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Quaternized chitosan/polyvinyl alcohol/sodium carboxymethylcellulose blend film for potential wound dressing application

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ABSTRACT

In this study, blends of N-(2-hydroxyl) propyl-3-trimethylammonium chitosan chloride (HTCC), polyvinyl alcohol (PVA), and sodium carboxymethylcellulose (CMC) were prepared by the solution-casting method to develop films. The blend films were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and light-transmission measurements. The results revealed that in the blend films, HTCC, PVA, and CMC interacted by hydrogen bonding and were partly miscible. The effects of varying amounts of CMC on the mechanical properties, water absorption, swelling properties, and moisture permeability of HTCC/PVA blend films were also examined. Improved strength and flexibility of the blend films were observed with the inclusion of CMC. Moreover, the incorporation of CMC resulted in enhanced water absorption capacity, improved swelling ratio, and appropriate moisture permeability. Furthermore, all the ternary blend films showed good antibacterial activity against *Escherichia coli* and *Staphylococcal aureus*. Sponges of HTCC/PVA/CMC blend films with these properties have the potential to be used as biomaterials in medical applications.

1. Introduction

In recent years, much attention has been focused on the research and development of polymer films for biomaterials such as wound dressings and drug delivery systems. In the medical field, the effective antimicrobial and antifungal agents of metal nanoparticles prevent most microorganisms from developing resistance are very important [1]. However, the antibacterial activity of metal nanoparticles (AgNPs) strongly depends on their size, shape, concentration, distribution, and stability [2]. Therefore, much work has been done on the preparation and study of polymers with good antibacterial activity for application in the medical field [3–5].

The ideal wound dressing material should have high liquid-adsorbing, biocompatible, and antibacterial properties to protect the wound from infections, dehydration, and subsequent tissue damaging [6]. Traditional dressings, including gauze, cotton, wool, and others, normally expose the open wound to adherent fibers, which causes inflammation and leads to wound debridement, thus delaying the wound-healing process [7]. Therefore, modern dressings such as bio-based polymeric films have drawn the attention of researchers as an alternative approach to deal with the problems of traditional dressing materials.

One of the widely studied polymers for wound-dressing applications is N-(2-hydroxyl) propyl-3-trimethylammonium chitosan chloride (HTCC), which is biocompatible, biodegradable, and nontoxic, and it possesses antibacterial and unique hemostatic capabilities. Hydrogels, membranes, scaffolds, and sponges of HTCC-based materials have been fabricated and investigated for wound care in different situations [8]. Generally, thin films or membranes materials are used for partial skin repair and to help regenerate new skin [9]. HTCC sponges with good fluid absorption capacity, hemostatic activity, cell interaction, and hydrophilicity can meet the above requirements for use in wound-dressing applications [10]. However, the use of single biopolymer films such as HTCC as functional materials for medical applications is limited because of their strong absorbent ability and the poor mechanical properties of wet films [11]. Composite film dressings with

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antimicrobial and anti-inflammatory properties have the potential to prevent and treat chronic wound infections for effective wound healing [12].

Therefore, it is important to blend HTCC with another mechanically stronger, hydrophobic material such as poly(vinyl alcohol) (PVA). PVA is a semicrystalline copolymer of vinyl acetate and vinyl alcohol that has been widely utilized in the chemical and medical industries because of its highly biocompatibility, non-toxicity, hydrophilicity, and film-forming ability [13]. It can be processed easily to improve the physical properties of a film through mixing with other materials that have poor physical properties. However, the hydrophilic nature of PVA is a disadvantage when considering the use of PVA films as protective barriers because they tend to swell or dissolve upon contact with a surface with a high moisture content.

Sodium carboxymethylcellulose (CMC), a natural polyelectrolyte derived from cellulose by introducing a carboxyl methyl group (-CH_2COOH), has attracted much attention in medical and pharmaceutical applications owing to its biodegradability, biocompatibility, non-toxicity, good film-forming properties, and pH sensitivity, characteristics that are important for wound dressings and the growth of artificial bone and skin [14,15]. The blending of two or more polymers has increasingly become an important technique for developing new biomaterials that exhibit combinations of properties that could not be obtained from individual polymers [16]. Therefore, it would be interesting to investigate the formation of polymer blend films using the unique properties of HTCC, PVA, and CMC.

