Carbohydrate Polymers 200 (2018) 468–476

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Interpenetrating polymer networks in polyvinyl alcohol/cellulose nanocrystals hydrogels to develop absorbent materials

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ARTICLE INFO

Keywords:
Polyvinyl alcohol
Cellulose nanocrystals
Photo-crosslinking
Interpenetrating polymer networks
Hydroxyethyl methacrylate
N, N'-methylenebisacrylamide

ABSTRACT

Polyvinyl alcohol/cellulose nanocrystals/poly(2-Hydroxyethyl methacrylate) (PVA/CNC/polyHEMA) and PVA/CNC/poly(N'-methylenebisacrylamide) (PVA/CNC/polyMBA) hydrogels were prepared by photo-crosslinking followed by freezing/thawing (F-T) cycle and this novel preparation method was reported. The formation of interpenetrating polymer networks (IPN) resulted from the addition of crosslinking HEMA or MBA monomers displayed improved interfacial adhesion. The produced hydrogels were measured by scanning electron microscopy (SEM), real-time fourier transform infrared (RTIR), thermogravimetric analysis (TGA), mechanical, swelling and adsorption tests. The results showed both PVA/CNC/polyHEMA with semi-IPN and PVA/CNC/polyMBA with dual network (DN) hydrogels had higher thermal stability, lower water loss rate and better swelling and reswelling and mechanical properties, comparing to PVA and PVA/CNC hydrogels. The adsorption behaviors of hydrogels using xylenol orange (XO) and methylene blue (MB) as model dyes were evaluated, indicating that PVA/CNC/polyHEMA and PVA/CNC/polyMBA hydrogels could hold some dyes. Overall, this work provided a good way for increasing mechanical, swelling, reswelling, thermal, and adsorption properties of PVA/CNC, which will be a promising water-manageable material for agriculture application and a candidate for dye carrier.

1. Introduction

Hydrogels as a soft material have extensive researches and applications in the biological medicine, agriculture, forestry, horticulture and environmental protection (Enas, 2015; Lee & Mooney, 2001; Wichterle & Lim, 1960). Polyvinyl alcohol (PVA) is one of the traditional raw materials for the preparation of hydrogels, because of its biocompatibility and high hydrophilicity (Oka, Cha, & Hyon, 1995;Suciu , Iwatsubo , Matsuda, & Nishino, 2004 Suciu, Iwatsubo, Matsuda, & Nishino, 2004). Nonetheless, PVA hydrogels can hardly meet some high requirements because of its unsatisfied properties, such as higher water loss ratio and worse reswelling behavior, as well as lower mechanical strength. So, it is particularly necessary to enhance these properties of PVA based hydrogels. Yang et al. (Yang et al., 2012; Yang, Zhao, Xu, & Sun, 2013) provides valuable knowledge for designing high performance nanocomposite hydrogels from cellulose as a raw material.

Cellulose, which is the most abundant polysaccharide, is widely present in the biomasses, such as cotton, trees, and bacteria (Valentini, Cardinali, Fortunati, Torre, & Kenny, 2013). In the start materials, the cellulose has amorphous regions and crystalline regions. Cellulose nanocrystals (CNC) can be obtained by hydrolyzing the amorphous regions of cellulose under acid conditions. Depending on its resources, the nanocrystalline domain of CNC is 1–100 nm in diameter and 10–100 nm in length (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Valentini et al., 2013). CNC could be modified owing to a lot of hydroxyl groups on its surface. And the modified CNC is beneficial to the dispersion in the matrix and improves the compatibility with the polymer (Dash & Ragauskas, 2012; Menezes, Siqueira, Curvelo, & Dufresne, 2009; Hu, Ballinger, Pelton, & Cranston, 2015; Liu & Berglund, 2013; Tang et al., 2014). The properties of PVA reinforced by CNC has been widely concerned (Medeiros, Mattoso, Offeman, Wood, & Orts, 2008; Peresin et al., 2014; Popescu, 2017; Spoljaric, Salminen, Luong, & Seppala, 2014; Voronova, Surov, Guseinov, & Barannikov, 2015). Voronova et al. (2015) found that PVA/CNC composites had better thermal stability and Peresin et al. (Peresin et al., 2014) indicated that CNC can improve the thermomechanical properties of PVA. Nowadays, many researchers try to add CNC to PVA hydrogels. The results showed that the addition of CNC improved the compressive and absorption properties of the PVA hydrogels (Butylina, Geng, & Oksman,

