



Characterization of composite hydrocolloid films

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Abstract

Chitosan (CH) and methylcellulose (MC) are hydrocolloids with good film-forming properties. The objectives of the present work were to characterize: (i) rheological and surface tension properties of the filmogenic suspensions and (ii) water solubility, color, mechanical properties and water vapor permeability of the composite films.

Suspensions of 1 and 2% CH and 1% MC were mixed in different proportions. Surface tension of filmogenic suspensions ranged between 72 and 87.5 dyn cm⁻¹. All suspensions were pseudoplastic; apparent viscosity and consistency index of the mixtures were higher than those of MC or CH suspensions. Films were obtained by casting. Water vapor permeabilities for CH and MC films were $9.03 \pm 0.12 \times 10^{-11}$ and $7.55 \pm 0.60 \times 10^{-11}$ g s⁻¹ mPa⁻¹, respectively; intermediate values were obtained for the composite films. CH films showed rigid characteristics (high elastic modulus and small elongation). Film flexibility increased with increasing MC content, the higher elongation and lower elastic modulus of composite films indicated the relevance of hydrocolloid interactions.

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1. Introduction

Environmental concerns enhance and stimulate the use of renewable resources producing economically convenient applications to maintain or even improve life quality. Low cost agricultural and seafood commodities, commonly found in developing countries, produce high amounts of surplus and wastes that are under-utilized sources of biopolymers. Research on alternative uses and reprocessing of these biopolymers will add commercial value and reactivate depleted economies, as well as reduce pollution problems.

Specifically, several polysaccharides have good film-forming capacities, including cellulose derivatives, chitosan (CH), starch, alginate, carrageenan and pectin. Cellulose and chitin are chemically treated to obtain cellulose derivatives and CH with higher water solubility and enhanced properties (Butler, Vergano, Testin, Bunn, & Wiles, 1996).

CH is a high molecular weight polymer formed by N-acetyl-D-glucosamine units with $\beta(1-4)$ glycosidic

bounds. The cationic nature of CH is owed to the free amino groups left by partial remotion of acetyl groups of chitin. CH is a linear polyelectrolyte at acidic pH with good film-forming capacity among other applications (Sandford & Hutchings, 1987). Because of its antifungal, good mechanical and oxygen barrier properties, CH is a promising edible film component (Anker, 1996; Caner, Vergano, & Wiles, 1998; Chen, Yeh, & Chiang, 1996).

Cellulose derivatives are polysaccharides composed of linear chains of $\beta(1-4)$ glucosidic units with methyl, hydroxypropyl or carboxyl substituents. Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) exhibit thermo-gelation (Grover, 1993) and have excellent film-making properties, high solubility, efficient oxygen and lipid barrier properties (Donhowe & Fennema, 1993a,b; Nisperos-Carriedo, 1994; Park, Weller, Vergano, & Testin, 1993).

Composite films may be designed to take advantages of pure components. Even tough, as with synthetic polymers, the mechanical and barrier properties of composite biofilms strongly depend on the constituting polymer characteristics and their compatibility (Butler et al., 1996; Donhowe & Fennema, 1993b).

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The objectives of the present work were: (a) to develop composite biodegradable films based on CH and MC, (b) to evaluate water solubility, optical properties, water vapor permeability (WVP) and mechanical properties of the films and (c) to characterize surface tension and rheological properties of the filmogenic suspensions from which films were obtained by casting.

2. Materials and methods

2.1. Hydrocolloid suspensions

MC (A4M, Methocel) was provided by Dow Chemical (USA), CH was provided by Sigma (St Louis, USA). Suspensions of 1% (w/w) of MC, were prepared; this concentration was selected in a previous work (García, Ferrero, Bértola, Martino, & Zaritzky, 2002).

For CH suspensions, concentrations of 1 and 2% (w/w) were tested to select appropriate formulations for film applications. CH was solubilized in 1% (v/v) acetic acid solution during continuous agitation for 12 h approximately, followed by a vacuum filtration to eliminate insolubles (No & Meyers, 1989). For CH suspensions, concentrations above 2% were very difficult to solubilize.

