Carbohydrate Polymers 99 (2014) 508–516

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Chitosan–caseinate bilayer coatings for paper packaging materials

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ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form 24 August 2013
Accepted 27 August 2013
Available online 1 September 2013

Keywords:
Caseinate
Chitosan
Paper
Composite coating
Bilayer coating
Functional properties

ABSTRACT

Papers coated with caseinate and caseinate/chitosan bilayer films were developed. Caseinate, chitosan and caseinate/chitosan films were preliminary characterized by FTIR spectroscopy and thermal stability analyses. The effects of coating weight, caseinate concentration (7%, 10%, and 12%, w/w), and coating application methods (single layer and bilayer) on the physical and mechanical properties of coated papers were studied. Increasing the concentration of caseinate led to a decrease in water vapor permeability (WVP) of the resulting coated paper sheets. Chitosan significantly ($p < 0.05$) increased the elongation at break (%*E*) of coated paper. However, the application of chitosan as a second layer on wet or dry caseinate films did not significantly affect ($p > 0.05$) the tensile strength (TS) of coated paper. The greatest reduction in paper WVP is achieved by addition of a chitosan layer to the dried preformed caseinate-coated paper.

1. Introduction

Naturally renewable biopolymers can be used for improving the durability of paper sheets (Basta, 2003; Basta & El-Saied, 2008). They may also serve as barrier coatings on paper packaging materials (Khwaldia, Tehrany, & Desobry, 2010). Renewable biopolymers originated from proteins, polysaccharides, and lipids or combinations of those components have already been associated to paper to provide interesting functionalities while maintaining environment-friendly characteristic of the material (Aloui, Khwaldia, Ben Slama, & Hamdi, 2011; Despond, Espuche, Cartier, & Domard, 2005; Ham-Pichavant, Sèbe, Pardon, & Coma, 2005; Khwaldia, Linder, Banon, & Desobry, 2005; Khwaldia, 2010).

Sodium caseinate (SCAS) is commercially available and can easily form cohesive films from aqueous solutions because of its random coil nature and its ability to form extensive intermolecular hydrogen, electrostatic, and hydrophobic bonds. Films made of SCAS are colorless, tasteless, odorless, transparent, flexible, highly impermeable to oil and oxygen and resistant to thermal denaturation (Schou et al., 2005). Moreover, SCAS is an attractive polymer for the coating of cellulose-based materials for food packaging purposes due to its low cost, availability, and complete biodegradability. However, films made of caseinate are rather sensitive to moisture and have low stiffness and strength, especially in moist environments (Debeaufort, Quezada-Gallo, & Voilley, 1998), which may restrict their use in food applications.

Composite coatings or multilayer coatings on paper packaging materials, applied either in the form of an emulsion or in successive layers (multilayer coating), have been prepared to combine the good structural and gas-barrier properties of hydrocolloid coatings with the good moisture-barrier characteristics of lipids. In a previous study, Khwaldia (2010) processed a water vapor-barrier packaging material with paper, caseinate, and paraffin wax. She found that the greatest reduction in paper water vapor permeability (WVP) is achieved by addition of a wax layer to the paper already coated with caseinate, due to the high resistance to moisture transfer of the paraffin wax. Unfortunately, the content of paraffin wax of packaging materials makes it difficult to separate, recycle or compost them after use.

Chitosan, the linear and typically 20% acetylated (1-4)-2-amino-2-deoxy β-D-glucan, is versatile and useful for the development of composite materials even in case of elaborated applications (Busilacchi, Gigante, Mattioli-Belmonte, Manzotti, & Muzzarelli, 2013; Muzzarelli, Greco, Busilacchi, Sollazzo, & Gigante, 2012). Chitosan-based films and coatings have good mechanical properties and can act as excellent oxygen and grease barriers (Kittur, Kumar, & Tharanathan, 1998). Moreover, chitosan is readily compatible with paper and is one of the most interesting and the most studied paper coating materials (Bordenave, Grelier, Pichavant, & Coma, 2007; Despond et al., 2005; Kjellgren, Gällstedt, Engström,

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http://dx.doi.org/10.1016/j.carbpol.2013.08.086

& Järnström, 2006; Reis, Yoshida, Reis, & Franco, 2011; Vartiainen et al., 2004).

Although the properties of composite films based on caseinate have been studied in several publications, there are very few published data on caseinate–chitosan films (Pereda, Aranguren, & Marcovich, 2008). Moreover, most of the cited literature about bilayer coatings on paper described systems where a lipid forms a second layer over the polysaccharide or protein-coating (Despond et al., 2005; Khwaldia, 2010). To our knowledge, no research has been reported on bilayer systems including two hydrocolloid layers for paper coating.

Therefore, the objectives of this study were to develop caseinate and caseinate/chitosan bilayer coatings on paper, and to investigate the effects of coating weight, caseinate contents (7%, 10%, and 12%, w/w), and coating application methods (single layer and bilayer) on the functional properties of coated papers.

2. Materials and methods

2.1. Materials

Paper packaging used as a support for coating was supplied by SOTEFI (Soukra, Tunisia) with a grammage of $77.80 \pm 0.85\ g/m^2$ and an average thickness of $98 \pm 1.09\ \mu m$ at 23 °C and 50% RH. SCAS (molecular weight ~25,000 Da, Sigma Aldrich, Steinheim, Germany) and chitosan (deacetylation degree >75%, viscosity ≤200 mPa s in 1% acetic acid, molecular weight ~150,000 Da, Sigma Aldrich, Steinheim, Germany) were used as coatings materials.

