Carbohydrate Polymers 92 (2013) 982–988

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

# Characterization and controlled release aloe extract of collagen protein modified cotton fiber

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ARTICLE INFO

*Article history:*
Received 23 July 2012
Received in revised form 3 October 2012
Accepted 17 October 2012
Available online 23 October 2012

*Keywords:*
Cotton fiber
Collagen protein
Modification
Sodium periodate oxidation
Release aloe anthraquinone

ABSTRACT

For exploiting the novel multifunctional cotton fibers, a collagen protein modified cotton fiber (CPMCF) was prepared by the oxidation of cotton fiber with sodium periodate solution and subsequent crosslinking reaction with an aqueous solution of collagen protein in acetic acid. Infrared spectra and X-ray photoelectron spectrometry (XPS) analysis of the CPMCF illuminated that the C=N double bond was formed through the imine reaction of the aldehyde group on oxidized cotton fiber with the amino group of collagen protein. X-ray diffractograms indicated that the crystallinity of the oxidized cotton fiber increased from 65.6 to 69.3% after collagen protein treatment. Scanning electron microscopy photographs displayed that the collagen protein combined on the surface of oxidized cotton fiber. The resulting optimum conditions to prepare the CPMCF achieved the sufficient aldehyde groups in oxidized cotton fiber and the collagen protein content on CPMCF, whereas the mechanical strength of the oxidized cotton fiber had no significant change. Meanwhile, a model experiment for the controlled release of aloe anthraquinone extract on CPMCF showed a satisfactory result compared with those release of the original cotton fiber, demonstrated potential application of the synthetic collagen protein–cotton fiber as a carrier for the sustained release of drugs.



## 1. Introduction

Collagen protein, consisting mostly in the skin, bone, tendon, ligaments and blood vessel of animal, is one of the most abundant natural protein resources inside mammalian body with a large unexplored commercial potential. Collagen has the special three-ply helix construction formed through three polypeptide chains, one is the α(I) chain and the other two are the α(II) chains (Gelse, Pöschl, & Aigner, 2003; Giuseppe, Alexandre, Murray, Rolf, & Robert, 2000). Collagen protein is a vital structural protein of connective tissue which can support the organs and protect the organism, and is also the most important functional protein composing the substrate among cells. In recent years, a number of investigations have been carried out to exploit the potential applications of collagen protein (Cavallaro, Kemp, & Kraus, 1994; Takezawa, Ozaki, & Takabayashi, 2007; Wallace & Rosenblatt, 2003). Since collagen has unique structure, physiological and biological activities, low antigen, predominant biocompatibility and biodegradability, it has been applied widely in biomedical material, drug delivery carrier, tissue engineering, cosmetic, foodstuff and feedstuff, etc. (Brown, 2009; Ellis & Yannas, 1996; Fujioka, Takada, Sato, & Miyata, 1995; Madhan, Muralidharan, & Jayakumar, 2002; Wang, Su, & Chen, 2008). It is well known that the collagen protein not only is similar to the human skin collagenic structure but also has the perfect biocompatibility with the human body, which can supply necessary nutrition for the human skin and various amino acids that are helpful to the human body. In addition, the collagen protein can accelerate the skin tissue metabolism so as to moisten the human skin and delay the aging (Chvapil, Kronenthal, & Winkle, 1973; Stein, Vader, Weitz, & Sander, 2011).

Cotton fiber is a greatly vital natural cellulose fiber, which has been extensively utilized as textile, industrial product, construction material and medical commodity. Presently, lots of chemical modification methods by using crosslinking agents treatment, or irradiation of the gamma ray for bonding collagen protein on the poly(vinyl alcohol) and polypropylene fibers have been necessarily applied to improve the properties and find more versatile applications of these fibers (Lin, Dan, & Dan, 2012; Tyan, Liao, Lin, & Chen, 2003; Wang, Tang, Wu, Xu, & Ye, 2007; Wang, Wu, & Chen, 2011). However, the studies on collagen protein modified cotton fiber have not been reported previously. Our work now report a novel modification method by oxidizing the cotton fiber with sodium periodate, the periodate oxidation cleaves the C-2 and C-3 of the glucose units in the cotton fiber molecule, giving the reactive aldehyde groups in the oxidized fiber (Maekawa & Koshijima, 1991; Potthast, Kostic, Schiehser, Kosma, & Rosenau, 2007), subsequently treated with the

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0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.10.042

collagen solution in aqueous acetic acid, then the imine bond produced by the reaction of aldehyde groups on the oxidized cotton cellulose with amino groups of the collagen protein. The resulting collagen protein modified cotton fiber (CPMCF) is a green ecological fiber material, and the preparing process is nonpolluting and eco-friendly without using chemical crosslinking agents.

Additionally, the aloe anthraquinone is extracted from the succulent leaves of a Chinese crude drug, Aloe vera. Aloe anthraquinone has antibacterial, anti-inflammatory, anti-hypersusceptible, anti-ultraviolet radiation, deodorizing and wound healing activities (Abd-Alla et al., 2009; Genovese et al., 2010; Ji & Jia, 2009; Mwale & Masika, 2010; Ranjani, Rajan, & Brindha, 2010). The loading and controlled release of aloe anthraquinone using our newly synthesized CPMCF would be significant to make full use of aloe extract pharmaceutical functions and achieve the efficacies of antibacteria, diminishing inflammation, moistening skin and anti-ultraviolet light, which is applicable to making underwear, bedding and medical commodity for atopic dermatitis.