Suspensions of CH (1 and 2%) and suspensions of 1% MC were prepared and mixed in the proportions showed in Table 1. Filmogenic suspensions were divided in two groups, one with the same total solid content and the other with different total solids content (Table 1). The effect of composition was analyzed with mixed filmogenic suspensions containing different proportions of 1% CH and 1% MC and those containing 2% CH and 1% MC. These last formulations also gave an insight into total solids effect.

Table 1
Composition of CH–MC filmogenic suspensions

CH concentration	Mass ratio of each suspension in 100 g of the filmogenic mixture ^a	Concentration of each component in 100 g of filmogenic suspension (g CH: g MC)	Solid content (mass of polymer per 100 g suspension)
0% CH	0:100	0:1	1
1% CH	25:75	0.25:0.75	1
	50:50	0.5:0.5	1
	75:25	0.75:0.25	1
	100:0	1:0	1
2% CH	25:75	0.5:0.75	1.25
	50:50	1:0.5	1.5
	75:25	1.5:0.25	1.75
	100:0	2:0	2

^a Suspensions of 1 or 2% CH were mixed in the indicated proportions with 1% MC suspensions (mass of CH suspension:mass of MC suspension).

2.1.1. Surface tension

Surface tension of each suspension was measured using the Ring Method in a CSC-DUNOUY 70535 (Fairfax, VA). Four measurements were performed for each formulation.

2.1.2. Rheological characterization of hydrocolloid suspensions

Rheological characterization of the filmogenic suspensions was performed in a Haake RV2 (Haake, Germany) rotational viscometer, at controlled constant temperature (20 °C) A NV type sensor system of coaxial cylinders was used for the measurements of suspensions that contain 1% CH and a MV IP profiled coaxial cylinders was used for suspensions that contain 2% CH. Rheological curves were obtained after a stabilization time of 3 min at 20 °C. Shear stress was determined as a function of shear rate between 0 and 512 s⁻¹ with the following program: 3 min to attain the maximum shear rate, 1 min at the maximum shear rate and 3 min to attain 0 shear rate. Apparent viscosities were calculated at 256 s⁻¹.

2.2. Hydrocolloid films

To obtain the films, 40 g of suspensions were poured on rectangular acrylic plates (10 × 20 cm²). The suspensions were dried (60 °C) in a ventilated oven to constant weight (about 6 h); translucent films, which could be easily removed from the plate, were obtained. Films were stored at 20 °C and at a relative humidity (RH) of 65% to measure barrier and mechanical properties.

2.2.1. Humidity

Water content of films was determined measuring weight loss of films, upon drying in an oven at 110 °C until constant weight (dry sample weight). Samples were analyzed at least in triplicate. Equilibrium humidity content (%) was calculated as follows:

$$\text{Humidity (\%)} = \left(\frac{\text{Initial sample weight}}{\text{Dry sample weight}} - 1 \right) \times 100 \quad (1)$$

2.2.2. Thickness measurements

Thickness of the films was determined using a digital coating thickness gauge Elcometer A 300 FNP 23 (England) for non-conductive materials on non-ferrous substrates. Informed values are an average of at least 15 measurements.

2.2.3. Film solubility in water

Pieces of film of 2 × 3 cm² were cut from each film and were stored in a dessicator (0% RH) for 7 days. Samples were weighed to the nearest 0.0001 g and placed into test beakers with 80 ml deionized water. The samples were maintained under constant agitation for 1 h at room temperature (approximately 25 °C) or at boiling temperature. The remained pieces of film after soaking were dried again in

an oven at 60 °C to constant weight. The percentage of total soluble matter (% solubility) was calculated as follows:

$$\% \text{Solubility} = \left[\frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \right] \times 100 \quad (2)$$

Samples were analyzed at least in duplicate.

2.2.4. Colorimetric measurements

Film color was determined by a Minolta colorimeter CR 300 Series (Japan) calibrated with a standard ($y = 93.2$, $x = 0.3133$, $y = 0.3192$) The CIELab scale was used, lightness (L) and chromaticity parameters a^* (red–green) and b^* (yellow–blue) were measured. Measurements were performed placing the film sample over the standard. Samples were analyzed in triplicate, recording four measurements for each sample.

