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Beeswax–chitosan emulsion coated paper with enhanced water vapor barrier efficiency

Weiwei Zhang[a,b], Huining Xiao[a,*], Liying Qian[b]

[a] Department of Chemical Engineering, University of New Brunswick, 15 Dineen Drive, Fredericton, NB E3B 5A3, Canada
[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

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ABSTRACT

For lipid–hydrocolloid emulsion based film, the increase of lipid amount would improve its water vapor barrier property, but also reduce the mechanical strength of the film in the meantime thus leading to a compromised lipid content in the film. However, when the emulsion is coated on paper surface, more lipid could be used for emulsion preparation to enhance the moisture resistance without considering the weakened strength of the film induced by lipid, because the mechanical properties of emulsion coated paper is mainly governed by the strength of base paper instead of the coating layer. In this study, beeswax–chitosan emulsion was first prepared and then coated on paper surface to improve paper's water vapor barrier and water resistance properties. The range and variance analysis of orthogonal test design showed that the order of priorities of the factors accordingly was beeswax solid content, drying temperature and chitosan concentration. The effect of drying temperature on water vapor transmission rate (WVTR) and water contact angle of coated paper was further investigated using 1.2 wt% chitosan and 96% beeswax solid content in the coating layer. The results indicated that water vapor barrier property was in accordance with the density of the coating layer. Atomic force microscope (AFM) was also used to characterize the surface morphology and explain the hydrophobicity of beeswax–chitosan coated paper. It was found that surface beeswax particles melted to wrinkle at high drying temperatures, while roughness values maintained at micro-scale over the temperature range investigated.

Introduction

In recent decades, green packaging has attracted substantial interests from both laboratorial research and industrial applications [1–3]. Proteins, polysaccharides and lipids are the three main green-based materials, which are often used to coat paper surface via filming for packaging application. Films formed by proteins and/or polysaccharides possess excellent mechanical properties and barrier resistance to oxygen, nitrogen and carbon dioxide due to the presence of hydrogen bond within inter-/intro-molecules. However, these films are susceptible to moisture because water molecules can easily open the hydrogen bonds and transport rapidly within polysaccharide or protein chains. On the contrary, hydrophobic lipids display effective barriers to moisture but inferior in structural strength. Therefore, composite films are explored to combine the good structural properties of hydrocolloid with good moisture barrier characteristics of lipids [4,5]. To take advantage of water vapor barrier property of lipids, they are usually used in the form of hydrocolloid-based emulsion or lamination on hydrocolloid film. Although water vapor transmission rate is much larger in emulsion-based film than in laminated bilayer film [6], the former has its advantages in mechanical properties and only requires one step for film-forming. Since emulsion-based film can be dried at room temperature, it is favored in some foods and fruits packaging as edible film to extend their shelf lives [7,8]. Moreover, delamination, which is a potential problem in lamination film, would never happen to emulsion film [9,10].

In traditional emulsion-based films, lipid particles, typically kinds of waxes, are dispersed in continuous matrix such as polysaccharides or proteins. The presence of lipid particles only prolongs the transfer distance of water molecules, since moisture migrates much more rapidly in hydrophilic matrix than in lipid phase. Obviously, lipid content and its globule size influence the final water vapor barrier property of emulsion-based film [11–13]. Enhancing the "apparent tortuosity" of the film could be obtained by increasing lipid content or decreasing its globule size. However, the addition of lipids to hydrocolloid-based film based on saccharides or proteins, often leads to a decrease of mechanical properties, which means that the in lipid content in edible film should be controlled in a certain range. In fact, an apparent bilayer structure

* Corresponding author. Tel.: +1 506 453 3532; fax: +1 506 453 3591.
E-mail address: hxiao@unb.ca (H. Xiao).

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within the emulsion-based film can be produced through drying process. In a relative high temperature, lipid emulsion stabilization decreases with phenomena such as creaming, aggregation and/or coalescence, resulting in a hydrophobic layer on the upper side. The lower part of the emulsified film mainly consists of a homogeneous hydrocolloid matrix network [14]. This also well explains the water vapor permeability (WVP) difference of the same emulsion-based film, prepared at high temperature, when it was measured on a test cup facing either the low relative humidity (RH) environment ("facing up") and the high RH environment ("facing down") [15].

