Effect of rosemary oil on functional properties of HPMC films at different concentration

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ABSTRACT

The objective of this work was to study the effect of rosemary oil on the mechanical properties and water vapour permeability of HPMC films. Films with different concentrations of HPMC, 2% and 6%, and with different rosemary oil concentrations- 0.0, 0.4, 0.7 and 1.0%, were prepared. Mechanical properties were measured by tensile test, using a dynamometer (Instron Universal, 4467). Water vapour transmission rate (WVTR) was evaluated by a gravimetric method according to ASTM (1993) by means of a Fisher permeability cup. The experimental results showed that HPMC concentration have a significant effect on mechanical and barrier properties. The use of rosemary oil did not have any effects on mechanical properties of HPMC film, but reduced the water vapour permeability, mainly for film at 6% of HPMC. The greatest effect on the reduction of WVP was achieved with a concentration of oil equivalent to 0.4% at 6% of HPMC.

Keywords: HPMC; rosemary oil; mechanical properties; water vapour permeability

INTRODUCTION

Active packaging is one of the innovative food packaging concepts that has been introduced as a response to the continuous changes in current consumer demands and market trends. Among active substances, it is increased the demand for replacing synthetic chemicals with natural compounds. In this context, the essential oils (EOs) are interesting for their potential use as natural preservatives. EOs are volatile, natural, complex compounds characterized by a strong odour and are formed by aromatic plants as secondary metabolites. They can contain about 20–60 components at quite different concentrations, but are characterized by two or three major components at fairly high concentrations (20–70%) compared to others components present in trace amounts. The main group is composed of terpenes and terpenoids and the other of aromatic and aliphatic constituents, all characterized by low molecular weight [1,2].

The in vitro efficacy of EOs against food borne pathogens and spoilage bacteria and their action mechanism has been extensively reviewed [1, 2]. Recently, it is increasing the interest in using these molecules as active compound in edible film or coating [3, 4]. But few works concern on the role of these additive on the film network formation and its functional properties.

Pranoto et al. [5] reported that adding garlic oil into alginate based film have detrimental effect on barrier and mechanical properties. Whereas, the presence of oregano oil/carvacrol, cinnamon oil/cinnamaldehyde and lemongrass oil/citral did not significantly affect water vapour and oxygen permeability of the alginate-apple edible film but did significantly modify tensile properties [6].

Du et al. [7, 8] reported that allspice, garlic and oregano oil, cinnamon, and clove bud did not effect the WVP of tomato-pectin film and apple-pectin edible film, but cinnamon and clove bud caused a significant reduction in tensile strength and elastic modulus of apple-pectin film.

The effect of cinnamon and ginger oils on functional properties of caseinate-based and soy protein edible film has been studied by Atarés et al. [9, 10]. They reported that the effect of the EO depends by the nature of the oil and film composition. In fact, ginger oil did not affect any functional properties of the studied film, whereas in presence of cinnamon oil, the WVP of soy protein film was significantly reduced.

Cinnamon essential oil has been also reported to decrease the moisture content, the water solubility, the water vapour permeability and the elongation at break of chitosan edible film [11]. Incorporation of carvacrol essential oil into Geladiuim corneum edible film caused an increase of the tensile strain and elongation at break and a significantly decrease of WVP [12].

The effect of essential oil on HPMC film is reported in only two work. Sanchez-Gonzales et al. [13] reported that tea tree essential oil added to HPMC edible film reduced their WVP and moisture sorption capacity and reduce the tensile strength and elastic modulus of the composite films. Kiam wood extract added to HPMC edible film reduced significantly tensile and water barrier properties film [14].
Although rosemary essential oil (Rosemary officinalis) has been widely studied as antimicrobial and antioxidant agent [15, 16, 17, 18, 19] and a wide spectrum of action against alterative pathogens has been reported [1], no application of this oil in edible film are reported. Thus, the objective of this work was to study the effect of rosemary oil on the mechanical properties and water vapour permeability of HPMC edible films.

MATERIALS & METHODS

Materials
Hydroxypropylmethylcellulose (HPMC) (1.8-2.0 methyl substitution (DS); 0.20-0.3 hydroxypropyl substitution (MS)), rosemary essential oil and Tween 80 were purchased by Sigma Aldrich (Milan, Italy).

Film making procedure
HPMC film were prepared by dissolving 2% and 6% of HMPC in deionised water at room temperature for all night. Different concentration of rosemary oil (0.0, 0.4; 0.7; 1%) were added to the HPMC solutions as emulsion with tween 80 at 6:1 ratio. Rosemary oil-Tween 80 were emulsified by using a vortex (IKA MS 3 Digital) for 5 min at 2000rpm. HPMC-rosemary oil/tween 80 were emulsified by using a Blender (Osterizer) to maximum power for 10 minutes. Prior to film casting, solutions were de-aerated under vacuum to prevent pinhole formation. 20 ml of film forming solutions were poured onto levelled 56.7 cm² polystyrene Petri dishes and allowed to dry at 20 °C and 50% relative humidity (RH) for 48h under air circulation. The dried films were peeled from the Petri dishes and stored at 20°C and 50% relative humidity prior to testing.