2.2. Coating solutions

Preparation of caseinate-based coating solutions was adapted from Khwaldia (2010). SCAS dispersions with concentrations of 7, 10, and 12% (w/w) were obtained by dispersing the appropriate SCAS powder in distilled water at 60 °C while stirring for 30 min. Chitosan coating solutions were prepared by dissolving chitosan 1% (w/v) in 1% (v/v) acetic acid solution with agitation using a magnetic stirrer at 45 °C (Vartiainen et al., 2004). All coating solutions were degassed to remove the entrapped air bubbles during mixing.

2.3. Coating method

Three coating application methods were investigated for paper coating. Single-layer method in which caseinate solution was applied to paper by coater machine. Bilayer coatings were prepared by application of chitosan solution either on wet caseinate-coated paper (bilayer coatings 1) or on dry caseinate-coated paper (bilayer coatings 2).

A control coater (model KCC 101, RK Print-Coat Instruments, Hertz, UK) was used to deposit the coating solutions on the paper at ambient temperature. This automatic machine uses standard wire-wound bars to produce a uniform and repeatable coating. Four coat weights were applied: 5, 9, 12 and $16\ g/m^2$, where the coat weight was varied by varying the diameter of the wire on the rod. The coating process was performed at a speed of 6 m/min. After wet coating, the papers were dried at 40 °C for 30 min (dryer model 400, TECHPAP, Gières, France). Before properties' testing, all samples were conditioned for two days in an environmental chamber at 50% RH and 23 °C. Coating weights (g/m^2) were obtained by subtracting from the weight of a defined area of coated paper, the weight of the same size area of the uncoated paper.

2.4. Characterization of caseinate/chitosan films

2.4.1. FTIR spectroscopy

FTIR spectra have been examined for the observation of changes occurred in various peaks when chitosan is blended with caseinate. IR-spectra ($4000–400\ cm^{-1}$) were recorded on a FTIR Bruker Equinox55 spectrometer at a nominal resolution of $4\ cm^{-1}$, using KBr discs. The technique of O'Connor, Du Pre, and Mitchoum (1958) was used to calculate the crystallinity index (Cr.I). The mean strength of hydrogen bonds (MHBS) was calculated according to Levdik, Inshakov, Misyurova, and Nikitin (1967).

2.4.2. Non-isothermal theromgravimetric analysis

Thermogravimetric analysis (TGA) was carried out to study the thermal stability of caseinate, chitosan and caseinate/chitosan films using a Setaram TG92 thermal analysis system. The thermograms were obtained under helium atmosphere at a uniform heating rate of 10 °C/min in the temperature range of 25–1000 °C.

*TG-curve analysis

Kinetic studies, based on the weight loss data, were obtained by TG curve analysis. The activation energy was evaluated by applying an analytical method proposed by Coats and Redfern (1964). For pseudo homogeneous kinetics, the irreversible rate of conversion of the weight fraction of reactant was expressed by the following equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where α is the fraction of material decomposed at time t, k is the specific rate constant and n is the order of reaction. The temperature dependence of k is expressed by the Arrhenius equation:

$$k = Ae^{E_a/RT} \quad (2)$$

where A is the frequency factor (s^{-1}) and T is the absolute temperature.

For linear heating rate, a, (deg min^{-1}):

$$a = \frac{dT}{dt} \quad (3)$$

For calculating the activation energy of thermal decomposition (E_a), when $n = 1$, Eq. (4) was used.

$$\log\left[-\log\frac{1-\alpha}{T^2}\right] = \log\frac{AR}{aE_y}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \quad (4)$$

When $n \neq 1$, Eq. (5) was used;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \quad (5)$$

Plotting the left-hand-side value of the equation [i.e., log $[1-(1-\alpha)^{1-n}/T^2\ (1-n)]$ against $1/T$ using various values of "n" should give a straight line with the most appropriate value of "n" (Basta, 1999). The least square method was applied to the equation, using values of "n" ranging from 0.0 to 3.0 in increments of 0.5. The correlation coefficient (r) and the standard error (SE) were calculated for each value of "n". The "n" value, which corresponds to the maximum r and minimum SE, is the order of the degradation process. The activation energies and frequency factors were calculated from the slope and intercept, respectively, of the Coats–Redfern equation with the most appropriate value of "n".

2.5. Characterization of coated paper sheets

2.5.1. Paper thickness measurements

Paper thickness was measured using a ProGage thickness tester (Thwing-Albert Instrument company, Philadelphia, PA) in accordance with ISO 534-2005. Ten replicates were done on each sample.

2.5.2. Water vapor permeability (WVP)

WVP measurements were determined with the gravimetric method described in the AFNOR NF H00-030 standard (AFNOR, 1974). The test film was sealed in a permeation cell containing

a desiccant (silica gel) to maintain an RH of 0% in the cell. The permeation cells were 6.4 cm (internal diameter) by 8.9 cm (external diameter) by 4.8 cm deep with an exposed area of 26.42 cm^2. The permeation cells were placed in a controlled temperature ($38 \pm 1\,^{\circ}C$) and relative humidity ($90 \pm 3\%$) chamber fitted with a variable-speed fan to provide a strong driving force across the film for water-vapor diffusion. The water-vapor transport was determined from the weight gain of the cell. Changes in the weight of the cell were recorded as a function of time. Slopes of weight changes vs. time (after steady state was reached) were calculated by linear regression, and the correlation coefficient for all reported data was >0.99. The steady transfer rate was reached after ~1 h. The water-vapor transmission rate (WVTR) was defined as the slope (g/d) divided by the transfer area (m^2). After the permeation tests, film thickness was measured and WVP was calculated as follows,

$$WVP = \frac{WVTR \cdot X}{\Delta p} \quad [\text{g mm/m}^2\text{/d/kPa}] \tag{6}$$

where X is the coated paper thickness, Δp is the difference of partial water-vapor pressure across the film ($\Delta p = p(RH_2 - RH_1) = 5.942$ kPa, where p is the saturation vapor pressure of water at 38 °C, $RH_2 = 90\%$, $RH_1 = 0\%$). Four replicates were made from each type of paper.

