Carbohydrate Polymers 96 (2013) 487–494

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Evaluation of anisotropic chitosan hydrogels using analytical Mueller matrix method and scanned laser pico-projector☆

Chih-Ling Huang[a], Chin-Ho Chuang[a], Yu-Lung Lo[a,b,*]

[a] Department of Mechanical Engineering, National Cheng Kung University, 701 Tainan, Taiwan
[b] Advanced Optoelectronic Technology Center, National Cheng Kung University, 701 Tainan, Taiwan

ARTICLE INFO

Article history:
Received 24 January 2013
Received in revised form 2 April 2013
Accepted 12 April 2013
Available online 22 April 2013

Keywords:
Chitosan
Anisotropic material
Gel
Mueller matrix
Speckle
Scanned laser pico-projector

ABSTRACT

Chitosan has excellent biodegradable, biocompatible and bio-absorbable properties and has been found increasing use in the biomedical field in recent decades. The linear birefringence (LB), linear diattenuation (LD), circular birefringence (CB), circular diattenuation (CD), and depolarization properties of chitosan hydrogel films crosslinked in citrate acid buffer solution (CBS) are extracted using an analytical Mueller matrix method. It is shown that the optical phase retardance property of the hydrogel films provides a reliable indication of both the chitosan concentration of the film and the pH value of the CBS crosslinking environment. In addition, chitosan hydrogel suspension with low-concentration crosslinked in CBS environments with various pH values are studied by the speckle contrast of the projected images obtained when illuminating the suspension with a scanned laser pico-projector (SLPP). It is found that for the samples crosslinked in an acidic environment, the speckle contrast decreases with an increasing pH value. By contrast, for the samples crosslinked in an alkaline CBS environment, the speckle contrast increases as the pH value increases. It is concluded that both the phase retardance and the speckle contrast enable the pH value of the CBS crosslinking solution to be reliably determined. However, of the two methods, the SLPP method yields improved measurement sensitivity. Overall, the results presented in this study show that the analytical Mueller matrix method and SLPP method provide an effective means of characterizing the optical properties, concentration and crosslinking environment of chitosan hydrogel films and suspensions.

1. Introduction

Chitin, a naturally-occurring linear polysaccharide found in arthropods such as crabs, shrimps and lobsters, is the main source of production for chitosan, which has many applications in the agricultural, industrial and biomedical fields (Carreira, Gonçalves, Mendonça, Gil, & Coelho, 2010). Chitin deacetylated under heterogeneous conditions to a degree of deacetylation (DD) of 60% or more is soluble in dilute aqueous acids, while chitin deacetylated under homogeneous conditions to a DD of approximately 50% is soluble in water. Min et al. (2004) fabricated a chitin nano-fibrous matrix for wound dressings using an electro-spinning method and then treated the as-spun matrix with a 40% aqueous NaOH solution to form a chitosan matrix with a DD of 85%.

Chitosan has many favorable biodegradable, biocompatible and mechanical properties and has been found to improve cell adhesion, proliferation and function (Huang, Liao, Yang, Chang, Ju, & Lin, 2009; Naahidi, Jafari, Edalat, Raymond, Khademhosseini, & Chen, 2013). As a result, it is widely used in the biomedical field for such applications as wound healing and controlled drug delivery (Bernkop-Schnürch & Dünnhaupt, 2012). Furthermore, chitosan has a homeostatic property and is therefore an ideal medium for tissue regeneration or cell culture growth. (Giri et al., 2012) For example, Jebahi et al. (2012) used bioglass-chitosan as a pharmaceutical drug to repair bone defect and indicated that bioglass-chitosan seemed to promote an excellent structural response in terms of bone integration. Crompton, Forsythe, Horne, Finkelstein, and Knott (2009) showed that for chitosan hydrogels with a chitosan concentration of 0.25–1.5 w/v%, the chitosan chains are arranged into polymer-rich aggregates with a diameter of 1–2 μm. Berger, Reist, Mayer, Felt, Peppas, and Gurny (2004) showed that ionically crosslinked chitosan hydrogels have a higher swelling sensitivity to pH changes than covalently crosslinked chitosan hydrogels and are therefore better suited to pH-controlled

* Corresponding author at: Department of Mechanical Engineering, National Cheng Kung University, 701 Tainan, Taiwan. Tel.: +886 6 2757575x62123; fax: +886 6 2352973.
E-mail address: loyl@mail.ncku.edu.tw (Y.-L. Lo).

0144-8617/$ – see front matter © 2013 The Authors. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.04.032

drug delivery applications. Additionally, the studies (Fen, Yunus, & Yusof, 2012; Montembault, Viton, & Domard, 2005) showed that the physico-chemical properties of chitosan render chitosan an ideal immobilization agent for the active layer in surface plasmon resonance (SPR) sensors. It was found that the extensive interspaces in the resulting polymer network enabled the storage of a large quantity of detecting material, thereby rendering the chitosan gel an ideal immobilization agent for polarimetery-based sensing applications.

The optical characterization for biological materials is advanced inspection and diagnostic applications with non-invasion (Wang, 2002). There is much motivating in the investigation by polarized light according to anisotropic chitosan hydrogels. For example, Dobashi, Tomita, Maki, Chang, and Yamamoto (2011) prepared chitosan hygrogel strings and films with birefringence by immersing a sandwiched chitosan in aqueous acetic acid into aqueous sodium hydroxide. They observed that the photo images of chitosan hygrogel strings and films showed crossed nicols due to an orientation of domains such as polymer aggregation. Also, Csoka, Appel, Eitner, Jirikowski, and Makovitzky (2013) showed that insect chitosan is characterized by birefringence; with the result that its structure is amenable to analysis via polarization microscopy.

