora* EO in CMC (Dashipour et al., 2015), Zataria EO in starch (Ghasemlou et al., 2013), Zataria EO in κ-carrageenan (Shojaee-Aliabadi et al., 2014), bane EO in gelatin-CMC (Ranjibar et al., 2017), cinnamon EO in starch (Souza et al., 2013), lemongrass EO in starch-alginate (Maizura et al., 2007), and oregano EO in starch-chitosan (Pelissari et al., 2009). In these papers, the addition of an EO usually decreased the TS and increased the EAB. An exception was noted in the paper by Dashipour et al. (2015), where a more complex behavior was observed; at 1% Zataria EO in CMC, both the TS and EAB were found to increase. This result qualitatively agreed with our data for EO-embedded CMC 0.7 DS films, where both TS and EAB increased. In contrast, our data for CMC 1.2 DS films showed the more conventional behavior of decreasing TS and increasing EAB with EO addition.

3.2 Water Vapor Permeation (WVP)

The WVP data for the CMC films embedded with different EO's are shown in Table 2. The WVP values for CMC control films at DS 0.7 and 1.2 were similar (about 2.1 - 2.2 g-mm/kPa-h-m^2), indicating no significant difference. When an EO was added, the WVP value stayed roughly the same for the CMC 0.7 DS films, except for eugenol, but all the values increased noticeably for the CMC 1.2 DS films. Thus, the EO-embedded CMC 0.7 DS films performed better than the CMC 1.2 DS films as far as the water barrier property was concerned.

In order to gain a better understanding of the observed data, the tensile strength was plotted against WVP in Figure 3, and the Young's modulus against WVP in Figure 4. An inverse relationship was observed in each case for CMC 1.2 DS, but not for CMC 0.7 DS. Thus, for CMC 0.7 DS films, both the YM and the WVP showed only very small changes with EO addition. However, for CMC 1.2 DS films, the EO addition seemed to decrease interchain molecular interactions, such that the tensile strength was reduced, while at the same time making the film more permeable so that water could diffuse more readily through the CMC film.

In the literature for water-soluble polymers, some papers reported reductions in WVP with EO incorporation (Pelissari et al., 2009; Ghasemlou et al., 2013; Shojaee-Aliabadi et al., 2014; Ranjibar et al., 2017), and some reported increases (Maizura et al., 2007; Souza et al., 2013; Dashipour et al., 2015). Basically two factors are at play. First, the addition of EO and glycerol can increase molecular mobility and facilitate the migration of water vapor molecules, thereby increasing WVP. Secondly, the presence of the hydrophobic EO (especially at higher dosages) can cause discontinuities in the hydrophilic polymer phase, thus increasing the tortuosity for mass transfer in the continuous matrix and decreasing WVP. Thus, the observed WVP depends on these two opposing effects, and the observed behavior depends on the polymer involved, the level of glycerol, and the nature and amount of EO used.

Table 2. Opacity and water vapor permeation (WVP) for CMC films embedded with different EO's

DS of CMC	EO	opacity (A/mm)	WVP (g-mm/kPa-h-m^2)
0.7	control	1.196±0.072	2.209±0.433
	eugenol	1.511±0.170	2.691±0.674
	rosemary	1.267±0.104	2.214±0.382
	coriander	1.190±0.099	2.246±0.272
	nutmeg	1.452±0.413	2.246±0.575
	average	*1.323*	*2.321*
1.2	control	1.290±0.339	2.117±0.230
	eugenol	1.671±0	3.015±0.597
	rosemary	1.269±0.101	3.007±0.373
	coriander	0.951±0.134	3.789±0.588
	nutmeg	1.272±0.194	4.116±0.397
	average	*1.291*	*3.209*

3.3 Opacity

The opacity data for the same set of films are given in Table 2. The opacity values for CMC control films at DS 0.7 and 1.2 were similar (about 1.2 - 1.3 A/mm). When an EO was added to CMC 0.7 DS, there was an increase in opacity with all EO samples, except for coriander oil. Eugenol showed the largest increase from the CMC 0.7

DS control value of 1.196 to 1.511 A/mm. For CMC 1.2 DS films, EO addition for eugenol still showed a large increase from the CMC 1.2 DS control value of 1.29 to 1.671 A/mm; the addition of EO to the other three films showed somewhat reduced opacity, but the trend was less clear because of the experimental errors involved. These opacity differences may reflect the degree of incompatibility of the CMC and the EO involved. With increasing incompatibility, the EO forms a separate phase as tiny droplets, leading to increased opacity. In the literature for EO-embedded water-soluble polymers, usually increased opacity was observed with EO addition (Ghasemlou et al., 2013; Shojaee-Aliabadi et al., 2014; Dashipour et al., 2015; Ranjibar et al., 2017).