2.5.3. Tensile testing

A material testing machine (Lloyd LRX, Lloyd Instruments, Royston, UK) with a 0.5 kN static load cell was used to determine tensile strength (TS) and elongation at break (%*E*) in the machine direction of the papers, according to a standard method of ISO 1924-2-1994. The experiments were performed under controlled conditions, at 23 °C and 50% RH. Ten rectangular paper samples (15 mm wide × 100 mm long) were cut from each type of paper and were tested using a double clamp with a separation of 30 mm at a test speed of 20 mm/min. The clamp separation was 100 mm and the strain rate was 20 mm/min. The curve load vs. extension was recorded until the elongation at break was reached. The TS was expressed in MPa and was calculated by dividing the maximum load (N) by the cross-sectional area (m^2). Maximum elongation at break or percent elongation at break (%E) was determined by dividing the extension at the moment of breakage by the initial gauge length of the samples and multiplying by 100.

2.5.4. Scanning electron microscopy (SEM)

The surface morphology of the papers was examined using scanning electron microscopy (SEM), using a FEI Quanta 200 scanning electron microscope (FEI Company, Eindhoven, the Netherlands). Samples were previously coated with gold using "Sputta Coater S150" under vacuum. SEM was carried out to give further insight on homogeneity of the coatings. All samples were examined using an accelerating voltage of 20 kV.

2.6. Statistical analysis

Data were subjected to a multifactor analysis of variance with 95% significance level using Statgraphics® Plus 5.1 (Manugistics Inc., Rockville, MD, USA), while least significant difference test (LSD, $p < 0.05$) was used to compare the different treatments at the 95% confidence level.

3. Results and discussion

3.1. Characterization of hydrocolloid films

3.1.1. FTIR spectra

Table 1 shows the FTIR spectra of caseinate, chitosan, and caseinate/chitosan films. In FTIR spectrum of caseinate, absorption peaks at ~3279 cm^{-1} are attributed to the OH stretching, which

Table 1
Main IR-absorption bands and measurements of caseinate, chitosan and caseinate/chitosan films.

Sample	MHBS[a]	Cr./I[b]	ν_{OH} or ν_{NH} (stretching)		ν_{CH} (stretching)		$\nu_{C\equiv N}$ (stretching)		$\nu_{C=O}$ (stretching) Amide I and II (1558–1705 cm^{-1})		ν_{OH} or ν_{NH} (bending)		ν_{C-O} 1000–1280 cm^{-1}		ν_{CH} (rocking)	
			cm^{-1}	A	cm^{-1}	A	cm^{-1}	A	cm^{-1}	A	cm^{-1}	A	cm^{-1}	A	cm^{-1}	A
Caseinate	1.658	1.947	3279	0.029	2939	0.019	2343	0.004	1632	0.075	1441	0.045	1230	0.039	966	0.022
			3051	0.017					1513.9	0.068	1387	0.037	1155	0.031	896.8	0.021
													1057	0.032		
Chitosan	1.261	1.380	3333	0.024	2852	0.019			1637	0.020	1412	0.022	1145	0.030	889	0.048
									1567	0.020	1371	0.026	1049	0.067		
											1302	0.022				
7% caseinate/chitosan	1.253	2.217	3267	0.019	2932	0.015	2341	0.005	1625.8	0.047	1438.7	0.033	1230	0.031	894.9	0.022
			3049	0.013					1516	0.046	1386	0.033	1149	0.027	918	0.023
											1309	0.027	1068	0.034		
10% caseinate/chitosan	1.285	1.496	3255	0.096	2955	0.074	2571	0.037	1621	0.231	1438	0.120	1240	0.099	919	0.013
			3070	0.069	2919	0.074	2161	0.043	1517	0.205	1390	0.111	1157	0.065	874	0.008
							2033	0.036					1060	0.072		
12% caseinate/chitosan	1.366	1.415	3261	0.089	2956	0.065	2580	0.030	1624	0.208	1438	0.103	1239	0.086	916	0.010
			3045	0.058	2929	0.065	2161	0.039	1518	0.475	1388.6	0.092	1072	0.057	873.6	0.007
							2003	0.029								

[a] MHBS: $A_{OH(Str.)}/A_{CH\ (Str.)}$.
[b] Cr. I: $A\,A_{\sim 1370\ cm^{-1}}/A_{\sim 2920\ cm^{-1}}$

overlaps the NH stretching in the same region (Jiang et al., 1997). The peak at 2939 cm^{-1} is assigned to C—H stretching. An intense peak at 1632 cm^{-1} is due to the C=O stretching vibrations of the amide groups (coupled with N—H in-plane bending and C—N bond stretching vibrations) (amide I) (Wan, Wu, & Wen, 2006), the band at 1514 cm^{-1} is NH bending (amide II) (Duan, Donq, Yuan, & Yao, 2004). The peaks at 1441 cm^{-1} correspond to the CH_3 symmetrical deformation mode and those at 1236–1240 cm^{-1} range to the PO_2 asymmetric stretching (Derkach, Dyakina, & Levachev, 2005).

The comparison of FTIR spectra of caseinate and chitosan revealed that the bands assigned to OH and NH stretching, and C=O stretching vibrations of the amide groups are blue shifted from 3279 cm^{-1} to 3333 cm^{-1} and 1632 cm^{-1} to 1637 cm^{-1}, respectively. Due to their lower ability to form hydrogen bonds, the functional groups of chitosan vibrate more easily than those of caseinate molecules, which include electronegative hydrophilic and neutral hydrophobic domains. This view is supported by the lower crystallinity index and MHBS values of chitosan compared with caseinate (Table 1).

