

Study on microstructure and physical properties of composite films based on chitosan and methylcellulose

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Abstract

Biodegradable films obtained from chitosan (CH) and methylcellulose (MC) can reduce environmental problems associated with synthetic packagings. Biodegradable films still need a cost reduction to be economically profitable; the use of CH, a by-product obtained from wastes of the fishing industry would be a good alternative. The objectives of the present work were to characterize physical, mechanical and water vapor barrier properties and microstructure of films of CH, MC and their mixtures.

Solutions of 2% CH and 1% MC were mixed in different proportions. Films were obtained by casting. Film microstructure was characterized by SEM, X-ray diffraction and FTIR spectroscopy. Water vapor permeabilities for CH and MC films were $6.67 \pm 0.74 \times 10^{-11}$ and $7.55 \pm 0.60 \times 10^{-11}$ g/s m Pa, respectively; composite film permeabilities did not differ significantly from these values. CH films showed rigid characteristics (high elastic modulus and low elongation). Flexibility of composite films 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

Edible films and coatings are thin films prepared from biopolymers that act as a barrier to the external elements (factors such as moisture, oil and water vapor) and thus protect the product and extend its shelf life. Biodegradable film properties depend on the material type used and obtention conditions that determine their applications (Krochta & De Mulder-Johnston, 1997). Biological materials used are polysaccharides, proteins, lipids and their derivatives. Specifically, within polysaccharides cellulose derivatives, chitosan (CH), starch, alginate, carrageenan and pectin are preferred because their high film forming capacity.

Cellulose derivatives are polysaccharides composed of linear chains of β (1–4) glucosidic units with methyl, hydroxypropyl or carboxyl substituents. Methylcellulose

(MC) has excellent film-making properties, high solubility and efficient oxygen and lipid barrier properties (Donhowe & Fennema, 1993a, 1993b; Nisperos-Carriedo, 1994; Park, Weller, Vergano, & Testin, 1993).

Chitin and its deacetylated product, CH, have received much interest for its application in agriculture, biomedicine, biotechnology and the food industry due to their biocompatibility, biodegradability and bioactivity (Kumar, 2000; Muzzarelli, et al., 1988; Tharanathan & Kittur, 2003). Among these potential applications, the use of chitin and CH as food antimicrobials and biopesticides are especially attractive (Wu, Zivanovic, Draughon, Conway, & Sams, 2005). Due to its antifungic, good mechanical and oxygen barrier properties (Caner, Vergano & Wiles, 1998; Chen, Yeh, & Chiang, 1996), CH film is a promising packaging material that can be included in the active film category (Vermeiren, Devlieghere, van Beest, de Kruijff, & Debevere, 1999).

Composite films of CH and MC may result in improved mechanical and physical properties since these two

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polysaccharides have compatible structures. Thus, a deep insight into component interactions would help to understand and control the physical properties of composite films. In a previous work (García, Pinotti, Martino, & Zaritzky, 2004), solutions with different CH–MC ratios were characterized rheologically; films obtained from these solutions were analyzed as well.

The objectives of the present work were: (a) to develop composite biodegradable films based on CH and MC, (b) to characterize film microstructure by SEM, X-ray diffraction and Fourier transform infrared (FTIR), (c) to evaluate mechanical properties of the films and some physical characteristics like equilibrium moisture content, film solubility in water and permeability to water vapor.

2. Materials and methods

2.1. Film preparation

Commercial MC, (A4M, Methocel, Dow, USA) with a substitution degree of 27.5% was purchased from Colorcon (Buenos Aires, Argentina). Commercial CH from crab shells with a minimum deacetylation degree of 85% was purchased from Sigma (St. Louis, USA). Solutions of 1% (w/w) of MC, and 2% (w/w) of chitosan were prepared. CH was solubilized in 1% (v/v) acetic acid solution, followed by a vacuum filtration to eliminate insolubles (No & Meyers, 1989).

Mixture solutions were prepared with the following (w/w) CH: MC proportions: 25:75, 50:50 and 75:25.

To obtain films, 40 g of solutions were poured on rectangular acrylic plates (10 × 20 cm). The solutions were dried at 60 °C in a ventilated oven to constant weight. Films were stored at 20 °C and a relative humidity (RH) of 65% in a controlled temperature and humidity room for measuring barrier and mechanical properties.

