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Effects of murta (*Ugni molinae* Turcz) extract on gas and water vapor permeability of carboxymethylcellulose-based edible films

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Abstract

The effect of murta (*Ugni molinae* Turcz) leaves extract on water vapor permeability (WVP) and gas permeability (GP) of carboxymethylcellulose (CMC)-based films was studied. Two ecotypes of murta leaves "Soloyo Grande" (SG) and "Soloyo Chico" (SC), were analyzed for their composition (HPLC-MS) and SC extract revealed a higher concentration of flavonols than the SG extract. The film forming solution was prepared with 2 g of CMC, 0.4 ml of glycerol and 0.5 ml of sunflower oil in 100 ml of water (Control), 50 ml of water and 50 ml of each exctract (SC50 or SG50) and 100 ml of each extract (SC 100 or SG 100). The addition of murta leaves extract modified the WVP and GP of the films. The WVP decreased significantly ($P \leqslant 0.05$) with the incorporation of SG extract in the film but not with the SC extract ($P > 0.05$). The CO_2 and O_2 permeability of the films were influenced by the kind and concentration of murta leaves extract used. The CO_2 permeability, with SG extract was higher than without extract ($P \leqslant 0.05$) and with SC extract was not modified. The O_2 permeability with murta leaves extract were lower than without extract. Therefore, it is possible to consider that films with SC acts only as barrier to the oxygen, but with SG the water vapor and gas barrier properties were modified, being more permeable to the CO_2 and acting as barrier to O_2 and water vapor.

Keywords: Carboxymethylcellulose; Murta leaves extracts; Edible films; Water vapor permeability; Gas permeability

1. Introduction

There has been a considerable interest in edible film research in recent years, because of the potential applications of films as effective moisture and gas barriers in foods (Guilbert, Cuq, & Gontard, 1997; Turhan & Şahbaz, 2004). Edible coatings have long been known to protect perishable food product from deterioration by retarding dehydration, suppressing respiration, improving textural quality, helping retain volatile flavor compounds and reducing microbial growth (Han, Zhao, Leonard, & Traber, 2004; Mauer, Smith, & Labuza, 2000; Peressini, Bravin, Lapasin, Rizzotti, & Sensidoni, 2003; Yang & Paulson, 2000). Also it can be used as a vehicle for incorporating functional ingredients, such as antioxidants, flavor, colors, antimicrobial agents and nutraceuticals (Guilbert et al., 1997; Kester & Fennema, 1986).

The main biopolymers used in the edible film preparaton are polysaccharides and proteins (Gontard, Guilbert, & Cuq, 1992; Mali, Grossmann, García, Martino, & Zaritzky, 2006; Peressini et al., 2003; Sobral, Menegalli, Hubinger, & Roques, 2001). Some additives, such as plasticizer and emulsifiers, may also be used (Cuq, Gontard, Cuq, & Guilbert, 1997; Peressini et al., 2003; Shaw, Monahan, O'Riordan, & O'Sullivan, 2002). Protein and polysaccharides are good film-forming materials that are used for their mechanical and structural properties, but they provide only poor moisture barrier. This poor barrier is the result of their hydrophilic character (Anker, Berntsen, Hermansson, & Stading, 2002; Petersson & Stading, 2005). Cellulose is the most abundant organic

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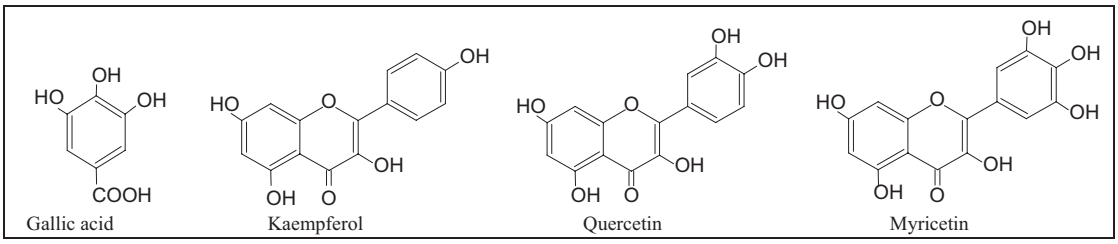

Fig. 1. Chemical structure of gallic acid, and of the flavonols kaempferol, quercetin, myricetin.

renewable resource in the plant kingdom, and the cellulose derivatives have excellent film-making properties (Park, Weller, Vergano, & Testin, 1993). Carboxymethylcellulose (CMC) is an anionic linear polysaccharide derived from cellulose. The solubility of CMC increases with the degree of substitution (Girard, Turgeon, & Paquin, 2002). As an amylose with many hydroxyl and carboxylic groups, it can absorb water and moisture, and the resulting hydrogel has many excellent properties, such as high water content, good biodegradation, and a wide range of applications due to its low cost (Nie, Liu, Zhan, & Guo, 2004). The various properties of CMC depend upon three factors: molecular weight of the polymers, average number of carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituents along the polymer chains (Biswal & Singh, 2004).

The addition of a plasticizing agent to edible films is required to overcome film brittleness caused by extensive intermolecular forces. Plasticizers such as glycerol, reduce these forces and increase the mobility of polymer chains, thereby improving flexibility and extensibility, affecting gas, water vapor and solute permeability of the films (Aydinli & Tutas, 2000; Debeaufort & Voilley, 1997; García, Martino, & Zaritzky, 2000; Gontard, Guilbert, & Cuq, 1993; Kim, Ko, & Park, 2002; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2004).

