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## Characteristics of hydroxy propyl methyl cellulose (HPMC) based edible film developed for blueberry coatings

Fernando A. Osorio<sup>a\*</sup>, Paulina Molina<sup>a</sup>, Silvia Matiacevich<sup>a</sup>, Javier Enrione<sup>a</sup>,  
Olivier Skurtys<sup>a</sup>

<sup>a</sup>Dpto. Ciencia y Tecnología Alimentos, Facultad Tecnológica, Universidad de Santiago de Chile-USACH Av.Ecuador N° 3769, Estación Central, Santiago, Chile. [fernando.osorio@usach.cl](mailto:fernando.osorio@usach.cl)

### Abstract

Edible film coatings (EFC) represent a viable preservation technology, they often constitute a water vapor barrier that delays deterioration and maintain the product structural integrity. EFC is a food covering film which can be eaten as part of the food. Hydroxy propyl methyl cellulose (HPMC), a cellulose derivative used in pharmaceutical industries, was employed as the basic formulation component to coat fresh blueberries. Addition of carrageenan, plasticizer and carnauba wax emulsion add value to film structure and functionality. The present work developed and characterized edible films from a food grade additive that is from a natural vegetable and biodegradable origin.

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### 1. Introduction

Edible food coating (EFC) is a food covering film which can be eaten as part of the food [1]. It imparts some characteristics to the food, maintaining coated food product quality by diminishing main alteration causes through different mechanisms such as avoiding moisture losses, decreasing adverse chemical reaction rates, acting as gas interchange barriers, improving microbiological stability, etc. [2,3].

EFC can be grouped into three categories depending upon the type of compound included in their formulations [1]: hydrocolloids, lipids and mixed hydrocolloid - lipid compounds. In addition, EFC may incorporate other components which help to improve final film characteristics such as plasticizers, surfactants and emulsifiers. Other kind of interesting ingredients for ECF are antioxidants, antimicroorganisms, and texture modifiers; all of them utilized to improve coating properties.

\* Corresponding author. Tel.: 56-2-718 550; fax: 56-2-682-3536.

E-mail address: [fernando.osorio@usach.cl](mailto:fernando.osorio@usach.cl)

Hydroxypropyl Methyl Cellulose (HPMC) is a water soluble cellulose ether hydrocolloid with good film forming properties. The degree of substitution, types of functional groups substitution, and chain length of this polymer affect permeability, mechanical properties and water solubility [4]. The EFC cellulose ether hydrocolloids based have been applied to a variety of foods to impart both moisture and oxygen barrier [4]. Carrageenan type K, a natural hot water (65-70°C) soluble hydrophilic gum [5], generates a thermo reversible strong and rigid gel. It can be applied as EFC to delay moisture loss and to avoid oxidations [6].

Plasticizers weaken polymer chain cohesion forces, increasing chain mobility and improving polymeric matrix flexibility [7]. In the food industry plasticizers are used for moisture stabilization, filling agent and/or edulcorants. Sorbitol, a polyalcohol, incorporated into EFC imparts higher traction resistance, lower elongation force and lower vapor water permeability than glycerol [8]. Propylene glycol was classified by the U. S. Food and Drug Administration as "generally recognized as safe" (GRAS) for use as a direct food additive; is totally miscible in water, alcohol, aldehyde, ether, ester; this property is utilized for stabilize and solubilize food products.

Waxes are long chain fatty acid esters with a long chain alcohol. They are more water diffusion resistant than the majority of lipids. Natural waxes currently employed in EFC are: candelilla wax, Carnauba wax, rice bran wax and beeswax [9]. Carnauba is a plant exudate from the Brazilian 'tree of life' (*Copernicia cerifera*), composed almost entirely of esters of C24 and C28 carboxylic acids and C32 and C34 straight-chained primary alcohols. Compared to other waxes, carnauba wax is significantly less viscous, more elastic, and more resistant to deformations [10]. In foods, it is used as a formulation aid, frostings, gravies, sauces etc. Waxes have also been used extensively as carriers for various types of drugs in pharmaceutical applications [11]. In EFC mixed hydrocolloid - lipid compound based, the lipid fraction may be emulsified in the hydrocolloid matrix forming the emulsified coatings, or forming a double layer known as bilayer coating [7].

Among preservation techniques, edible films represent a viable technology because they often constitute a barrier to water vapor that delays deterioration and helps to maintain the product structural integrity.

The present work developed and characterized edible films from a food grade additive that is from a natural vegetable and biodegradable origin.

