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Enhanced water vapour barrier and grease resistance of paper bilayer-coated with chitosan and beeswax

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ABSTRACT

In order to overcome the deficiencies of single layer coating, bilayer coated papers were prepared by two separate coating procedures using various combinations of proteins or polysaccharides with beeswax. Among those combinations, chitosan–beeswax bilayer coated paper showed the best water vapour barrier property. It was observed that as the concentration of chitosan solution increased from 1.0 to 3.0 wt%, its water vapour transport rate (WVTR) decreased from 171.6 to 52.8 $g/m^2/d$ but using reduced beeswax coating weight (from 10.1 to 4.9 g/m^2). It also displayed an enhanced performance of grease resistance. Scanning electron microscopy (SEM) showed that beeswax layer was fitted to chitosan layer so closely that these two layers are indistinguishable. Confocal laser scanning microscope (CLSM) further confirmed the existence of an integrated chitosan film between beeswax layer and paper base and a thin composite layer consisting of chitosan and beeswax.

1. Introduction

Paper and paperboard are composed of cellulose derived from wood resources. They are flexible, renewable and biodegradable, and therefore, are widely used as packaging materials. However, because of the hygroscopic cellulose and the porosity of fiber network or paper, physical and mechanical strength of paper-based materials are easily reduced or even lost when they are contacted with moisture during storage and transportation process. For food packaging, grease permeation through paper packaging affects products appearance. Moreover, mass of moisture and oxygen exchange (gain or loss) with surrounding environment would accelerate physical, chemical and microbiological deterioration (Andersson, 2008), and therefore shorten shelf-life of foods. Usually the surfaces of paper and paperboard packaging are coated with fossil-based synthetic polymer to improve barrier property or mechanical strength. In recent years, the replacement of these plastics with natural polymers for surface-coating has become a trend out of necessity in alleviation of energy crisis and environmental protection (Khwaldia, Arab Tehrany, & Desobry, 2010).

Common natural polymers used for paper coating include proteins, polysaccharides and lipids. Films made of proteins, such as zein (Trezza & Vergano, 1994), whey protein (Han & Krochta, 2001), caseinate (Khwaldia, Banon, Desobry, & Hardy, 2004) and polysaccharides like chitosan (Kjellgren, Gällstedt, Engström, & Järnström, 2006), starch (Matsui et al., 2004), alginate (Rhim, Lee, & Hong, 2006), cellulose derivatives, displayed good barrier resistance to grease and oxygen, nitrogen and carbon dioxide, due to the presence of hydrogen bond within inter-/intra-molecules. However, these films are susceptible to moisture because water molecules can easily open the hydrogen bonds and transport rapidly within polysaccharide or protein macromolecules, which results in a deterioration of barrier performance. On the contrary, hydrophobic lipids, such as long-chain fatty acid (Kester & Fennema, 1989a) and waxes (Donhowe & Fennema, 1993), are considered to be effective barriers to water vapour but insufficient to retard grease and oxygen. What is more, lipid film would cause problems with application, brittleness, stability and organoleptic property (Gontard, Marchesseau, & Guilbert, 1995). Hence, considerable work and effort has been put into the combination of lipids and proteins or polysaccharides for surface coating. One of the feasible approaches is to coat paper with a latex-based composite film which was prepared by emulsifying lipids with the assistance of proteins or polysaccharides. It combined the excellent film-forming properties of proteins or polysaccharides and the good water vapour resistance of lipids. However, this kind of film is much less efficient in water vapour barrier performance compared to the corresponding pure lipid films. Apart from the latex technique, composite coating layer could also be obtained by laminating molten lipids on the proteins or polysaccharides pre-coated paper. Bilayer-films composed of cellulose ether–beeswax (Kester & Fennema, 1989b), wheat gluten–lipids (Gontard et al., 1995),

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zein–sorghum wax/carnauba wax (Weller, Gennadios, & Saraiva, 1998) and sodium caseinate–paraffin wax (Khwaldia, 2010) were verified to be effective barriers to the transport of water vapour. Lipids in the form of an integrate film instead of dispersion in substance ensures its efficiency in moisture resistance.

In this study, molten beeswax was cast onto the proteins or polysaccharides pre-coated paper to investigate the water vapor and grease barrier properties. The concentration and coating weight of chitosan was particularly evaluated for the optimization of the bilayer coating conditions. Scanning electron microscopy (SEM) and confocal laser scanning microscope (CLSM) were used to reveal the structures of bilayer coated paper. The key objective was to develop bilayer coated papers for food packaging that could provide both of competitive water vapor and grease resistances compared with plastics.

2. Materials and methods

2.1. Materials

Chitosan (medium molecular weight), sodium alginate (SA), hydroxymethyl cellulose (HMC), hydroxyl starch (HS) and zein (Sigma Aldrich, Canada) were used for the first layer coating on copy paper (Xerox Corporation, with a grammage of ca. 76 g/m^2) and beeswax (F.O.B. Tweed, Ontario, Canada) as the second layer. All other chemicals and reagents were analytical grade and used as received.