Ferulic acid, a phenolic acid derivative existing ubiquitously in the plant kingdom, was used to prepare satisfactory gels from arabinoxylans and pectin (Oosterveld, Beldman, & Voragen, 2000) and soy protein isolate (Ou, Wang, Tang, Huang, & Jackson, 2005). This suggests that componds like ferulic acid or polyphenols could act as cross-linking agent in preparation of CMC-based edible films. Traditionally, the hot water extract of leaves of the native plant of the South of Chile, known as murta or murtilla (*Ugni molinae* Turcz), are highly valued as a folk medicine by the chilean indigenous ethnia mapuche for its physiological benefits, mainly as kidney-protective effect (Montenegro, 2002); besides, the red fruits of this plant are eaten fresh or processed, because of its pleasant flavor. Therefore, the germoplasm of this plant has been collected and characterized (Seguel, Peñalosa, Gaete, Montenegro, & Torres, 2000) and the methanolic, ethanolic and water extracts of the leaves were found high in polyphenols content and antioxidant abilities measured through DPPH and TBARS (Rubilar et al., 2006). Rubilar et al. (2006) found also that HPLC-MS analysis revealed that epicatechin and kaempferol were the single polyphenols participating in the antioxidant capacity of the alcoholic extract, whereas gallic acid was only present in water extract. The structure of these polyphenols are shown in Fig. 1. Myricetin and quercetin glycosides were detected in both aqueous and alcoholic extracts, but the derivatives of the gallic acid could not be individualized from the HPLC-MS analysis realized.

In this study, the aqueous extracts of two murta ecoptypes, the "Soloyo Chico" (SC) and "Soloyo Grande" (SG) ecotypes, grown in Pumalal near Temuco, were analyzed for their polyphenols content through HPLC-MS, and because of the differences observed, the effect of the addition of either one or the other of these two extracts, in different amounts, to the CMC-based film-forming solution was determined on the water vapor, O_2 and CO_2 permeability of the films formed.

2. Materials and methods

2.1. Materials

Fresh leaves of murta (*Ugni molinae* Turcz) of two ecotypes of Pumalal, SG and SC, were sampled near Temuco (38°35′39″ South latitude) at the Instituto de Investigación Agropecuaria INIA Carillanca. Sodium carboxymethylcellulose, molecular weight (MW) 280–400 kDa, degree of substitution (DS) 07–09, was purchased from Prinal, glycerol at 87% from Merck and sunflower oil from a grossery store.

2.2. Obtaining murta leaves extract

Leaves samples were air-dried for 18 h to about 12% moisture content in a convection oven/shaking incubator (GFL-3032, Germany), at 35 °C. Dried leaves were milled and sieved. Particles ranging from 1.00 to 2.38 mm were selected, placed in sealed polyethylene bags and stored, protected from the light, until extraction. Dried and milled murta leaves (1.5 g) were extracted at 25 °C for 10 min with 20 ml of distilled water in an Erlenmeyer flask placed in the shaking incubator at 170 oscillation min^{-1}. Then the mixture was filtered on Whatman No. 3 filter paper to obtain the water extract.

2.3. HPLC-MS analysis of extracts

As described before (Rubilar et al., 2006), filtered crude extract (20 μl) were directly injected into the HPLC system. The reverse-phase HPLC apparatus with a pump PU-980 connected to a quaternary gradient unit LG-1580-04, a JASCO UV-1575 UV–vis detector, and a Rheodyne model 7725 loading sample injector with a 20 μl sample loop were used to determine the phenolic composition of the different fractions. The column ($250 \times 4.6\,mm^2$) was a C_{18} Hypersil ODS (5 μm particle size) (Supelco). The two solvents used to make the gradient were (A) 0.5 g/100 g acetic acid Milli-Q water solution and (B) methanol. The solvent gradient in volumetric ratios of solvent A and B was as follows: 0–10 min, 95A/5B; 10–60 min, 50A/50B; 60–80 min, 30A/70B; and 80–90 min 95A/5B. Detection was carried out using 280 nm as a preferred wavelength. The flow rate was set to 0.7 ml/min. Three determinations were made on each extract obtained. The equipment used for electrospray mass spectrometry in positive ion mode was a HP-Serie 1100-MSD, working with nitrogen as the drying gas at 13 l/min and 350 °C, nebulizer pressure at 40 psig, and fragmentor voltage at 60 V. Murta extracts, dissolved in water, were filtered through a 0.45 μm nylon filter, and then injected at 10 μl volume.

2.4. Film solution preparation

The leaves extracts of each murta ecotype were used for the preparation of the filmogenic solutions: without dilution (SC 100 and SG 100), mixing 50% extract with 50% water (SC 50 and SG 50), only distilled water (control). In 100 ml of each of these solutions, 2 g of CMC were completely dispersed in the shaking incubator at 170 oscillation min^{-1}, 25 °C, for 24 h. Glycerol (0.4 ml) and sunflower oil (0.5 ml) as plasticizers were added to the CMC film solution, and mixed at 45 °C. Then film solution was sonicated with a CO_2 electrode (Ultrasonic processor, XL 2020) with a pulse-wave on–off of 30 s during 4 h to eliminate the air bubbles incorporated during the agitation, to avoid errors in the permeability measuring. The composition of each sample is shown on Table 1.