## 2. Materials & Methods

Carrageenan type K (Carragel PGU 5289) (K1) samples were provided by Gelymar® S.A. (Santiago, Chile). HPMC (Methocel E19) was provided by Dow Wolff Cellulosics® (Bomlitz, Germany); Propilenglycol (PG) was provided by LyondellBasell® (LyondellBasell Industries Holdings, Rotterdam, The Netherlands); Sorbitol (70% v/v) (S), oleic acid, triethanolamine and Carnauba wax were provided by Blumos® S.A. (Santiago, Chile).

Previous to EFC preparation it was necessary to hydrate the HPMC in distilled water for 24 h at 10 C to obtain EFC forming suspensions at 0.5; 1.5 and 3% w/w. After this step, 30 ml of each suspension was added to a 500 ml beaker. Each beaker was stirred and heated (MSH 300, Boeco, Germany) at 4 rpm and ~50 C, temperature at which 0.2 % w/v carrageenan type K was added to each EFC forming suspension. Stirring continued for ~30 minutes at 4 rpm. After the elapsed time, temperature is decreased and maintained to ~30 C during 15 minutes and 2%v/v plasticizer -either S or PG- was added. To prepare the 0.2 %w/v carnauba wax emulsion (C) require to add to the previous suspension, carnauba wax is heated to 95 C and once it is melted 4%w/w oleic acid, 3%w/w triethanolamine and distilled water were carefully added maintaining constant agitation. Once the emulsion is homogenized it is filtrated an added to the previous suspension. Six different EFC forming suspension formulations were obtained. To compare, blank suspension formulations without carnauba wax emulsion were prepared. The carnauba wax emulsion drop size is a key variable for EFC forming suspension characterization. carnauba wax

emulsion drop size was determined through image analysis obtained with a light microscope (Olympus BX50, Optical Co. Ltd., Tokyo, Japan) and recorded with a digital camera (Meyer Instruments. CCD Coolsnap Pro Color). Each image (1392×1040 pixels) was saved as a 24 bits TIFF image file of approximately 1.38 MB, without compression. The image processing analysis was performed with an algorithmic segmentation process developed by Software Matlab 7.6 (R2009) (The Mathworks Inc. MA, USA). Drop size distribution was generated by grouping bubbles belonging to common class intervals. Frequency size distribution was calculated using MS-Excel (Microsoft Excel 2007). The frequency volume for any class interval was calculated as the ratio of drop number in that class (frequency class) to the drop total number.

To determine the rheological properties, a rheometer (Carri Med, CSL2 100, TA Instruments, England) using a 40 mm diameter parallel plate fixture was used to carry out the experiments. The lower plate is equipped with a Peltier temperature control system. An 800  $\mu\text{m}$  gap between the two parallel plates was applied for small amplitude oscillatory measurements. EFC forming suspension formulation samples were placed into cylinders (40 mm diameter and 5 mm height) and stored at  $\sim 4$  C for 24 hours to gel. Then, the gels were placed on the lower plate and it was raised to the desired gap. To ensure that the samples reach and maintain working temperature, a routine temperature stabilization provided by the instrument software was used. Preliminary tests, to determine the strain which assures the region of linear viscoelasticity, were performed in strain sweep mode, with a torque range from 0.008 to 80 Pa at a frequency of 1 Hz for  $10^\circ\text{C}$ . To determine EFC gels melting temperatures, temperature sweeps from 20 to 50 C with a heating rate of 1.5 C/min at frequency 1Hz were applied. To determine gel gelling temperature, temperature sweeps from 50 to 20 C with a cooling rate of  $1^\circ\text{C}/\text{min}$  at frequency of 1 Hz were applied. In both cases the strain applied was 0.5%. When the curves corresponding to the storage ( $G'$ ) and loss ( $G''$ ) modulus intercept, this corresponds to the melting temperature for the heating process and to the gel temperature for the cooling process, respectively [12].

Films from EFC forming suspension formulations were prepared by casting the polymer suspension onto a teflon covered metallic plate (135 mm diameter and 30 mm deep). Films were placed in an oven for 48 hours at  $\sim 20$  C to remove residual solvent. Films are stored on aluminum foil bags and these bags are placed into sealed PET bags for further measurements. Film thickness, measured using a Mitutoyo (700-117, Japan) instrument, ranged from  $\sim 20$  to 100  $\mu\text{m}$ . A dynamic mechanical analyzer (DMA 8000, Perkin Elmer, England) in tension mode was used to test the edible film structural behavior; triplicate samples were heated from  $-90\text{C}$  to  $90\text{C}$  at a heating rate of  $3\text{C min}^{-1}$  at a frequency of 1 Hz with 0.5% of strain.

