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Research paper

# Effects of formation and penetration properties of biodegradable montmorillonite/chitosan nanocomposite film on the barrier of package paper

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ABSTRACT

The conventional package paper was coated with biodegradable montmorillonite/chitosan nanocomposite, in order to extend the application scope of paper. The effect of coating weight, montmorillonite dispersion rate, montmorillonite and dispersant content on the surface and penetration properties of montmorillonite/chitosan nanocomposite coated paper were being investigated. The surface properties of the coated paper were observed by using scanning electron microscope (SEM) and atomic force microscope (AFM). The water permeation and water vapor barrier properties were confirmed through penetration dynamics analyzer (PDA) and water vapor permeability tester (WVP), respectively. The results indicated that montmorillonite/chitosan nanocomposite had a poorer formation than pure chitosan, but it had better water vapor barrier properties. The paper coated with lower content of montmorillonite, or with higher dispersion speed and dispersant content, had better smoothness and elongation. Additionally, the coated paper had excellent barrier properties under the conditions of high montmorillonite and dispersant content, dispersion rate and coating weight.


## 1. Introduction

Due to environmental pollution and resources shortage had limited the development of packaging materials, people began to turn attention to bio-based materials. Bio-based packaging materials are made from cellulose, starch, protein, chitosan and their bio-derivative, which chitosan is widely favored because of its good film, biocompatible, biodegradable and antibacterial properties (Kampeerapappun et al., 2007; Dias et al., 2014; He et al., 2014).

Biodegradable paper was a kind of conventional packaging material and applied widely in the packaging sector. Paper consisted mainly of natural plant fibers. Fibers connected each other by hydrogen bonding. Because the main compositions of fibers were hydrophilic cellulose and hemicellulose, paper was hydrophilic and porous. So paper has weaker the barrier properties against oxygen and water vapor penetration, compared with plastics material. Pure chitosan had a disadvantage for the application in the high-humid condition because of its hydrophilic nature and its poor mechanical properties. Moreover, its thermal stability, hardness, and gas barrier property were not adequate enough to meet the wide ranges of potential applications (Reis et al., 2011; Lertsutthiwong et al., 2012; Lewandowska et al., 2014). But the barrier of paper against water vapor and oxygen could be improved by coating montmorillonite/chitosan nanocomposite (Mt/Cs) on the surface of paper (Xu et al., 2005).

The addition of layered silicates and in particular montmorillonite (Mt) in chitosan has been extensively studied in some fields. (Han et al., 2010; Kittinaovarat et al., 2010; Hsu et al., 2012; Azhar and Olad, 2014; Giannakas et al., 2014). Mt, a clay mineral, is the most widely used silicate in polymer nanocomposites (Lin et al., 2005). Mt is a dioctahedral smectite with a total (negative) layer charge between 0.2 and 0.6 per half unit cell. Its layer consists of an Al-O octahedral sheet sandwiched between two *Si*-O tetrahedral sheets. The sheets are covalently connected by common oxygen atoms (Brigatti et al., 2006). Because of the hydrophilic and polycationic nature of chitosan in acidic media, this biopolymer has good miscibility with Mt and can easily intercalate into the interlayer spaces by means of cationic exchange (Wang et al., 2005). It has been proved that chitosan has been intercalated via ionic exchange into negatively charged Mt interlayer spaces (Margarita et al., 2003). Salcedo et al. (2014) studied the intestinal permeability of oxytetracycline from montmorillonite/chitosan nanocomposite. Giannakas et al. (2014) investigated the characterization, mechanical and water barrier properties of montmorillonite-chitosan nanocomposite and found that a reflux treatment of solution led to a significant improvement of the tested properties of montmorillonite-chitosan nanocomposite films. It had research on the effect of the Mt concentration on the mechanical, barrier properties (Pechyen and Ummartyotin, 2016).

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In order to improve the barrier of traditional package paper against water and vapor, the paper focused on studying the surface properties of package paper by coating montmorillonite/chitosan nanocomposite on the surface of paper. The film forming property and film permeability property were also researched. The effect of Mt dispersion rate, the content of Mt and dispersant in the mixed solution on the surface properties and barrier properties of the coated paper were studied. Scanning electron microscope (SEM), atomic force microscope (AFM), and penetration dynamics analyzer (PDA) were used to analyze the film formation and permeability of montmorillonite/chitosan nanocomposite.

## 2. Materials and methods

### 2.1. Materials

The basis weight of kraft paper was 120 g/m$^2$ (smoothness: 18.5 s with Bekk smoothness tester, elongation: 1.51% with Frank tensile testing machine). Chitosan (Cs) (degree of deacetylation of 80% to 95%, the molar mass (Mm) is about $1.26 \times 10^5$ g/mol), supplied by Guoyao Chemical Co., Ltd., China. The acetic acid (99%), was obtained from Nanjing Chemical Industry Group (China). Montmorillonite (Mt) was bought from Beijing Yue Wei specialized technology companies. Sodium polyacrylate as a dispersant was purchased from Ningbo Jiahua (China).

