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Investigation of PVA/ws-chitosan hydrogels prepared by combined γ-irradiation and freeze-thawing

Xiaomin Yang [a,b], Qi Liu [a,b], Xiliang Chen [a,b], Feng Yu [a,b], Zhiyong Zhu [a,*]

[a] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, P.O. Box 800-204, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

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Abstract

γ-Irradiation combined with freeze-thawing, i.e. irradiation followed by freeze-thawing and freeze-thawing followed by irradiation, was applied to prepare poly(vinyl alcohol) (PVA)/water soluble chitosan (ws-chitosan) hydrogels for wound dressing. The properties of these hydrogels were investigated and compared to those prepared by freeze-thawing and by irradiation, respectively. Hydrogels made by irradiation followed by freeze-thawing show larger swelling capacity and mechanical strength, higher thermal stability, lower water evaporation rate, and are less turbid than those made by pure freeze-thawing and freeze-thawing followed by irradiation. Hydrogels made by irradiation alone cannot be used as wound dressing due to their poor mechanical strength. SEM results show that the final structure of hydrogels made by combined irradiation and freeze-thawing is mainly determined by the first processing step. It is found that the appropriate amount of ws-chitosan can endow hydrogels with large swelling capacity and mechanical strength. The presence of ws-chitosan provides the hydrogels with good antibacterial activity against *Escherichia coli (E. coli)*.

Keywords: Hydrogels; Freeze-thawing; Irradiation; Rheology; Water soluble chitosan

1. Introduction

Hydrogels are cross-linked hydrophilic polymer networks which can absorb large amounts of water without dissolution. Owing to their similar physical properties to human tissues and their excellent tissue compatibility, hydrogels have been studied extensively for biomedical applications. They can be used as soft contact lenses (Opdahl, Kim, Koffas, Marmo, & Somorjai, 2003), tissue engineering scaffolds (Nowak et al., 2002), controlled drug-release vehicles (Qiu & Park, 2001) and wound dressings (Sen & Avci, 2005; Wu et al., 2004; Yang & Lin, 2004). Hydrogels have many advantages as wound dressings. For instance, they can absorb excess of wound exudates, protect the wound from secondary infection and effectively promote the healing process by providing a moisturized wound healing environment (Winter, 1962). They can also be removed without causing trauma to the wound.

Chitosan, the partially deacetylated form of chitin, is a well known material in the wound dressing field. It has excellent biocompatibility, biodegradability, hemostatic, and antibacterial activity. In general, chitosan with a high molecular weight is insoluble in water but can dissolve in acid solution. Hydrogels made from chitosan acid solution often need a repeated washing process to neutralize the acid. The use of water-soluble chitosan (ws-chitosan) can simplify the process of making hydrogels. Poly (vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer. It has been used in practical applications because of its easy preparation, excellent chemical resistance and physical properties, and it is completely biodegradable and cheap. With these considerations, the blends of ws-chitosan and PVA were used as the hydrogel materials for wound dressing in this experiment.

* Corresponding author. Tel./fax: +86 21 59556904.
E-mail address: zhuzhiyong@sinap.ac.cn (Z. Zhu).

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Hydrogels can be made by irradiation, freeze-thawing or chemical methods. Irradiation is considered as a suitable tool for the formation of hydrogels. It has the advantages of easy control of processing, no necessity to add any initiators or cross-linkers which may be harmful and difficult to remove, and possesses the possibility of combining hydrogel formation and sterilization in one technological step. The main disadvantage of hydrogels prepared by irradiation is their poor mechanical strength. Hydrogels prepared by freeze-thawing from PVA aqueous solutions have shown many interesting properties. They have good mechanical strength, are stable at room temperature, and with no initiators or cross-linkers. The main disadvantages of this kind of hydrogel are its opaque appearance and the limited swelling capacity and thermal stability.