Film thickness measurement
Film thickness was measured using a micrometer model HO62 with sensitivity of ±2 μm (Metrocontrol Srl, Casoria, NA, Italy). Film strips were placed between the jaws of the micrometer and the gap reduced until the first indication of contact. Mean thickness (μm) of films was determined by averaging ten measurements at different locations.

Film mechanical properties
The tensile strength of the films was measured by using an Instron Universal Testing Instrument Model No 4301 (Instron Engineering Corp., Canton, MA) equipped with a 1,000-N load cell. Film samples were cut into 25 wide and 100mm length strips using a sharp razor blade. The strips were equilibrated overnight at 50±5% RH and 23±2 °C in an environmental chamber. Ten samples of each film type were tested. Tensile properties of the films were measured according to the ASTM (1991) Standard Method D882 using Test Method A, the Static Weighing, Constant Rate-of-Grip separation test. The initial grip separation was 50 mm and crosshead speed was 15 mm/min in a Tension Mode. Tensile strength (TS) and percent elongation at break (ε%), Young modulus (EM) were calculated. Results are reported as average of ten replications of each sample.

Water vapour permeability
Water vapour permeability of films was evaluated by gravimetric test according to ASTM E96 (1993) by means of a Fisher/Payne permeability Cup (Carlo Erba, Milan, Italy). Three grams of silica gel were introduced in each cup. Film sample having diameter of about 6 cm was placed on top of the cup and sealed by means of a top ring kept in place by three tight clamps. The film area exposed to vapour transmission was 10 cm². The cups containing silica gel were weighed and then placed in desiccators containing a saturated KCl solution which provided a constant water activity at 25 °C equal to 0.8434. The desiccators were stored in a Heareus thermostated incubator at 25.0±0.1 °C. At regular time intervals the cups were weighed until a constant increment in weight was achieved. The amount of Water vapour transmission rate (WVTR) through the film was estimated by the linear portion of the diagram obtained by plotting the weight increment of the cup as a function of time. It was assumed that steady-state was reached once the regression analysis made by using the last four data points resulted in $r^2 > 0.998$. From WVTR data, the value of vapour pressure on film’s inner surface (p2) was obtained taking into account the method proposed by Mc Hugh et al. [20] to correct the effect of concentration gradients established in the stagnant air gap inside the cup.
Where, $P$ is the total pressure; $D$ is the diffusivity of water through air at 25°C; $R$ is the gas law constant; $T$ is the absolute temperature; $\Delta z$ is the mean stagnant air gap height, considering the initial and final $z$ value; $P_1$ is the water vapour pressure on the solution surface; $P_2$ is the corrected water vapour pressure on the film’s inner surface in the cup. Then permeance was calculated as followed:

$$\text{Permeance} = \frac{WVTR}{P_3 - P_2}$$

Where $P_3$ is the water vapour partial pressure at the film outer surface. Permeability was obtained by multiplying the permeance by the average film thickness. Results are reported as average of three replications of each sample.

**RESULTS & DISCUSSION**

**Thickness**

Thickness of HPMC film is reported in Table 1. By increasing the HPMC concentration from 2% to 6%, the film thickness increased from 0.062 ± 0.005 mm to 0.23 ± 0.01 mm. ANOVA highlighted a significant effect of HPMC concentration on film thickness ($p<0.01$), and results showed that the thickness increased linearly with HPMC concentration ($R^2>0.999$). The addition of rosemary oil to HPMC films did not have a significant effect on the thickness of the film ($p>0.05$).

**Mechanical properties**

Mechanical properties of HPMC film at different rosemary oil concentration are reported in Table 1. By increasing the HPMC concentration from 2% to 6% a reduction of the EM (MPa) and an increment of the $\varepsilon$ (%) was observed. On the contrary, the addition of the rosemary essential oil did not affect the mechanical properties of the film. This last result was in accordance with Atarés et al. [10] which reported that cinnamon oil did not affect film mechanical properties most probably for the low concentration of oil. However, many authors agree that additives can induce the development of a heterogeneous film structure by interact with the polymer, resulting in the decrease in TS and $\varepsilon$% of the film [5, 13, 7, 8, 11].

**Water vapour permeability**

One of primary function of an edible film is to restrict moisture transfer between the food and surrounding atmosphere or between two compounds of heterogeneous food product.