### 2.2. Preparation of montmorillonite/chitosan nanocomposite

Montmorillonite/chitosan nanocomposite (Mt/Cs) were prepared by the solution intercalation method. 200 g 1.5 wt% chitosan acetic acid solution was prepared, which the dosage ratio of chitosan (dry weight) to glacial acetic acid was 1:0.5. Then added the Mt dispersion (be dissolved in 1.0 wt% glacial acetic acid), which the content of Mt (dry weight) with respect to the weight of chitosan (dry weight) respectively was 2%, 5%, and 8%. The dispersion speed of Mt dispersion was respectively 1200 rpm, 1500 rpm, and 1800 rpm. The content of dispersant was respectively 0.5% and 0.9% of the Mt (dry weight). The mixed solution was magnetically stirred for 4 h, then purified by the 200 mesh sieve filter and standing for 30 min to eliminate foam.

### 2.3. Coating and calendering

The kraft paper were single-side coated by the roll coating machine (PK Print Coat Instruments Ltd., Litlington, Royston, Herts, SG8 0QZ, U.K.). Then the coated paper were dried in the electric heated blast drying oven (105 °C) and calendered by the Calender (pressure 1 MPa). After calendered, the coated paper were placed at the constant temperature and humidity environmental to balance water.

### 2.4. SEM and AFM

Scanning electron microscope (SEM) was applied to observe the surface coverage of nanocomposites. The sample paper was imaged with the FEI Quanta 200 environmental scanning electron microscopy (SEM) at 15 kV acceleration voltage. Through the test of atomic force microscope, it can see the change of surface Root Mean Square (RMS) roughness of the coated paper. The sample paper was drawn in a 2-dimensional and a 3-dimensional picture with supporting software NanoScope Analysis 1.40.

### 2.5. The paper surface properties analysis

The smoothness and elongation properties of the coated paper were tested according to GB/450-455/1989.

### 2.6. Penetration dynamics analysis (PDA)

PDA was used to study the properties of the coated paper against water molecular penetrating through it. The PDA curve was applied to represent the penetration and absorption properties of the sample paper (Liu and Chen, 2011). When the curve was steeper, indicated that the liquid penetrated fast.

### 2.7. Water vapor permeability (WVP)

Water vapor permeability (WVP) of the coated paper were measured at the temperature of 35 ± 2 °C and a humidity of 70 ± 2 RH% using W3/060 WVP tester. The sample paper were tested once every 15 min, a total of three times. Finally, the last data for the final results.

## 3. Results and discussion

### 3.1. Effects of montmorillonite/chitosan nanocomposite film on the surface of the Kraft paper

The surface and cross section SEM of the uncoated and the coated paper with 1.5 wt% chitosan or 5 wt% montmorillonite/chitosan nanocomposite (be dispersed at 1500 rpm without dispersant) were shown in Figs. 1 and 2. Compared to the uncoated paper, there were better and smoother surface for paper coated by chitosan or montmorillonite-chitosan nanocomposite. It was contributed to the better film formation of chitosan. It was also found that there were a little solution

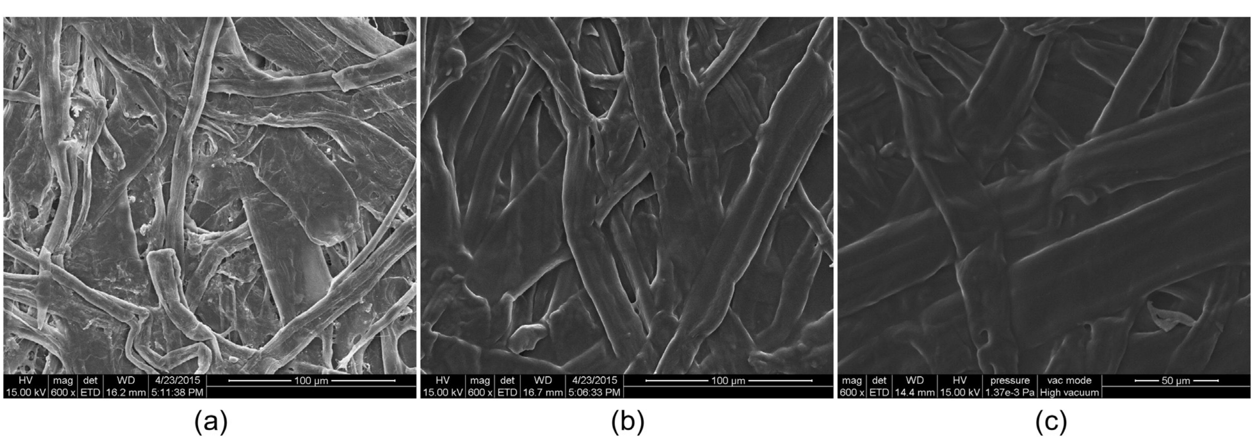


**Fig. 1.** The kraft paper surface topography. (a) for the uncoated paper, 600×; (b) for Cs coated paper, 1.59 g/m$^2$, 600×; (c) for Mt/Cs coated paper, 1.59 g/m$^2$, 600×.