In the case of caseinate/chitosan films, spectra revealed that the absorption peaks dominated by chitosan at 3333, 1637, 1567, 1412, and 1371 cm^{-1} decrease, confirming the incorporation of chitosan during the formation of caseinate/chitosan films. The bands corresponding to OH (str.), NH (st), amide(I) of caseinate and chitosan are shifted from 3279 cm^{-1} and 3332.7 cm^{-1} to 3267–3273 cm^{-1}, while those corresponding to amide groups are shifted from 1632 cm^{-1} and 1637.4 cm^{-1} to 1624–1625 cm^{-1}, respectively. This shift is indicative of the ionic interaction developed between anion carboxylate and phosphates groups of caseinate and NH_3^+ formed groups of chitosan in acetic acid. Similar trends are observed for the bands assigned to carboxylate groups (C=O and CO gps) at 1643, 1510 and 1435 cm^{-1}. It can be seen that caseinate/chitosan films showed higher crystallinity index ($A_{1370\ cm^{-1}}/A_{2920\ cm^{-1}}$) compared with chitosan. The maximum interaction was achieved with 7% caseinate/1% chitosan system. Indeed, caseinate molecules have amphiphilic chemical characteristics and contain hydrophilic and hydrophobic regions. On the other hand, the structure of commercial chitosan shows positively charged hydrophilic domains (~75% glucosamine) and neutral hydrophobic domains (25% N-acetylglucosamine). This can be useful for ionic interaction and the formation of caseinate–chitosan complexes.

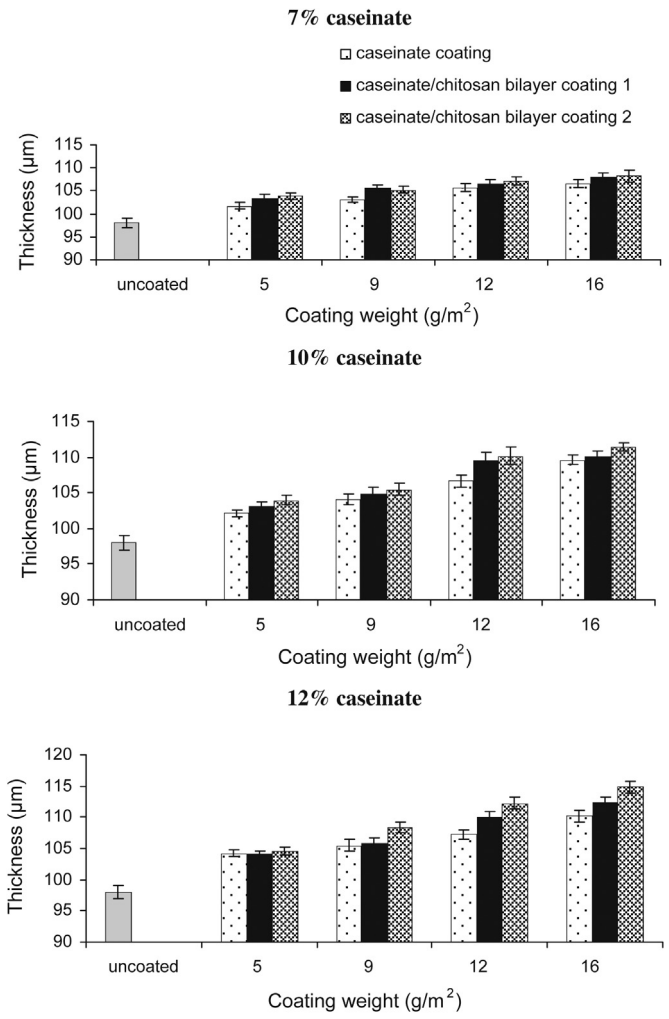

Fig. 1. Thickness of paper coated with caseinate and caseinate/chitosan bilayer coatings. Chitosan was applied as a second layer to wet (bilayer coating 1) and dry (bilayer coating 2) caseinate films.

3.1.2. Thermal stability of caseinate/chitosan films

The kinetic measurements of caseinate, chitosan and caseinate/chitosan films are recorded in Table 2. Two degradation stages are observed in TG curves of films made from different caseinate concentrations (7%, 10% and 12%). The first stage at 26–187 °C is due to the loss of the absorbed moisture. At 184–525 °C, the main degradation stage is attributed to the decomposition of caseinate constituents. Increasing caseinate concentration from 7% to 12%, decreased the onset temperature of degradation, DTG peak temperature and the activation energy from 184 °C to 209 °C, 305 °C to 309 °C, and ~75 kJ/mol to ~81 kJ/mol (high thermal stability), respectively.

As shown in Table 2, the thermal degradation of 7% caseinate −1% chitosan complex is observed at higher temperature (~350 °C) than that of the individual caseinate and chitosan films (~304 °C). Increasing the concentration of caseinate from 7% to 12% provided films with relatively higher thermal stability. The main 2nd degradation stages of caseinate and chitosan occur in two degradation stages at maximum temperatures of 235–242 °C and 323–338 °C, respectively, with total degradation activation energies of 229–300 kJ/mol. These values are higher than those of caseinate (81.30 kJ/mol) and chitosan (126.77 kJ/mol). This may be attributed to the degradation of ionic bonds formed by interaction between caseinate and chitosan, followed by degradation of the main biopolymer chains. The remaining weight percentages for caseinate and chitosan are 26–29% and 45%, respectively; while those of their complexes are constant ~26%, and not increased due to combination of caseinate with chitosan. This result confirmed the complexation occurred via carboxylate and phosphate groups with removal of Na^+ ions.