Then, for the edible films preparation, according to the casting technique, 20 ml of the CMC-based film solutions was poured and spread onto an acrylic plate level fitted with rims around the edges to give a 18×9 cm film-forming area. The solution was allowed to dry at room temperature (25 °C) for about 24 h. Films that formed were peeled off and kept in polyethylene bags.

2.5. Film analysis

2.5.1. Thickness measurements

Film thickness was measured at eight random positions with a micrometer of sensitivity of 0.001 mm (Mitutoyo, Japan). The thickness of the films produced ranged from 0.016 to 0.046 mm.

2.5.2. Water vapor permeability measurements

The cup method with some modifications was used to determine water vapor permeability (WVP) (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002). The film samples were mounted over an acrylic cup sealed with O-rings, with a circular opening of 0.00151 m^2. Gel silicate (0% RH) was placed inside the cups and a sodium chloride saturated solution (75% RH) was used in the desiccator maintained at 25 °C. The RH inside the cell was always lower than outside. The water vapor transport was determined from the weight gain of the cup. After steady-state conditions were reached (about 2 h), the change in the weight of the cup was recorded to the nearest 0.0001 g and plotted as a function of time. The WVP of films was calculated and expressed in ($g\,m^{-1}\,s^{-1}\,Pa^{-1}$). All tests were conducted in duplicate, from films formed with extracts from different leaves.

2.5.3. Gas permeability (GP) measurements

Carbon dioxide (CO_2) and oxygen (O_2) permeabilities of the films were assessed by the accumulation method, in a specially designed stainless-steel cell formed by two chambers of 29.45 cm^3 volume separated by the test film with a trasmission area of 0.00049 m^2 (García et al., 2000). The GP determinations were done by placing the test-film between these chambers after closing the cell tightly. The total pressure difference across the film was zero and the partial pressure difference for the gas was approximately 1 atm.

The quasi-isostatic method used was based on the measurement of the amount of gas diffusing through the film. To measure this concentration, 1000 μl gas sample was withdrawn with a syringe from the test chamber, initially filled with air. Gas concentration was measured in a Shimadzu (Kyoto-Japan) gas chromatograph with an Alltech CTR1 column (Alltech Associates, Deerfield-USA) of 180 cm, thermal conductivity detector (TCD) with

Table 1
Composition of forming solution of carboxymethylcellulose-based edible film with murta extracts

Sample	CMC (g)	Glycerol (ml)	Sunflower oil (ml)	Water (ml)	SC extract (ml)	SG extract (ml)
SC50	2.000	0.40	0.50	0	100.00	0
SC100	2.000	0.40	0.50	50.00	50.00	0
SG50	2.000	0.40	0.50	0	0	100.00
SG100	2.000	0.40	0.50	50.00	0	50.00
Control	2.000	0.40	0.50	100.00	0	0

temperature of detector at 120 °C, temperature of column at 30 °C, temperature of injector at 120 °C, carrier gas He. GP of films, expressed in $cm^3\,gas\,m^{-1}\,s^{-1}\,Pa^{-1}$, was calculated at 20 °C and 100% RH. The gas was stabilized by passing through distilled water (García et al., 2000). All tests were conducted in duplicate, from films formed with extracts from different leaves.

2.5.4. Statistical analysis

Duncan's multiple range test was applied to compare the means for water vapor and GP of the films, with a level of significance of 5%.

3. Results and discussion

3.1. Characterization and identification of murta phenolics

The chemical structure of the main polyphenols that appeared on different amounts in both murta ecotypes through the HPLC-MS analysis is shown in Fig. 1. The chromatograms obtained in the reverse phase HPLC-MS analysis for the aqueous murta leaves extracts of the Pumalal ecotypes SG and SC are shown in Fig. 2. It can be appreciated the typical elution pattern of reverse phase chromatography described by Robards, Prenzler, Tucker, Swatsitang, and Glover (1999) and Rubilar et al. (2006) for SC murta leaves extract, where polar compounds like phenolic acids elute first (gallic acid derivatives at retention time 11.7 min) followed by those of decreasing polarity: phenolic acids < cinnamic acids < flavonoids. At retention times between 46 and 62 min, Rubilar et al. (2006) found 6 peaks at decreasing polarity: myricetin xyloside, myricetin dirhamnoside, myricetin glucoside, myricetin rhamnoside, quercetin glucoside, quercetin xyloside.

At Fig. 2, the chromatograms showed 3 peaks which are large for the SC and small for the SG extracts, which corresponds to the retention times of 48.052, 49.655, 57.753 min for SC (Fig. 2, bottom) and of 48.505, 50.115, 58.123 min for SG (Fig. 2, up). This main difference in flavonoids between the SC and the SG extracts at these three peaks, identified as flavonol compounds (Fig 1), are attributed to myricetin dirhamnoside, myricetin glucoside or galactoside, and quercetin dirhamnoside (Table 2). There can be seen in Fig. 3 the masses spectrum for the peaks of retention times 50.115 min of the SG extract (Fig. 2 up) and of 49.655 min of the SC extract (Fig. 2 down), which corroborates the presence of the compounds before mentioned.

