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Preparation, characterization and functional evaluation of chitosan-based films with zein coatings produced by cold plasma

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ABSTRACT

Chitosan-based films with zein coatings were prepared in order to modify the drug release properties. The adhesion of zein layers to the films was ensured via a cold plasma treatment. Using ciprofloxacin hydrochloride as model, the effect of cold plasma on the functional properties and structures was evaluated. The results suggest that the encapsulation efficiency, chemical composition and crystal type of ciprofloxacin hydrochloride in chitosan/drug films were not altered by cold plasma treatment, while the wettability and surface free energy displayed a notable increase. After being coated with zein, the chitosan interacted with the zein through hydrogen bonding and electrostatic interactions. The burst release phenomenon of the chitosan/drug films was prevented by the zein coating. Furthermore, the plasma treatment provided the coated film with a slower release rate within 24 h, from 72.8% to 49.3%. The enhanced coating thickness and the more compact interface structure were responsible for this improvement.

1. Introduction

Bacterial infection is one of the major sources of morbidity and mortality for patients in the world. Various antimicrobial wound dressings encapsulating drugs can be used to prevent bacterial penetration into the wound or to avoid microbial growth, and these dressings form an important part of the medical and pharmaceutical wound care market worldwide (Fu, Wang, Zhou, & Wang, 2009; Simões et al., 2018). Chitosan, the deacetylated product of chitin, is the second most abundant linear polysaccharide in nature. During the past decade, chitosan as an encapsulant for antimicrobial drug has attracted much interest in the delivery system field due to its excellent biocompatible, biodegradable, nontoxic, wound-healing and hemostatic properties (Barata et al., 2016; Caetano et al., 2015). Compared to many biodegradable natural or synthetic polymer-based drug delivery materials, chitosan shows better biocompatibility, which contributes to cell adhesion, proliferation and differentiation (Li, Maciel, Rodrigues, Shi, & Tomás, 2015). It also exhibits high antibacterial activity against pathogenic and spoilage micro-organisms. Thus, chitosan offers an additional antimicrobial effect for wound dressings (Aranaz, Harris, Navarro-García, Heras, & Acosta, 2016). Chitosan can be easily processed into various forms such as gels, microspheres, scaffolds, films, implant membranes, and polymer blends, which provides many biomedical applications in the delivery system field (Aranaz et al., 2009; El-Leithy, 2009; Fu, Ji, Yuan, & Shen, 2005; Patil & Sawant, 2011; Sohrabi, Haeri, Mahboubi, Mortazavi, & Dadashzadeh, 2016). The drug loaded film is a common form of chitosan-based wound dressings. However, previous studies have shown that chitosan films are strongly absorbent carriers and that the chitosan/drug films have a high swelling property in solution. This property causes a phenomenon called drug burst release, which is considered a negative characteristic in the drug delivering process (Luo & Wang, 2014). To prevent the burst release phenomenon and develop the chitosan-based films to be used in a controlled-release manner, numerous studies have been performed on chitosan surface modifications by formulating double or multilayer films with other biopolymers, such as alginate, hyaluronic acid and gellan gum (Amin & Panhuis, 2011; Elgadir et al., 2015; Manna, Bharani, & Patil, 2009; Wong, Lai, Kho, & Heng, 2002).

As a water-insoluble protein extracted from corn, zein is a promising coating candidate for this purpose. It provides lower possibility to provoke zoonotic disease transmission than animal proteins and is an attractive biopolymer for human use. The high biocompatibility, biodegradability and nontoxicity have made it recognized as a useful biomaterial for controlled drug delivery and tissue engineering (Paliwal & Palakurthi, 2014). Additionally, the intermolecular disulfide bonds and hydrophobic interactions among zein molecules mean that zein can be easily and quickly transformed into a coating that is more resistant to abrasion, heat and humidity than most plant proteins are (Dong

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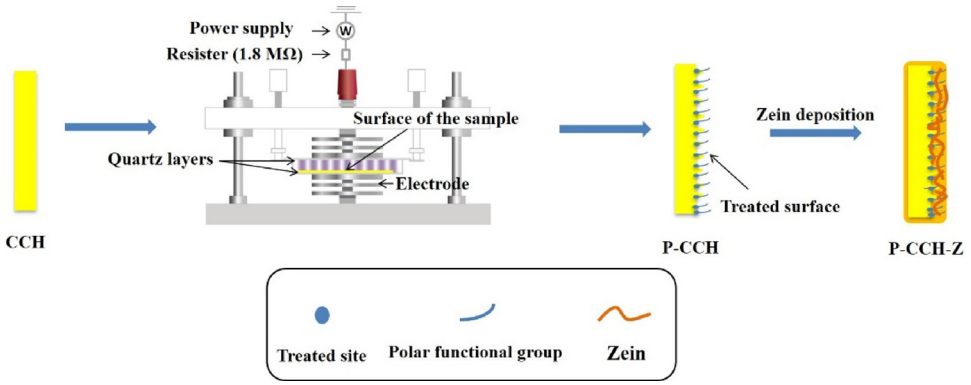

Fig. 1. The formation process of a zein-coated film with cold plasma treatment.

et al., 2018). Previous studies suggested that the hydrophobic nature of zein coatings has great advantages in decreasing the disintegration profile, increasing the encapsulation efficiency of the drug, prolonging drug release properties, and improving mechanical and colloidal stability properties of multilayer films (Lawton, 2002; Luo, Zhang, Cheng, & Wang, 2010; Piai, Rubira, & Muniz, 2010; Zhang et al., 2015). With those excellent characteristics, zein has been exploited as an attractive coating material for improving the release properties of chitosan-based films.