3.2. Characterization of coated papers

3.2.1. Thickness

Fig. 1 shows thickness of paper coated with caseinate and caseinate/chitosan bilayer coatings. An ANOVA reveals that coating application method, coating weight and coating composition significantly affected ($p < 0.05$) thickness values. By increasing coating weight from 5 to 16 g/m^2, the dried thickness of coated paper increased. Thickness of coating layers on the surface of paper ranged between 3.70 and 16.88 µm for all coated papers. Coating thicknesses in this study are higher than those reported for HPMC coating (Khwaldia, 2013) and chitosan coating (Aloui et al., 2011). The low thickness increase observed after deposition of some biopolymers onto paper was attributed to their penetration into the cellulose matrix (Guillaume, Pinte, Gontard, & Gastaldi, 2010).

Table 2
Kinetic parameters of caseinate, chitosan and caseinate/chitosan films.

Sample code in chart	Stage	Temp. range (°C)	DTG peak temp. (°C)	n	$-r$	Se	E_a (kJ/mol)	Wt. (final)
7% caseinate	1st	26–187	125	–	–	–	–	96.020
	2nd	184–525	305.3	1.5	0.969	0.195	75.313	25.740
10% caseinate	1st	35–184	139	–	–	–	–	96.556
	2nd	184– 487	304.6	1.5	0.988	0.155	77.923	25.650
12% caseinate	1st	26– 187	125	–	–	–	–	96.024
	2nd	209 –486	209.4	1.5	0.990	0.186	81.369	29.736
Chitosan	1st	32.7–146.68	98.06	–	–	–	–	96.514
	2nd	204.1–421.8	304.04	1.5	0.963	0.244	126.768	45.899
7% caseinate/chitosan	1st	25.9–179.8	83.37	–	–	–	–	96.024
	2nd	186.6–541.4	349.55	2.0	0.955	0.184	86.238	25.736
10% caseinate/chitosan	1st	40.2–145.4	92.75	–	–	–	–	98.687
	2nd	169.3–264	242.9	2.0	0.938	0.169	98.374	82.320
	3rd	268.3–463.9	322.6	2.0	0.946	0.199	$\frac{130.642}{\Sigma}$ $E_a = 229.016$	26.570
12% caseinate/chitosan	1st	37.2–136.9	95.52	–	–	–	–	99.810
	2nd	197.9–282.5	235.06	1.5	0.921	0.2068	144.690	76.790
	3rd	282.5–424.0	338	2.0	0.928	0.198	$\frac{155.305}{\Sigma}$ $E_a = 299.995$	26.576

On the other hand, increasing the concentration of caseinate led to an increase in thickness of the paper sheets coated with caseinate and caseinate/chitosan bilayer coatings. Moreover, chitosan application as a second layer on caseinate-coated paper tends to increase coating thickness. "bilayer coatings 2" produced by application of chitosan solution on dry caseinate-coated paper were thicker compared with single-layer coatings, and the 12% caseinate/chitosan "bilayer coatings 2" were the thickest (Fig. 1).

3.2.2. WVP

The effectiveness of packaging materials is generally related to their mass-transport properties. The ability to ovoid or at least to decrease moisture transfer between the food and the surrounding atmosphere is critical for food quality and safety concerns. Transport properties of coated packaging materials are influenced by the type of coating material used, coating composition, and coating weight (Aloui et al., 2011). Therefore, the detailed study of the water-vapor-barrier properties of paper coated with caseinate and chitosan as influenced by coating composition and method of application is of great importance for practical and commercial purposes.

The WVP of coated papers varied significantly ($p < 0.05$) with coating weight and coating method (Fig. 2). By increasing coating weight from 5 to 16 g/m^2, the WVP of coated paper was decreased consistently. A similar effect of coating weight also has been reported after biopolymer coating because of clogging by the coating material of the pores of the cellulose structure of paper (Khwaldia, 2010). At 7% caseinate concentration, caseinate coating on paper reduced WVP by 64% for 9 g/m^2 coating weight compared with that of the uncoated paper. Chitosan was added to investigate the effect of the cationic polysaccharide on barrier and mechanical properties of caseinate-based coatings. The WVP of paper coated with "bilayer coatings 1", produced by application of chitosan as a second layer on wet caseinate films (7%, w/w), increased slightly compared with that of paper coated with pure caseinate coating, and then decreased for higher caseinate content. At 12% caseinate concentration, "Bilayer coating 1" on paper reduced WVP by 37% for 16 g/m^2 coating weight compared with that of the pure caseinate-coated paper at the same concentration. This may be due to the interactions that develop between the cationic polymer (chitosan) and the caseinate carboxyl groups, which should lead to polyelectrolyte complexation in forming the composite coating. This complexation might decrease the free volume of the polymeric matrix and lead to the formation of a denser polymeric matrix, thus decreasing the diffusion rate of water molecules through the bilayer coatings. The enhanced water-vapor-barrier properties of composite films as compared with those obtained from the pure polymers have been reported for gelatin/chitosan (Hosseini, Rezaei,