3.2. Water vapor permeability

The effect of both murta ecotype extracts in CMC-based edible films on WVP are shown in Table 3. It can be seen that the incorporation of the leaves extracts affected significantly ($P \leqslant 0.05$) the WVP. The results showed that the WVP of the films without extract was $7.144 \times 10^{-11}\,g\,m^{-1}\,s^{-1}\,Pa^{-1}$ and, with SG extract, the values decreased significantly ($P \leqslant 0.05$) as the concentration of the extract increased, reaching a WVP of $5.655 \times 10^{-11}\,g\,m^{-1}\,s^{-1}\,Pa^{-1}$ for 97.18 g/100 g of extract, but the WVP values for the film with SC extract were not significantly different ($P > 0.05$). The films containing the same concentration of SG or SC extracts also showed significant difference

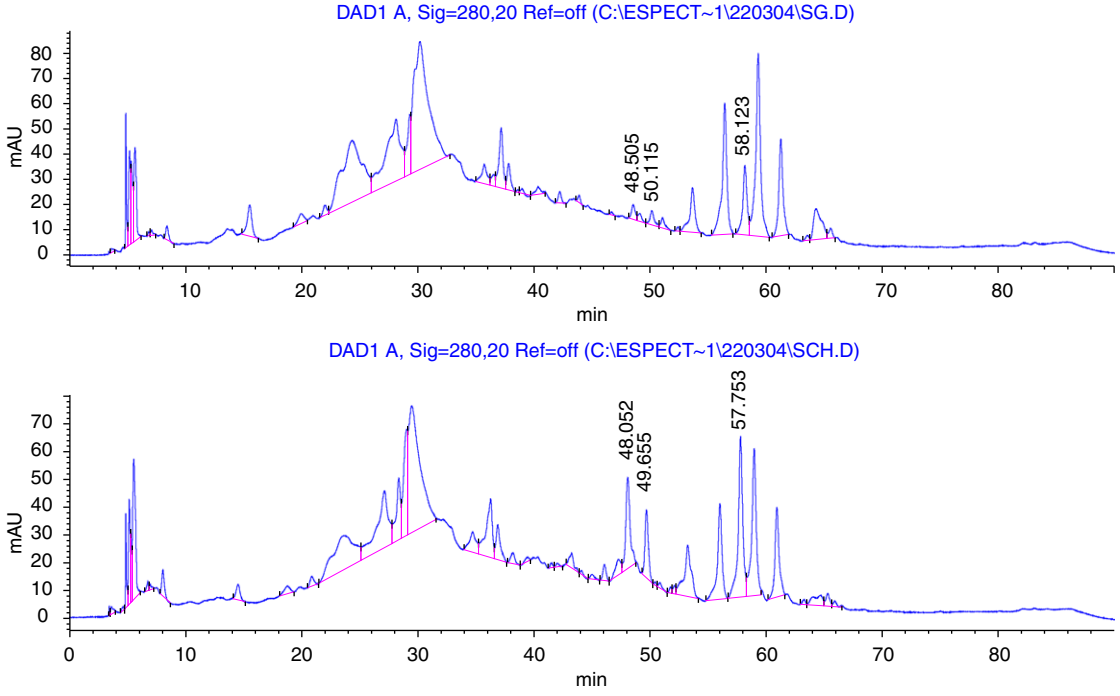

Fig. 2. Chromatograms corresponding to murta leaves aqueous extracts of the ecotypes Soloyo Grande (top) and Soloyo Chico (bottom).

Table 2
Identification of phenolic species contained in the aqueous extracts of murta leaves

Ecotype	Retention time peak (min)	$\lambda_{máx}$ (nm)	(m/z)	Positive ion (m/z)	Identification
SG	48.505	276	335, 318	(318 + 146 + 146 + 23) 633	Myricetin dirhamnoside
SG	50.115	272	318	(318 + 162 + 23) 503	Myricetin glycoside or galactoside
SG	58.123	264, 356	302	(302 + 146 + 146 + 23) 617	Quercetin dirhamnoside
SC	48.052	274	335, 318	(318 + 146 + 146 + 23) 633	Myricetin dirhamnoside
SC	49.655	276	318	(318 + 162 + 23) 503 (318 + 162 + 1) 481	Myricetin glycoside or galactoside
SC	57.753	262, 358	302	(302 + 146 + 146 + 23) 617	Quercetin dirhamnoside glycoside or xyloside