2.2. Film Characterization

2.2.1. Equilibrium moisture content

Water content of the 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 moisture content (%) was calculated as follows:

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

2.2.2. Thickness

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. Presented values are an average of at least 15 measurements.

2.2.3. Film solubility in water

From each film pieces of 2 × 3 cm were cut and stored in a desiccator with silica gel 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 at 200 rpm for 1 h at room temperature (25 °C approximately). After soaking, the remaining pieces of film were collected by filtration and dried again in an oven at 60 °C to constant weight (final dry 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.

2.3. Film microstructure

2.3.1. Microscope observations

Scanning electron microscopy (SEM) analysis was performed with a JEOL JSPM 100 electron microscope (Japan). Film pieces were mounted on bronze stubs using a double-sided tape and then coated with a layer of gold (40–50 nm), allowing surface and cross-section visualization. All samples were examined using an accelerating voltage of 5 kV.

2.3.2. X-ray diffraction

Film samples were cut into rectangular pieces (3 × 2 cm), mounted on glass supports and used for analysis. Samples were analyzed between $2\theta = 4^\circ$ to 60° with a step size $2\theta = 0.02^\circ$ in a X-ray diffractometer X'Pert Pro PANalytical Model PW3040/60 (Almelo, The Netherlands) using a Cu K α radiation ($\lambda = 1.543$), 40 kV and 40 mA. The diffractometer was equipped with 1° divergence slit and a 0.3 mm receiving slit.

2.3.3. FTIR analysis

The Fourier transform infrared (ATR-FTIR) spectrometry was used to analyze the functional groups of the films in order to determine the possible interactions between CH and MC in composite systems. Samples were analyzed between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} in a Bruker 66 spectrometer (Germany).

2.4. Water vapor permeability (WVP)

WVP tests were conducted using a modified ASTM (1995) method E96 as described in a previous work (García, et al., 2004) using an especially designed permeation cell that was maintained at 20 °C. After steady-state conditions were reached (about 2 h), eight weight measurements were made over 24 h. A driving force of 1753.55 Pa, expressed as water vapor partial pressure, was used.

2.5. Mechanical properties

Tensile tests were performed in a texturometer TA.X-T2i—Stable Micro Systems (England) as described in a previous work (García, et al., 2004) using a tension grip system A/TG and probes of 6 cm in length and 0.7 cm width.

Puncture tests were performed using a cylindrical probe 2 mm in diameter at a constant rate of 1 mm/s. Tests were carried out with samples of 3 × 3 cm from each film formulation. For both, tensile or puncture tests, each reported value corresponded to at least five determinations.

Curves of force (N) as a function of deformation (mm) were automatically recorded by the Texture Expert Exceed software. Maximum breaking force (N), deformation at break (extension at the moment of rupture, mm), percent of elongation at break (deformation divided by initial sample length and multiplying by 100, %) and elastic modulus (N/mm) were calculated as the slopes of force–deformation curves according to the ASTM D882-91 method (1996). Tensile strength (MPa) was calculated by dividing maximum force by film cross-section (thickness × width).

2.6. Statistical analysis

Systat-software (SYSTAT, Inc., Evanston, IL, USA) 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. Film characterization

Homogeneous, thin, flexible and transparent films were obtained from MC, CH and mixture solutions. Visually, MC films were colorless and CH films had a slightly yellow appearance, increasing yellowness with CH concentration for composite films. Even though, the intensity of the yellowness is negligible when compared to values reported for whey protein based films (Trezza & Krochta, 2000a, 2000b).

All films were easily removed from the cast plate and no pores or cracks were detected as seen by SEM (Fig. 1) even though film formulation did not include a plasticizer. Besides, a compact structure was observed (Fig. 1). Composite films showed multilayer structures (Fig. 1c) this could be possibly attributed to the limited chain mobility even though both CH and MC are compatible polymers.

