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# Preparation and characterization of antibacterial films based on polyvinyl alcohol/quaternized cellulose

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ABSTRACT

Quaternized cellulose (YM) was homogeneously synthesized by grafting 3-chloro-2-hydroxypropyldodecyldimethylammonium groups onto cellulose molecules in a NaOH/urea aqueous solution. YM was blended with a poly(vinyl alcohol) (PVA) matrix to prepare composite films via co-regeneration from the alkaline solution. The PVA film and the blend films were characterized by Fourier transform infrared spectroscopy, X-ray diffraction measurements, thermogravimetric analysis, and scanning electron microscopy. Mechanical properties, water vapor barrier properties, light transmission, and antibacterial activity against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria were also evaluated. The results reveal that PVA and YM in the composite films interacted by hydrogen bonding. Compared with pure PVA film, the PVA/YM blend films had higher tensile strength, higher thermostability, lower water permeability, and especially, higher antibacterial activity. The blend films exhibited good UV-shielding performance. Our study demonstrates a simple and efficient method for preparing a functional, environment-friendly composite film.



## 1. Introduction

The massive use of non-degradable plastic materials has caused serious "white pollution". Many efforts have been made to develop environment-friendly biomaterials to solve environmental problems while reducing the dependence on petroleum-based fuel and products. Cellulose, a natural polymer, has become an attractive solution to the increasing demand for environment-friendly and biocompatible materials [1,2]. Many works have intensively investigated materials from regenerated cellulose films because of their high mechanical strength, thermal stability, biocompatibility, and nontoxicity [3–6]. However, pure regenerated cellulose films are highly hydrophilic, have poor barrier properties, and lack antimicrobial activity. These characteristics have limited their potential applications [7–9]. Chemical modification or combination with other polymers effectively overcomes these problems.

Poly(vinyl alcohol) (PVA) is a highly biocompatible, nontoxic synthetic polymer with high water solubility. It can be blended with other natural polymers to produce biodegradable composites. It has promising industrial applications in many fields because of its film-forming, emulsifying, and adhesive properties [10–12]. PVA films have remarkable barrier properties due to their small, dense, and closely packed monoclinic crystal structure. Cellulose is often used as reinforcement filler for PVA. However, cellulose-reinforced PVA-based films have limited application in functional packaging because of their lack of antibacterial activity. Thus, improving the antimicrobial activity of PVA-based composite films is of importance.

The use of natural and synthetic antibacterial agents is considered as a promising approach to control the growth of microorganisms [13]. Antibacterial agents include nanometal or metal oxides [14,15], antibiotics, halogens [16], and essential oils from herbs and spices [17]. However, there are several disadvantages associated with the use of these antibacterial agents. Use of nanometal or metal oxides, antibiotics, and halogens can readily lead to secondary pollution. The antibacterial activity of essential oils is transient because of their volatility. On the other hand, quaternary ammonium compounds are widely used because of their antibacterial properties, low toxicity, low cost, and environmental compatibility [18]. They have recently been used to modify cellulose derivatives used as bioadsorbents, flocculants, and gene carriers [19,20]. However, there are no reports on the incorporation of quaternized cellulose (YM) in the preparation of antibacterial films with PVA as matrix.

In the present study, 3-chloro-2-hydroxypropyldodecyldimethylammonium chloride (YB) was synthesized through a reaction between *N*,*N*-dimethyl-1-dodecylamine and epichlorohydrin (EH) in alkali/urea aqueous solution. The obtained YB was used to modify cellulose for synthesis of the quaternized cellulose (YM). The PVA/YM composite films were regenerated from the alkali/urea aqueous solution. YM, PVA film, and YM/PVA films were characterized by Fourier transfer infrared (FTIR) spectroscopy, X-ray diffraction (XRD) measurements, thermogravimetric analysis (TGA), scanning electron microscopy, tensile tests, oxygen permeability (OP) measurements, water vapor permeability (WVP) tests, and light-transmission measurements. Their activity against

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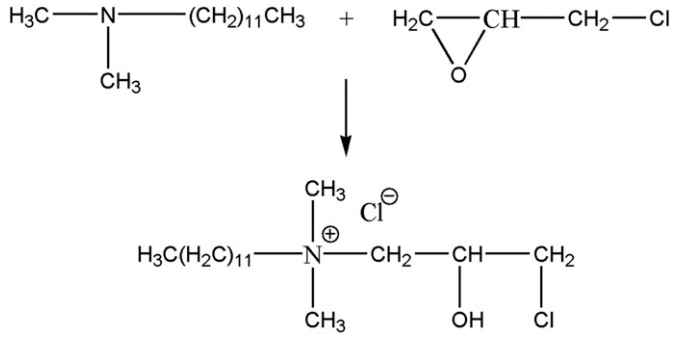

**Fig. 1.** Synthetic reaction for the YB.

Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria were also investigated.

## 2. Materials and methods

### 2.1. Materials

Microcrystalline cellulose (MCC, Comprecel M101; degree of polymerization (DP) = 200), was purchased from Shanghai Shenmei Pharmaceutical Technology Co., Ltd. (Shanghai, China). PVA (average molecular weight $M_W$ = 84,000–89,000; DP = 1700–1800; degree of hydrolysis = 88%) was purchased from Sinopec Shanghai Petrochemical Co., Ltd. (Shanghai, China). *N*,*N*-Dimethyl-1-dodecylamine ($C_{14}H_{31}N$; 98% pure; $M_W$ = 213.4) was obtained from Heowns Chemical Reagent Co. Ltd. (Tianjin, China). All other reagents and solvents were of analytical grade and were used as received. The microorganisms used in this study were obtained from Qingdao Hope Bio-Technology Co., Ltd. (Qingdao, China) and were stored at 4 °C before use. Biochemical reagents for the nutrient agar were purchased from AoBoXing Bio-tech Co., Ltd. (Beijing, China).

