



# Glutaraldehyde–chitosan and poly (vinyl alcohol) blends, and fluorescence of their nano-silica composite films

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## ABSTRACT

In this study, a commercial chitosan cross-linked with glutaraldehyde (GA–chitosan) having the autofluorescent property was effectively blended with a poly (vinyl alcohol) (PVA) matrix, in the formation of a transparent and fluorescent blend film. The fluorescent efficiency of the film was enhanced with red-shifted emission band by increasing the concentrations of the GA–chitosan and decreasing the PVA crystallinity. It was found that the incorporation of silica nanoparticles could further decrease the PVA crystallinity, enhance the fluorescent efficiency, and largely redshift the emission band, as compared with the neat GA–chitosan–PVA blend film. This fluorescent property could be finely tuned by careful doping of the silica nanoparticles and change of the PVA crystallinity. These phenomena could be reasonably explained by high extent of isolation of the fluorophores, increase of the stiffness of the fluorescent conjugated planar structure, and further decrease of the PVA crystallinity. In addition, the introduction of the nano-silica could improve the water and heat resistances of the GA–chitosan–PVA based silica nanocomposites.

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## 1. Introduction

Isolated chitosan, a polysaccharide, is the linear and partly acetylated (1-4)-2-amino-2-deoxy- $\beta$ -D-glucan (Muzzarelli, 1977; Ravi Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004), which has polymorphism forms of anti-parallel fashion similar to that of  $\alpha$ -chitin (Wang, Turhan, & Gunasekaran, 2004). Isolated chitosan is sensitive to acidic solution, and hydrophilicity is a very important characteristic for this material and it is, in part, due to the presence of the amine groups (Neto et al., 2005). Therefore, it is important to prevent it from readily dissolving in acid media and to enhance its chemical resistance, and at the same time, to maintain its hydrophilicity and long-term biological degradation. That can be realized by removing a certain amount of amine groups from it through the cross-linking reaction, but still preserving a part of free amine groups (Neto et al., 2005). Glutaraldehyde is a commonly used cross-linking agent. Recently, it has been found that the pristine chitosan cross-linked with glutaraldehyde (GA–chitosan) is autofluorescent, without the need of conjugating any external fluorochromes. By contrast, there is no fluorescent signal in the pure chitosan or glutaraldehyde emulsions (Wei et al., 2007). However,

the neat autofluorescent GA–chitosan has some limitations such as brittleness and low air barrier properties. Blending the pure chitosan with poly (vinyl alcohol) (PVA) could be an effective way to improve its properties for practical applications.

Poly (vinyl alcohol) (PVA) is one of the widely used synthetic polymers owing to its excellent physical properties such as high tensile strength and flexibility, superior barrier to oxygen and aroma, and ease of formation in films. It is also biodegradable under suitable conditions. In addition, PVA is biocompatible and non-toxic. Because of these excellent properties, PVA films have been developed for biomedical applications.

Considering the usefulness of the chitosan and PVA in biological activities, a combination of these two polymers may have beneficial effects on the biological characteristics of the resulting composites. Besides, there is a huge amount of hydroxyl functional groups in the PVA molecular chains. The GA–chitosan also has abundant hydroxyl groups and preserved amine groups. These groups can lead to the formation of strong hydrogen bonds in the GA–chitosan–PVA blend system. As the PVA and GA–chitosan molecules can interpenetrate and intertwine with each other, the homogeneous blend can be formed. The specific inter-molecular interactions between the PVA and chitosan make the PVA/chitosan blend have good mechanical properties. The toughness and water resistance of the blends can be markedly enhanced as well as compared with the chitosan homopolymer and the pure PVA, respectively. Various applications of the PVA/chitosan blends has been widely reported, such as medical devices and controlled

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delivery of drugs (Chandy & Sharma, 1992; Chuang, Young, Yao, & Chiu, 1999; Koyano, Koshizaki, Umehara, Nagura, & Minoura, 2000; Minoura et al., 1998; Nakatsuka & Andraday, 1992; Srinivasa, Ramesh, Kumar, & Tharanathan, 2003; Yang, Su, Leu, & Yang, 2004; Yu, Song, Shi, Xu, & Bin, 2011).

In this study, the chitosan partially cross-linked with glutaraldehyde was blended with a PVA matrix to form a transparent blend film having fluorescent property. The partial cross-linking reaction between the amine groups of chitosan and the aldehyde groups of glutaraldehyde leads to the formation of the autofluorescent chitosan with the residual amine groups in it. Due to the abundant hydroxyl and preserved amine groups, the GA–chitosan can be dissolved into hot acidic water solution, and easily compounded with PVA matrix, without the sacrifice of the autofluorescent properties.