2.2. Bilayer coated paper preparation

The main procedure for the preparation of bilayer coated paper is described as follows: certain concentration of proteins or polysaccharides solution were prepared by dispersing corresponding qualities of solid powder and 25 wt% (to proteins or polysaccharides) glycerol which was used as plasticizer, in water or 0.2 mol/L acetic acid aqueous solution (for chitosan) or water/alcohol (3:7 by volume, for zein) with vigorous stirring. Then solutions were filtered using gauze and degassed under vacuum. Paper was first coated with the above solutions on K303 Multicoater (RK Print Coat Instruments Ltd., U.K.) at a speed of 10 m/min and then dried at room temperature for 1 h. In particular, three different concentrations of chitosan, 1 wt%, 2 wt% and 3 wt%, were used for the first layer coating. A thin-layer chromatography spreader (heated to 100 °C) was used to spread molten beeswax (80 °C) over the pre-coated paper. Excess beeswax was scraped off the paper to make the wax coating weight as low as possible.

Before the characterization of various properties, all coated papers were conditioned for 2 days in an environmental chamber of 50% RH and 23 °C. The paper was weighted before and after coating with film-form materials and beeswax separately.

2.3. Water vapor transmission rate (WVTR) measurements

WVTR of all paper samples were performed on IGA-003 (Hiden-Isochema, Warrington, UK) which consists of a high sensitivity microbalance (0.1 μg) and a turbomolecular high vacuum pumping system, in accordance to the methods described in TAPPI standard T464 om-12 (2012) and ASTM E96/E96M-05 (2005). The round paper samples were clamped in a permeation cell which was tightened by six screws (see Fig. 1). The 90% of relative humidity (RH) difference was achieved by saturated potassium nitrate solution inside and flowing dry nitrogen gas at a flow rate of 10 mL/min outside.

After the permeation cell was placed in a chamber, the data was collected after 1 h to allow the transmission to reach a steady state. The chamber temperature was controlled at 38 °C. The weight (including paper sample, permeation cell and salt solution) reduced is proportional to the testing time. The WVTR was calculated according the following equation:

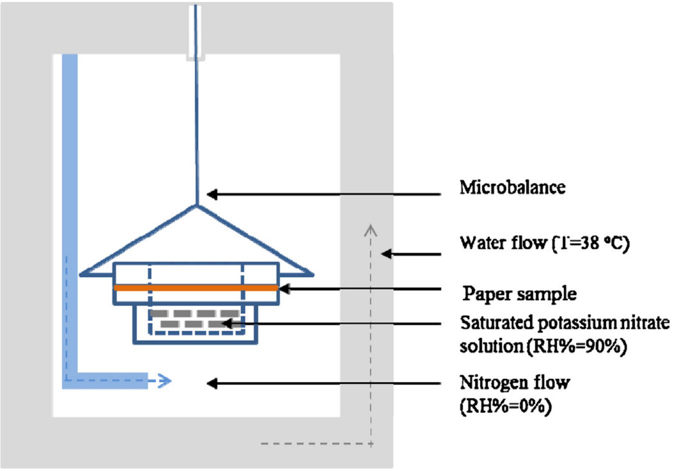

Fig. 1. Schematic illustration of IGA set-up for WVTR testing.

$$\text{WVTR} = \frac{\text{weight reduced}}{\text{area} \times \text{time}}$$

When the film thickness and water vapor pressure difference of both paper sides were considered, water vapor permeability (WVP) was then introduced to reflect the properties of film materials. However, in this study, bilayer coated paper was heterogeneous, which had a relatively denser coating layer and a porous base. The apparent WVP value of these multilayer composites was meaningless because it would fluctuate seriously by not only the thickness of coating layer but also the thickness of paper. The WVP value would have no comparability when coating was applied at papers with varying thicknesses. However, these coated papers samples would have similar WVTR values, at least in the same order of magnitude. Therefore, WVTR, instead of WVP, was used in our research.

2.4. Measurements of grease resistance

The grease resistance was evaluated according to the standard method TAPPI T507 cm-99. However, in our detecting procedure, the area of the stained spots on the stain absorber paper was detected by scanning images, and then determined by calculating pixels using the software-Image Pro Plus (Version 6.0).

2.5. SEM and CLSM

Surface and cross section morphologies of bilayer coated papers were examined with scanning electron microscopy (JEOL 6400 SEM, JEOL Ltd., Japan). Samples were mounted on aluminum stubs using double-sided scotch tape and then coated with about 10 nm gold (S150A SPUTTER coater, Edwards). An accelerating voltage of 15 kV was used to scan the samples.

In order to determine the distribution of chitosan lay in cross section, fluorescein isothiocyanate (FITC) labeled chitosan was prepared according to the method reported by Huang, Khor, and Lim (2004), and detected with confocal laser scanning microscope. Small piece of coated paper was embedded in Epofix resin and polymerized at room temperature overnight. The embedded paper in the block of resin was trimmed and cut in cross-section using a Leica T Ultramucrotome with a Diatome diamond Histo-knife. About one micrometer thick sections were collected from water and heat-sealed onto glass slides and covered with immersion oil and a glass coverslip. Cross-sections of paper samples were