In this study, various concentrations of CMC were added to a binary blend of HTCC and PVA to study the chemical composition, mechanic properties, water absorption, moisture permeability, and antibacterial activities of various mass ratios of HTCC/PVA/CMC in edible films. The HTCC/PVA/CMC blend films were characterized by Fourier transfer infrared (FTIR) spectroscopy, X-ray diffraction (XRD) measurements, scanning electron microscopy (SEM), light-transmission measurements, tensile tests, water vapor permeability (WVP) tests, water absorption and swelling tests, and antibacterial tests.

2. Experimental

2.1. Materials

N-(2-hydroxyl) propyl-3-trimethylammonium chitosan chloride (HTCC, >91% degree of substitution) with an average molecular weight of 50,000 was purchased from Tianhua Bio-Assistants Co., Ltd. (Shandong, China). PVA (average M_w = 84000–89000 g/mol; degree of polymerization (DP) = 1700–1800; 88% alcoholysis) was purchased from Sinopec Shanghai Petrochemical Co., Ltd. (Shanghai, China). CMC with a 0.55–1.0° of substitution and a viscosity of 800–1200 mPa s (20 g L^{-1}, 25 °C) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 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). All the commercial products were used without further purification.

2.2. Preparation of HTCC/PVA/CMC films

HTCC and CMC were each dissolved in distilled water under stirring to obtain concentrations of 5.0 wt%, respectively. PVA was dissolved in distilled water under constant stirring at 80 °C for 2 h to achieve a clear solution of 5.0 wt%. To obtain HTCC/PVA/CMC blend solutions, given amounts of HTCC, PVA, and CMC solutions were mixed in different mass ratios, and the resulting solutions were stirred vigorously for 30 min. The solutions were degassed in a vacuum oven, then transferred into a Teflon pane (30 cm × 30 cm × 3.5 cm) and dried at 50 °C to obtain films with uniform thickness. The HTCC/PVA/CMC films were denoted as 40HTCC/60PVA, 40HTCC/50PVA/10CMC, 40HTCC/30PVA/30CMC, 40HTCC/50PVA/10CMC, and 40HTCC/60CMC in weight proportions of 40:60:0, 40:50:10, 40:30:30, 40:10:50, and 40:0:60, respectively.

2.3. Characterization

FTIR spectroscopic images of the films were recorded on a Nicolette 6700 spectrometer (Thermo Fisher Scientific Co., Ltd., MA, USA) in attenuated total reflection (ATR) mode at a resolution of 4 cm^{-1}. X-ray diffraction (XRD) was performed with a D/max-2200 diffractometer (Rigaku, Japan) at a voltage of 40 kV and a current of 30 mA using Cu Kα radiation with a scanning rate of 5°/min. The scanning scope of 2θ ranged from 5 to 40° at ambient temperature. The morphology of the upper surfaces and cross sections of the films was observed by a Quanta 200 scanning electron microscope (Philips-FEI Co., AMS, The Netherlands) with an accelerating voltage of 5 kV. Samples were coated with a thin gold layer prior to observation. Thicknesses of the films were measured with an ID-C112XBS micrometer (Mitutoyo Corp., Tokyo, Japan) and reported as the average from ten random points. Tensile tests were carried out by using an auto tensile tester (XLW-PC, PARAM, Jinan, China) equipped with a 500 N load cell. Measurements were performed at a strain rate of 300 mm/min at 25 °C. The WVP values of the films were determined at 23 °C and 60% relative humidity by using a Mocon Permatran-W 3/61 (MOCON, MN, USA) according to GB/T 26253 (GB/T, 2010).

2.4. Light transmission and opacity measurements

The visible-light transmittance curves through the films (4 × 3 cm) were recorded in the range of 200–800 nm on an ultraviolet-visible (UV-vis) spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan). The opacity of the films was calculated as follows:

$$\text{Opacity measurement} = \frac{A_{600}}{T}$$

where A_{600} is the absorbance at 600 nm and T is the film thickness (mm).

2.5. Water absorption

The films were cut into 2 cm × 2 cm pieces and the initial weight of the dry films was measured. The films were subsequently immersed in distilled water until equilibrium was reached. Before measuring the weight of the wet films, the extra surface water of the wet films was carefully removed by filter paper. The water absorption capacity (WAC) was calculated as follows:

$$\%\text{WAC} = \frac{W_f - W_0}{W_0} \times 100$$

where W_0 and W_f are the weight of the initial dry and wet films at equilibrium, respectively.

2.6. Swelling studies

The swelling behavior of the films was determined by measuring the initial weight of the dry films (2 cm × 2 cm) and subsequently immersing them into a phosphate buffer solution (PBS) of pH 7.4 at 37 °C [17]. Before measuring the weight of the swollen films at different time intervals, the extra surface solution of the wet films was removed by filter papers. This process was