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Wheat-gluten/montmorillonite clay multilayer-coated paperboards with high barrier properties

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ABSTRACT

This study presents the oxygen-barrier properties of paperboards with a wheat gluten (WG)/montmorillonite clay (MMT) multilayer coating, in which MMT was sandwiched between two layers of WG. Urea was added to the WG to facilitate the coating procedure and the clay was applied as an aqueous dispersion. With a coating thickness of ~20 μm, oxygen transmission rates were 8–10 $cm^3/(m^2\ day\ atm)$ at 50% RH, which meant that the oxygen barrier was ca. 25 times better than that given by a single-layer WG-coated paperboard (uncoated paperboard showed infinite values). The water vapor transmission rate (WVTR) was 28–39 $g/(m^2\ day)$ using a 50–0% RH gradient, which was 6- to 8-fold lower than the value for uncoated paperboard. Tensile tests revealed small, if any, mechanical effects when the paperboard was coated. A protein solubility analysis indicated that urea-containing WG films were slightly more intermolecularly cross-linked than urea-free WG films. X-ray diffraction revealed that the MMT layer consisted of unswollen tactoids similar to those observed in the MMT powder. The $Cobb_{60}$ data showed that both WG and clay increased the water absorbency.

1. Introduction

Paper and paperboard are commonly used in packaging applications because of their good mechanical properties, biodegradability, renewability, recyclability and printability (Aloui et al., 2011; Rhim et al., 2007). However, paper-based packaging materials show poor barrier properties against oxygen, water vapor, grease and aroma compounds due to their hydrophilic nature and porous structure (Han et al., 2010). To improve their barrier properties, they are often coated with a synthetic polymer such as latices, polyethylene, poly(ethylene-co-vinyl alcohol), poly(vinylidene chloride), poly(ethylene terephthalate) and polyamide-6 (Hong and Krochta, 2006), but the use of synthetic (petroleum-based) polymers reduces the "renewability", biodegradability and recyclability of the paper/paperboard-based packages (Khwaldia et al., 2010). Thus, there is a growing interest in the use of biodegradable polymers from renewable sources on paper substrates to produce environment-friendly packaging materials (Han and Krochta, 2001; Kjellgren et al., 2006; Ben Arfa et al., 2007; Gastaldi et al., 2007; Rhim et al., 2006).

Different types of proteins, polysaccharides and lipids or combinations of these are used as coatings on paper-based packaging materials (Khwaldia et al., 2010; Weber, 2000). Among the proteins, wheat gluten (WG) is considered to be a valuable candidate for packaging applications due to its low price, biodegradability, renewability, good film forming and adhesive/cohesive properties. It has also been shown that WG-based films have good barrier properties under dry conditions (Türe et al., 2011; Gällstedt et al., 2004; Khosravi et al., 2010).

Dispersion coating, lamination and extrusion coating are common methods used to obtain barrier coatings on paperboard. Dispersion coating is fast and is considered to be a more environment-friendly alternative with regard to composting and re-pulping than conventional lamination or extrusion coating (Schuman et al., 2004; Bollström et al., 2012).

Several studies have been reported where renewable biodegradable polymers such as polylactic acid (PLA) (Rhim et al., 2007), hydroxypropylmethylcellulose (Sothornvit, 2009), soy protein (Rhim et al., 2006), zein (Trezza et al., 1998), chitosan (Ham-Pichavant et al., 2005), whey protein isolate (Chan and Krochta, 2001) and wheat gluten (Guillaume et al., 2010) have been applied to paper/paperboard by dispersion/solution coating. Most of these studies focus on improving the oxygen-, water-vapor- or grease-barrier properties. Previous work has indicated that it is still a great challenge to obtain barrier properties on the same level as those of

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the best synthetic polymers. The incorporation of montmorillonite clay into polymers is expected to enhance the barrier properties, but success has been limited since it has been difficult to achieve a homogeneous dispersion of the clay in the polymer (Sinha Ray and Okamoto, 2003).

In this work, we present a novel approach to improve the barrier properties of paperboard using a wheat gluten/montmorillonite clay (MMT) multilayer coating. In this multilayer structure, wheat gluten was used as the first barrier layer (on top of the pre-coated paperboard) and the top layer, while MMT was deposited between the two WG layers. The main purpose of the study was to investigate the effect of the WG–clay multilayer on the oxygen- and water-vapor-transmission properties of the paperboard. The idea of using a separate clay layer was to have locally as high concentration of clay as possible in order to effectively reduce the permeability.

