Materials Science and Engineering C 34 (2014) 54–61

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

# Poly(vinyl alcohol)/cellulose nanowhiskers nanocomposite hydrogels for potential wound dressings

Jimena S. Gonzalez [a], Leandro N. Ludueña [a,*], Alejandra Ponce [b], Vera A. Alvarez [a]

[a] Composite Materials Group, Research Institute of Material Science and Technology (INTEMA) (CONICET-UNMdP), Solís 7575, B7608FLC Mar del Plata, Argentina
[b] GIIA Group, Research Institute of Material Science and Technology (INTEMA) (CONICET-UNMdP), Juan B. Justo 4302, B7608FDQ Mar del Plata, Argentina

ARTICLE INFO

*Article history:*
Received 2 June 2013
Received in revised form 27 August 2013
Accepted 10 October 2013
Available online 18 October 2013

*Keywords:*
Polymer-matrix composites
Nano-composites
Nano-particles
Composite hydrogel
Cellulose nanowhiskers

ABSTRACT

Polyvinyl alcohol (PVA)/cellulose nanowhisker (CNW) nanocomposite hydrogels to be used for wound dressing were obtained by freezing–thawing technique and characterized by means of morphological, physical, thermal, mechanical, barrier and antimicrobial properties. First, cellulose nanowhiskers were obtained by the acid hydrolysis of commercial crystalline microcellulose (MCC) and characterized by its size, shape, morphological, structural and thermal properties. Then, PVA/CNW nanocomposites with several CNW contents (0, 1, 3, 5 and 7 wt.%) were obtained. Morphological, thermal, chemical and physical characterization of the PVA/CNW nanocomposite hydrogels was carried out. It was found that the addition of CNW to the hydrogel allows controlling the pore morphology of the samples. On the other hand, the transparency of the samples was maintained, the thermal stability was increased, the mechanical properties were improved and the water vapor transmission rate was in the range of wound dressing applications after CNW incorporation inside the PVA hydrogel matrix. The evaluation of microbial penetration showed that the prepared hydrogels can be considered as a good barrier against different microorganisms. All obtained results indicate that the PVA/CNW materials are promising to be used as wound dressing.



## 1. Introduction

Substantial efforts are being lately expended to develop new materials for protecting the damaged skin from infections and dehydration [1]. The development of a new generation of wound dressings with improved healing attributes that provide an antimicrobial effect has been encouraged [1,2]. These dressings still require to be frequently changed, which may be painful to the patient, harm the vulnerable underlying skin and increase the risk of secondary contamination.

An ideal dressing should meet some requirements: creating and remaining a moisture environment, being biocompatible, absorbing fluids and exudes effectively, showing higher gas permeation, exhibiting high elasticity and also adequate mechanical strength, being transparent, and acting as a barrier against the bacterials, ensuring a protection of wound from infection and dehydration [1,3].

Hydrogel is seen as an essential component in many different types of wound care. This is because these kinds of dressings are designed to hold moisture in the surface of the wound, providing the ideal environment for cleaning the wound, absorbing the exudates and promoting the healing process [4]. The moisture in the wound is also essential in pain management for the patient, and hydrogels are very soothing and cooling.

Poly(vinyl alcohol) (PVA) hydrogels are biocompatible, non-toxic and they can absorb a huge amount of exudates [5]. Hydrogels consist in a hydrophilic polymer that forms a three-dimensional network, which swells and retains a lot of water (or biological fluids) without being dissolved. They can be obtained based on natural or synthetic polymers. Synthetic hydrogels, that have over 50% water, are notoriously brittle and have poor microstructural and mechanical stabilities [6]. For all these features PVA hydrogels can be as the right option for dressing applications. However they lack in mechanical properties.