### 2.2. Preparation of blend films

#### 2.2.1. Preparation of YB

YB was synthesized from *N*,*N*-dimethyl-1-dodecylamine and EH. EH solution (219 mL, 2.79 mol) was added dropwise to a 300 mL (1.11 mol) solution of *N*,*N*-dimethyl-1-dodecylamine [21]. The mixture was stirred at 60 °C for 2 h to obtain a highly viscous solution, and the residual EH was removed by a procedure using vacuum–rotary evaporation. After the product was cooled to room temperature, it was dissolved in acetone (500 mL). Crystals began to separate in a few minutes. After the mixture was stored for 8 h at 25 °C, it was filtered. The crystal-like products were washed with diethyl ether and then dried at 60 °C under vacuum for 24 h. The product obtained was labeled as YB. The yield was 76% which approximated to the yield of 77% in the reference [21]. The reaction involved in this process is shown in Fig. 1. Results of its analysis are given below:

Elemental analysis (YB, $C_{17}H_{37}Cl_2NO$). Measured (%): N 4.14%, C 59.73%, H 10.86%; calculated (%): N 4.09%, C 59.65%, H 10.82%.

YB: $^1$H nuclear magnetic resonance spectrometer ($^1$H NMR) ($D_2O$, 300 MHz): δ 0.75 (t, 3H, $J$ = 3.75), 1.16 (q, 18H, $J$ = 8.2), 1.57 (q, 2H, $J$ = 7.8), 3.20 (s, 6H), 3.45 (t, 2H, $J$ = 4.8), 4.15 (d, 2H, $J$ = 2.4), 6.18 (d, 2H, $J$ = 8.4), 6.29 (q, 1H, $J$ = 2.8).

#### 2.2.2. Preparation of YM

A cellulose solution was prepared according to a previously reported method [22]. Predetermined amounts of NaOH, urea, and distilled water (7:12:81 by weight) were combined in a 100 mL beaker to obtain a solution. MCC (2 g) was dispersed in the NaOH/urea solution, which was then cooled to −12.5 °C. The frozen mixture was then thawed and vigorously stirred for 5 min at ambient temperature to obtain a transparent solution of 2 wt.% cellulose. A specified amount of YB was added to the cellulose solution, and the mixture was stirred at 25 °C for 24 h. The mole ratio of YB to anhydroglucose units in the cellulose molecules was 6:1. The resulting solution of quaternized MCC derivative was separated into two parts. One was used to obtain the purified quaternized MCC derivative (YM) [23] for further analysis. The other was stored at 0 °C for direct use in the preparation of YM/PVA blend films. The possible synthesis scheme of YM is shown in Fig. 2.

#### 2.2.3. Preparation of YM/PVA blend films

PVA was stirred into distilled water at 80 °C for 2 h to achieve a clear PVA solution (8.80%). Specified amounts of PVA and YM solution were mixed, and the resulting solution was stirred vigorously for 30 min. After the solution was degassed in a vacuum oven, it was spread onto a glass sheet to form a gel with a thickness of ~0.2 mm. The sheet was immersed in a coagulation bath containing of 5 wt.% $CaCl_2$ and 3 wt.%

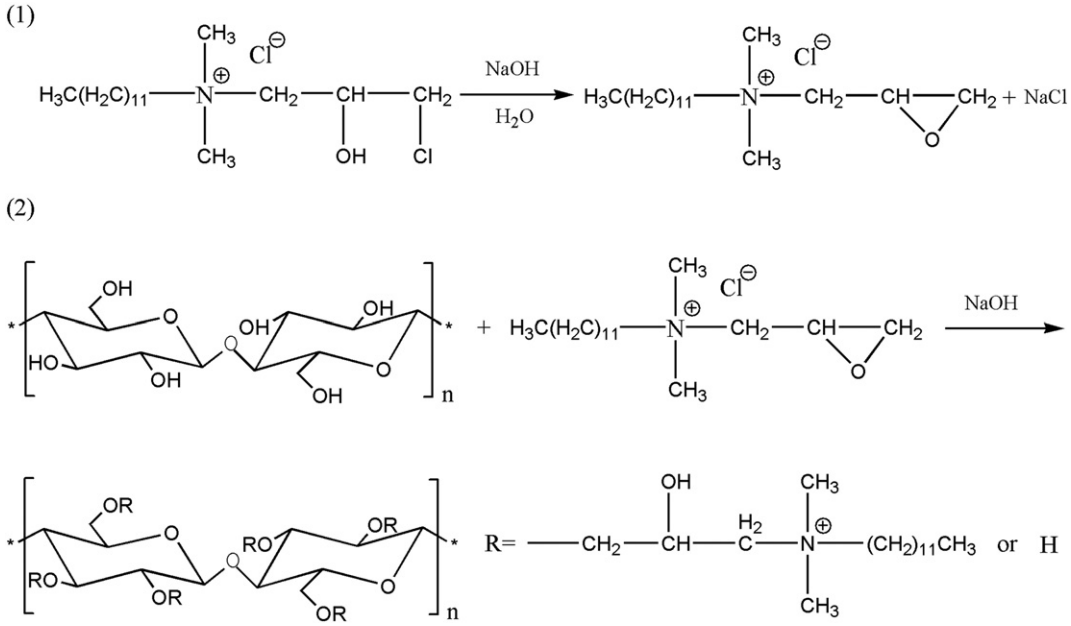

**Fig. 2.** Synthetic reactions for the YM.