Up to now, much work has been done on preparing hydrogels by irradiation (Lopergolo, Lugao, & Catalaini, 2002; Park & Nho, 2004; Sen & Avci, 2005; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003a) or by freeze-thawing (Bajpai & Saini, 2005; Hickey & Peppas, 1997; Nugent, Hanley, Tomkins, & Higginbotham, 2005; Ricciardi, Gaillet, Ducouret, Lafuma, & Laupretre, 2003). However, there is very little information on preparation of hydrogels by combining the two processing techniques (Nho & Park, 2002), especially by irradiation followed by freeze-thawing. In this research, PVA hydrogels with or without ws-chitosan were prepared by combined γ-irradiation and freeze-thawing, namely irradiation followed by freeze-thawing and freeze-thawing followed by irradiation. The properties of these hydrogels including the gel fraction, the swelling behavior, the water evaporation rate, the rheological properties, and the antibacterial behavior, as well as their relationship to ws-chitosan content were investigated. The results were discussed in comparison with hydrogels prepared by pure irradiation and pure freeze-thawing.

2. Experimental

2.1. Materials

PVA-1750 (M_w: 80 500) was bought from Sinopharm Chemical Reagent Co. Ltd., China. Ws-chitosan, manufactured by protonation of chitosan in HCl/CH_3CH_2OH solution, was obtained from Jinhu Chitin Co. Ltd., China. The weight-average molecular weight and deacetylation degree of the chitosan before protonation were 200 000 and 91.7%, respectively. Agar (Bacteriological Grade) was bought from Xiamen Xinglongda Chemical Reagent Co. Ltd., China. Nutrient broth was purchased from Shanghai Kangrun Biotech Co. Ltd., China.

2.2. Preparation of the hydrogels

Aqueous solutions of PVA were obtained by dissolving PVA in distilled water at 96 °C under refluxing for 3 h. The solution was mixed with ws-chitosan solutions at 45 °C and stirred for 30 min with a physical stirrer. In order to remove bubbles, the solutions were placed in an ultra sonic water bath at 45 °C for 15 min. The aqueous solutions with 7 wt% PVA and various contents of ws-chitosan were then poured into Petri dishes. Hydrogels were obtained by γ-irradiation (Irra.), γ-irradiation followed by freeze-thawing (Irra. + FT), freeze-thawing (FT), and freeze-thawing followed by γ-irradiation (FT+Irra.), respectively. Irradiation was performed in N_2 atmosphere with ^{60}Co γ-ray to a dose of 30 kGy and at a dose rate of 0.76 kGy/h. Freezing and thawing were repeated up to three times to form hydrogels. Each cycle of freeze-thawing involved lowering the temperature to −20 °C, standing at this temperature for 1.5 h, and then raising the temperature to 25 °C, standing at this temperature for 1 h.

2.3. Gel fraction

Hydrogels made by various methods were first dried at 60 °C for 48 h until a constant weight (W_d) was reached. Then the sol part was extracted by immersing the dried gels in hot distilled water at 45 °C for 72 h with water being changed every 5 h. The extracted hydrogels were dried at 60 °C for 48 h to a constant weight (W_r). The gel fraction was defined as $\text{Gel}\ (\%) = (W_r/W_d) \times 100$.

2.4. Swelling behavior

Hydrogels made by various methods were extracted in distilled water at 45 °C for 72 h. After the water on the surface of the extracted gels was removed with cellulose paper, the gels were immersed in various buffer solutions (0.01 mol/L) for at least 24 h until an equilibrium state of swelling (with a weight of W_s) was achieved. Then the swollen gels were dried at 60 °C for 48 h to a constant weight (W_d). The degree of swelling (DS) of gels in various buffer solutions was calculated as $DS = W_s/W_d$.

The swelling kinetics of hydrogels in distilled water at 37 °C was followed by measuring the weight (W_t) of hydrogels at regular intervals until the gels reached the equilibrium state of swelling (weight = W_s). The swelling kinetics of hydrogels was calculated by the following equation

$$\text{Water retained}(\%) = (W_t - W_d)/(W_s - W_d) \times 100$$

where W_d was the weight of the initially dried gels.

2.5. Evaporation rate of water from hydrogel

The swollen hydrogels (with a weight of W_s) were kept at 37 °C and 40% relative humidity in an incubator. After regular intervals of time, the weight (W_t) was measured. Water loss percentage was calculated by the following equation

$$\text{Water lost}(\%) = (W_s - W_t)/(W_s - W_d) \times 100$$

where W_d was the weight when the gel lost all its water.