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https://doi.org/10.1016/j.carbpol.2018.08.041

2016). However, the improvements are not obvious. So we further improve the overall performance of PVA/CNC hydrogels through interpenetrating polymer networks (IPN) strategy in this paper.

IPN has been thought to be an appropriate method to facilitate interfacial interactions between polymers and improve properties of hydrogels because of its more stable internal structure (Chen, Zhu, Zhao, Wang, & Zheng, 2013, 2015; Li, Zhang, Fortin, Xia, & Zhao, 2015).

IPN is composed of two polymers, which are crosslinked by strong interlocking crosslinking to form a network. Owing to the entanglement of polymer chains, the material with IPN has exceptional properties. In the related research, the presence of poly (HEMA) or poly (MBA) could improve polymer interpenetration. As such, tertbutyl acrylate-co-2-hydroxyethyl methacrylate (HEMA) or N, N'-methylenebisacrylamide (MBA) was susceptible to free radical polymerization and used as a component in the IPN. Therefore, CNCs are expected to have excellent reinforcing effects in both PVA/CNC/polyHEMA and PVA/CNC/polyMBA systems, in which the IPN structure formed and the CNC in the IPN embedded in the PVA matrix.

As a new type of cross-linking technology, photo-crosslinking technology uses low-energy ultraviolet light as a radiation source, and has the advantages of simple operation, quick environmental protection and low cost. The UV-responsive initiator decomposes and produces highly reactive free radicals under UV light, causing polymerization to propagate rapidly (Halake & Lee, 2014).

In this study, PVA/CNC based hydrogels with added HEMA or MBA was prepared through in situ photo-crosslinking followed by freezing/thawing (F–T) cycle. The structures and properties of PVA, PVA/CNC, PVA/CNC/polyHEMA, and PVA/CNC/polyMBA hydrogels were studied. The effect of IPN resulted from photo-crosslinking and F-T on the mechanical, water loss rate, swelling, reswelling, thermal, and adsorption properties of the resulted hydrogels was investigated in detail. Furthermore, PVA/CNC/polyHEMA and PVA/CNC/polyMBA hydrogels had higher mechanical strengths, lower water loss rate, higher thermal stability, and better swelling and reswelling and adsorption properties.

2. Materials and methods

2.1. Materials

PVA-1799 was purchased from Sinopharm Chemical Reagent Co., Ltd., China. HEMA solution (96 wt % solution) was purchased from Aladdin while 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone (commercial name Irgacure 2959, I2959) was purchased from BASF Kaisten AG. MBA powder was supplied from Sigma Aldrich. Xylenol orange (XO) (AR) and methylene blue (MB) (AR) were supplied by Aladdin Chemical Reagent Corp., Shanghai, China.

2.2. Material preparation

2.2.1. The pure PVA hydrogels

PVA was added to deionized water at a weight ratio of 1:11.5 and a PVA solution was obtained by keeping PVA in a water bath at 95°C and stirring for 1.5 h. Subsequently, the PVA solution was cooled to room temperature, until the bubble completely disappeared. Afterward, through F-T cycle (freezing at -10°C for 8 h followed by thawing for 2 h at room temperature), a large number of crystallites were generated, and the PVA solution would form into PVA hydrogels.