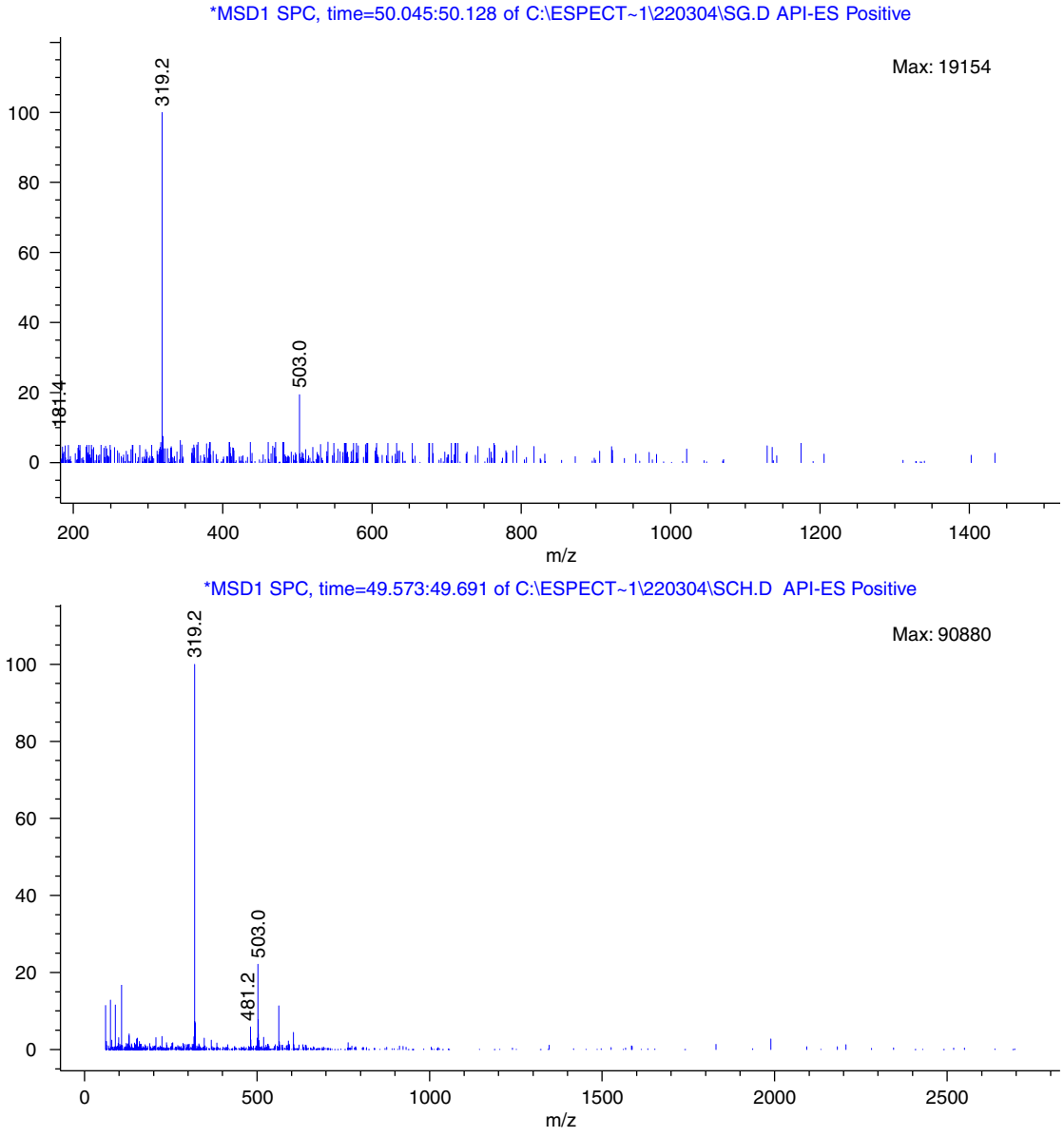

Fig. 3. Mass spectrum for Soloyo Grande (SG) extract on peak of retention time 50.115 min (top) and Soloyo Chico (SC) extract on peak of retention time 49.655 min (bottom).

($P \leqslant 0.05$) in WVP. These results could be related to the structural modification of the CMC network produced by the extract. Generally, water vapor transmission through a hydrophilic film depends on both diffusivity and solubility of water molecules in the film matrix (Yang & Paulson, 2000).

Table 3
Water vapor permeability of carboxymethylcellulose film with murta leaves extracts in different concentrations, and other literature cited films

Water vapor permeability $\times 10^{11}$ ($g\,m^{-1}\,s^{-1}\,Pa^{-1}$)[a]		
Extract concentration (g/100 g)	Soloyo Grande	Soloyo Chico
This work[a,b]		
0	7.144 ± 0.130[b] Aa	7.144 ± 0.130 Aa
48.57	6.738 ± 0.032 Bb	7.200 ± 0.038 Aa
97.18	5.655 ± 0.049 Cc	7.188 ± 0.064 Aa
Literature references		
Yam starch	$0.99–1.88 \times 10^{-10}$	Mali et al. (2002)
Whey protein isolate	38.3×10^{-10}	Anker et al. (2002)
Corn	3.68×10^{-10}	García et al. (2000)
Corn + glycerol	2.57×10^{-10}	García et al. (2000)
Amylomaize	2.62×10^{-10}	García et al. (2000)
Amylomaize + glycerol	2.14×10^{-10}	García et al. (2000)
Methylcellulose	$8.4–12.1 \times 10^{-10}$	Park et al. (1993)
Methylcellulose	$0.49–0.60 \times 10^{-10}$	Turhan and Şahbaz (2004)
Methylcellulose + polyethylen glycol	0.747×10^{-10}	Turhan and Şahbaz (2004)
Hydroxypropyl cellulose	$5.2–6.6 \times 10^{-10}$	Park et al. (1993)
Potato starch	$1.36–2.17 \times 10^{-10}$	Petersson and Stading (2005)
Bovine gelatine	$4.7–10.6 \times 10^{-10}$	Sobral et al. (2001)
Pig skin gelatine	$5.0–8.9 \times 10^{-10}$	Sobral et al. (2001)
Gellan	1.58×10^{-10}	Yang and Paulson (2000)
β casein	$1.82–4.79 \times 10^{-10}$	Mauer et al. (2000)

[a]Means in same row with different capital letters are significantly different ($P \leqslant 0.05$); means in same column with different small letters are significantly different ($P \leqslant 0.05$).
[b]Means value ± standard deviations of two replicates.