## 2. Experimental

### 2.1. Materials

Cotton fibers were obtained from Hongxiang Spinning and Dyeing Co. Ltd. (Suzhou, China) and used with preliminary treatment to remove any additives and prevent interference from extraneous substances. Collagen protein with the average molecular weight about 10 kDa and aloe anthraquinone extract were purchased from Mingrang Biotechnology Co. Ltd. (Shanghai, China) and Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan), respectively. All chemicals used for the following investigations were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and of analytical grade. Deionized water was used throughout the following work.

### 2.2. Sodium periodate oxidation of cotton fiber

Desired amount of cotton fiber was immersed in aqueous solutions of sodium periodate ranging in concentrations from 0.1 to 5.0 g/l at a liquor ratio 1:100. The cotton samples were stirred gently at 50 °C for 1 h in the absence of light. Then the oxidized cotton fiber was soaked in 0.1% (w/w) excess ethylene glycol solution with stirring for 30 min at ambient temperature to remove the remaining oxidant, and washed with deionized water up to neutral conditions. The oxidized cotton fiber was used for the next reaction without drying.

### 2.3. Imine reaction of oxidized cotton fiber with collagen protein

A collagen protein solution was prepared by stirring a dispersion of collagen in aqueous acetic acid solution at pH value of 4.0, then the above mentioned oxidized cotton fiber was immersed in 1.0% (w/w) collagen protein solution with constant oscillating for 1 h at 40 °C, subsequently submitted to thermal treatment at 60 °C under vacuum for 3 h, then scoured with deionized water several times. The resultant cotton fiber was air-dried at ambient temperature to produce the collagen protein modified cotton fiber (CPMCF).

### 2.4. Measurement

#### 2.4.1. Aldehyde group content of oxidized cotton fiber

The aldehyde group content in oxidized cotton fibers was determined by the Schiff base reaction with hydroxylamine hydrochloride (Marte & Owens, 1956). Hydrochloric acid released from hydroxylamine hydrochloride was titrated by 0.03 M NaOH methanol solution which of concentration was determined with the titrimetry of potassium hydrogen phthalate (Qian & Li, 2001). The formula is as follows:

$$\text{Aldehyde group content } (\text{mmol/g}) = 30V/W \quad (1)$$

where $V$ is the volume of sodium hydroxide methanol solution used in titrimetry (l); $W$ is the mass of oxidized cotton fiber sample (g).

#### 2.4.2. Collagen protein content in CPMCF sample

The modified cotton fiber samples were precisely weighed and then suspended in concentrated sulfuric acid (5 ml). Five drops of hydrogen peroxide (30%) was added to the suspension and the mixture was heated under reflux until the solution became transparent and colorless. The resulting solutions were subjected to Kjeldahl nitrogen analysis by the DS-20 analyzer (Tecator Instrument Co. Ltd., Sweden). The collagen protein content in the CPMCF was calculated from the nitrogen percentage on the basis of the calibration curve for the weight of collagen protein and test value.

#### 2.4.3. Instrumental measurements

The Fourier transform infrared spectra of the oxidized fiber and the CPMCF were recorded with a NEXUS-870 FT-IR spectrometer (Nicolet Instrument Co. Ltd., USA) using a Globar source. Approximately 1 mg of sample was pressed into discs of variable thickness of potassium bromide, and samples were analyzed in transmittance, with accumulation of 50 scans and a resolution of 2/cm. Scanning electron microscopy photographs were taken on a Japan Hitachi S-4800 electronic instrument operating at 2–8 kV after sputtering the samples with gold. The X-ray diffractometry profile was recorded for dry pellet of the samples in reflection mode using a Japan RINT 2027 X-ray generator equipped with a Cu Kα target and β Ni filter. Diffractometer scans at a rate of 2°/min and a $2\theta$ range of 5–45°. The breaking strength of the cotton thread was measured with a YG-021A electronic automatic graph tension tester (Changzhou Textile Instrument Factory, China). The length of the sample thread was 250 mm, the rate of extension was 100 mm/min, each sample was measured 10 times and the tests were performed at 20 °C and a relative humidity of 65%.

### 2.5. XPS of the oxidized cotton fiber and the CPMCF

X-ray photoelectron spectrometry (XPS) of the oxidized fiber and the CPMCF were performed in FAT mode with the X-ray gun of Mg target (1253.6 eV) at the power of 12 kV × 15 mA, and the analytical background vacuum of $2 \times 10^{-7}$ Pa, the channel energy of 100 eV and the step length of 0.1 eV/s, using a Kratos XSAM-800 multifunctional spectrometric apparatus (VG Science Instrument Co. Ltd., Britain). The surface of samples were sputtered with the $Ar^+$ ion to eliminate interference from contaminated substances and subsequently preserved in high vacuum.

### 2.6. Loading and controlled release aloe extract of CPMCF

The CPMCF (2.5 g) was added into the 2.0% (w/w) aloe anthraquinone extract solution and stirred slightly for 2 h at 60 °C, subsequently dried in vacuum oven at the same temperature for 1 h, then the colored cotton thread was vigorously washed with deionized water to remove the aloe extract adsorbed physically on the surface of the fiber. The original cotton thread (2.5 g) was also treated by aloe extract using the same procedure to produce the control sample. The aloe extract-treated thread and the control sample were separately added to an isotonic sodium chloride solution (200 ml) in two Erlenmeyer flasks. Each flask was shaken at 37 °C for different days (4, 6, 8 and 10 days), and the solutions were replaced with fresh sodium chloride solutions every 24 h. The aloe anthraquinone extract released into the sodium chloride