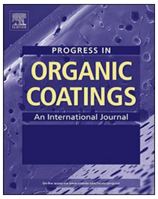
Progress in Organic Coatings 112 (2017) 66–74

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat



Effects of montmorillonite on the properties of cross-linked poly(vinyl alcohol)/boric acid films

Chenwei Chen[a,b,c], Youji Chen[b], Jing Xie[a,b,c,*], Zhewei Xu[b], Zhipeng Tang[b], Fuxin Yang[a,b,c], Kaijia Fu[b]

[a] Institute of Packaging Engineering, Shanghai Ocean University, Shanghai 201306, China
[b] Colleague of Food Science and Technology, Shanghai Ocean University, Shanghai 201306, China
[c] Shanghai Engineering Research Center of Aquatic-Product Processing & Preservation, Shanghai 201306, China

ARTICLE INFO

Keywords:
Poly(vinyl alcohol)
Montmorillonite
Boric acid
properties
packaging film

ABSTRACT

The cross-linked poly(vinyl alcohol)/boric acid(PVA/BA) films incorporated with montmorillonite (MMT) was developed via a solution blending-casting method. The effects of MMT concentrations of 0%, 1%, 3%, 5% and 7% on the structural, mechanical, barrier, water resistance, thermal stability and morphology properties of cross-linked PVA/BA film was investigated. It was found that the properties of the films changed as the MMT content varied. As the MMT content increased from 0% to 3%, the tensile strength increased, while the oxygen permeability and water vapour permeability reduced. However, these properties deteriorated slightly due to partially aggregations of MMT in the PVA film structure with increasing MMT content from 5% to 7%. The results showed the films incorporated with MMT became a little darker and tendency toward yellowness, the opacity increased, the water resistance and thermal stability was improved with the increasing amount of MMT. X-ray diffraction patterns, transmission electron microscopy (TEM) and scanning electron microscope (SEM) results revealed that the MMT was well dispersed in the PVA matrix and it was predominantly exfoliated. The cross-linked PVA/BA film incorporated with 3% MMT showed the best comprehensive properties among all films.

1. Introduction

Nowadays, the majority of packaging plastic materials are non-biodegradable petroleum base materials which have caused serious environmental problems. The biodegradable materials have received an increasing attention by numerous research groups recently. Poly-(vinyl alcohol) (PVA) is one of such a kind of material, a biodegradable and non-toxic water-soluble synthetic polymer, which has been widely applied in a broad range of adhesives, textile industrial, medical devices and packaging material [1,2]. It exhibits excellent properties of film forming, emulsifying, adhesive, transparency, oxygen barrier and biodegradability.

However, PVA is sensitive to moisture for hydroxyl groups in the molecular chain and its barrier properties strongly decreases by increased relative humidity, which limits its applications in many fields and would be also a major obstacle for using in the packaging. Therefore, improvement in the hydrophobic and other comprehensive properties of PVA is of great concern to expand its scope of application. Several attempts have been made to improve the hydrophobic property of PVA by physical methods, such as heat treatment, UV radiation and electron beam irradiation [3]. And many researches focused on chemical cross-linking method by using chemical agents such as glutaraldehyde [4,5], glyoxal [6–8], and boric acid (BA) [9–12]. Particularly, many studies about the cross-linked PVA by BA demonstrated that improved water resistant property, oxygen barrier property, thermal stability and mechanical properties, which showed a very promising application in the preparation of biomedical materials and films or coatings for various packaging material [13,14] were proposed.

On the other hand, polymer/clay nanocomposites are of much current attention since the pioneering development of nylon-6/montmorillonite (MMT) nanocomposite showed great improvements in physical and mechanical properties with only a small amount of MMT in the early 1990s [15–17]. MMT was the most widely studied type of clay fillers owing to its low cost and its ability to be well dispersed and exfoliated in the polymer matrix [18,19]. In the past researches, the results showed that incorporating appropriate amount of MMT or modified MMT into the PVA could obtain intercalated or exfoliated composite materials, lead to improve mechanical, gas barrier and thermal properties comparing with the pure PVA [20–26]. However, the effect of MMT on the properties of cross-linked PVA/BA film has not

---

[*] Corresponding author at: Colleague of Food Science and Technology, Shanghai Ocean University, Shanghai 201306, China.
E-mail addresses: cwchen@shou.edu.cn (C. Chen), jxie@shou.edu.cn (J. Xie).

http://dx.doi.org/10.1016/j.porgcoat.2017.06.003
Received 14 January 2017; Received in revised form 30 May 2017; Accepted 1 June 2017
0300-9440/

been reported. Based on the works of cross-linked PVA film by BA [13], this study was about incorporating MMT into the cross-linked PVA/BA film in order to combine advantages of MMT and BA to get PVA films with better properties. The effect of MMT on the structural, mechanical, barrier, water resistance, thermal stability and morphology properties of cross-linked PVA/BA film was investigated.

2. Materials and methods

2.1. Materials

PVA with a degree of polymerization of 1799 and an alcoholys is degree of 99% was obtained from SINPEC Shanghai Petrochemical Co. Ltd (China). Montmorillonite was purchased from Nanocor Inc. (USA). It is Na^+-MMT and the purity is great than 98%. Its general physical properties are as follow: Gray color; Avg. dry particle size is 16–22 um; aspect ratio is 200–400; specific gravity is 2.6 g/cm^3; moisture content is 12%. Glycerol and boric acid (BA) were purchased from Sinopharm Chemical Reagent Co., Ltd (China).