Color differences (ΔE) were also calculated by the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$

where:

$$\Delta L^* = L^* - L_0^*$$

$$\Delta a^* = a^* - a_0^*$$

$$\Delta b^* = b^* - b_0^*$$

being: L_0^* , a_0^* , b_0^* , the color parameter values of the standard and L^* , a^* , b^* , the color parameter values of the sample.

2.2.5. Water vapor permeability

WVP tests were conducted using a modified ASTM (1995) method E96. Each film sample was sealed over a circular opening of 0.00181 m² in a permeation cell that was stored at 25 °C in a dessicator. To maintain a 75% RH gradient across the film, anhydrous calcium chloride (0% RH) was placed inside and a sodium chloride saturated solution (75% RH) was used in the dessicator. This difference in RH corresponds to a driving force of 1753.55 Pa, expressed as water vapor partial pressure.

The RH inside the cell was always lower than outside, and water vapor transport was determined from the weight gain of the permeation cell. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by linear regression ($r^2 > 0.99$) and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g s^{-1}) divided by the test area (m²). After the permeation tests, film thickness was measured and WVP ($\text{g Pa}^{-1} \text{s}^{-1} \text{m}^{-1}$) was calculated as

$$\text{WVP} = [\text{WVTR}/S(R_1 - R_2)]d \quad (4)$$

where S is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1 is the RH in the dessicator, R_2 is the RH in the permeation cell and d is the film thickness (m).

2.2.6. Mechanical properties

Puncture tests were performed in a texturometer TA XT2i, Stable Micro Systems (England). A cylindrical probe 2 mm in diameter at a constant rate of 1 mm s⁻¹ was used. Tests were performed on probes of 3 × 3 cm² from each film formulation; each informed value corresponded to at least four determinations.

Tensile tests were also performed with the same equipment using a tension grip system A/TG. Probes of 6 cm in length and 0.7 cm width were used; at least 4 probes were used for each film formulation.

For both, tension and puncture assays, the curves of force (N) as a function of deformation (mm) were automatically recorded by the Texture Expert Exceed software.

Maximum breaking force (N), breaking factor (maximum breaking force divided by film thickness, N μm⁻¹), deformation at break (extension at the moment of rupture, mm), percent elongation at break (deformation divided by initial probe length and multiplying by 100, %) and elastic modulus (slope of force–deformation curve, N mm⁻¹) were obtained from force vs. deformation curves according to the ASTM (1996) D882-91 method. For tensile assays, tensile strength (MPa) was calculated by dividing maximum force by film cross-section (thickness × width). For puncture assays, tensile strength (MPa) at break was calculated by dividing force at break by probe cross-section.

2.3. Statistical analysis

Systat-software (SYSTAT, Inc, Evanston, IL) version 5.0 was used for all statistical analysis. Analysis of variance (ANOVA), linear and non-linear regressions and Fisher LSD mean comparison test were applied. The significance levels used were 0.05 and 0.01.

3. Results and discussion

3.1. Characterization of the hydrocolloids suspensions

Surface tensions of MC and CH and suspensions of their mixtures are shown in Table 2. MC suspensions exhibited the highest surface tension, while CH ones were in the order of water values (72.8 dyn cm⁻¹).

Power law model satisfactory fitted experimental data ($r^2 > 0.99$). All suspensions showed pseudoplastic behavior ($n < 1$); apparent viscosities of suspensions were calculated at 256 s⁻¹ shear rate (Table 2).

According to the manufacturer description, the cellulose derivative used (MC) is a modified cellulose that contains only methyl groups as substituents allowing stronger interactions between hydrocolloid chains; thus, suspensions with high apparent viscosities should be expected. Similar considerations could apply to CH chains. Rheological parameters of either MC or CH suspensions at 1% concentration showed similar values in all rheological parameters (Table 2).