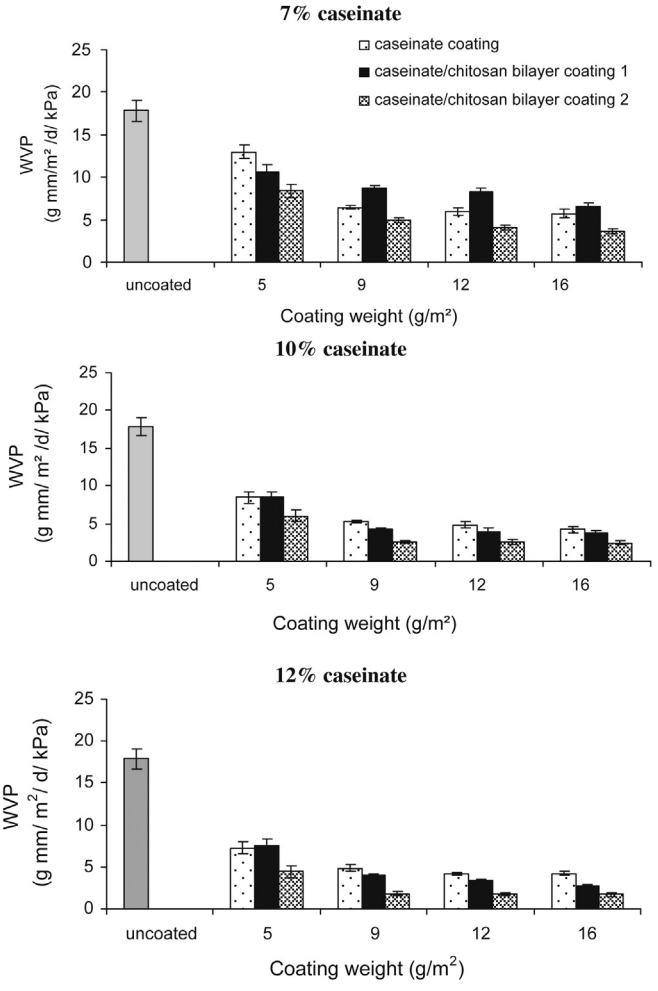

Fig. 2. Water vapor permeability (WVP) of paper coated with caseinate and caseinate/chitosan bilayer coatings. Chitosan was applied as a second layer to wet (bilayer coating 1) and dry (bilayer coating 2) caseinate films.

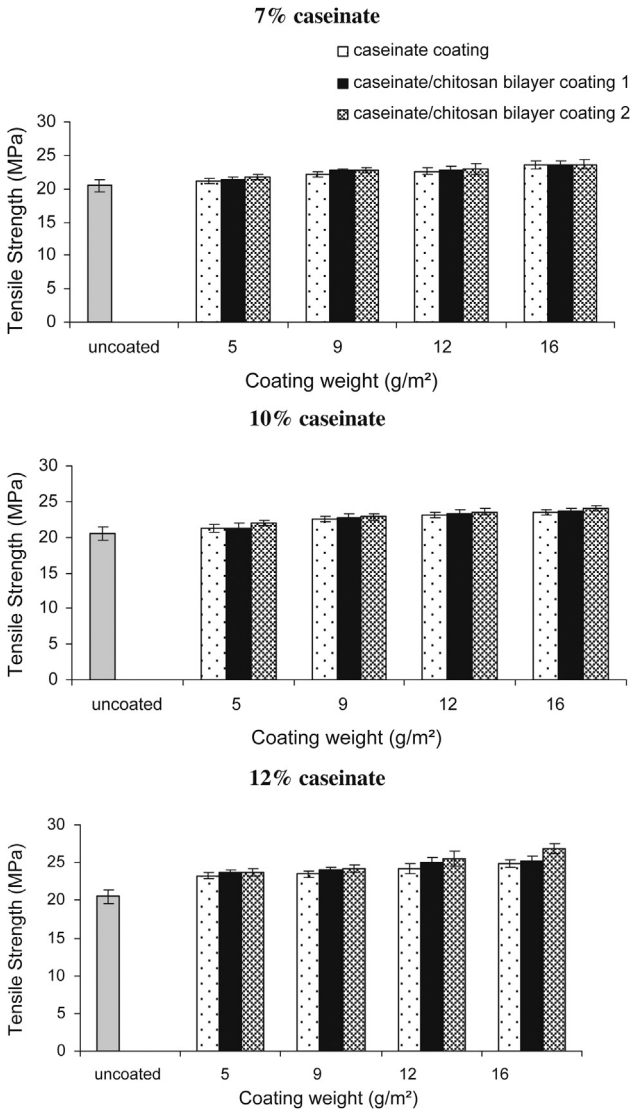

Fig. 3. Tensile strength (TS) of paper coated with caseinate and caseinate/chitosan bilayer coatings. Chitosan was applied as a second layer to wet (bilayer coating 1) and dry (bilayer coating 2) caseinate films.

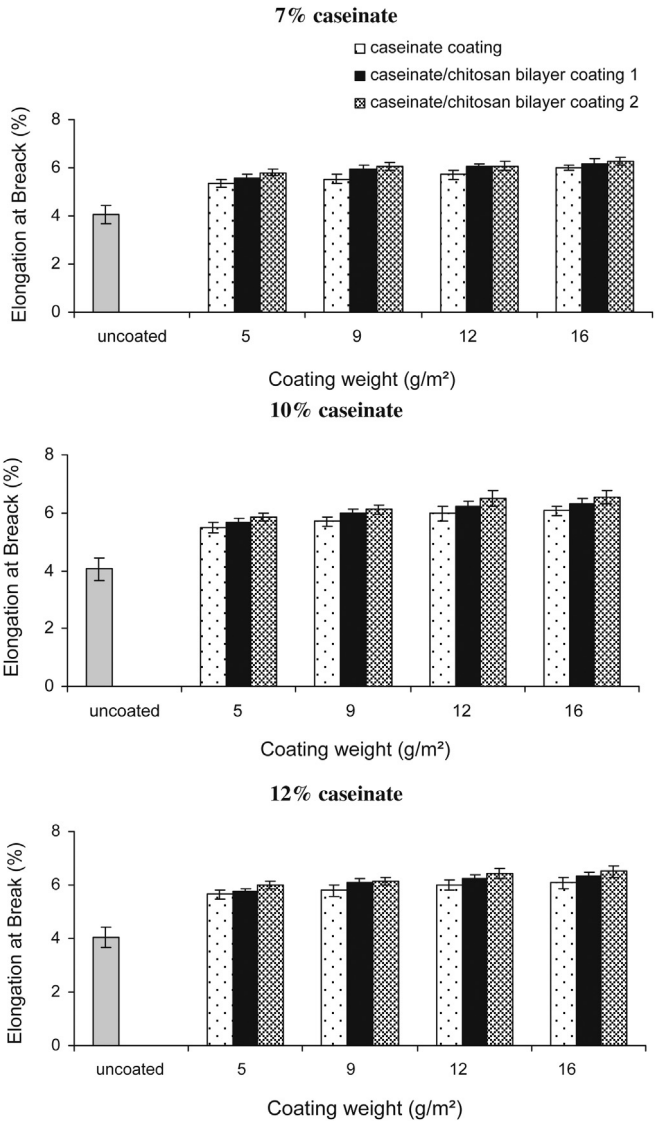

Fig. 4. Elongation at break (%*E*) of paper coated with caseinate and caseinate/chitosan bilayer coatings. Chitosan was applied as a second layer to wet (bilayer coating 1) and dry (bilayer coating 2) caseinate films.