Figure 1 shows the WVP value of HPMC film measured at 25°C and 87% RH gradient. Results showed that WVP was influenced by HPMC concentration, and in particular it increased from 1.07*10^-10 g m^-1 s^-1 Pa to 2.68*10^-10 g m^-1 s^-1 Pa, as HPMC concentration increased from 2% to 6% ($p<0.05$).

<table>
<thead>
<tr>
<th>Film composition</th>
<th>Thickness (μm)</th>
<th>$\varepsilon$ (%)</th>
<th>TS (MPa)</th>
<th>EM (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMC - 2%</td>
<td>62 ± 8 th</td>
<td>7.5 ± 2.7th</td>
<td>33.2 ± 1.4th</td>
<td>1264 ± 51th</td>
</tr>
<tr>
<td>HPMC - 2% - 0.4% EO</td>
<td>62 ± 9 th</td>
<td>6.5 ± 2.8th</td>
<td>27.3 ± 6th</td>
<td>1336 ± 79th</td>
</tr>
<tr>
<td>HPMC - 2% - 0.7% EO</td>
<td>63 ± 7 th</td>
<td>4.76 ± 0.5th</td>
<td>34.9 ± 4.9th</td>
<td>1308 ± 201th</td>
</tr>
<tr>
<td>HPMC - 2% - 1% EO</td>
<td>65 ± 3 th</td>
<td>6.4 ± 2.2th</td>
<td>31.5 ± 5th</td>
<td>1342 ± 141th</td>
</tr>
<tr>
<td>HPMC - 6%</td>
<td>220 ± 15 xx</td>
<td>15.5 ± 2.6xx</td>
<td>33 ± 1.6xx</td>
<td>1062 ± 42xx</td>
</tr>
<tr>
<td>HPMC - 6% - 0.4% EO</td>
<td>222 ± 10 xA</td>
<td>14.3±3 xA</td>
<td>34.5±2.6xA</td>
<td>1090±50 xB</td>
</tr>
<tr>
<td>HPMC - 6% - 0.7% EO</td>
<td>225 ± 12 xA</td>
<td>11.7±1.3 xAbA</td>
<td>37.8±3.6xAbA</td>
<td>974.5±28 xAb</td>
</tr>
<tr>
<td>HPMC - 6% - 1% EO</td>
<td>230 ± 14 xA</td>
<td>9 ± 1.7 xAa</td>
<td>37 ± 4.5xAbA</td>
<td>1100 ± 86 xM</td>
</tr>
</tbody>
</table>

Table 1. Thickness (μm), percentage of elongation at break $\varepsilon$%, tensile strength (TS) and elastic modulus (EM) of HPMC and HPMC- rosemary oil composite film. Different letters indicate significant differences ($p<0.05$). effect of oil: a,b; AB: effect of HPMC
This effect can be attributed to the higher number of polar group, enhancing interaction with water and favoring water transmission through film [21]. Similar behavior was reported for pectin film [22], chitosan whey protein film [23], Chitosan-ovoalbumine film [24].

The addition of rosemary oil had a significant effect on WVP of both film at 2% and 6% of HPMC. The major effect has been observed for film at 6% of HPMC for which WVP decreased from $2.68 \times 10^{-10}$ g m$^{-1}$ s$^{-1}$ Pa to a value of $1.2 \times 10^{-10}$ g m$^{-1}$ s$^{-1}$ when 0.4% of rosemary oil has been added to the film. Rosemary oil concentration of 0.7% and 1% also caused a decrease of the WVP to a value slightly higher than at 0.4%. For film at 2% of HPMC the adding of rosemary oil at 0.4% and 0.7% did not affect WVP of HPMC film, but at concentration of 1% of rosemary oil, an increased of WVP has been observed. The increment of WVP at oil concentration higher than 0.4% can be justified by a not optimal distribution of the oil particles into the film structure that is recognized having a negative impact on film barrier properties [25, 21, 26]. In fact, the water vapour effectiveness of a lipid has been relate to type of lipid, particle size, [25, 26, 27], chain length [27, 28, 29], and insaturation number [30]. Moreover, Atarés et al. [8] reported that lipids with similar size distribution in film forming emulsion may exhibit different water barrier effectiveness at specific lipid to protein ratios, depending on the interactions between components and the destabilizing phenomena taking place during drying. So a determinant factor that affects the water vapour barrier is the impact of the lipid addition on the microstructure of the emulsified film.

CONCLUSION

The use of rosemary oil did not have any effects on mechanical properties of HPMC film, but reduced the water vapour permeability, mainly for film at 6% of HPMC. The results suggest that HPMC film enriched with rosemary oil could be used as system to release odorous molecules capable to reduce microbial growth in foods with low humidity. Further studies should be conducted to optimize the concentration of oil in relation to the specific food.

REFERENCES