2.2. Film preparation

The PVA/BA film was prepared by using solution-casting method. BA (1.1 g) and MMT of different content (0%, 1%, 3%, 5%, 7%, w/w relative to PVA on a dry basis) were immersed in 200 mL distilled water and stirred continually until uniformly mixed. Then the PVA resin pellets (22 g) were added into the mixture. It was heated to 95 °C and stirred continually until they were dissolved completely. The glycerol (1 g) used as plasticizer was added into the solution and stirred continually for 1 h. Then the solution was cooled down to room temperature and was placed in the vacuum drying oven (Shanghai Yiheng Instruments Co., Ltd. China) to eliminate air bubble in the solution. The gelatinous solution was poured onto a glass plate and spread for the wet film using a film steel spreader (Shanghai Xiandai Environmental Engineering Technology Co., Ltd. China). The casted glass plates were dried onto flat heating stage at 60 °C for 40 min and then the films were peeled from the glass plate. At last the films were vacuum packed in the high barrier bag for using. The films containing 0%, 1%, 3%, 5% and 7% MMT were marked as PVA-5BA-0MMT, PVA-5BA-1MMT, PVA-5BA-3MMT, PVA-5BA-5MMT and PVA-5BA-7MMT respectively. The pure PVA film was prepared without adding BA and MMT.

2.3. Film characterization

2.3.1. Film thickness

Thickness of the films was measured at five different locations of each film sample randomly using a digital micrometer (Guilin Guanglu Measuring Instrument, Co., Ltd, China) with an accuracy of 0.001 mm. The average film thickness was used for determining mechanical properties, water vapor permeability and oxygen permeability.

2.3.2. Fourier transforms infrared (FTIR) spectroscopy analysis

The FTIR spectroscopy of films was carried out on FTIR-650 spectrophotometer (Tianjin Ganggong science and technology development CO, LTD, Tianjin, China). The spectra in the range of 4000–400 cm^{-1} were recorded in 32 scans with a resolution of 4 cm^{-1} and were ratioed against a background spectrum recorded from the clean empty cell with air. Prior to measurement, films were placed in a desiccator containing dried silica gel for 2 weeks at room temperature to obtain the most dehydrated films.

2.3.3. X-ray diffraction (XRD) analysis

The XRD was measured by X'Pert PRO X-ray diffractometer (PANalytical B.V., Almelo,Holland) with a nickel-filtered CuKα radiation source (40 kV, 40 mA and $\lambda = 0.15406$ nm). Small angle X-ray diffractometer (SAXD) and wide angle X-ray diffractometer (WAXD) analysis were used. The data were collected in the scattering range from $2\theta = 2°$ to $10°$ for SAXD and $2\theta = 5°$ to $60°$ for WAXD at a step of 0.01° with a scan speed of 1.0°/min. The interlayer distance (d or d-spacing) between silicate layers (d_{001}) was calculated by Bragg's equation [2] as following:

$$d = \frac{\lambda}{2\sin\theta}$$

Where d is the interplanar distance, λ is the wavelength of X-ray beam and θ is the diffraction angle.

2.3.4. Transmission electron microscopy (TEM)

The morphology of the film samples were visualized by a transmission electron microscope (JEOL JEM-1230, JEOL Ltd., Tokyo, Japan) operating at 90 kV. The film samples were cut into thin slices with about 100 nm thickness along the direction of the films' thickness using ultramicrotome (Leica EM UC7, Leica Microsystems Inc., Buffalo Grove, United States) under −100 °C. Then they were attached to the copper grid and were viewed under the transmission electron microscope.

2.3.5. Scanning electron microscope (SEM)

The surface and cross-section morphologies of the film samples were carried out by using a S-3400N scanning electron microscope SEM (Hitachi Ltd, Japan) under the standard high-vacuum conditions at a voltage of 5 kV. The film samples were fractured in liquid nitrogen for cross-section morphology measurement. Then all film samples were fixed on the bronze stub with conductive adhesive and sputtered with gold layer prior to SEM observation. Photographs were taken at selected magnification.

2.3.6. Film color and opacity

The film color was determined in terms of the Hunter L*, a*, and b* value by using a Konica Minolta CR-400 Chroma Meter (Minolta Co., Tokyo, Japan). The white standard plate was $L^* = 94.36$, $a^* = -0.6$, and $b^* = 4.29$. Each film was put on top of the white standard plate for measurement and five measurements were taken. The total color difference (ΔE^*) was expressed as follows:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$

Where L^* is the lightness, 0 for black and 100 for white; a^* is redness, from green (−) to red (+);b^* is yellowness, from blue (−) to yellow (+).

The film opacity was measured according to the method described by Park and Zhao [27], measuring the absorbance at 600 nm with a UV 2100 spectrophotometer (Unico Instruments Co., Ltd., Shanghai, China). The films were cut into rectangle strip (10 mm × 40 mm) and inserted into cuvette directly. An empty cuvette without film was used as the reference. The film opacity was calculated as follows:

$$Opacity = Abs600/t$$

Where Abs600 is the value of absorbance at 600 nm and t is the thickness of film (mm). Three repetitions were performed for each film.

2.3.7. Mechanical properties

The tensile strength (TS (MPa)) and percentage of elongation at break (E(%)) of film samples were performed using a XWL Auto Tensile Tester (Labthink mechanical and electrical technology Co. Ltd., China) according to the ASTM D638-08.The films were cut into 15 mm long and 100 mm wide strips. The film samples were clamped between the grips with 50 mm initial distance and stretched at a cross-head speed 50 mm/min. All film measurements were performed on three specimens and averaged.

2.3.8. Gas permeability

2.3.8.1. Water vapor permeability. The water vapor permeability of the films was determined by using a PERMANTRAN-W® Model 1/50 water