Composites have been introduced to improve mechanical stiffness and durability [7]. The composites can be designed to meet the mechanical and physiological requirements of target application by controlling the volume fraction, morphology and physico-chemical characteristics of the reinforcement [8]. This is due to the fact that these features are responsible for the interface interaction between the polymer and the filler; the aspect ratio of the filler [9] and the dispersion of them inside the matrix [10].

Over the past decade, composite materials have attracted a great deal of interest and particular attention has been focused on the use of cellulosic fibers as reinforcements in polymer matrices for biomedical applications [11] due to their good biocompatibility [12]. The hydrolysis of cellulosic materials with a strong acid (sulfuric or hydrochloric acid) yields highly crystalline, well-defined, slender rod-like nanoparticles called cellulose nanowhiskers (CNWs) [13]. These can be about 5–10 nm in diameter and range from 100 nm to several micrometers in length depending on the origin of the cellulose (such as wood, cotton,

* Corresponding author. Tel.: +54 223 4816600x321.
*E-mail address:* luduena@fi.mdp.edu.ar (L.N. Ludueña).

0928-4931/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2013.10.006

bacteria, among others). The CNW shows elastic modulus as high as 130–150 GPa and strengths of 10 GPa along the axial direction [14].

Therefore, PVA/CNW nanocomposite hydrogels are ideal for different applications such as water treatments [15], soft tissue replacement [16] and drug delivery [17].

The aim of this work was to improve specific properties of PVA hydrogels as required for their use as dressings. For this purpose, composite hydrogels based on PVA and different concentrations of cellulose nanowhiskers were synthesized and characterized by means of thermal and swelling analysis, scanning electron microscopy, X-ray diffraction, mechanical and water vapor permeation measurements. Herein it was developed a reliable and a facile way to obtain nanocomposite hydrogels based on PVA with reasonable mechanical properties and excellent swelling behavior.

## 2. Experimental part

### 2.1. Materials

The PVA used in this study was a commercial product purchased from Sigma-Aldrich (USA) (Mw: of 89000–98000 g/mol, hydrolysis degree of 98–99%). The microcrystalline cellulose (MCC) was purchased from Aldrich (USA). Sulfuric acid with analytical grade was supplied by laboratory Cicarelli (Argentina).

### 2.2. Cellulose nanowhisker (CNW) production

CNW was prepared by the acid hydrolysis of MCC. The acid hydrolysis was carried out with sulfuric acid ($H_2SO_4$) solution 60 wt.% at 45 °C for 30 min under continuous stirring [15]. That solution was dialyzed for 5 days and then was spray dried in a BUCHI Mini-Spray Dryer B-290 at 185 °C.

### 2.3. Preparation of nanocomposite hydrogels

Aqueous solutions of 10 wt.% PVA were prepared by dissolving the polymer in distilled water at 85 °C and slowly stirring (with magnetic stirrer) for 1 h. After stirring, 1, 3, 5 and 7 wt.% of CNW (1CNW, 3CNW, 5CNW and 7CNW) were added and the stirring continued for 3 h more in order to completely dissolve the polymer. After this step, the solutions were placed in an ultrasonic bath for 30 min to remove all bubbles. The solutions were allowed to reach room temperature. Then, the PVA-based solutions were cast onto anti-adherent containers and frozen for 1 h, cooling down to −18 °C and afterward placed at room temperature (25 °C, thawing process) for the same time in order to crosslink the polymer. This procedure was repeated 3 times. To obtain the neat PVA hydrogel (PVA) the same steps were followed but without the addition of filler.

### 2.4. Methods

#### 2.4.1. Characterization methods

*2.4.1.1. Fourier transformed infrared (FTIR) spectroscopy.* FTIR spectra of MCC and CNW were obtained in transmission mode. Samples were ground with KBr, pressed and then analyzed in a Thermo-Scientific Nicolet 6700 spectrometer, with a resolution of 4 $cm^{-1}$. 32 scans were performed over each sample from 600 to 4000 $cm^{-1}$. In the case of hydrogels, the ATR (Attenuated Total Reflectance) accessory was utilized to perform the measurements.