Water vapor transmission rates (WVTR) of EFC films were measured using the methodology proposed by Sobral et al. [13] (ASTM E96-80 test). Eppendorf tubes (1.5 mL; surface area of  $0.93\text{ cm}^2$ ) were filled with silica gel, EFC sample films were tightly attached to the tube mouth and placed in plastic containers with supersaturated salt solutions with relative humidity from  $\sim 23$  to  $\sim 75\%$ . Plastic containers were placed at different constant temperatures ambients (5C, 20C and 30C). Weight and time were recorded during 8 days.

WVTR ( $\text{g}_{\text{H}_2\text{O}}\cdot\text{mm}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ ) was calculated from Equation 1 [13]:

$$\text{WVTR} = \frac{w \times x}{t \times A} \quad (1)$$

Where  $w$  is weight gain (grams),  $x$  is the average film thickness (mm),  $t$  is the elapsed time (hour) and  $A$  is the mass transfer area ( $0.93\text{ cm}^2$ )

Water vapor permeability (WVP) was calculated from Equation 2:

$$\text{WVP} = \frac{w \times x}{t \times A \times \Delta P} \quad (2)$$

Where  $\Delta P$  is the pressure difference between internal pressure (silica gel side) and external pressure (supersaturated salt solution side).

The statistical analysis was performed through ANOVA tests, and Tukey tests were applied to analyze differences among averages. The GraphPad Prism v.4.0 (GradPad Systems Inc.) program was utilized. Treatment averages were considered significantly different at  $P < 0.05$ .

### 3. Results & Discussion

Figure 1 shows the percentage of equivalent drop diameter frequency versus drop equivalent diameter for carnauba wax emulsion.

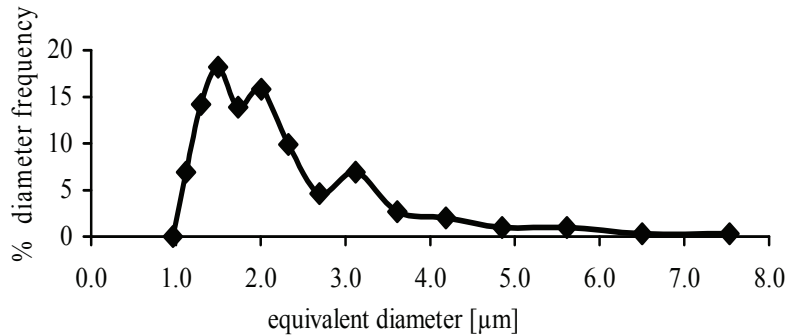


Fig. 1. Percentage of equivalent drop diameter frequency versus drop equivalent diameter for carnauba wax emulsion

The carnauba wax emulsion drop diameter varied from 1 to 7.5  $\mu\text{m}$  and the 18% of the total drop size population is within 1 to 1.5  $\mu\text{m}$ . Average drop size population is 1.92  $\mu\text{m}$ . Although drop size population is very small it doesn't form a micro emulsion, but it is adequate for film formation because water vapor barrier increases with lipid particle size reduction and also with homogeneous lipid distribution within hydrocolloid matrix [3, 14-15]; a large number of lipid particles homogeneously distributed in the matrix makes water vapor transmission difficult since diffusion occurs mainly through the hydrophilic phase avoiding lipid particles [7].

Figure 2 shows storage ( $G'$ ) and loss ( $G''$ ) modulus versus temperature sweeps from 50 to 20 C to determine gelling temperature for a cooling rate of 1.5 C/min at frequency of 1 Hz. Strain applied was 0.5%.

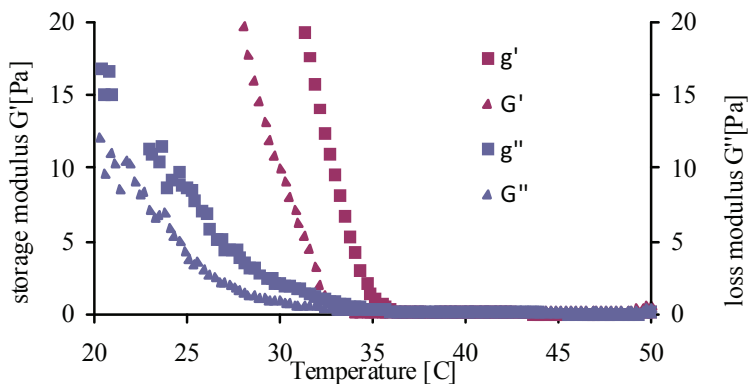


Fig. 2. Storage ( $G'$ ) and loss ( $G''$ ) modulus versus Temperature sweeps from 50 to 20 C to determine gelling temperature. Cooling rate of 1.5 C/min at frequency of 1 Hz. Strain applied was 0.5%.

