



Chitosan–caseinate bilayer coatings for paper packaging materials



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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.

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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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& 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 $77.80 \pm 0.85 \text{ g/m}^2$ and an average thickness of $98 \pm 1.09 \mu\text{m}$ at 23°C and 50% RH. SCAS (molecular weight $\sim 25,000 \text{ Da}$, Sigma Aldrich, Steinheim, Germany) and chitosan (deacetylation degree $>75\%$, viscosity $\leq 200 \text{ mPa s}$ in 1% acetic acid, molecular weight $\sim 150,000 \text{ Da}$, 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 ($4000\text{--}400 \text{ cm}^{-1}$) 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 Levdiik, Inshakov, Misyurova, and Nikitin (1967).

2.4.2. Non-isothermal thermogravimetric 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 $10^\circ\text{C}/\text{min}$ in the temperature range of $25\text{--}1000^\circ\text{C}$.

*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

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