Thickness of films varied between 14.12 ± 1.59 and $26.07 \pm 3.17 \mu\text{m}$, as shown in Table 1. As expected, CH films, obtained from a 2% solution, were thicker than MC ones, obtained from 1% solution, this was also evidenced by SEM observations (Figs. 1a and b). Composite films

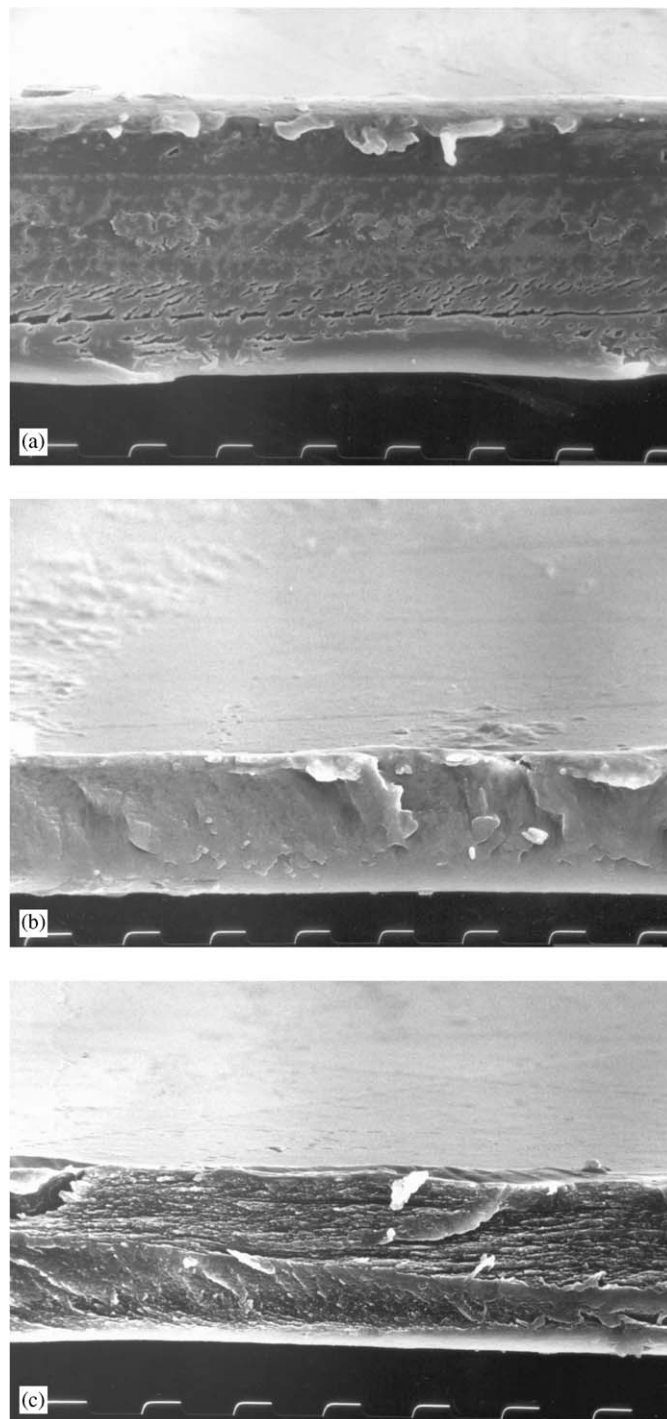


Fig. 1. SEM micrographs of the cross-section of: (a) CH, (b) MC and (c) 50:50 CH:MC films. Magnification: 10 μm between marks.

exhibited intermediate thickness values within the range of those of one component film (Table 1).

All films reached after drying low moisture, MC films exhibited the lowest equilibrium moisture while the highest value was observed for CH ones (Table 1). MC films were completely soluble in water while CH films had lower solubility values. Composite films had intermediate water solubilities, decreasing film solubility with increasing CH

Table 1
Film solubility in water, equilibrium moisture content, thickness and water vapor permeability of CH–MC films

Film composition	Concentration of each component in 100 g of filmogenic suspension (g CH: g MC)	Film solubility in water (%)	Equilibrium moisture content (g water/100 g film)	Film thickness (μm)	Water vapor permeability $\times 10^{11}$ (g/m s Pa)
MC	1:0	98.4 ± 2.2^b	0.91 ± 0.16	16.32 ± 2.46	7.55 ± 0.60
25:75 ^a	0.5:0.75	40.7 ± 6.3	1.12 ± 0.01	21.22 ± 0.68	6.77 ± 0.92
50:50	1:0.5	27.7 ± 1.6	2.41 ± 0.16	23.35 ± 2.72	6.67 ± 0.74
75:25	1.5:0.25	14 ± 2.1	2.22 ± 0.01	22.75 ± 1.69	7.24 ± 0.35
CH	2:0	9.3 ± 0.9	6.33 ± 0.58	26.07 ± 3.17	7.24 ± 0.81

^aCH:MC (w/w) proportion in film formulation.