*2.4.1.2. Thermogravimetric analysis (TGA).* Dynamic thermogravimetric measurements of MCC and CNW were performed by using a Shimadzu TGA-50 instrument. Tests were run from 20 to 900 °C at a heating rate of 10 °C/min under $N_2$ atmosphere. In the case of hydrogels, the samples were dried (37 °C, 48 h) before test.

*2.4.1.3. X-ray diffraction (XRD).* Analytical Expert Instrument equipped with an X-ray generator ($\lambda = 0.154$ nm) was used to characterize the crystalline structure of the composites, fillers and matrix. Samples were scanned in 2θ ranges varying from 2 to 50° (2°/min).

*2.4.1.4. Field emission scanning electron microscopy (FESEM).* The morphology of MCC and nanocomposite hydrogels was analyzed by FESEM micrographs with a FE-SEM Zeiss Supra. Microcrystalline cellulose was dispersed in water, ultrasonicated and then casted in a glass, then the water was evaporated, this glass covered by MCC was coated by gold. Nanocomposite hydrogel samples were swollen, frozen, lyophilized and then cryofractured with liquid $N_2$ and coated by gold before testing.

*2.4.1.5. Atomic force microscopy (AFM).* The morphology of CNW was observed by AFM in a 5500 Scanning Probe Microscopy from Agilent Technologies operating in the contact mode in air. Samples were prepared by dispersing 5 mg of CNW in 250 mL of bidistilled water in an ultrasonic bath at room temperature for 30 min. A droplet of the resulting solution was cast onto an AFM mica disk from TED PELLA and dried in vacuum oven at 70 °C for 1 h. The resulting dispersed CNW was exposed to the AFM so as to collect contact mode images.

*2.4.1.6. Differential scanning calorimetry (DSC).* DSC measurements were carried out in a TA Instrument Q2000. Samples were scanned from room temperature to 250 °C at a heating rate of 10 °C/min, under $N_2$ atmosphere. Before DSC analysis, the hydrogel samples were dried for 24 h at 37 °C. The degree of crystallinity ($X_{cr}$%) was calculated from the following equation:

$$X_{cr}\% = \frac{\Delta H}{w_{PVA} \times \Delta H_c} \times 100 \quad (1)$$

where $\Delta H$ was determined by integrating the area under the melting peak over the range 190–240 °C, $w_{PVA}$ was the PVA weight fraction and $\Delta Hc$ was the heat required for melting a 100% crystalline PVA sample, 138.6 J/g [18].

#### 2.4.2. Swelling and permeation studies

*2.4.2.1. Gel fraction determinations.* To perform gel fraction (*GF%*) measurements, a slice of each sample was placed in oven at 37 °C until constant weight was reached. Each sample was immersed into distilled water at room temperature for 4 days to rinse away un-reacted species. Subsequently, the immersed sample was removed from distilled water and dried at 37 °C until constant weight was reached. Therefore the gel fraction can be calculated as follows:

$$GF\% = \frac{W_f - W_F}{W_i - W_F} \times 100 \quad (2)$$

where $W_i$ and $W_f$ are the weights of the dried hydrogels before and after immersion, respectively, and $W_F$ is the weight of the cellulose nanowhiskers added.

*2.4.2.2. Swelling degree measurements.* Swelling determinations were carried out in distilled water at 25 °C. All samples were dried before immersion at 37 °C for 48 h. The equilibrium swelling degree ($M_\infty$ %) was determined by the following equation:

$$M_\infty\% = \frac{M_f - M_i}{M_i} \times 100 \quad (3)$$

where $M_i$ is the weight of the samples before immersion and $M_f$ is the weight of the sample at equilibrium water content.

*2.4.2.3. Water vapor transmission rate (WVTR).* For these measurements, dried hydrogel samples with a diameter of 28 ± 2 mm and a thickness