Table 1 shows melting (Tf) and gel (Tgel) temperatures for some formulations. Gelling and melting temperatures varied from  $29.9 \pm 0.5\text{C}$  to  $35.5 \pm 0.1\text{C}$ .

Table 1. Melting (Tf) and gel (Tgel) temperatures for some formulations

Formulation	Tf, C	Tgel, C
(E)	$34 \pm 0.42$	$29.85 \pm 0.49$
(B)	$35.5 \pm 0.14$	$35 \pm 1.41$

Higher Tgel and Tf temperatures were obtained for samples using propylene glycol as plasticizer, meaning this formulation requires higher energy to deform or to change state to melt.

Figure 3 shows complex ( $\eta^*$ ) and dynamic( $\eta'$ ) viscosity versus frequency for Formulation (B). Temperature was 10 C and strain 0.5 %. The film forming suspensions showed pseudoplastic behavior.

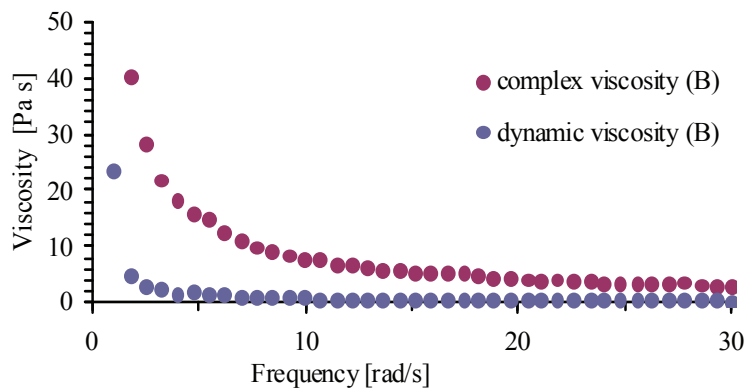


Fig. 3. Complex ( $\eta^*$ ) and dynamic( $\eta'$ ) viscosity versus frequency. Temperature 10 C; strain 0.5 %.

Figure 4 shows the storage modulus ( $G'$ ) and  $\tan \delta$  versus temperature sweep for edible film formed from Formulation (E) suspension. Frequencies were 1 ; 10 and 20 Hz; heating rate was  $3 \text{ C min}^{-1}$  and strain 0.5%

Data from DMA analysis showed a drastic change on storage modulus ( $G'$ ) at  $-22.5\text{C} \pm 4.8\text{C}$ , change which was coincidental with  $\tan \delta$  peak value. These drops in both  $G'$  and  $\tan \delta$  values are associated to a film structural change from glassy to rubbery state related to the glass transition temperature

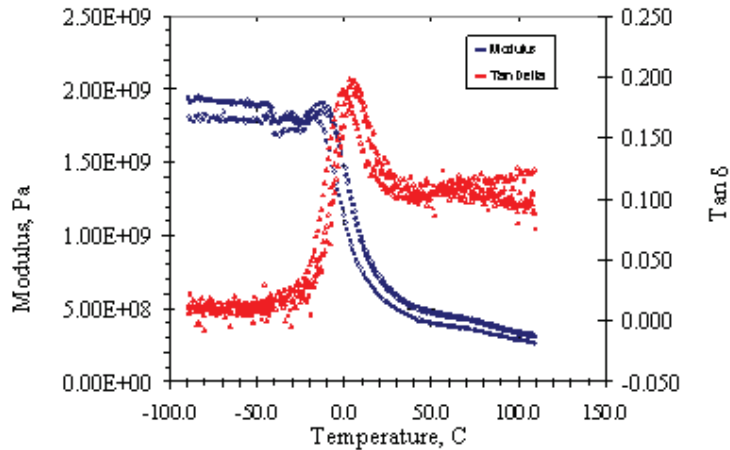


Fig. 4. Storage modulus ( $G'$ ) and  $\tan \delta$  versus temperature sweep for edible film formed from Formulation (E) suspension. Frequencies 1; 10 and 20 Hz;  $3 \text{ C min}^{-1}$  heating rate ; strain of 0.5%

