



Macromolecular Nanotechnology

Properties of as-prepared and freeze-dried hydrogels made from poly(vinyl alcohol) and cellulose nanocrystals using freeze-thaw technique



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ABSTRACT

Poly(vinyl alcohol), PVA hydrogels are potential materials for biomedical and biotechnological applications. However, their low mechanical properties restrict their use. In this study, the effect of PVA concentration, addition of nanocrystalline cellulose, CNC, number of freeze-thaw cycles and freeze-drying stage on properties of resulting hydrogels were investigated. The results showed that increase in PVA concentration and the addition of CNC improved the compressive properties of the hydrogels. Overall, increase in number of freeze-thaw cycles from 3 to 5 did not show any improvements in properties of hydrogels. Concentration of PVA had great effect on morphology of freeze-dried hydrogels. The CNC reduced crystallinity of PVA/CNC hydrogels as compared to PVA hydrogels. Rehydrated PVA and PVA/CNC hydrogels had higher compressive characteristics than their as-prepared analogues. In general, an improvement of compressive properties of hydrogels was achieved via reduction of their water content. In case of 5% PVA hydrogel, an addition of CNC was found to be beneficial because it increased degree of swelling and water content on rehydration.

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1. Introduction

Polyvinyl alcohol (PVA) is a water-soluble, non-toxic, biodegradable and biocompatible synthetic polymer. Due to its hydroxyl groups present in each repeating unit, PVA exhibits a strong hydrophilic and hydrogen bonding character; thus it is able to form cross-linked hydrogels [1]. Physical hydrogels can be obtained by exposing PVA aqueous solutions to repeated cycles of freezing and thawing, which resulted in formation of crystallites. The preparation of ultrapure PVA hydrogels using freeze-thaw method was first reported by Peppas in 1975 [2]. Typically, freeze/thaw PVA hydrogels are elastic, they manifest a long-term dimensional stability, they can be extended up to 5–6 times their initial length and they do not lose elasticity even after immersion in water for a long time [3].

Tested biocompatibility of freeze-thaw PVA hydrogels and their ability to incorporate and release large amounts of host molecules of different size in their structure make these systems particularly attractive for biomedical and biotechnological applications. For example, Peppas and Mongia [4] and Păduraru et al. [1], demonstrated that the PVA has potential application as carrier for bioactive components. PVA-based hydrogels mimics the nonlinear mechanical properties displayed by cardiovascular tissue and their anisotropic behaviour [5]. Vasanthan et al. [6] have tested PVA/gelatin hydrogels as scaffolds for liver tissue. Commercially available PVA hydrogel called Salubria™ (Salumedica, Atlanta, GA) displays

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similarities to natural cartilage tissue in terms of water content and, furthermore, shows promise in terms of its mechanical integrity and biocompatibility. Salubria™ biomaterial made of a freeze-thawed organic polymer (PVA) molecular backbone and 0.9% saline [7]. The mechanical properties of the Salubria™ biomaterial may be influenced by several factors. These factors include weight percentage of the respective components of the cryogel (water and PVA), the molecular weight of the initial PVA polymer element, the number of freeze-thaw cycles and the duration of the freeze cycle [8].

While PVA hydrogels possess similar water content to articular cartilage, a critical barrier to their use is a lack of sufficient mechanical properties to withstand the severe loading conditions imposed on articular joint surfaces. The incorporation of functional materials into PVA hydrogels have been studied with the general aims of either reinforcement for artificial tissue applications or for drug delivery [9]. Scientific literature presented different types of cellulose incorporated into PVA films and hydrogels, such as bacterial cellulose [10,11], cellulose whiskers (CNW) [12], cellulose nanofibres (CNF) [13,14], and cellulose nanocrystals (CNC) [9,15,16].