Table 2
Characterization of CH–MC filmogenic suspensions

CH concentration	Mass ratio CH:MC ^a	Surface tension (dyn cm ⁻¹)	Consistency index <i>k</i> (Pa s ^{<i>n</i>})	Flow behavior index <i>n</i> (dimensionless)	Apparent viscosity η_{ap} at $\lambda = 256 \text{ s}^{-1}$ (mPa s)
0% CH	0:100	87.00 ± 1.14 ^b	1.66 ± 0.21	0.570 ± 0.009	102.49 ± 7.40
1% CH	25:75	86.35 ± 0.07	3.42 ± 0.07	0.509 ± 0.003	140.68 ± 0.62
	50:50	81.07 ± 0.47	2.83 ± 0.38	0.531 ± 0.011	134.57 ± 8.43
	75:25	70.38 ± 1.48	2.21 ± 0.12	0.559 ± 0.003	127.11 ± 4.48
	100:0	72.17 ± 0.21	1.43 ± 0.07	0.605 ± 0.002	112.73 ± 5.44
2% CH	25:75	68.07 ± 1.01	4.84 ± 0.17	0.549 ± 0.001	410.68 ± 14.18
	50:50	66.40 ± 0.56	7.09 ± 1.37	0.547 ± 0.025	589.22 ± 33.44
	75:25	67.87 ± 2.20	8.70 ± 1.10	0.541 ± 0.027	702.65 ± 13.07
	100:0	74.53 ± 0.57	19.36 ± 3.13	0.445 ± 0.025	945.05 ± 31.93

^a Mass proportions of CH suspensions (1 or 2%) and 1% MC suspensions. Key to compositions in Table 1.

^b Value ± standard deviation.

Mixtures of 1% MC and CH suspensions showed a synergistic effect, apparent viscosities and consistency indices were higher than those of individual components (Fig. 1). Chen et al. (1996) working on MC and CH suspensions with different MC concentrations found similar results.

However, when 2% CH suspension was mixed with 1% MC suspension, results were completely different. Rheological parameters of composite suspensions formulated with 2% CH differed significantly ($P < 0.05$) from the other suspensions. Viscosities of these composite suspensions fell between those of individual components, 2% CH suspension viscosity was 9 times higher than that of 1% MC (Table 2). Dilution effect as seen by total solid content detailed in Table 1 may explain intermediate viscosity values obtained for mixed suspensions (Fig. 1). Besides, consistency index increased and flow behavior index decreased with CH concentration.

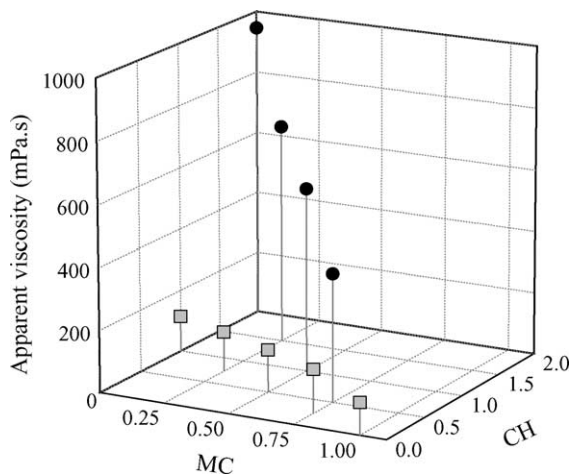


Fig. 1. Apparent viscosity of suspensions (at 256 s^{-1}) as a function of the polysaccharide concentrations, CH, chitosan; MC, methylcellulose. 1% CH series (●) and 2% CH series (□). Values of CH and MC on the axes correspond to concentration in 100 g of the filmogenic suspensions (third column of Table 1). Maximum standard deviation for 1% CH series = 8.43 and maximum standard deviation for 2% CH series = 31.93.

3.2. Film characterization

Homogeneous, thin, flexible and transparent films were obtained from MC, CH and mixture suspensions. All the films were easily removed from the cast plate and showed smooth surfaces. Thickness of films varied between 14.12 ± 1.59 and $26.07 \pm 3.17 \mu\text{m}$, as shown in Table 3. Films with the same total solid content did not differ significantly ($P > 0.05$) in thickness; increasing total solid content increased film thickness (Tables 1 and 3). All films reached after drying low humidities (Table 3); MC films exhibited the lowest equilibrium humidity while the highest value was observed for 2% CH films.