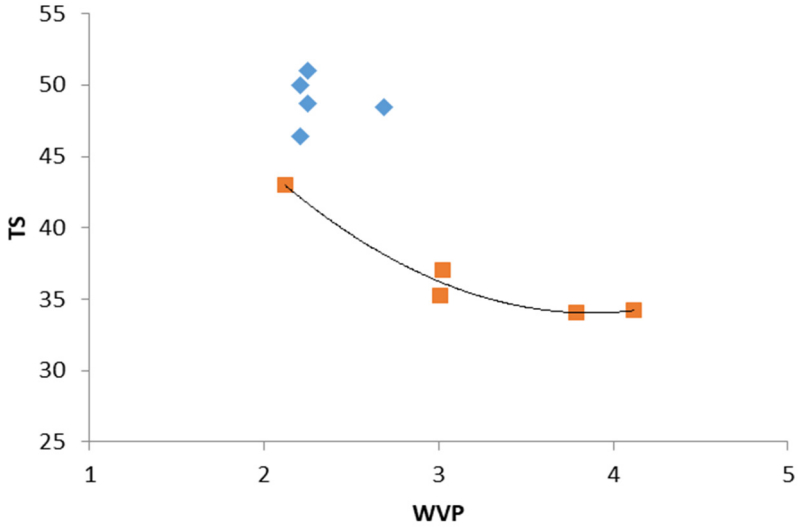

Figure 3. The correlation of tensile strength (TS, in MPa) with water vapor permeability (WVP) for EO-embedded CMC films. CMC DS 0.7 data are in blue diamonds, CMC DS 1.2 data in red squares

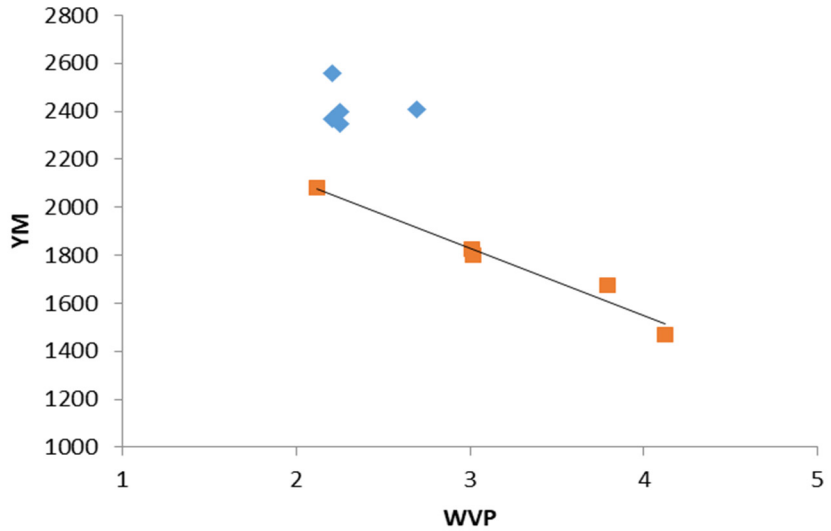

Figure 4. The correlation of Young's modulus (YM, in MPa) with water vapor permeability (WVP) for EO-embedded CMC films. CMC DS 0.7 data are in blue diamonds, CMC DS 1.2 data in red squares

An increased opacity would be a benefit for food packaging if reduced photo-oxidation of the food item is desired. Conversely, a decreased opacity would be useful for the consumer to observe the food item in the package before the purchase. The fact that some EO's can increase the opacity and coriander oil can decrease the opacity permits us to vary the opacity as needed for a given application.

3.4 Surface Morphology

The SEM photomicrographs of the surfaces of CMC 0.7 DS films with and without embedded nutmeg oil are shown in Figure 5. The CMC control film had a smooth continuous surface. However, the EO-embedded CMC surface showed some spherical pits of about 0.2-1.0 μm in diameter, probably due to the presence of droplets of EO. This observation was consistent with the report of Dashipour et al. (2015), who also saw some pitted structures on the surface of CMC that embedded Zataria oil.

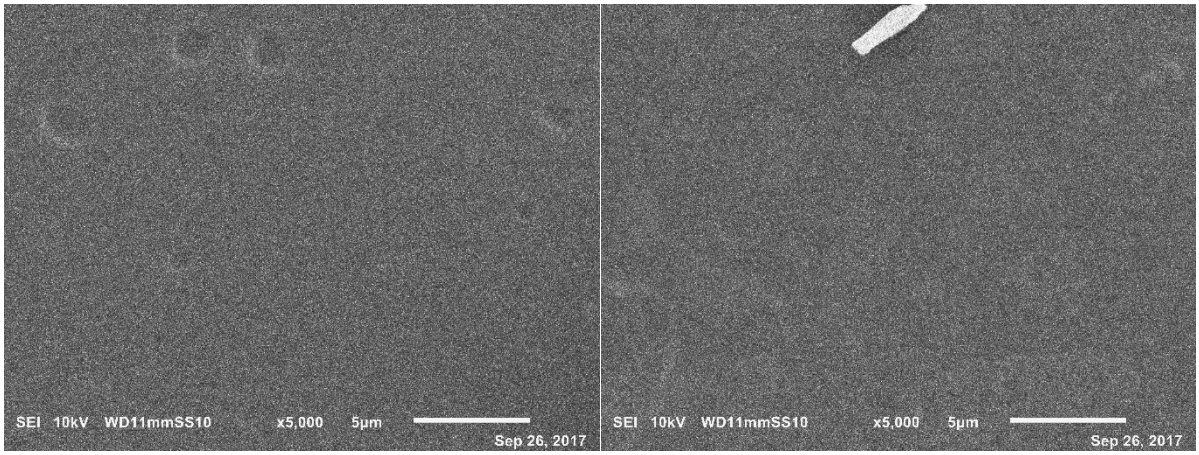

Figure 5. Scanning electron photomicrographs for the surface of CMC 0.7 DS film (left) and the surface of CMC 0.7 DS with 3% nutmeg oil (right)

