



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



Weiwei Zhang^{a,b}, Huining Xiao^{b,*}, Liying Qian^a

^a State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

^b Department of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3, Canada

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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/m²/d but using reduced beeswax coating weight (from 10.1 to 4.9 g/m²). 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.

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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 (Khwalidia, Arab Tehrani, & 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 (Khwalidia, 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),

* Corresponding author. Tel.: +1 506 453 3532; fax: +1 506 453 3591.

E-mail address: hxiao@unb.ca (H. Xiao).

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/m²) 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

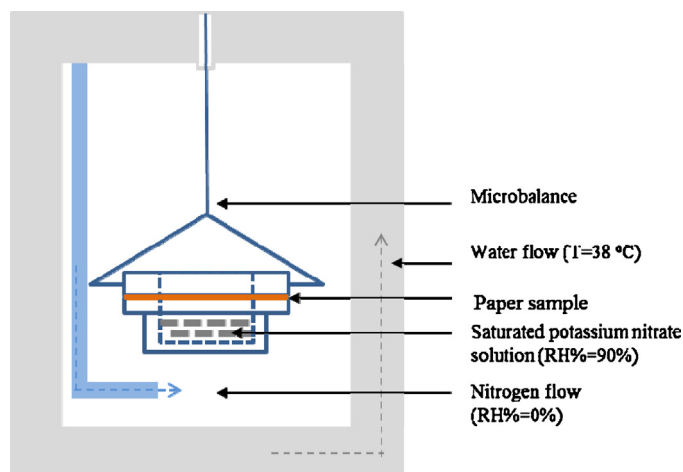


Fig. 1. Schematic illustration of IGA set-up for WVTR testing.

(including paper sample, permeation cell and salt solution) reduced is proportional to the testing time. The WVTR was calculated according the following equation:

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

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 Ultramicrotome 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

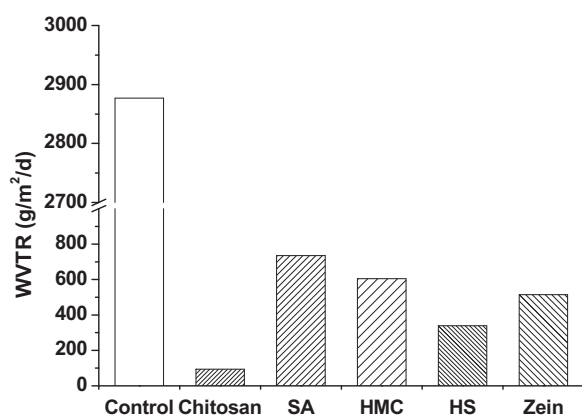


Fig. 2. WVTR of control and the paper samples coated with chitosan-, SA-, HMC-, HS- and zein-beeswax.

photographed in bright field and fluorescence mode on a Leica DM R Upright light microscope with a DC 500 Leica digital camera.

3. Results and discussion

3.1. WVTR comparison of bilayer coating

The measured WVTR of control paper was as high as 2877 g/m²/d (Fig. 2). This was attributed to the obvious pore structure of fiber-based paper and the hydrophilic fibers. When these pores were filled with beeswax by dip coating (surface excess beeswax was absorbed), its WVTR was still kept at around 500 g/m²/d. Application of a bilayer coating consisting of proteins or polysaccharides and beeswax reduced WVTR at least one order of magnitude. The high efficiency of beeswax as a moisture-barrier is likely related to both of its chemical composition and physical structure. Since molten beeswax could easily permeate into paper base, which resulted in a massive coating weight but inferior barrier property (dip coating), it was necessary to pre-coat with proteins or polysaccharides to make up the smoothness deficiency of porous paper before beeswax coating.