Visually, MC films were colorless and CH films had a slightly yellow appearance, increasing yellowness with CH concentration for both CH alone and composite films. Similar results were reported by Butler et al. (1996). Besides, Caner et al. (1998) studying the effect of acids on CH solubilization, stressed that propionic acid led to almost

Table 3
Water vapor permeability (WVP), humidity content and thickness of CH–MC films

Concentration of each component in 100 g of filmogenic suspension (g CH:g MC)	WVP × 10 ¹¹ (g m ⁻¹ s ⁻¹ Pa ⁻¹)	Equilibrium humidity content in the film at 65% HR (g water/100 g film)	Film thickness (μm)
0:1	7.552 ± 0.604 ^a	0.91 ± 0.16	16.32 ± 2.46
0.25:0.75	7.834 ± 0.034	2.61 ± 0.48	15.32 ± 2.06
0.50:0.50	8.483 ± 0.819	1.65 ± 0.02	18.42 ± 2.84
0.75:0.25	8.764 ± 0.773	2.57 ± 0.51	14.12 ± 1.59
1:0	9.029 ± 0.123	2.18 ± 0.44	14.39 ± 1.84
0.50:0.75	6.767 ± 0.919	1.12 ± 0.01	21.22 ± 0.68
1:0.50	6.671 ± 0.744	2.41 ± 0.16	23.35 ± 2.72
1.5:0.25	7.236 ± 0.346	2.22 ± 0.01	22.75 ± 1.69
2:0	7.239 ± 0.811	6.33 ± 0.58	26.07 ± 3.17

^a Value ± standard deviation.

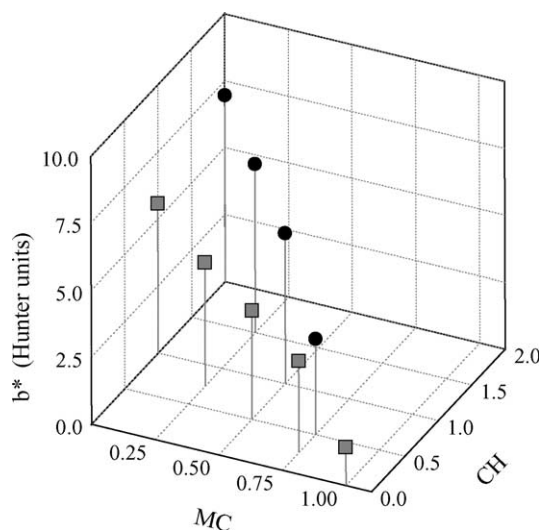


Fig. 2. Chromaticity parameter b^* of films as a function of the polysaccharide concentrations, CH, chitosan; MC, methylcellulose. 1% chitosan series (●) and 2% chitosan series (□). Values of CH and MC on the axes correspond to concentration in 100 g of the filmogenic suspensions (third column of Table 1). Maximum standard deviation for 1% CH series = 0.22 and maximum standard deviation for 2% CH series = 0.12.

colorless films. Anyway, the intensity of the yellowness is negligible when compared to values reported for protein-based films like whey protein ones (Trezza & Krochta, 2000a). Moreover, color modifications with storage are commonly reported in protein films due to Maillard reactions and in lipid-based films due to rancidity (Trezza & Krochta, 2000b). Polysaccharide films are free of these problems associated with proteins and lipids.

Instrumental color determinations showed non-significantly ($P > 0.05$) lightness (L) values, around 96.30 ± 0.30 , for all assayed films. The values of b^* of MC and CH films are shown in Fig. 2. The CH films formulated with concentrations 1 or 2% showed b^* values significantly ($P < 0.05$) higher than MC films. These results agreed with visual observations.