The WVP of CMC-based films with murta leaves extract, were lower than other edible films, as can be seen in the literature values cited in Table 3, such as yam starch films (Mali, et al., 2002), corn starch films with glycerol (García et al., 2000), but comparable with methyl cellulose films ($0.232–1.160 \times 10^{-10}\,g\,m^{-1}\,s^{-1}\,Pa^{-1}$) (Kester & Fennema, 1989; Turhan & Şahbaz, 2004) and higher than konjac glucomannan with CMC-based films ($1.92 \times 10^{-11}\,g\,m^{-1}\,s^{-1}\,Pa^{-1}$) (Cheng, Abd Karim, Norziah, & Seow, 2002). WVP of a film is believed to be dependent upon the number of "available" polar (–OH) groups that the polymers hold (Cheng et al., 2002). As can be seen in Fig. 2, Fig. 3 and Table 2, the SC extract has more myricetin derivatives than the SG extract; this means more –OH groups, which could explain the better permeability to water vapor of the films made with the 'more polar' SC extract, reaching the same values as the films made with pure water instead of the extract. Films with SG extracts, with less flavonols present, and therefore less –OH groups, reduces significantly the WVP. The lower WVP in the films of this work compared to the literature and shown in Table 3, could be on account of the low amount of glycerol added to the film forming solution. An increase in the interchains spacing due to inclusion of glycerol molecules between the polymer chains should promote water vapor diffusivity through the film and hence accelerate the water vapor transmission (Gontard et al., 1993; Mali et al., 2004). The values of WVP obtained in the present work may also be attributed to the low values of thickness s of the films: the thinness obtained in the present work, ranging between 0.016 and 0.046 mm, compared to values of the literature, ranging between 0.104 and 0.115 mm for corn and 0.128 and 0.137 mm for amylomaize (García et al., 2000), or 0.140 mm for whey protein isolate-based films (Anker et al., 2002).

3.3. Gas permeability

The ability of films to modify gas transport is important for tailoring such films to specific applications such as fresh fruit and vegetables, which are characterized by active metabolism even during refrigerated storage (Guilbert, Gontard, & Gorris, 1996).

According to Tables 4 and 5, CO_2 and O_2 permeabilities were influenced by the kind (SG or SC) and the concentration of the extracts. The CO_2 permeability of films with SG extract was significantly ($P \leqslant 0.05$) higher than without extract. As can be seen in Table 4, for the films with 48.57/100 g and 97.18/100 g of extract, SG permeabilities were 7.485×10^{-10} and $6.850 \times 10^{-10}\,cm^3\,m^{-1}\,s^{-1}\,Pa^{-1}$, respectively, and for the films without extract the permeability was $4.092 \times 10^{-10}\,cm^3\,m^{-1}\,s^{-1}\,Pa^{-1}$. Table 4 showed also that the SC extract did not modify CO_2 permeability.

Table 5 shows that O_2 permeabilities of films with murta leaves extract (SG or SC) were lower than those without extract. The O_2 permeability of the films containing 48.57/100 g and 97.18/100 g of SG extract were 3.260×10^{-10} and $4.382 \times 10^{-10}\,cm^3\,m^{-1}\,s^{-1}\,Pa^{-1}$, respectively; the O_2

permeabilities of the films containing 48.57/100 g and 97.18/100 g of SC extract were 2.344×10^{-10} and 5.941×10^{-10} $cm^3\,m^{-1}\,s^{-1}\,Pa^{-1}$. As can be seen in the literature values cited in Table 5, this is comparable with corn starch-based films (García et al., 2000), amylomaize-based films (Mali et al., 2002), but is higher than amaranth flour-based films (Tapia-Blácido, Sobral, & Menegalli, 2005) and hydroxypropyl starch/gelatin (Arvanitoyannis, Nakayama, & Aiba, 1998).

These results showed that O_2 permeability were lower ($P \leqslant 0.05$) than CO_2 permeability in films with SG extract, indicating a selective action of these films on GPs. This selective action can be attributed to a better solubility of CO_2 in the films with extract, comparable to the results of García et al. (2000). The SC extract with more flavonols than SG extract, mainly myricetin, with one more –OH groups at the B-ring than quercetin, could favor the GP. Othersides, through the heat treatment, although mild, for the extraction of components, some of the B ring of the flavonols myricetin and quercetin could be hydrolyzed, and this smaller molecules, together with gallic acid, could act filling part of the pores of the CMC-based films, reducing their sizes, avoiding some of the free passage of gases.

As Cuq, Gontard, and Guilbert (1998) already saved some time ago, the development of edible films and coatings with selective GP could be very promising for controlling respiratory gas exchange and improving the conservation of fresh or minimally processed vegetables. Our films presented here are shown to work in this direction.

4. Conclusions

The water extract of SC murta leaves showed a higher concentration of some polyphenolic species, like myricetin and quercetin glycosides, than the SG extract (HPLC-MS analysis). The present study showed that incorporation of these two murta leaves extracts in CMC-based films

Table 4
CO_2 permeability of carboxymethylcellulose film with murta leaves extracts in different concentrations, and other literature cited films

CO_2 permeability ($cm^3\,m^{-1}\,s^{-1}\,Pa^{-1}$)		
Extract concentration (g/100 g)	Soloyo Grande	Soloyo Chico
This work[a,b]		
0	$(4.092 \pm 0.095) \times 10^{-10}$ Aa	$(4.092 \pm 0.095) \times 10^{-10}$ Aa
48.57	$(7.485 \pm 0.002) \times 10^{-10}$ Bb	$(3.914 \pm 0.486) \times 10^{-10}$ Aa
97.18	$(6.850 \pm 0.007) \times 10^{-10}$ Cc	$(3.551 \pm 0.093) \times 10^{-10}$ Aa
Literature references		
Corn starch	29.21×10^{-10}	García et al. (2000)
Corn starch + glycerol	5.69×10^{-10}	García et al. (2000)
Amylomaize	28.05×10^{-10}	García et al. (2000)
Amylomaize + glycerol	3.85×10^{-10}	García et al. (2000)

[a]Means value ± standard deviations of two replicates.
[b]Means in same row with different capital letters are significantly different ($P \leqslant 0.05$); means in same column with different small letters are significantly different ($P \leqslant 0.05$).