Nevertheless, the application of chitosan-based films as the substance of multilayer films has been limited due to the poor surface adhesion of chitosan. Such limitations in surface adhesion constrained the storage stability and sustained drug release effect of multilayer films (Luna, Silva, Gomes, Mano, & Reis, 2011; Pankaj et al., 2017). Among many approaches for surface adhesion enhancement, cold plasma technology appears to be a promising one. Cold plasma is a quasineutral ionized gas that consists of free radicals, electrons, positive and negative ions, and excited or nonexcited molecules and atoms (Thirumdas, Sarangapani, & Annapure, 2015). Cold plasma technology is a novel nonthermal technology with widespread applications in various fields, such as textile processes, sterilization, life sciences, packaging and drug delivery systems (Hagiwara, Hasebe, & Hotta, 2013; Luna et al., 2011; Ma et al., 2015; Pankaj et al., 2014; Samanta, Jassal, & Agrawal, 2010). Cold plasma treatment is an environmentally friendly process, since it is chemical-free and produces no waste (Ren et al., 2016). For decades, cold plasma has been used as a commercial technology in packaging industries to enhance the adhesive bonding of polymers, and it is considered an attractive proposition in surface functionalization of heat-sensitive materials without adversely affecting their properties (Meenan, 2012; Thirumdas et al., 2015). Previous studies have proven that cold plasma treatment could induce several physical and chemical changes on plasma-polymer interfaces that modify the polymeric surface properties, such as surface roughness, wettability, printability and sealability (Pankaj et al., 2014). When the treated surface was exposure to air, hydroperoxides and peroxide species might be formed on the surface, which is a positive function for grafting (Ding et al., 2004; Wang, Yin, Ren, & Zhao, 2009).

Using ciprofloxacin hydrochloride (a water-soluble drug) as the model, a chitosan/ciprofloxacin hydrochloride film was treated by the cold plasma process in air and then immersed in a zein solution to obtain a hydrophobic coating. The influences of cold plasma on the thickness, encapsulation efficiency, wettability, chemical components, crystal structure, morphology and thermal stability of the chitosan-drug film, with or without the zein coating, were evaluated. The release properties in vitro and antimicrobial properties were also investigated.

2. Materials and methods

2.1. Materials

Chitosan (pharmaceutical grade), with the deacetylation degree of 91%, as determined by acid-based conductometric titration, and molecular weight (Mw) of 34 kDa, as determined by high-performance gel permeation chromatography (HPGPC), was purchased from Golden-Shell Pharmaceutical Co. Ltd., (Zhejiang, China). Ciprofloxacin hydrochloride (USP grade) with content ≥88.5% was purchased from Yuanye Biotechnology Co., Ltd., (Shanghai, China). Zein (regular grade) with a protein content of 94.7% was purchased from Gaoyourixing Industries Inc. (Jiangsu, China). Alcohol and glacial acetic acid were purchased from Tianyi Industries Inc. (Tianjin, China).

2.2. Preparation of chitosan/ciprofloxacin hydrochloride films

The chitosan/ciprofloxacin hydrochloride films were prepared by a casting-solvent evaporation method. Initially, the chitosan (2% w/v) was dissolved in a 1% (v/v) acetic acid solution under stirring overnight at room temperature (25 ± 2 °C). Then, ciprofloxacin hydrochloride was carefully dissolved in the chitosan solution to achieve a drug/chitosan ratio of 1:2 by weight. After heating at 70 °C for 10 min, the cooled solution was cast in a smooth, rimmed plastic plate and dried at room temperature until the solvent completely evaporated. The as-prepared chitosan/ciprofloxacin hydrochloride film was termed CCH.

2.3. Cold plasma treatment and zein deposition onto CCH surface

A DBD-50 Plasma Reactor (Suman Co., Ltd., Nanjing, China) was utilized to modify the CCH surface. The process of forming a zein-coated film with the cold plasma treatment is shown in Fig. 1. Using dielectric barrier discharge as the cold plasma generation mode, the cold plasma was formed between two plane-parallel electrodes, which were covered with the quartz layers (5 mm thickness). In the treatment process, the CCH was placed onto the lower quartz layer and subjected to the cold plasma with a treatment intensity of 100 W (65 V, 1.5 A) for 30 s. Both surfaces of the film were treated. Next, the freshly treated CCH was exposed to the air for approximately 1 h to allow the formation of surface active groups (Ding et al., 2004). Then, the CCH was smashed into pieces. The cold plasma-treated CCH was termed P-CCH.

The zein (10%, w/v) was dissolved in an aqueous ethanol solution (80% v/v). Then, the solution was stirred for 30 min and heated at 60 °C for 10 min. In the coating process, the pieces of P-CCH were immersed into the zein solution for 60 min to form a coating. Finally, the zein-coated films were air-dried at room temperature. The zein-coated films with plasma treatment were termed P-CCH-Z, and the cold plasma untreated films were termed CCH-Z. All films were preconditioned at 25 ± 2 °C and a relative humidity of 50 ± 5% before testing.