The water vapour barrier property of bilayer coated paper was also associated with film-forming behavior of coating materials. The abilities of decreasing WVTR were in the following order: chitosan → hydroxylated starch → zein → hydroxymethyl cellulose → sodium alginate/beeswax. The WVTR of paper coated with SA-beeswax was 735.6 g/m²/d, while with chitosan-beeswax, the WVTR was decreased to 93.6 g/m²/d. The dramatic difference among these protein-/polysaccharide-beeswax combinations was unexpected since these film-forming materials were considered to seal porous paper surface and then render beeswax as a continuous layer. The possible reasons could be explained in two aspects. First, the roughness of the first coating layer determined the coating weight of beeswax, which directly influenced the final water vapour barrier property. Second, the cohesion between proteins/polysaccharide and beeswax layers might have a “boundary effect” on WVTR measurement. Since chitosan was insoluble in water in the absence of acetic acid or pH higher than 5, it could be inferred that chitosan was most “hydrophobic” among the tested materials, therefore, the chitosan-beeswax combination had some mutual interaction between chitosan and beeswax molecules to reduce WVTR values.

3.2. WVTR of chitosan-beeswax coated paper

Chitosan had an excellent film-forming property (Fang, Chen, Liu, & Chai, 2012). The films made of chitosan displayed smooth

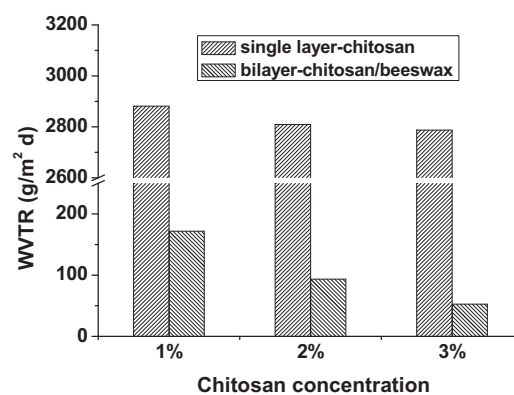


Fig. 3. The effect of chitosan concentration on WVTR of coated paper.

surface and good oxygen resistance. However, its water vapour barrier property was quite limited due to its hydrophilic nature. As shown in Fig. 3, the WVTR of only chitosan coated paper was slightly reduced comparing to blank paper. Even for the sample using 3 wt% chitosan, the reduction of WVTR was less than 100 g/m²/d compared to the blank control (Fig. 2). In contrary, after coated with hydrophobic beeswax, the WVTR significantly decreased to the value of less than 200 g/m²/d. More than that, the water vapour barrier property was enhanced as the chitosan concentration increased. The best WVTR of bilayer coated paper using 3 wt% chitosan-beeswax was reduced to 52.8 g/m²/d. When the coating weight was taken into account, an interesting phenomenon was observed. As can be seen in Fig. 4, it was reasonable that chitosan coating weight increased when a high concentration of chitosan solution was applied (mainly due to a high viscosity). However, the second coating layer showed an opposite trend in terms of coating weight. That meant paper coated with the least beeswax coating weight (4.9 g/m²) displayed the best resistance to water vapour (52.8 g/m²/d).

The water vapour permeability (P) of beeswax, reported by Donhowe and Fennema (1993), was $5.81 \pm 0.26 \times 10^{-13}$ g/m/s/Pa at 25 °C; and activation energy (E_p) for permeation of water vapor through beeswax film was 29 ± 3 kJ/mol. According to Arrhenius equation:

$$P = P_0 e^{-\frac{E_p}{RT}}$$

the calculated water vapor permeability of beeswax should be 9.47×10^{-13} g/m/s/Pa at 38 °C. In a cup method for WVTR testing, the diffusion flow of water vapor through the covered film did not

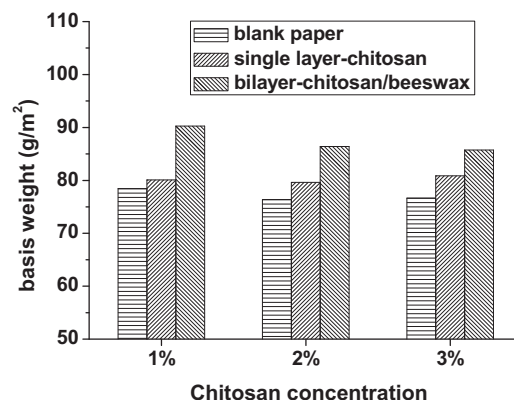


Fig. 4. The effect of chitosan concentration on coated paper basis weight.

Table 1
The grease resistance of single-layer and bi-layer coated paper.