In performing a quantitative analysis of an anisotropic sample, effective optical parameters are of interest, namely the linear birefringence (LB), the linear diattenuation (LD), the circular birefringence (CB), the circular diattenuation (CD), and the depolarization index. In recent studies (Pham & Lo, 2012a, 2012b), the current group presented a decoupled analytical technique based on the Mueller matrix method and Stokes polarimetry for extracting the effective optical parameters. The proposed method not only yields high measurement accuracy due to its decoupled nature, but also provides the means to extract the parameters of optical samples having only LB, CB, LD or CD properties without the need for any form of compensation on system or pretreatment on samples. Recently, the current group (Chuang, Sung, Huang, & Lo, 2012) presented a method for measuring the two-dimensional (2-D) concentration of solid and liquid solutions via an inspection of the speckle contrast of the images projected by a scanned laser pico-projector (SLPP). The feasibility of the proposed approach was demonstrated by measuring collagen concentrations (Collagen type I from calf skin was used for measurements and dissolved in 0.1 M acetic acid solution) ranging from 0.025 to 0.125%.

The optical characteristics of chitosan hydrogels are generally examined qualitatively by means of polarization microscopy. By contrast, in the present study, a quantitative examination of the optical characteristics of chitosan hydrogels is performed. Specifically, the analytical Mueller matrix method is applied to extract the effective optical parameters of chitosan hydrogel films with various chitosan concentrations crosslinking in acidic or alkaline citrate acid buffer solutions (CBS). Moreover, SLPP method is also applied to measure the chitosan hydrogel suspensions under the various pH value of the CBS crosslinking environment.

2. Materials and methods

2.1. Extraction of effective optical parameters of anisotropic chitosan hydrogel films using Mueller matrix method

2.1.1. Experimental methodology

According to the studies (Pham & Lo, 2012a, 2012b), the Mueller matrix for a LB material with principal axis angle (α) and phase retardance (β) can be expressed as

$$M_{lb} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(4\alpha)\sin^2(\beta/2)+\cos^2(\beta/2) & \sin(4\alpha)\sin^2(\beta/2) & -\sin(2\alpha)\sin(\beta) \\ 0 & \sin(4\alpha)\sin^2(\beta/2) & -\cos(4\alpha)\sin^2(\beta/2)+\cos^2(\beta/2) & \cos(2\alpha)\sin(\beta) \\ 0 & \sin(2\alpha)\sin(\beta) & -\cos(2\alpha)\sin(\beta) & \cos(\beta) \end{pmatrix} \quad (1)$$

Meanwhile, the Mueller matrix for a LD material with diattenuation axis angle (θ_d) and diattenuation (D) has the form

$$M_{ld} = \begin{pmatrix} \frac{1}{2}\left(1+\frac{1-D}{1+D}\right) & \frac{1}{2}\cos(2\theta_d)\left(1-\frac{1-D}{1+D}\right) & \frac{1}{2}\sin(2\theta_d)\left(1-\frac{1-D}{1+D}\right) & 0 \\ \frac{1}{2}\cos(2\theta_d)\left(1-\frac{1-D}{1+D}\right) & \frac{1}{4}\left(\left(1+\sqrt{\frac{1-D}{1+D}}\right)^2+\cos(4\theta_d)\left(1-\sqrt{\frac{1-D}{1+D}}\right)^2\right) & \frac{1}{4}\sin(4\theta_d)\left(1-\sqrt{\frac{1-D}{1+D}}\right)^2 & 0 \\ \frac{1}{2}\sin(2\theta_d)\left(1-\frac{1-D}{1+D}\right) & \frac{1}{4}\sin(4\theta_d)\left(1-\sqrt{\frac{1-D}{1+D}}\right)^2 & \frac{1}{4}\left(\left(1+\sqrt{\frac{1-D}{1+D}}\right)^2-\cos(4\theta_d)\left(1-\sqrt{\frac{1-D}{1+D}}\right)^2\right) & 0 \\ 0 & 0 & 0 & \sqrt{\frac{1-D}{1+D}} \end{pmatrix} \quad (2)$$

The Mueller matrix for a CB material with optical rotation (γ) is given as

$$M_{cb} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\gamma) & \sin(2\gamma) & 0 \\ 0 & -\sin(2\gamma) & \cos(2\gamma) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (3)$$

The Mueller matrix for a CD material with circular diattenuation (R) can be expressed as

$$M_{cd} = \begin{bmatrix} 1+R^2 & 0 & 0 & 2R \\ 0 & 1-R^2 & 0 & 0 \\ 0 & 0 & 1-R^2 & 0 \\ 2R & 0 & 0 & 1+R^2 \end{bmatrix} \quad (4)$$

Finally, the Mueller matrix for a non-uniform depolarizing material has the form

$$M_{\Delta} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ p_1 & e_1 & 0 & 0 \\ p_2 & 0 & e_2 & 0 \\ p_3 & 0 & 0 & e_3 \end{bmatrix} \quad \text{and} \quad |e1|, |e2|, |e3| \le 1 \quad (5)$$