Cellulose based paper and paperboard are green packaging materials due to their renewability, recyclability and biodegradability. However, prior to industrial application in packaging, paper needs to be coated with other materials like polyethylene, polyethylene terephthalate, polybutylene terephthalate, etc., to improve their water or water vapor barrier properties. These fossil derived polymers are difficult for either recovery or degradation. Thus, they have been gradually replaced by biopolymer materials in papermaking industry for surface coating nowadays. Beeswax, as a typical green-based commercial wax, has been widely used as food grade additive in cosmetics manufacturing, pharmaceutical industry and food industry. Due to its high hydrophobicity and excellent moisture resistance, beeswax is a favorable candidate for preparation of edible film with combination of polysaccharides or proteins [16,17].

In this work, beeswax–chitosan emulsion was prepared and then used for paper surface coating. The effects of chitosan concentration, beeswax content and drying temperature on water vapor permeability and wetting ability of the emulsion film coated paper were examined using range and variance analysis of orthogonal array experimental design. With relatively high beeswax content in the coating layer, which has not been reported previously, the influence of drying temperature on water vapor barrier and hydrophobicity was further investigated. The key objectives of this work were to reveal the influence of beeswax on moisture barrier property of the emulsion-based film; and to create the paper coater with green-based emulsion with enhanced moisture barrier property for packaging application.

Materials and Methods

Materials

Chitosan (medium molecular weight) was supplied by Sigma Aldrich (Canada) with 75–85% deacetylated. Bleached beeswax was obtained from F.O.B. Tweed (Ontario, Canada). Copy paper, received from Xerox Corporation (Canada, in a grammage of about 75 g/m^2) was used as base paper for coating. Other chemicals and regents were chemical pure and used without further purification.

Preparation of beeswax–chitosan emulsion and paper surface coating

Chitosan solution was prepared by dispersing x g chitosan powder in 100 mL diluted acetic acid solution which contained x g acetic acid, at room temperature for at least 1 h under a 500 rpm magnetic stirring ($x = 1, 2, 3$). Glycerol was added in a chitosan-plasticize ratio of 4:1 for all chitosan solutions. Then the chitosan solutions were heated up to around 80 °C in a water bath to melt certain amount of beeswax. The weight of beeswax was added precisely such that it occupied 30 wt%, 60 wt% and 90 wt% of the emulsion film dry matter. Homogenization was carried out using a high-shear probe mixer (Power Tool X120, Ingenieurbüro CAT, Germany) for 3 min at 28,000 rpm. After that, the hot beeswax–chitosan latex was quickly cooled to room temperature in an ice bath.

Copy paper was coated with the beeswax–chitosan latex on K303 Multicoater (RK Print Coat Instruments Ltd, U.K.) with a bar coating speed at10 m/min and then dried at varying temperatures for 2 h.

WVTR and water contact angle 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 [18] and ASTM E96/E96M-05 [19]. The round paper samples were clamped in a permeation cell which was tightened by six screws. The 90% of relative humidity (RH) difference was produced 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 water vapor 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:

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

Water contact angle measurements were performed using Theata Optical tensiometer (Attension, Finland). A C311 automatic single liquid dispenser is used to automatically dispense a precise volume of water drop (5 μL) and then descended until the drop contacted with paper samples. It was raised again such that the water drop stayed at sample surface. An image of water drop, taken by a camera of the instrument, was analyzed by Attension software to obtain the water contact angles. Each paper sample was measured at least five times to get its average value.

Orthogonal test design

The major factors, chitosan concentration (factor A), beeswax content (factor B), drying temperature (factor C), were arranged in an orthogonal array experimental design (3^4 matrix), as seen in Table 1. Each column was assigned to a factor and the last column was used to indicate experimental error. Data was analyzed through range analysis and variance analysis to optimize the coating film preparation conditions. In the range analysis, sum or mean of the evaluation indexes of each level in each factor was used to determine the optical level and the optical combination of factors. In the variance analysis, F value, the ratio of the sum of the square of each factor's mean deviation to that of the experimental error, was introduced to indicate the magnitudes of each factor effects.

Characterization

Surface morphology of beeswax–chitosan emulsion coated paper was characterized using AFM (Nanoscope IIIa, Veeco Instruments, CA) in tapping mode with a silicon tapping probe (NP-S20) with setting of 512 pixels/line and 1 Hz scan rate.

Results and discussion

Under acidic condition, chitosan showed excellent capacity as an emulsifier to prepare stable lipid latex due to the electrostatic interaction between positively-charged chitosan with negatively-charged lipids or beeswax [20]. The negative charges on beeswax could be contributed from the carboxyl groups presented in the wax. The particle size of beeswax–chitosan emulsion ranged from 400 to 1000 nm and phase separation occurred after standing for