Table 4
Comparison of WVP values of biodegradable and synthetic films

Film formulation	WVP ($\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$)	Reference
Wheat gluten plasticized with glycerol	7.00×10^{-10}	Gennadios, Weller, and Gooding (1994)
Corn zein plasticized with glycerol	8.90×10^{-10}	Aydt, Weller, and Testin (1991)
Whey protein plasticized with sorbitol	7.17×10^{-10}	Mc Hugh et al. (1994)
Corn starch plasticized with sorbitol	1.75×10^{-10}	García et al. (2000)
Hydroxypropylmethylcellulose (HPMC) with plasticizer and oil	1.90×10^{-10}	Gennadios et al. (1994)
Methylcellulose	8.70×10^{-11}	Donhowe and Fennema (1993a)
Methylcellulose 1%	7.55×10^{-11}	Present study
Methylcellulose 3%	$8.4\text{--}12.1 \times 10^{-11}$	Park et al. (1993)
Chitosan 2% (unknown source)	$3.66\text{--}4.80 \times 10^{-11}$	Wong et al. (1992)
Chitosan 3%	$6.19\text{--}15.27 \times 10^{-11}$	Caner et al. (1998)
Chitosan 1%	9.03×10^{-11}	Present study
Cellophane	8.4×10^{-11}	Shellhammer and Krochta (1997)
Low density polyethylene	9.14×10^{-13}	Smith (1986)
High density polyethylene	2.31×10^{-13}	Smith (1986)
Nylon 6	2.09×10^{-9}	Smith (1986)

In the composite films (1% MC and 1 or 2% CH), b^* increased continuously with CH concentration. Color difference (ΔE) showed a similar trend.

With regard to water solubility, while MC films were completely soluble in water at both, 25 and 100 °C, CH films had low solubilities; below 4.5% at 25 °C and 11.5% at 100 °C after 1 h dipping; as expected, solubility increased with temperature. Although, CH films became rubbery when they were dipped in water, they maintained their integrity. Films from CH–MC mixtures had intermediate water solubilities, which were between the values of one component film. With increasing CH concentration film solubility decreased. Films of 25:75 CH:MC gave the highest solubility (39.9%) and showed a gel-like structure at the end of the solubility test.

Thus, film solubility can be tailored by controlling CH concentration allowing a wide range of possible applications. Some applications may require water insolubility to enhance product integrity and water resistance. However, in other cases, water solubility of the film before consumption of the product might be beneficial.

3.3. Water vapor permeability

Table 3 shows WVP of individual MC and CH films and also of the composite films; WVP of MC films was lower than 1% CH films. Composite films of 1% CH–MC mixtures had intermediate WVP values with a slight tendency to increase towards CH values. Films of 2% CH gave similar WVP values to those of MC; composite films did not differ significantly ($P > 0.05$) from the values of one component film. Even though, all films formulated with 2% CH suspensions had lower WVP values than those obtained with 1% CH suspensions. Our obtained results agree with those of Park et al. (1993), Caner et al. (1998) and Wong, Gastineau, Gregorski, Tillin, & Pavlath (1992) (Table 4).

Table 5
Tensile and puncture properties of CH–MC films

Concentration of each component (g CH:g MC) in 100 g of filmogenic suspension	Tensile properties		Puncture properties	
	Elongation (%)	Elastic modulus (N mm ⁻¹)	Deformation (mm)	Elastic modulus (N mm ⁻¹)
0:1	14.020 ± 1.426 ^a	2.281 ± 0.548	2.019 ± 0.192	6.332 ± 0.654
0.25:0.75	8.271 ± 1.120	1.881 ± 0.164	1.815 ± 0.098	5.050 ± 0.739
0.50:0.50	7.240 ± 0.842	2.337 ± 0.368	1.799 ± 0.337	4.821 ± 0.759
0.75:0.25	6.309 ± 1.160	2.194 ± 0.161	1.894 ± 0.193	5.427 ± 1.398
1:0	4.341 ± 0.403	2.234 ± 0.507	1.828 ± 0.243	5.981 ± 0.869
0.50:0.75	6.219 ± 0.169	2.397 ± 0.361	2.263 ± 0.167	6.217 ± 1.148
1:0.50	6.273 ± 0.339	3.522 ± 0.606	2.115 ± 0.291	8.139 ± 1.271
1.5:0.25	4.893 ± 0.427	3.705 ± 0.603	2.258 ± 0.053	8.075 ± 0.410
2:0	3.956 ± 0.423	4.923 ± 0.636	2.257 ± 0.056	10.389 ± 1.056

^a Value ± standard deviation.