Table 5
Comparison of O_2 permeability of carboxymethylcellulose film with murta leaves extracts in different concentrations, and other literature cited films

O_2 permeability ($cm^3\,m^{-1}\,s^{-1}\,Pa^{-1}$)		
Extract concentration (g/100 g)	Soloyo Grande	Soloyo Chico
This work[a,b]		
0	$(8.096 \pm 0.077) \times 10^{-10}$ Aa	$(8.096 \pm 0.077) \times 10^{-10}$ Aa
48.57	$(3.260 \pm 0.035) \times 10^{-10}$ Ab	$(2.344 \pm 0.011) \times 10^{-10}$ Cb
97.18	$(4.382 \pm 0.078) \times 10^{-10}$ Ac	$(5.941 \pm 0.141) \times 10^{-10}$ Bc
Literature references		
Corn starch	4.61×10^{-10}	García et al. (2000)
Amylomaize	3.21×10^{-10}	Mali et al. (2002)
Amaranth flour	0.00065×10^{-10}	Tapia-Blácido et al. (2005)
Hydroxypropyl starch/gelatin	0.0002×10^{-10}	Arvanitoyannis et al. (1998)

[a]Means value ± standard deviations of two replicates.
[b]Means in same row with different capital letters are significantly different ($P \leqslant 0.05$); means in same column with different small letters are significantly different ($P \leqslant 0.05$).

modified the barrier properties to water vapor, oxygen and carbon dioxide. The SG extract caused a reduction in the WVP and oxygen permeability of the films, but the permeability to carbon dioxide was increased. The films with SC extract did not have effect on the permeability, except on the oxygen permeability where it acted as barrier. It can be also concluded that the films with SG extract hold a selected effect on the GP; very important thinking in a future application as coating of fruits with high respiration metabolism.

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References

Anker, M., Berntsen, J., Hermansson, A. M., & Stading, M. (2002). Improved water vapor barrier of whey protein films by addition of an acetylated monoglyceride. *Innovative Food Science & Emerging Technologies*, *3*(1), 81–92.

Arvanitoyannis, I. S., Nakayama, A., & Aiba, S. (1998). Edible films made from hydroxipropyl starch and gelatin and plasticized by polyols and water. *Carbohydrate Polymers*, *36*(2–3), 105–119.

Aydinli, M., & Tutas, M. (2000). Water sorption and water vapor permeability properties of polysaccharide (Locust bean gum) based edible films. *Lebensmittel- Wissenschaft und Technologie*, *33*(1), 63–67.

Biswal, D. R., & Singh, R. P. (2004). Characterization of carboxymethylcellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers*, *57*(4), 379–387.

Cheng, L. H., Abd Karim, A., Norziah, M. H., & Seow, C. C. (2002). Modification of the microstructural and physical properties of konjac glucomannan-based films by alkali and sodium carboxymethylcellulose. *Food Research International*, *35*(9), 829–836.

Cuq, B., Gontard, N., Cuq, J. L., & Guilbert, S. (1997). Selected functional properties of fish myofibrillar protein-based films as affected by hydrophilic plasticizers. *Journal of Agricultural and Food Chemistry*, *45*(3), 622–626.

Cuq, B., Gontard, N., & Guilbert, S. (1998). Proteins agricultural polymers for packing production. *Cereal Chemistry*, *75*(1), 1–9.

Debeaufort, F., & Voilley, A. (1997). Methylcellulose-based edible films and coating, 2: Mechanical and thermal properties as a function of plasticizer content. *Journal of Agricultural and Food Chemistry*, *45*(3), 685–689.

García, M. A., Martino, M. N., & Zaritzky, N. E. (2000). Lipid addition to improve barrier properties of edible starch-based films and coating. *Journal of Food Science*, *65*(6), 941–946.

Girard, M., Turgeon, S. L., & Paquin, P. (2002). Emulsifying properties of whey protein–carboximethylcellulose complexes. *Journal of Food Science*, *67*(1), 113–119.

Gontard, N., Guilbert, S., & Cuq, J. L. (1992). Edible wheat gluten films: Influence of the main process variables on film properties using response surface methodology. *Journal of Food Science*, *57*(1), 191–195,199.

Gontard, N., Guilbert, S., & Cuq, J. L. (1993). Water and glycerol as plasticizer affect mechanical and water vapor barrier properties of an edible wheat gluten film. *Journal of Food Science*, *58*(1), 206–211.

Guilbert, S., Cuq, B., & Gontard, N. (1997). Recent innovations in edible and/or biodegradable packing materials. *Food Additives and Contaminants*, *6*(6–7), 741–751.