Zandi, & Ghavi, 2013) and gelatin/gellan (Pranoto, Lee, & Park, 2007) composite edible films. However, Pereda, Aranguren, and Marcovich (2009) found increased WVP of caseinate based edible films when chitosan was added. These authors concluded that the high-humidity conditions (100/64.5 RH gradient) might affect the interactions between chitosan and caseinate and cause a conformational change in the microstructure of the blend film, as a result of swelling.

On the other hand, increasing the concentration of caseinate led to a decrease in WVP of the paper sheets coated with caseinate and caseinate/chitosan bilayer coatings (Fig. 2). It was also observed that there were significant differences between WVP values of coatings made with 7%, 10% and 12% caseinate ($p < 0.05$). The WVP of uncoated papers was 17.87 ± 1.23 g mm/m^2/d/kPa. So, "bilayer coatings 1" formulated with 7% caseinate reduced this value by 53% for 12 g/m^2 coating weight. This result was further improved to 81% by the application of chitosan on wet caseinate films (12% w/w). This seems to be consistent with the finding of Rhim, Lee, and Hong (2007) who reported that the Poly(lactide) (PLA) coating on paperboard reduced WVP significantly depending on the concentration of PLA coating solution. Depending on coating weight and caseinate content, the WVP of the paper coated with caseinate-chitosan "bilayer coatings 2" are generally 2–10 times lower than those of uncoated paper. It can be noted that no significant difference ($p > 0.05$) occurred between WVP of the paper sheets coated with caseinate-chitosan "bilayer coatings 2" at 9–16 g/m^2 of coating weight. At a content of 12% caseinate, the WVP of paper coated with caseinate-chitosan "bilayer coating 2" with 9 g/m^2 was about 10 times lower than that of the uncoated paper. It was 64% lower than that of paper coated with caseinate/chitosan "bilayer coating 1" with 9 g/m^2 (Fig. 2). It seems that the greatest reduction in paper WVP is achieved by addition of a chitosan layer to the dried preformed caseinate-coated paper, due to the thickness effect. In contrast to hydrophobic synthetic polymeric materials, the WVP of films prepared from biopolymers depend on their thickness (McHugh, Avena-Bustillos, & Krochta, 1993). "Bilayer coatings 2" produced by application of chitosan solution as a second layer on dry caseinate films were thicker compared with single-layer coatings, and the 12% caseinate/chitosan "bilayer coatings 2" were the thickest (Fig. 1). Literature demonstrates that bilayer systems are more effective barrier against water vapor transfer than composite films (Rivero, Garcia, & Pinotti, 2009).