^bvalue \pm standard deviation.

proportion (Table 1). Thus, by controlling CH concentration in film formulation, solubility can be tailored enhancing the possible applications of these materials.

3.2. Microstructural characterization

For film materials, an insight into film microstructure is critical since it determines their barrier and mechanical properties. Thus, film microstructure was studied by X-ray diffraction and Fourier transforms infra red (FTIR) spectroscopy.

X-ray diffraction patterns of films showed an amorphous–crystalline structure (Fig. 2). The X-ray diffraction patterns of the MC films exhibited a sharp peak in the region of $2\theta = 8^\circ$ (d_{101} spacing, 10.7–11.2 Å) and a broad peak with a maximum at $2\theta = 20.5$ – 21.5° (d_{101} spacing, 4.13–4.33 Å), (Donhowe & Fennema, 1993a and 1993b). Kato, Yokoyama, and Takahashi (1978) stressed that the presence of the sharp d_{101} peak in the diffraction patterns of MC films corresponds to trimethylglucose-type crystalline order in these films. Chitosan films exhibited a typical X-ray diffractogram associated to a more amorphous material (Fig. 2a). The X-ray diffractograms of composite MC–CH films are similar to those obtained with MC ones, although intensity of diffraction peak at $2\theta = 8^\circ$ decreased with increasing CH proportion as observed in Fig. 2b. The decrease of peak intensity at $2\theta = 8^\circ$ with increasing CH concentration indicates that CH interferes with MC ordering. Similar results were reported by Chen et al. (2003) who attribute the crystallinity decrease of composite CH–gelatin films mainly to the broken hydrogen bonding in the CH molecules and the resulting amorphous structure of the polyelectrolyte complex.

Fig. 3a shows the IR spectra of MC, CH and the blend 50:50 CH–MC films. The position of the peaks of CH film spectrum is similar to those described by different authors (Chen et al., 2003, Sionkowska, Wisniewski, Skopinska, Kennedy, & Wess, 2004; Wu et al., 2005). The IR spectra of chitosan films had characteristic bands at 3400 – 3480 cm^{-1} that responded to OH-3 and CH_2OH intra and intermolecular hydrogen bonds, 1650 cm^{-1} for