Guilbert, S., Gontard, N., & Gorris, L. G. M. (1996). Prolongation of the shelf-life of perishable food products using biodegradable films and coating. *Lebensmittel- Wissenschaft und Technologie*, *29*(1–2), 10–17.

Han, C., Zhao, Y., Leonard, S. W., & Traber, M. G. (2004). Edible coating improve storability and enhance nutritional value of fresh strawberries (*Fragaria* × *ananassa*) and raspberries (*Rubus ideaus*). *Postharvest Biology and Technology*, *33*(1), 67–78.

Kester, J. J., & Fennema, O. R. (1986). Edible films and coatings: A review. *Food Technology*, *40*(12), 47–59.

Kester, J. J., & Fennema, O. R. (1989). An edible film of lipids and cellulose ethers: Barrier properties to moisture vapor transmission and structural evaluation. *Journal of Food Science*, *54*(6), 1383–1389.

Kim, K. W., Ko, C. J., & Park, H. J. (2002). Mechanical properties, water vapor permeability and solubilities of highly carboxymethylated starch-based edible films. *Journal of Food Science*, *49*(1), 1478–4181,1485.

Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. N., & Zaritzky, N. E. (2002). Microstructural characterization of yam starch films. *Carbohydrate Polymers*, *50*(4), 379–386.

Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. N., & Zaritzky, N. E. (2004). Barrier, mechanical and optical properties of plasticized yam starch films. *Carbohydrate Polymers*, *56*(2), 129–135.

Mali, S., Grossmann, M. V., García, M. A., Martino, M. N., & Zaritzky, N. E. (2006). Effect of controlled storage on thermal, mechanical and barrier properties of plasticized films different starch sources. *Journal of Food Engineering*, *75*(4), 453–460.

Mauer, L. J., Smith, D. E., & Labuza, T. P. (2000). Water vapor permeability, mechanical, and structural properties of edible β-casein films. *International Dairy Journal*, *10*(5–6), 353–358.

Montenegro, G. (2002). Ugni molinae Turcz. In G. Montenegro, & B. N. Timmermann (Eds.), *Chile nuestra flora útil. Guía de uso apícola, medicinal folclórica, artesanal y ornamental* (2nd ed., pp. 241–242). Santiago: Ediciones Universidad Católica de Chile.

Nie, H., Liu, M., Zhan, F., & Guo, M. (2004). Factors on the preparation of carboxymethylcellulose hydrogel and its degradation behaviour in soil. *Carbohydrate Polymers*, *58*(2), 185–189.

Oosterveld, A., Beldman, G., & Voragen, A. G. J. (2000). Oxidative crosslinking of pectic polysaccharides from sugar-beet pulp. *Carbohydrate Research*, *328*(2), 199–207.

Ou, S., Wang, Y., Tang, S., Huang, C., & Jackson, M. G. (2005). Role of ferulic acid in preparing edible films from soy protein isolate. *Journal of Food Engineering*, *70*(2), 205–210.

Park, H. J., Weller, C. L., Vergano, P. J., & Testin, R. F. (1993). Permeability and mechanical properties of cellulose-based edible films. *Journal of Food Science*, *58*(6), 1361–1365.

Peressini, D., Bravin, B., Lapasin, R., Rizzotti, C., & Sensidoni, A. (2003). Starch–methylcellulose based edible films: Rheological properties of film-forming dispersions. *Journal of Food Engineering*, *59*(1), 25–32.

Petersson, M., & Stading, M. (2005). Water vapor permeability and mechanical properties of mixed starch–monoglyceride films and effect of film forming conditions. *Food Hydrocolloid*, *19*(1), 123–132.

Robards, K., Prenzler, P. D., Tucker, G., Swatsitang, P., & Glover, W. (1999). Phenolic compounds and their role in oxidative processes in fruits. *Food Chemistry*, *66*, 401–436.

Rubilar, M., Pinelo, M., Ihl, M., Scheuermann, E., Sineiro, J., & Núñez, M. J. (2006). Murta leaves (*Ugni molinae* Turcz) as a source of antioxidant polyphenols. *Journal of Agricultural and Food Chemistry*, *54*(1), 59–64.

Seguel, I., Peñalosa, E., Gaete, N., Montenegro, A., & Torres, A. (2000). Colecta y caracterización molecular de germoplasma de murta (*Ugni molinae* Turcz.) en Chile. *Revista Agro Sur*, *28*(2), 32–41.

Shaw, N. B., Monahan, F. J., O'Riordan, E. D., & O'Sullivan, M. (2002). Physical properties of WPI films plasticized with glycerol, xylitol, or sorbitol. *Journal of Food Science*, *67*(1), 164–167.

Sobral, P. J. A., Menegalli, F. C., Hubinger, M. D., & Roques, M. A. (2001). Mechanical, water vapor barrier and thermal properties of gelatin based edible films. *Food Hydrocolloids*, *15*(4–6), 423–432.

Tapia-Blácido, D., Sobral, P. J., & Menegalli, F. C. (2005). Development and characterization of biofilms based on Amaranth flour (*Amaranthus caudatus*). *Journal of Food Engineering*, *67*(1–2), 215–223.

Turhan, K. N., & Şahbaz, F. (2004). Water vapor permeability, tensile properties and solubility of methylcellulose-based edible films. *Journal of Food Engineering*, *61*(3), 459–466.

Yang, L., & Paulson, A. T. (2000). Mechanical and water vapor barrier properties of edible gellan films. *Food Research International*, *33*(7), 563–570.