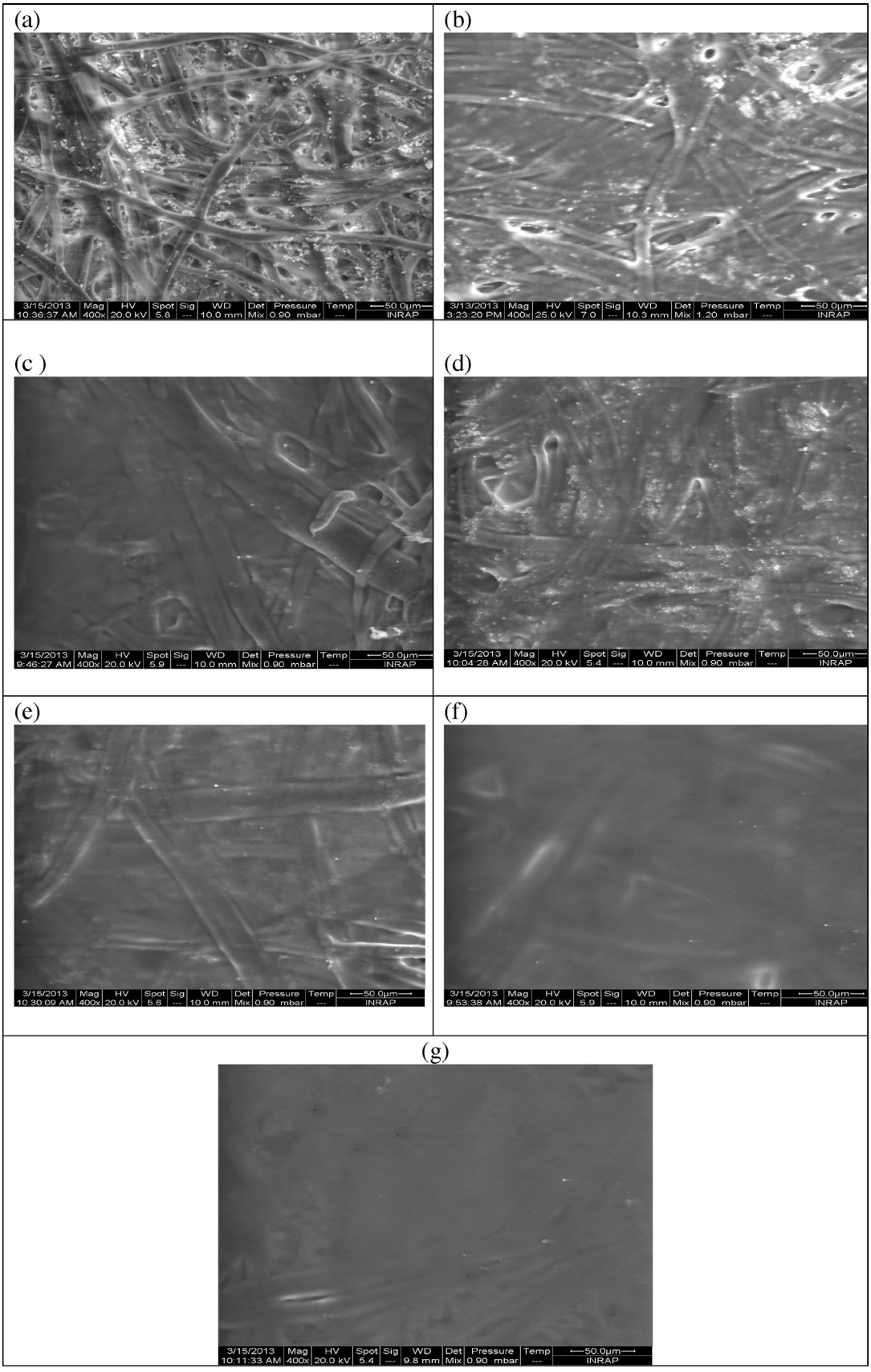

Fig. 5. Scanning electron microscopy images (400×) of (a) uncoated paper, (b) paper coated with 12% caseinate at 5 g/m^2, (c) paper coated with 12% caseinate at 16 g/m^2, (d) paper coated with 12% caseinate/chitosan "bilayer coating 1" at 5 g/m^2, (e) paper coated with 12% caseinate/chitosan "bilayer coating 1" at 16 g/m^2 and (f) paper coated with 12% caseinate/chitosan "bilayer coating 2" at 5 g/m^2, and (g) paper coated with 12% caseinate/chitosan "bilayer coating 2" at 16 g/m^2.

3.2.3. Tensile properties

Tensile strength (TS) and elongation at break (%*E*) are the most commonly reported responses to describe mechanical properties of paper-based packaging materials. Adequate mechanical strength and flexibility are required to maintain packaging integrity during shipping, handling, and storage. In general, the mechanical properties of the coated/laminated films in composite structure are controlled by the substrate or base film (Hong, Lee, & Son, 2005). However, tensile properties of coated papers were shown to be mainly dependent on the coating weight (Figs. 3 and 4). The TS of coated papers increased with increasing coating weight from 5 to 16 g/m^2. However, neither the addition of chitosan nor the coating application methods (single layer and bilayer) affected significantly ($p > 0.05$) the TS of coated paper (Fig. 3). Conversely, Pereda et al. (2008), who worked with chitosan/caseinate composite films, had reported that the addition of chitosan produced stronger films as compared with caseinate film. The complexation established between the two macromolecules is proposed as the reason for this improvement. A similar behavior was observed by Hosseini et al. (2013), who studied composite films made from gelatin and chitosan.

On the other hand, the %*E* of coated papers increased with increasing coating weight from 5 to 16 g/m^2 (Fig. 4). At 10% caseinate concentration, caseinate coating on paper enhanced %*E* by 50% for 16 g/m^2; 41% for 9 g/m^2, and 35% for 5 g/m^2, compared with that of the uncoated paper (4.05 ± 0.39%). The increase in %*E* as coating level increased, as shown in Fig. 4, may be attributed to a stress relaxation in the base paper during the coating process when the base paper was exposed to the water in the coating solution. Similar results were also observed by Kjellgren et al. (2006) and Khwaldia (2013) for greaseproof paper coated with chitosan and HPMC coated paper, respectively. Moreover, the application of chitosan as a second layer on wet or dry caseinate coatings led to an increase in %*E* of coated paper suggesting that the polysaccharide provides a more flexible structure to the caseinate–chitosan bilayer coatings. Similar results were also observed by Kristo, Biliaderis, and Zampraka (2007) in composite films based on caseinate and pullulan.

3.2.4. SEM

SEM photographs relative to the coated and uncoated papers (Fig. 5) show that, the porous structure typical of fiber-based materials was tightly covered by the caseinate-based coating. As coating level increased, uniformity and smoothness of the coating also increased. It can be noted that the resulting coated papers showed good appearance, flexibility and adhesion between the coating and the cellulosic substrate. Caseinate-chitosan "bilayer coatings 2" were more uniform than caseinate coatings and "bilayer coatings 1". The surface micrographs obtained by SEM revealed that "bilayer coatings 2" completely coated the cellulose fibers, and filled the pores of the paper. However, no observable differences were observed between microscopic views of single-layer coatings and "bilayer coatings 1".

4. Conclusions

The functional properties of paper coated with caseinate and caseinate/chitosan bilayer coatings were investigated as a function of coating weight, caseinate contents, and coating application methods. At high caseinate content, caseinate/chitosan bilayer coatings prepared by application of chitosan as a second layer on wet caseinate-coated paper showed lower WVP than the pure caseinate-coated paper. Tensile properties of coated papers were shown to be mainly dependent on the coating weight. The application of a chitosan layer on the dried preformed caseinate coatings provided paper with the highest water vapor barrier and mechanical properties and the resulting caseinate/chitosan-coated papers showed good appearance, flexibility, and adhesion between the bilayer coating and the cellulosic substrate. These bilayer systems seemed to be appropriate coating materials for paper-packaging materials.

Acknowledgments

The financial support of this work by the Egyptian Ministry for Scientific Research and the Tunisian Ministry of Higher Education and Scientific Research through the Executive Program of Scientific and Technological Cooperation between Egypt and Tunisia for the years 2012–2014, is gratefully acknowledged.

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