Preparation of Vanillin Modified Poly(Vinyl Alcohol)/ Ag Composite for Food Packaging

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Abstract. Film packaging preservation method is a new simple storage preservation method introduced in recent years, the effect of film preservation depends mainly on the choice of film material composition and film-forming method. The results show that polyvinyl alcohol/silver (PVA/Ag) composite film has some antibacterial properties, but it has not been reported to use this film for the preservation of agricultural products. Vanillin was used as cross-linker to improve the properties of the composites. The effect of crosslinker agent dosage, reaction time, film forming pH and film forming temperature were studied. The properties of PVA/Ag/V composites were characterized by FT-IR and XRD. The results show that the neutral reaction environment and the short reaction time are not conducive to the formation of hydrogen bonds in polymer materials with low crosslinker content.

Introduction

Traditional packaging film is mostly polyethylene film, using vacuum and other methods of preservation. Film packaging preservation method is a new simple storage preservation method introduced in recent year, the effect of film preservation depends mainly on the choice of film material composition and film-forming method[1,2]. Polyvinyl alcohol (PVA) which is easy to film and degradation, health and safety, has been widely used in food packaging; PVA with the hydrophilic properties of the film after a high permeability, which will affect the application of food packaging[3]. By increasing the polymer molecular chain length and polarity of the constituent film, the interaction between the intermolecular hydrogen bonds and the electrostatic attraction can be increased, thus forming a network structure with certain selectivity barrier properties. The grafting polymerization of maleic anhydride, acrylic acid and acrylamide has been used to improve the water resistance of PVA at home and abroad, and the modification of PVA by glutaraldehyde crosslinking has been made on the basis of acetal reaction principle. The addition of glutaraldehyde makes the fresh-keeping material of PVA composite film have antibacterial effect on Escherichia coli but the largest use of glutaraldehyde for fruits and vegetables 0.05g / kg. Therefore, the use of glutaraldehyde as a crosslinking agent is likely to cause residues, there are certain limitations.

Antibacterial materials are divided into inorganic, organic and natural antibacterial agents of these three categories[4]. Inorganic antimicrobial materials are mainly inorganic non-metallic materials as the carrier, through the ion exchange load of silver, copper, zinc and other antibacterial ions. Organic antibacterial materials through the antibacterial properties of organic matter to antibacterial, such as ethanol, Which is mainly small molecule organic matter. Natural antibacterial agent from nature, people obtain it by extracting and purifying. Although the inorganic antibacterial agent has various advantages, the application of inorganic antibacterial agent exist the stability of antibacterial agent and the influence of the carrier on the antibacterial agent and other issues; the organic small molecule antibacterial agent has the disadvantages of being volatile, difficult to be processed, poor in chemical stability and so on; natural antimicrobial agents due to geographical constraints and extraction
conditions can’t be effectively applied. With the antibacterial agent of organic high molecular compounds can overcome these shortcomings, so the synthesis and application of polymer antimicrobial agents is becoming a hotspot in research and development today.

The results show that polyvinyl alcohol/silver (PVA/Ag) composite film has some antibacterial properties[5,6], but it has not been reported to use this film for the preservation of agricultural products. Vanillin (3-methoxy-4-hydroxy benzaldehyde) is an active reagent which is widely used in food, pharmaceuticals and daily chemicals [7]. From a chemical standpoint of view, vanillin has both aldehydic and phenolic groups and it can create several types of reactions [8]. The purpose of this experiment was to prepare vanillin modified PVA/Ag (PVA/Ag/V) composites with different conditions and study the features of these composites.

Materials and Methods

Preparation of Composites

Vanillin, silver nitrate (AgNO₃) and PVA with a polymerization degree of 1750±50 were purchased from Chengdu Kelong Chemical Reagent Co., China. All the reagents used in this research were in AR grade. Vanillin was dissolved in ethanol to form the ethanol solution of vanillin at a concentration of 0.20g/mL.

The PVA/Ag/V composite membranes were prepared with following process. First, PVA powder was dissolved in deionized water and stirred continuously at 90 °C for 4 h to form a homogeneous viscous solution with PVA concentration of 10 wt%. 1 mL of 0.5% AgNO₃ solution was added into 50 mL PVA solution. The mixture was poured into a glass container which was dried in an oven at 80 °C. The different membrane solution was prepared by different reaction conditions.

In order to investigate the effect of crosslinking agent dosage (A), reaction time (B), film forming pH (C) and film forming temperature (D) on the physical and chemical properties of PVA/Ag composite film, three level of each factor were selected: crosslinker agent dosage (1%, 5%, 10%), reaction time B (0.5h, 1h, 2h) , film forming pHc (6,7,8),film forming temperature D (60%,75% 90%). Use 4 factors 3 levels of orthogonal experimental design method for experimental design, a total of nine treatment. As shown in Table 1.

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Physicochemical Characterization of Composite Membranes

The FT-IR spectra were obtained over a wavenumber range of 500–4000 cm⁻¹ using an infrared spectrometer (TENSOR 27, BRUKER Co. Germany). The composite films were analyzed by X-ray diffraction (XRD) of Philips company.

Experimental Results Analysis

IR Analysis

For the PVA (Fig. 1), the 1079 cm⁻¹ peak belongs to the C-O stretching vibration peak, the 2938 cm⁻¹ peak is the -CH₂-stretching vibration, and the 3276 cm⁻¹ peak is the vibration of the PVA
intramolecular hydrogen bond. The characteristic absorption peaks of vanillin benzene ring at 1508 cm\(^{-1}\) can be observed in Figure 1 (1, 3-7, 7-9), indicating that the crosslinking agent vanillin has entered the composite structure.

![Infrared spectra of composite films.](image)

**Figure 1.** Infrared spectra of composite films.

**XRD Analysis**

There is a large crystallization peak near the pure PVA \(2\theta = 20^\circ\) due to the PVA intramolecular hydrogen bonds and the role of intermolecular hydrogen bonds. It can be seen from Fig. 2 that the crystallization peak of PVA in treatment 2 is greatly weakened, indicating that the hydrogen bond may be destroyed. And the crystallization peak of PVA in the other treatments is enhanced to some extent compared with that of pure PVA. According to the literature reports, there are four characteristic diffraction peaks of Ag, corresponding to (111), (200), (220) and (311), one of which is located near \(2\theta = 39^\circ\). It can be seen from Fig. 2 that the crystallization peaks of PVA are observed in all the composite films except treatment 2, in which the characteristic diffraction peaks of Ag are clearly observed in the spectra of the four composite films 5, 6, 7, 8.

![X-ray diffraction pattern of the composite film.](image)

**Figure 2.** X-ray diffraction pattern of the composite film.

**Discussion**

The film-forming material determines the performance of the film. By increasing length and polarity of the polymer molecular chain of the constituent film, Hydrogen bonds and the electrostatic attraction between the polymers can be increased, thus forming a network structure
with certain selectivity barrier properties. The results of XRD shows that the crystallinity of the material in treatment 2 is the worst, and the infrared result shows that the vibrational peak of hydrogen bonds in PVA molecule is not observed at 3276 cm\(^{-1}\). The results show that the neutral reaction environment and the short reaction time are not conducive to the formation of hydrogen bonds in polymer materials with low crosslinker content. Therefore, treatment 2 is not an ideal reaction condition.

From the experimental results 5, 6, 7, 8 can be clearly observed in the diffraction peak of Ag, while PVA crystallization peak has been enhanced, is the better reaction conditions.

References