Chitosan concentration (h)	1%		2%		3%	
	Single-layer	Bi-layer	Single-layer	Bi-layer	Single-layer	Bi-layer
4	0	0	0	0	0	0
8	0	0	0	0	0	0
12	0	0	0	0	0	0
24	758	0	0	0	0	0
48	1623	0	0	0	0	0

The grease resistance was measured at room temperature (ca. 25 °C). Single-layer represented that paper was coated with chitosan alone while the bilayer meant that paper was coated with chitosan and beeswax.

change over time when the system reached in a steady state. Thus, WVTR could be calculated from the following equation:

$$\text{WVTR} = \frac{P\Delta p}{l}$$

where Δp is the water vapor difference between both sides of film, and l is the thickness of film. Suppose that beeswax on pre-coated paper formed an intact and thickness-uniform film, and the effect of chitosan layer on its final WVTR was negligible (seen the WVTR results of single layer and bilayer coating in Fig. 3), the calculated beeswax layer thickness needed to be 9.8 μm (equivalent coating weight at 9.5 g/m²) to reach the targeted WVTR at 50 g/m²/d. However, in sample of 3 wt% chitosan–beeswax bilayer coating, only about half of the theoretical beeswax coating weight (4.9 g/m²) was used to reduce the WVTR of coated paper to 52.8 g/m²/d. It seemed coating weight of beeswax was not the only reason for water vapour barrier property of coated paper. There might be some synergistic interactions between chitosan and beeswax layer which led to better water vapour resistance than the pure beeswax film.

3.3. Grease resistance of chitosan–beeswax coating

The ability of chitosan–beeswax coated papers to retard grease was carried out at room temperature instead of 60 °C as specified in the TAPPI standard T 507 cm-99, because the morphology of beeswax was between solid and liquid at 60 °C and the polymorphic

transitions of beeswax had already changed from an orthorhombic to a rotator phase (Gaillard et al., 2011).

The results of the grease resistance for coated paper were listed in Table 1. As expected, chitosan coated paper showed excellent grease resistance. There were no stained oil spots detected on all of the stain absorber papers except for the sample coated with only 1.0 wt% of chitosan after 24 h. Paper coated with 1.0 wt% chitosan–beeswax also successfully prevent grease from permeating, indicating that the ability of grease resistance was improved with assistance of beeswax. The reinforcement might be attributed to improved surface deficiency with beeswax casting. However, it was noticeable that the red grease spots appeared on the testing paper in the first two groups after 48 h, while no stain on the surfaces for the third group of samples, which implied that grease permeation still happened but the velocity was extremely low in the first two groups. It was also reflected in the beeswax coating weight that in the third group the usage was least because beeswax was totally isolated at chitosan film surface. That meant only an intact chitosan film could completely prevent grease from permeating into paper base and beeswax coating layer played a subsidiary role in grease resistance in the bilayer coated paper.

3.4. Surface and cross section morphology

Paper is composed of interlaced fibers and its surface displayed a porous structure. When chitosan solution was coated on paper,