4. Conclusion

In this work, two grades of CMC with degrees of substitution 0.7 and 1.2 were made into films with the help of 10% glycerol. The mechanical properties, opacity, and water vapor permeability of the two CMC films by themselves were similar within the limits of experimental error. However, when four essential oils were added, the film properties changed significantly. In general, the CMC 0.7 DS films embedded with EO's gave higher Young's modulus, higher tensile strength and higher elongation, whereas the corresponding CMC 1.2 DS films gave significantly lower values. The water vapor permeability of CMC 0.7 DS films was also not affected by EO incorporation (except for eugenol). Thus, if the food packaging application requires a film that is stronger, more flexible, and has good moisture barrier, the use of CMC 0.7 DS with one of the other EO's is a possible option. As for opacity, coriander oil or eugenol can be used to maintain or to increase opacity, respectively, as needed.

Although the CMC 1.2 DS films with embedded EO's have inferior mechanical properties and water vapor permeabilities, the CMC with 1.2 DS has a faster rate of water solubility and is less susceptible to enzymatic action. Perhaps these films can be used as edible food coatings or as water-soluble dissolvable bags and pouches for food items or for laundry detergents and cleaners.

Acknowledgments

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Appendix

Essential Oils Used in this Work

Table A1. Composition of essential oils used in this work

EO	composition	ref.
eugenol	pure compound	Marchese et al., 2017
rosemary	camphor (17.2-34.7%), α-pinene (10.2-21.6%), 1,8-cineole (12.1-14.4%), camphene (5.2-8.6%), borneol (3.2-7.7%), β-pinene (2.3-7.5%), verbenone (2.2-5.8%), β-caryophyllene (1.8-5.1%), limonene (2.0-3.8%), α-terpineol (1.2-2.5%), myrcene (0.9-4.5%), p-cymene (0.2-3.4%), bornyl acetate (0.2-2.3%), linalool (0.3-1.0%) and terpinen-4-ol (0.4-0.9%)	Salido et al., 2003
coriander	linalool (57.57%); geranyl acetate (15.9%); β-caryophyllene (3.26%), camphor (3.02%), and p-cymene (2.5%).	Khani & Rahdari, 2012
nutmeg	sabinene (21.38%), terpinen-4-ol (13.92%), myristicin (13.57%), α-pinene (10.23%), limonene (5.57%), safrole (4.28%), γ-terpinene (3.98%), α-terpinene (2.72%), myrcene (2.38%), methyl eugenol (0.77%), linalool (0.75%)	Muchtaridi et al., 2010

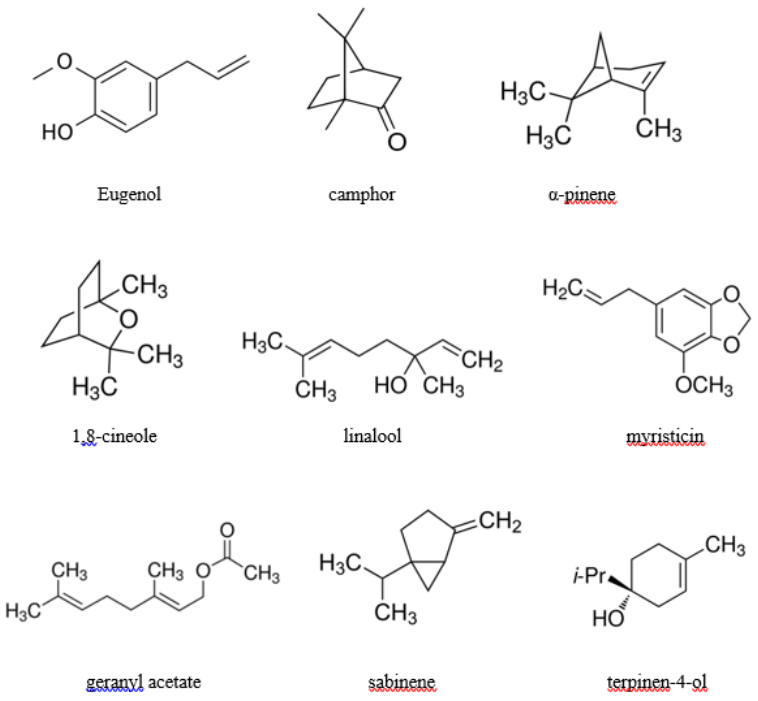

Figure A1. Chemical structures of some essential oil components

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