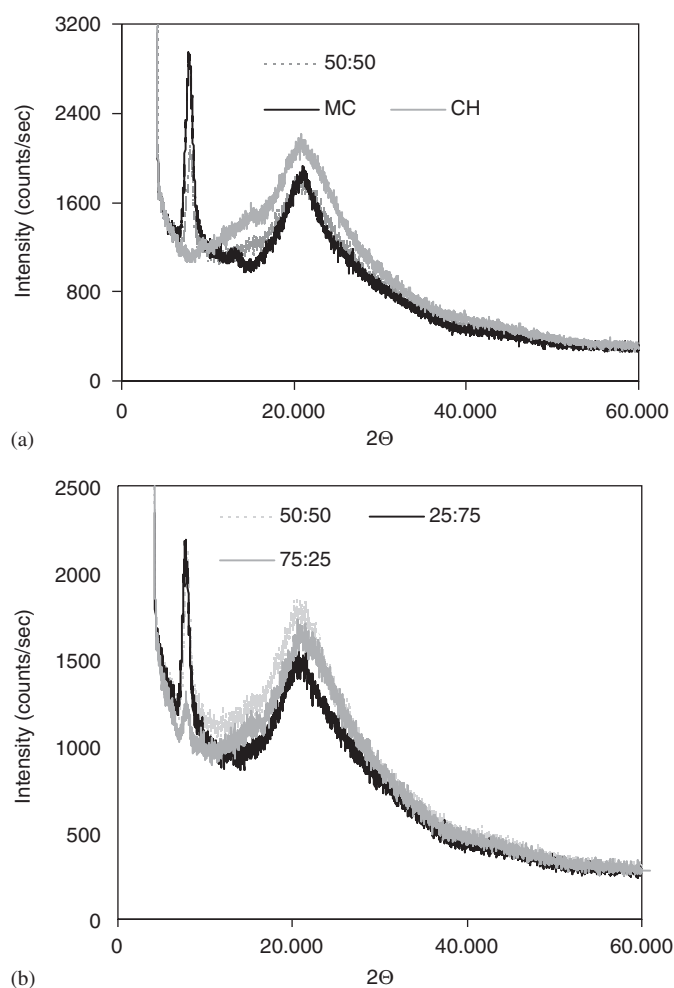


Fig. 2. Microstructural characterization by X-ray diffraction of: (a) MC, CH and 50:50 films and (b) composite films with different CH:MC ratios.

amide and 1557 cm^{-1} for amide II vibrational mode (Wu et al., 2005). The amino group has a characteristic absorption band in the region of 3400 – 3500 cm^{-1} , which is masked by the broad absorption band of the $-\text{OH}$ group (Sionkowska et al., 2004). Besides, peaks around 901 and 1155 cm^{-1} , and peak at 1591 cm^{-1} were observed (Fig. 3a); these peaks

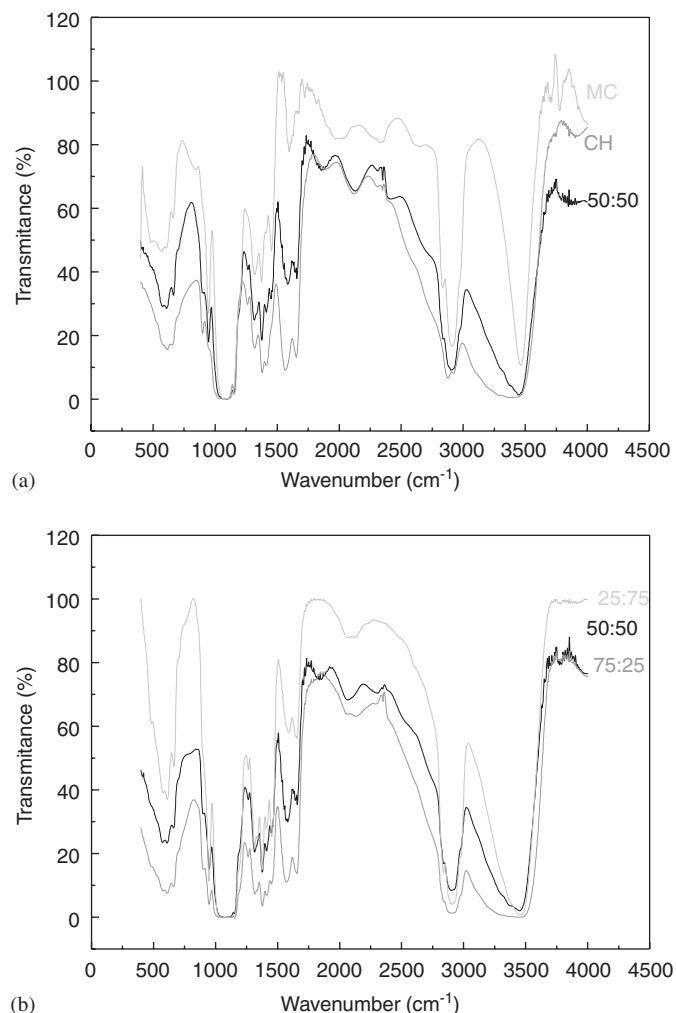


Fig. 3. Microstructural characterization by FTIR of: (a) MC, CH and 50:50 films and (b) composite films with different CH:MC ratios.

were assigned by Chen et al. (2003) to saccharide structure and amino groups, respectively.

According to Zaccaron, Oliveira, Guiotoku, Pires, and Soldi (2005) FTIR spectra of MC films had absorption bands at 3457 cm^{-1} (O–H stretching), 2904 cm^{-1} (C–H stretching), 1643 cm^{-1} (C–O) and 1066 cm^{-1} (C–O–C). Equivalent peak positions were observed in the spectrum of MC films of the present work.