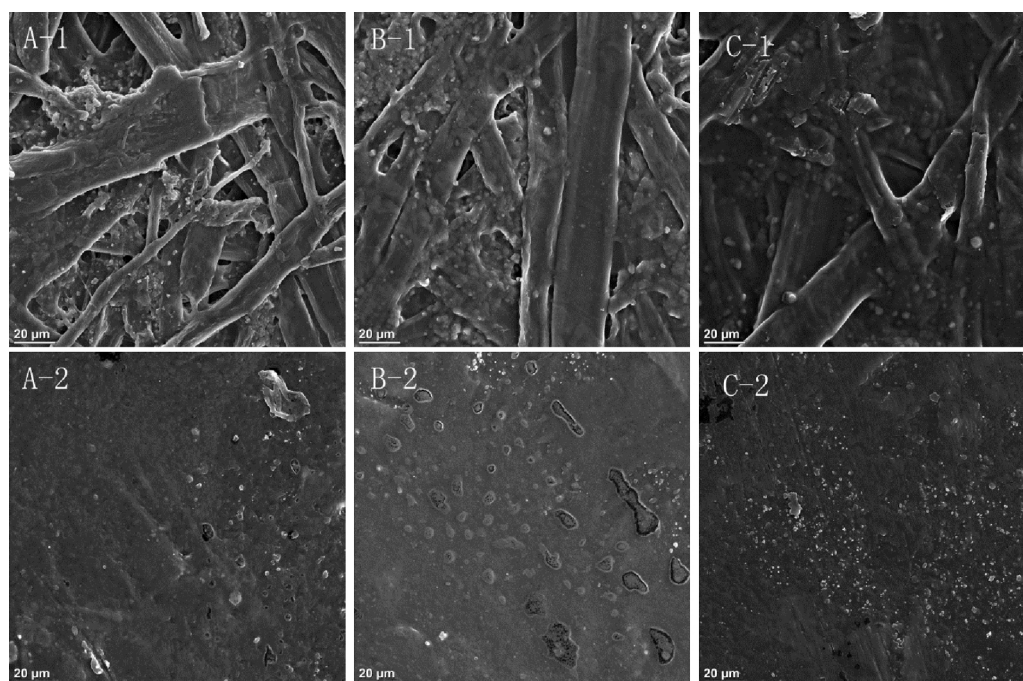


Fig. 5. The SEM images of the paper pre-coated with chitosan at the concentrations of 1.0 wt% (A-1), 2.0 wt% (B-1), 3.0 wt% (C-1) and the corresponding bilayer-coated paper with beeswax: 1.0 wt% chitosan–beeswax (A-2), 2.0 wt% chitosan–beeswax (B-2), 3.0 wt% chitosan–beeswax (C-2).

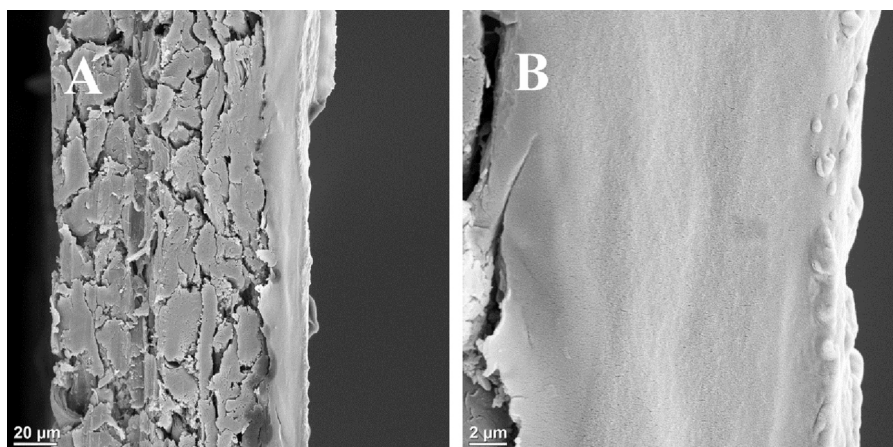


Fig. 6. The SEM images of the cross section of 3% chitosan-beeswax coated paper (A) and bilayer coating layer partial enlargement (B).

the surface pins or tiny voids were filled and the roughness was deduced significantly. Electron microscopic images of single-layer and double-layer coating were shown in Fig. 5. Obviously, the surface smoothness of chitosan pre-coated papers was improved as the concentration of chitosan increased. For the paper coated with chitosan (1.0 wt%), the pins were still visible on the surface; whereas the one treated with chitosan (3.0 wt%), an intact chitosan film covered on fibers and almost all the tiny air space among fibers was filled. After the casting of beeswax, the surfaces of three kinds of pre-coated papers appeared to be smooth and uniform. It was concluded that molten beeswax was held on the top surface because of chitosan layer. The coating weight of beeswax depended on the integrity of chitosan film. If the surface pins or tiny voids existed, the coating weight could increase since molten beeswax would penetrate into paper base.