2.2.2. The PVA/CNC hydrogels

Firstly, CNC aqueous suspension was prepared by sulfuric acid hydrolysis of cotton linters. Specific operations are as follows: 3 g cotton fiber was added to 62 mL 65% H_2SO_4 and treated at 50°C for 45 min under stirring. The mixture was centrifuged and dialysised with deionized water to remove the residual acid. The aqueous suspension was then subjected to ultrasonic dispersion in an ultrasonic cleaning machine for 30 min to disperse the CNC and break any agglomerates formed. The dispersed CNC was diluted to obtain an aqueous dispersion with concentration of 0.005 g/mL. Afterwards, PVA solution (see the preparation of pure PVA hydrogels) was added to the CNC aqueous suspension at given CNC/PVA mass ratios of 0.005:1, 0.01:1, 0.02:1, 0.03:1. These mixtures were stirred at 90°C for 2 h and ultrasonicated at room temperature for 20 min. Through a F-T cycle, the PVA/CNC solution would form PVA/CNC hydrogels. The results showed PVA/CNC hydrogels had better mechanical strength when the CNC/PVA mass ratio was 0.01:1. (see Fig. S1a,b of Supporting Information).

2.2.3. The photo-crosslinked PVA/CNC/polyHEMA hydrogels

Both HEMA solution and photo-crosslinker I2959 were added to PVA/CNC mixtures (CNC:PVA was 0.01:1). The HEMA:[PVA + CNC] mass ratios was 15:85 while the I2959:[PVA + CNC] mass ratio was kept at 2:100. The mixtures were crosslinked by being exposed to an F300 UVA lamp (Fusion UV systems, USA, the total incident light intensity is about 1600 mJ/cm^2 and the radiation intensity on the sample surface is about 400 mW/cm^2 when one pass is completed on band conveyor) operating with the band conveyor (5.0 inch/min speed) and using 5 passes. The obtained photo-crosslinked PVA/CNC/polyHEMA sol would form into hydrogels through a same F-T cycle. The specific preparation processes as shown in Fig. 1.

2.2.4. The photo-crosslinked PVA/CNC/polyMBA hydrogels

The preparation process is similar to that of photo-crosslinked PVA/CNC/polyHEMA hydrogels. The specific preparation processes is shown in Fig. 1.

2.3. Characterization

2.3.1. Real-time Fourier transform infrared (RTIR)

RTIR measurements were carried out by using a Nicolet 5700 FTIR spectrometer from Thermo Scientific. The PVA/CNC/HEMA and PVA/CNC/MBA solution were exposed to UV light for 300 s at intensity of 50.0 mW/cm^2 and cross-linked at room temperature. The progression of the reaction was followed by monitoring the change in absorption of the acrylate peak at 1635 cm^{-1}. The conversion was calculated from the absorption data as indicated in Eq. (1):

$$\text{Conversion degree (\%)} = (A_0 - A_t)/A_0 \times 100 \tag{1}$$

where A_0 and A_t are the absorption values before and UV irradiation at time t.

2.3.2. Scanning electron microscopy (SEM)

The micromorphology of PVA, PVA/CNC, PVA/CNC/polyHEMA, and PVA/CNC/polyMBA hydrogels was observed by using a Hitachi S4800 scanning electron microscope (Tokyo, Japan) at an accelerating voltage of 2 kV. The hydrogels were freeze-dried and then freeze-fractured in liquid nitrogen. All these samples were sputtered with a thin gold layer before measurement.

2.3.3. Mechanical properties

The tensile tests were performed using an Instron 5967 (Instron Co. Ltd.) at room temperature. Samples of PVA, PVA/CNC, PVA/CNC/polyHEMA, and PVA/CNC/polyMBA hydrogels were cut into dumb bell shaped samples with an initial notch (w = 4–5 mm, d = 2–3 mm, L = 30 mm; the length of the initial notch was 15 mm), respectively, according to GB1040-79. The average values of tensile strength (TS) and elongation at break (EB) of five replicates of each sample were taken. The initial Young's modulus was obtained by calculating the stress and strain between EB = 0 and 0.1.

Compressive tests were carried out on cylindrical samples of a diameter of 7–9 mm and a thickness of 3–5 mm using an Instron 5967 (Instron Co. Ltd.) at room temperature. The compression rate was 2 mm/min. The compressive stress (σ_c), defined as engineering stress,