Spectra of composite films showed characteristic peaks of both polymers and small modifications of the position of some bands within the range $1500\text{--}1700\text{ cm}^{-1}$ that are related to amino and carbonyl groups. Fig. 3b shows the effect of CH concentration in the blends; with increasing CH concentration spectra of composite films approaches to that of CH film. Besides, composite films showed between 2985 and 3600 cm^{-1} a broad band similar to CH that corresponds to N–H and –OH superposition according to Sionkowska et al. (2004) while MC only showed the characteristic –OH stretching at 3457 cm^{-1} (Zaccaron et al., 2005).

According to Wanchoo and Sharma (2003), hydrogen bonding or other interactions between chemical groups on dissimilar polymers should theoretically cause a shift in peak position of the participating groups. In the present work, this kind of behavior is observed for the OH stretching since this peak shifted from 3463 cm^{-1} for MC films towards 3450 cm^{-1} for CH–MC mixtures, as CH proportion increased. This could indicate that OH group movement is compromised in a different way when another polymer is present. A shift was also observed in amino group (–NH₂) of CH at 1560 cm^{-1} , when the amount of MC decreased in composite films. However, other characteristic peaks such as 1411 cm^{-1} (OH vibrations) and 2904 cm^{-1} (C–H stretching) assigned by Pawlak and Mucha (2003) and Zaccaron et al. (2005) did not show a significant shift. These results indicate that a low interaction is taking place and may be attributed to the similar chemical and geometrical linear structure of both MC and CH polymers. However, further studies should be carried out to establish the nature of this interaction.

3.3. Water vapor permeability

Table 1 shows WVP values of individual and composite films. CH and MC films showed lower WVP values, than those of some protein films and even lower than other polysaccharide based films reported in literature (García, Martino & Zaritzky, 2000; Krochta & De Mulder Johnston, 1997; Mali, Grossmann, García, Martino, & Zaritzky, 2002). Our obtained results are in agreement with those of Park et al. (1993), Wong, Gastineau, Gregorski, Tillin, and Pavlath, (1992) and Caner et al. (1998).

Permeability of composite films did not differ significantly ($p = 0.125$) from the values of one component film (Table 1). Since permeability is the contribution of diffusivity and solubility of the permeant through the solid matrix the obtained results for composite films indicate that the developed matrix should be similar to those of the individual component matrixes as seen by FTIR and X-ray diffraction analysis.

In comparison to commercial polymers, CH films appears to be good barriers to oxygen permeation, while exhibiting relatively low water vapor permeabilities. 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 both polymers. According to Shellhammer and Krochta (1997) cellophane exhibited a WVP value of $8.4 \times 10^{-11}\text{ g/m s Pa}$. Although, WVP values of our composite CH–MC films are higher than other synthetic films like low-density polyethylene (LDPE), with a WVP value of $9.14 \times 10^{-13}\text{ g/m s Pa}$ (Smith, 1986).

3.4. Mechanical properties

MC and CH films showed different behavior patterns under tensile tests; both films showed high resistance but