From the SEM images of the cross section of 3.0 wt% chitosan-beeswax coated paper shown in Fig. 6, the coating layer was firm

and compact, without structural defects. Although bilayer coating was carried out separately, no visible lamination occurred between the two layers. It confirmed previous conjecture that chitosan and beeswax layers were combined strongly. The composite coating layer attached tightly on paper surface. To further demonstrate the bilayer formed after sequential coating, the fluorescent-labeled chitosan was used and the resulting coated paper was observed using CLSM. As can be seen from CLSM images in Fig. 7, beeswax was completely obstructed at film surface and the majority of chitosan stayed between beeswax layer and base paper. Small amount permeated into superficial spaces among fibers. This laminating technology implied that the minimized penetration of the functional coating materials into the substrate was required to ensure the efficiency of barrier property (Andersson, 2008; Kimpimäki & Savolainen, 1997). It could be inferred that chitosan of lower concentration (1.0 wt%) would lead to greater infusion and therefore, some of molten beeswax permeated through those small pins and

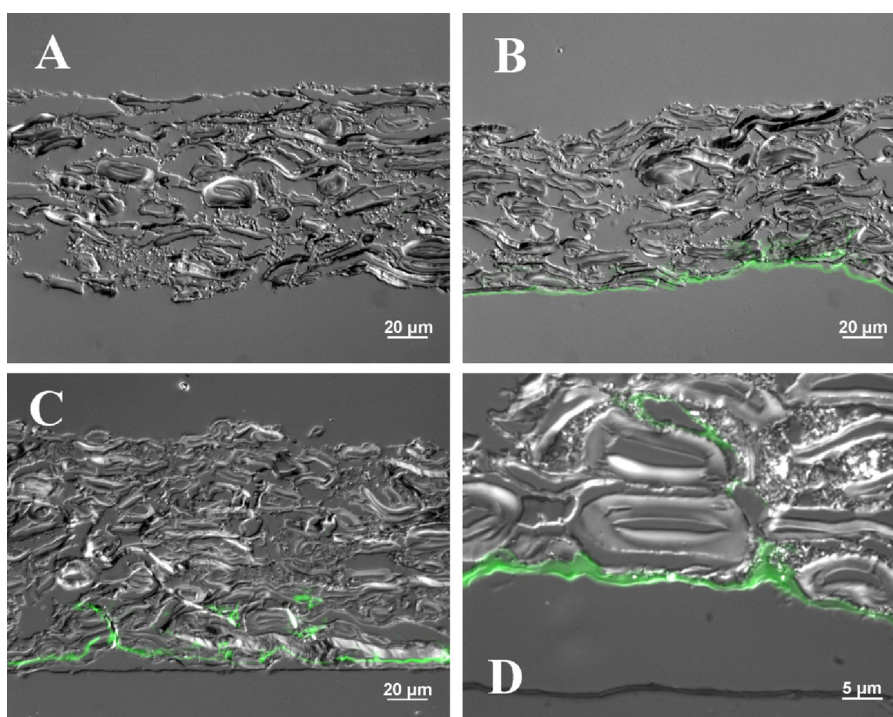


Fig. 7. Representative CLSM images of cross section in blank paper (A), chitosan coated paper (B), beeswax/chitosan coated paper (C) and partial enlargement of beeswax/chitosan coated paper (D).

holes (seen in Fig. 5, A-1 and A-2) which resulted in higher beeswax coating weight but worse water vapour barrier property. In the high-magnification image of chitosan–beeswax interface shown in Fig. 7D, a thin composite layer that belonged to beeswax layer but labeled in green was observed, thus demonstrating that chitosan was also included in this layer. This special layer might be formed through permeation of small amount of molten beeswax into chitosan layer in a thickness of less than 1 μm , named as synergistic interaction or “interface effect” between chitosan and beeswax layer, which explained the difference of coating weight between actual and theoretical values to reach specific WVTR values.

4. Conclusions

Among chitosan–, SA–, HMC–, HS– and zein–beeswax bilayer coated papers, chitosan–beeswax coating showed the best water vapour barrier property. An integrate chitosan film could be formed on the paper surface with high concentration (i.e. 3.0 wt%), resulting in a lower coating weight of beeswax but a reinforced water vapour resistance property. This is attributed to the minimized penetration of beeswax into base paper obstructed by chitosan (SEM and CLSM observation), and to the synergistic interactions between chitosan and beeswax layer (comparison of coating weight between actual and theoretical values). In respect to the grease resistance of bilayer coated paper, chitosan played a critical role while beeswax could promote its barrier efficiency.

Acknowledgments

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