The obtained results showed that water vapor transmission depends on storage conditions (temperature and relative humidity), film composition and thickness. On storage conditions, at 5C and 100% relative humidity, WVTR values for all formulations varied between  $1.5 \cdot 10^{-5} \pm 0.3 \cdot 10^{-5}$  and  $2.3 \cdot 10^{-4} \pm 0.3 \cdot 10^{-4}$  ( $\text{g mm h}^{-1} \text{ cm}^{-2}$ ), whereas WVP ranged between  $1.67 \cdot 10^{-8} \pm 0.37 \cdot 10^{-8}$  and  $2.61 \cdot 10^{-7} \pm 0.36 \cdot 10^{-7}$  ( $\text{g mm h}^{-1} \text{ cm}^{-2} \text{ Pa}^{-1}$ ). These values for WVP compare very well to those from the literature for films made only with HPMC [16] which gave  $3.79 \cdot 10^{-8}$  ( $\text{g mm h}^{-1} \text{ cm}^{-2} \text{ Pa}^{-1}$ ), and those prepared with starch [1] gave  $7.2 \cdot 10^{-11}$  ( $\text{g mm h}^{-1} \text{ cm}^{-2} \text{ Pa}^{-1}$ ).

#### 4. Conclusion

Rheological and water vapor transport properties are helpful tools to characterize HPMC based edible films developed for blueberry coatings.

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#### References

- [1] Pastor C., Vargas M. & González-Martínez C. 2005. Recubrimientos Comestibles: Aplicación a Frutas y Hortalizas. Alimentación, Equipos y Tecnología, 197, p.130-135.
- [2] Kester J. J., & Fennema O.R. 1986. Edible Films and Coatings: A Review. Food Technology, 40(12), 47-59.
- [3] Debeaufort F. & Voilley A. 1995. Effect of Surfactants and Drying Rate on Barrier Properties of Emulsified Edible Films. Int. J. Food Sci. Technol., 30,1 p.83-190.
- [4].Sanderson GR. 1981. Polysaccharides in Foods. Food Technology, 35,50–56, 83
- [5] Fennema O. 2000. Química de los Alimentos. Editorial Acribia S.A. Zaragoza. España. p 145-146,155.

- [6] Nieto M. 2009. Structure and Function of Polysaccharide Gum-Based Edible Films and Coatings. In: Embuscado M.E. & Huber K.C. (Eds.). *Edible Films and Coatings for Food Applications*. Springer. London /New York. USA. p 57–112
- [7] Navarro T. M. 2007. Efecto de la composición de recubrimientos comestibles a base de Hidroxipropilmetilcelulosa y cera de abeja en la calidad de ciruelas, naranjas y mandarinas. Trabajo de titulación para optar al grado de Doctor, Universidad Politécnica de Valencia, España
- [8] Park S. & Zhao Y. 2006. Development and Characterization of Edible Films from Cranberry Pomace Extracts. *Journal of Food Science*, 71(2), 97-98.
- [9] Baldwin EA. 2007. Surface Treatments and Edible Coatings in Food Preservation. In: Rahman M.S. (Ed.). *Handbook of Food Preservation*. CRC Press. Boca Raton, FL. USA.
- [10] Shellhammer T.H., Rumsey T.R. & Krochta J.M. 1997. Viscoelastic Properties of Edible Lipids. *Journal of Food Engineering*, 33, 305–320.
- [11] Milanovic J., Manojlovic V., Levic S., Rajic N., Nedovic V. & Bugarski B. 2010. Microencapsulation of Flavors in Carnauba Wax. *Sensors*, 10, 901-912.
- [12] Gudmundsson M. 2002. Rheological Properties of Fish Gelatins. *Journal of Food Science*, 67(6), 2172- 2173, 2174.
- [13] Sobral P., Menegalli F., Hubinger M. & Roques, M. 2001. Mechanical, Water Vapor Barrier and Thermal Properties of Gelatin Based Edible Films. *Food Hydrocolloids*, 15, 423-432.
- [14] Koelsch C.M. & Labuza T.P. 1992. Functional, Physical and Morphological Properties of Methyl Cellulose and Fatty Acid-Based Edible Barriers. *Lebensm. Wiss. u. Technol.*, 25, 404-411.
- [15] McHugh T. H. & Krochta J.M. 1994. Sorbitol-Vs Glycerol-Plasticized Whey Protein Edible Films: Integrated Oxygen Permeability and Tensile Property Evaluation. *J. Agr. Food Chem.*, 42(4), 841-845.
- [16] Hagenmaier R. D. & Shaw P.E. 1992. Gas Permeability of Fruit Coating Waxes. *J. Am. Soc. Hort. Sci.*, 117(1), 105-109.

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