2. Materials and methods

2.1. Materials

The commercial WG powder was kindly supplied by Lantmännen Reppe AB, Sweden. It had a gluten protein content of 77.7% of the dry weight (modified NMKL Nr6, Kjeltec, Nx5.7, (www.NMKL.org). Glycerol (99.5%) was supplied by Karlshamn Tefac AB, Sweden. Urea (≥99.5 wt.%) was purchased from Merck (Darmstadt, Germany). Sodium sulphite (98.0%) and anhydrous acetic acid (98.0%) were purchased from Sigma–Aldrich. Cloisite® Na^+ (natural sodium-rich montmorillonite, MMT) was obtained from Southern Clay Products, Inc. (USA). The paperboard, Korsnäs Duplex 260, supplied by Korsnäs Paper AB, Sweden, had a grammage of 242 g/m^2 and a thickness of 0.4 mm. The bottom layer consisted of unbleached softwood sulphite pulp and the middle layer of unbleached chemi-thermomechanical pulp (CTMP). The top layer consisted of a blend of bleached softwood and hardwood pulps. The board was made hydrophobic with a dual sizing agent of alkyl ketene dimer (AKD) and rosin. Two types of paperboard were obtained by pre-coating the bottom layer with a ~5.5 μm (type 1) and ~7 μm (type 2) layer of a commercial filler-containing barrier product (BIM BA8877, BIM Kemi AB, Stenkullen, Sweden). The effect of the pre-coating was to fill the pores of the paperboard and hence to reduce the absorption of the WG mixture into the paperboard. The air permeance of the paperboard of types 1 and 2 was 12 and 5.2 nm/Pa s and the grease resistance was 280 and 680 s, respectively. When referring to uncoated paperboard below it means the paperboard with the precoating but without the WG and clay layers.

2.2. Preparation of the coating mixture

The WG mixture was prepared by first dissolving 2 g of urea powder in 50 g deionized water containing 0.05 g of sodium sulphite using a magnetic stirrer. 20 g of WG powder was then added and the mixture was stored at ambient temperature for 30 min. After settling, any remaining air bubbles were removed from the mixture with a spatula and the pH of the WG mixture was adjusted to 4 with acetic acid. Finally, glycerol (38 wt.%, based on the total weight of WG and glycerol or 15 wt.% based on the total mixture) was added and the mixture was stirred with a magnetic stirrer for 45 min.

In order to prepare the clay slurry, MMT was mixed with deionized water at a weight ratio of 10:90 (MMT:water) using a homogenizer (IKA, 31 300 00) at 8000 rpm for 25 min.

2.3. Coating procedure

Prior to the coating, paperboard specimens were mounted on a flat bench table with tape applied around their edges to prevent wrinkling during the coating process. An Erichsen Applicator (Model 360 99227) with a 120 μm slit distance was used to deposit the coating mixture on the pre-coated side of the paperboard. For the multilayer coatings, the WG and clay solutions/dispersions were deposited on the paperboard sequentially. The paperboard was initially coated with a WG mixture as a first layer. After drying for two days under ambient conditions, the aqueous MMT dispersion was deposited on the WG layer and the drying process was repeated. Finally, a WG mixture was applied onto the clay layer as a top coating. The coated paperboards were allowed to dry under ambient conditions for three days. The following notation is used in this study; 1 + WG – c – WG indicates type 1 paperboard coated with WG, clay and WG. For protein solubility measurements, single WG films were produced by pouring 10 g of the WG mixture into plastic petri dishes and allowing the mixture to dry under ambient conditions. Pure MMT films were prepared, as described above, in plastic petri dishes from the aqueous MMT dispersion for X-ray measurements.

2.4. Oxygen permeability

The oxygen transmission rate (OTR) was determined in accordance with ASTM D 3985-95, at 23 ± 1 °C and 50 ± 1% RH, using a Mocon Ox-Tran 2/20, from Modern Controls, Inc., MN, USA. The test pieces were mounted in isolated diffusion cells that were subsequently purged with nitrogen gas (2% hydrogen) in order to measure the background oxygen leakage of the instrument. Each specimen was tightly sandwiched between two aluminum foils so that an area of 5 cm^2 was exposed for the measurements. One side of the sample was exposed to flowing oxygen (99.95%) at atmospheric pressure. The oxygen transmission rate was normalized with respect to the atmospheric pressure and coating thickness to yield the oxygen permeability (OP). Two replicates from each sample were used.

2.5. Water vapor transmission rate

The water vapor transmission rate was measured on two replicates of each sample using a Mocon Permatran-W 3/31 according to ASTM F 1249-90 at 23 ± 1 °C with a 50–0 ± 1% RH gradient across the film sample. Specimens were tightly sandwiched between two pieces of aluminum foil leaving a 5 cm^2 exposure area for the WVTR measurements. Before the measurements, the specimens were conditioned in isolated diffusion cells with one side at 50 ± 1% RH and the other side facing dry nitrogen gas.

2.6. Water absorbency by the $Cobb_{60}$ method

The water absorption of the paperboards was measured using the $Cobb_{60}$ method described by Cho et al. (2012), with some modifications. Samples were cut into dimensions of 10 × 10 cm^2 and conditioned at 23 ± 1 °C and 50 ± 1% RH for one week before measurement. The measurements were performed using an L&W Cobb Sizing Tester (Lorentzen & Wettre, AB, Kista, Sweden) at room temperature. A preconditioned paperboard was placed in the apparatus with the coating facing up and 100 mL of distilled water was poured onto the surface of the paperboard. After 45 s, the water was poured off and the test piece was removed from the instrument after an additional 15 s. The residual water on the surface was removed by shaking the samples gently for 2 min. The $Cobb_{60}$ value (X, g/m^2), i.e. the absorption during 60 s, was determined as $X = (W_2 - W_1)/A$, where W_1 and W_2 are the weights of the paperboard before and