Recently, a wide range of nano-materials has been designed and used in different areas, such as medicine, cosmetics, and foods (Hiromi et al., 2011). Among them, it is necessary to note that the nano-silica has been widely explored for various applications, such as fluorophore carrier (Ow et al., 2005), controlled release of drug molecules, antiseptic agents (Depla et al., 2011; Verraedt, Pendela, Adams, Hoogmartens, & Martens, 2010), and biosensor, etc. (Monton, Forsberg, & Brennan, 2012). It is well known that there exist plenty of the silanol groups in the nano-silica, which can increase hydrogen bonding effects in a composite system, change the crystalline behaviors of polymeric blended matrix, and affect the fluorescent properties of end products. On the other hand, thermal resistance is one of the most dominative properties for polymeric materials, as it ultimately governs the mechanical properties, durability, spectral stability, shelf lives, and life cycles of polymers (Cho, Jung, Cho, Lee, & Shim, 2003; Jin et al., 2003; Peng & Kong, 2007; Peng, Kong, Li, & Spiridonov, 2006; Xia et al., 2005). Once the degradation begins, the above properties will gradually deteriorate. Hence, the incorporation of inorganic nano-silica with the GA–chitosan–PVA blend matrix was also considered in this study to change the fluorescent property, and to improve the thermal resistance of the GA–chitosan–PVA blend. Due to the large amount of the silanol groups, the nano-silica can be well dispersed within the PVA matrix, facilitating the manufacturing of fluorescent nanocomposites. It is expected that the fluorescent PVA based blend and its silica nanocomposites developed in the present work could pave a way for the fluorescent probe, drug-carrier, and tracer applications.

## 2. Materials and methods

### 2.1. Materials

PVA powder (99% hydrolyzed) of a typical Mw 89,000–98,000 was supplied by Sigma–Aldrich Chemical Co. Inc. The GA–chitosan powder, with ~18% amine groups in its polymeric chains cross-linked with glutaraldehyde and ~70% free amine groups left behind, was kindly supplied by Sunshine Road Biomaterials Technology Co. Ltd. (Shenzhen, China). Silicon dioxide nanopowder with an average diameter of 5–15 nm (BET) was purchased from Sigma–Aldrich Chemical Co. Inc. Acetic acid (100%, A.R. grade) was obtained from Oriental Chemicals and Lab. Supplies Ltd., Hong Kong. All chemicals were directly used without further purification.

### 2.2. Preparation of GA–chitosan–PVA blend and its nanocomposite film with silica nanoparticles

A certain amount of GA–chitosan powder was dissolved in 100 mL of dilute acetic acid (2%, w/w) at 70 °C in a beaker placed in a thermostatic oil bath equipped with a mechanical stirring device (the reaction lasted for about 1 h until no insolubles were visible).

PVA pellets were dissolved in deionized water at about 85 °C for 1 h. Then, GA–chitosan and PVA solutions were compounded together by mechanical stirring at 75 °C for 2 h, followed by another 1 h of stirring under room temperature to obtain a homogeneous blend. The clear solution was then cast on a glass plate, and gradually dried at 60 °C for 48 h. To neutralize the acetic acid contained in the composite film, the latter was immersed in a 4% NaOH aqueous solution for 1 h, then thoroughly washed with deionized water, and finally dried at 60 °C for 48 h. Pure PVA and PVA based blend films with various concentrations of GA–chitosan were prepared with the same procedure.

A given amount of nano-silica powder was dispersed into deionized water with the assistance of mechanical stir and ultrasonic wave for about 2 h, and then a homogenous aqueous dispersion of nano-silica was obtained, followed by compounding GA–chitosan solution and nano-silica dispersion. The resultant clear dispersion was cast into a flat Petri dish and allowed to stand for about 2 h until no bubbles were observed. Finally, it was oven-dried at 60 °C for 48 h. A series of 8% GA–chitosan–PVA blend based nanocomposites with different loadings of silica nanoparticles were fabricated with the same procedure. As for the prepared samples, all percentages presented in this paper are the percentages of the weight of GA–chitosan or nano-silica related to the total weight of the composite.

### 2.3. Characterization

The structures of the powder and film samples were analyzed using a Fourier transformed infrared spectrometer (FTIR, Perkin Elmer System 2000). The FTIR spectra of the powder samples were recorded using KBr pellet technique, and the PVA based film samples were tested in the mode of attenuated total reflection (ATR). The UV–vis spectra of the composite film samples were measured with a UV–vis spectrometer (Lambda 2S, Perkin Elmer), and their fluorescence spectra were recorded with a Perkin-Elmer Luminescence spectrometer LS50B, which was equipped with a motor-driven linear polarizer on the detection side, at room temperature under isotropic excitation. The crystalline and glass transition behaviors of the pure PVA and its composites filled with the GA–chitosan and nano-silica were measured by a differential scanning calorimeter (DSC, Perkin Elmer DSC-7) according to the following way: 10 mg of sample was firstly sealed in an Al pans, heated from 25 to 250 °C with a rate of 10 °C/min, kept at 250 °C for 3 min, then cooled from 250 to 25 °C with a rate of –10 °C/min and kept at 25 °C for 3 min, and finally heated again from 25 to 250 °C with a rate of 10 °C/min. The cooling and second heating stages were selected for the analysis. Thermogravimetric analysis (TGA) of the samples was carried out on a Mettler Toledo TGA/SDTA851 under N<sub>2</sub> atmosphere with a heating rate of 10 °C/min. The morphologies of pristine GA–chitosan and nano-silica powders, and freeze-fractured sections of PVA based composites were investigated using a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F). Before SEM observation, all the samples were coated with a thin layer of platinum. The crystallinity of the pure PVA and its composite materials were studied by a X-ray diffraction device equipped with 9000 W Cu K $\alpha$  X-Ray tubes (XRD, Bruker D8 Advance X-ray diffractometer, Bruker AXS, Karlsruhe, Germany) operating at 45 kV and 200 mA.

## 3. Results and discussion

It is well known that the generation of fluorescence results from  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  transitions of the unsaturated bonds, and that the fluorescence of a material has a close relationship with the following special structure features: (1) the structure with large

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