CNCs are needle-shaped, high aspect ratio particles produced from the mineral acid hydrolysis of native celluloses. The amorphous regions of cellulose microfibrils are accessible to acidic degradation and controlled hydrolysis results in a narrow size distribution ($L \sim 100\text{--}300\text{ nm}$ and $d \sim 5\text{--}10\text{ nm}$) of highly crystalline residual particles. Sulfuric acid hydrolysis produces stable colloidal suspension of CNC in water and the CNCs are attractive as reinforcement for biopolymers because they are derived from affordable, renewable resources, and because of the high crystallinity, aspect ratio and apparent biocompatibility [17].

In this paper, the effect of 1.0 wt% CNC loading was studied because according to results published by Abitbol et al. [9] the loadings of CNCs greater than 1.5 wt% rather disturb the structure of PVA hydrogels than reinforced it. The PVA hydrogels were prepared with three different PVA concentrations and with varying number of freeze-thaw cycles. The mechanical properties, swelling behaviour, morphology and thermal characteristics of the hydrogel were evaluated. In 1986 Babayevskii et al. [18] showed that by means of controlled sorption-desorption of water PVA properties may be modified reversibly and within wide limits, particularly in the case of PVA transition from the state of elastic gel to solid glassy polymer, and vice versa. This means there should be much scope for applications of PVA in the production of materials and articles fabricated from them. In this study, the compressive properties of PVA and PVA/CNC hydrogels were evaluated for as-prepared hydrogels and for rehydrated freeze-dried hydrogels.

2. Experimental

2.1. Materials

PVA hydrogels were prepared by using commercial grade PVA (Aldrich Chemistry) with an average molecular weight, M_w of about 89,000–98,000 and a degree of hydrolysis of 99+%. Cellulose nanocrystals (CNC) (2013-FPL-CNC-0499) were provided by US Forest Service, Forest Product Laboratory, Madison, USA. The material is 10.3 wt% suspension of CNC in water, and it contains 1.02 wt% sulphur determined on the base of weight of dry CNC. Fig. 1 shows the AFM height and phase images of CNCs and their length and diameter (height) distributions. The length and the height were measured using the “FibreApp” software, the algorithm developed by Usov and Mezzenga [19] was used.

2.2. Preparation of materials

2.2.1. Preparation of PVA hydrogels

Aqueous solutions of PVA with concentrations 5, 7.5 and 10% (w/v) concentrations were prepared by dissolving the PVA polymer in distilled water at 90 °C, under stirring for about 3 h. The polymer was entirely dissolved and the obtained transparent solutions were slowly cooled to room temperature. The aqueous PVA solutions were then poured in plastic mould having 14 sections with dimensions: length \times width \times thickness: $16 \times 16 \times 10\text{ mm}^3$. PVA5, PVA7.5 and PVA10 hydrogels were obtained by subjecting the polymer aqueous solutions with corresponding concentrations to repeated freeze-thaw cycles (3 F-T and 5 F-T), consisting a 24 h freezing step at $-20\text{ }^\circ\text{C}$ followed by a 2 h thawing step at room temperature. The choice of number of freeze-thaw cycles was based on the previous studies by Ricciardi et al. [3] and Holloway et al. [20].

2.2.2. Preparation of PVA/CNC hydrogels

The CNC concentration used in this study was 1 wt% determined on the base of dry weight of PVA. A CNC suspension was dispersed in distilled water by using 24-h stirring followed by ultrasonication for 10 min. Ultrasonication was performed using Ultrasonic Processor UP 2005 (Hielscher Ultrasound Technology), the cycle was set to 0.5 and amplitude to 50%. After sonication PVA was added into CNC dispersion. The mixture was placed on magnetic stirrer and heated at 90 °C for about 3 h to dissolve PVA. Then the PVA5/CNC1, PVA7.5/CNC1 and PVA10/CNC1 solutions were slowly cooled to room temperature and after poured in plastic mould which was subjected to repeated freeze-thaw cycles (3 F-T and 5 F-T) consisting a 24 h freezing step at $-20\text{ }^\circ\text{C}$ followed by a 2 h thawing step at room temperature.

2.2.3. Freeze-drying

To determine the water content and re-absorption capacity, to study morphology, thermal properties as well as mechanical properties after rehydration, the PVA and PVA/CNC hydrogels prepared according to procedures described in Sections

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