Hydrocolloid films are characterized by their good gas barrier properties but poor water vapor permabilities (Baldwin, Nisperos-Carriedo, Hagenmaier, & Baker, 1997; Cuq, Gontard, & Guilbert, 1998; Debeaufort & Voilley, 1997; García, Martino, & Zaritzky, 1999, 2000; Krochta & De Mulder-Johnson, 1997; Mali, Grossmann, García, Martino, & Zaritzky, 2002; Park et al., 1993). Films developed in the present study showed lower WVP, with an order of magnitude below some protein films and even lower than other polysaccharide-based films reported in literature (Table 4).

With regard to synthetic polymers, CH–MC films have WVP values similar to those of cellophane, as expected due to the similar chemical structure of the components. Although, they are higher than low density polyethylene (LDPE), the most commonly polymer used in the food packaging industry (Table 4).

3.4. Mechanical properties

MC and CH films showed different behavior patterns under tensile tests. While MC and 1% CH films had similar elastic modulus and tensile strength, about 2.5 N mm⁻¹ and 10 MPa, respectively, MC films elongation was significantly ($P < 0.05$) higher than that of 1% CH films (Table 5). This indicates that both films were resistant and MC films were more flexible. Elongation values of films were 14.02% for MC, 4.33% for 1% CH and 3.96% for 2% CH and intermediate values were obtained with composite films. Similar mechanical properties were found in literature for MC films. Debeaufort & Voilley (1997) reported values of 7% elongation and 12 MPa for tensile strength in MC films from another suppliers. Other researchers working with 3% MC (Dow Chemical) found values of about 7–20% elongation and 71–80 MPa tensile strength (Donhowe & Fennema, 1993a,b; Park et al., 1993). For CH films, data reported in literature were higher than those obtained in

the present work, differences may be attributed to CH composition and suppliers, plasticizer presence and film preparation (Butler et al., 1996; Caner et al., 1998; Chen & Lin, 1994).

In composite films from 2% CH suspensions, elastic modulus and tensile strength increased with CH concentration and total solid content of films, leading to stronger films (Table 5). Accordingly, a decreasing elongation trend was observed with CH concentration and total solid content, indicating a reduction in film flexibility (Table 5).

All composite films containing 2% CH had higher elastic modulus and lower elongation values than those of 1% CH. Following this trend, Caner et al. (1998) reported values of 42% elongation and 19.60 MPa of tensile strength for 3% CH films. Synthetic polymers like LDPE and HDPE exhibit much higher elongation but similar tensile strength; however, cellophane shows higher tensile strength but similar elongation values when compared with our results (Cunningham, Ogale, Dawson, & Acton, 2000).

With regard to puncture tests, elastic modulus showed the same trend as in tensile test. However, all films have a similar value of deformation at break, about 2 mm, regardless CH:MC ratio (Table 5). CH may replace MC improving puncture resistance of films with economical benefits.

4. Conclusions

Variations of studied film properties could not be simply explained by additive effect of individual components; results indicated that a different interaction between 1 or 2% CH suspensions and MC ones may be produced leading to a different film structure. Moreover, rheological data previously described also showed great differences between 1 and 2% CH suspensions and the corresponding mixtures.

Considering that both polymers had linear backbones with a cellulose-like structure, intermolecular interactions should be facilitated and should be even reinforced by the different charge density of the substituents. Accordingly, Chen & Lin (1994) also stressed that physical properties highly depend on the interaction between polymer chains whose molecules are chemically or geometrically regular in structure.

Replacing MC by CH, a by-product obtained from wastes of the fishing industry, could help to reduce both environmental and economical problems. These combined biodegradable films with good water vapor barrier properties have the possibility to tailor mechanical and solubility properties, within a range, based on polymer ratio composition. Thus, MC–CH edible films can lead to many possible applications.

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