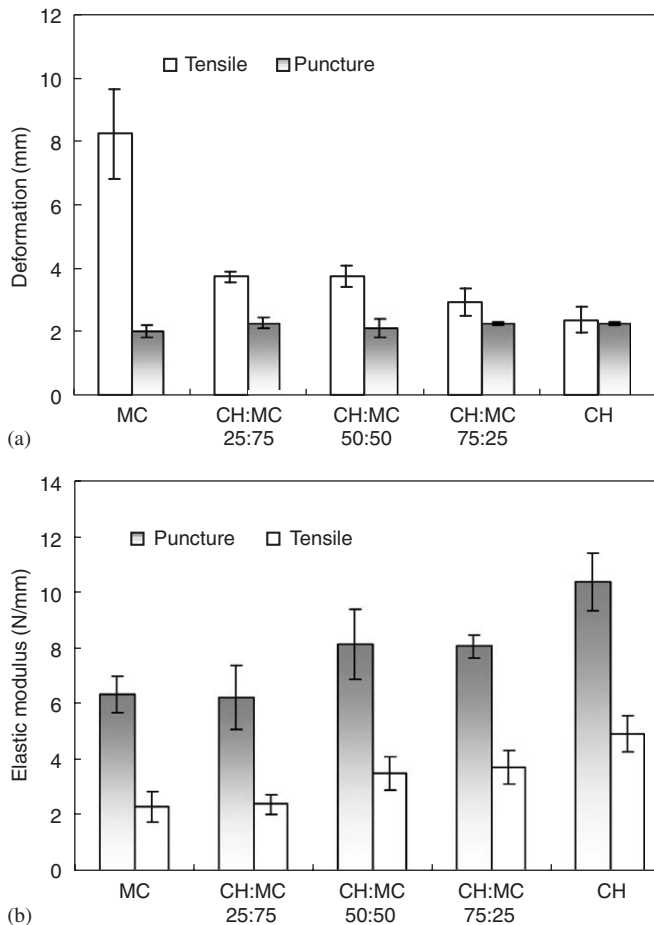


Fig. 4. Mechanical properties of MC, CH and composite films with different CH:MC ratios. Tensile and puncture tests: (a) deformation at break and (b) elastic modulus.

MC films were more flexible (Fig. 4). Percent elongation values of films were 12.7% for MC, and 3.9% for CH and intermediate values were obtained with composite films (Fig. 4a). Similar mechanical properties were found in literature for MC films (Debeaufort & Voilley, 1997; Donhowe & Fennema, 1993a and 1993b; Park et al., 1993). For CH films, data reported in literature for tensile test were higher than those obtained in the present work (Fig. 5), differences may be due to CH composition and suppliers, plasticizer presence and film preparation (Butler, Vergano, Testin, Bunn, & Wiles, 1996; Caner et al., 1998; Chen & Lin, 1994;). The main differences may be attributed to plasticizer type and content; Caner et al. (1998) reported a wide range of elongation (14–70%) depending on storage time, plasticizer and type of acid used in CH solubilization.

In composite films, tensile strength and elastic modulus increased with CH concentration, leading to stronger films, (Figs. 4b and 5). Accordingly, a decreasing deformation trend was observed with CH concentration, indicating a reduction in film flexibility (Fig. 4a).

Mechanical properties of CH–MC films were comparable to many medium strength commercial polymer films

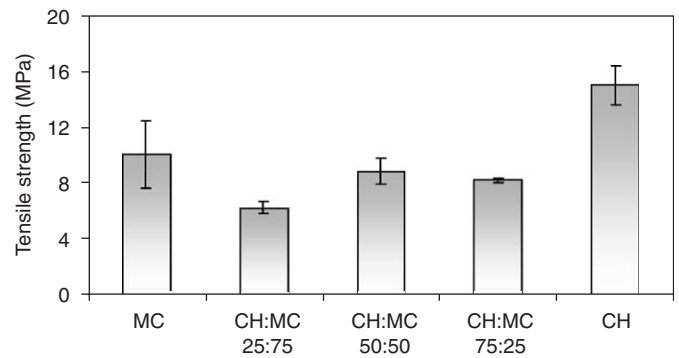


Fig. 5. Tensile strength of MC, CH and composite films with a different CH:MC ratios.

like cellophane. However, synthetic polymers like LDPE and HDPE exhibit similar tensile strength to those obtained in the present work but higher elongation (Cunningham, Ogale, Dawson, & Acton, 2000).

With regard to puncture tests, elastic modulus showed the same trend as in tensile tests (Fig. 4b). However, all films have a similar value of deformation at break, about 2 mm, regardless CH:MC ratio (Fig. 4a). Thus, CH may replace MC maintaining puncture resistance of films with economical benefits.

4. Conclusions

Physical properties of composite films showed intermediate (solubility and mechanical properties) values compared to those of individual component films or did not differ significantly (WVP) reinforcing the idea of compatibility of CH and MC polymer.

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. CH imparts rigid characteristics to composite films (high elastic modulus and small elongation) while MC contributes with a higher elongation and lower elastic modulus, increasing solubility as well. Thus, MC–CH edible films can lead to many possible applications in food, pharmaceutical and cosmetic industry considering the natural origin of both polymers.

Acknowledgments

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