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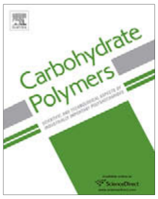

Preparation and characterization of optical property of crosslinkable film of chitosan with 2-thiophenecarboxaldehyde

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ABSTRACT

This article describes an elegant cross-linking technique for the preparation of chitosan-thiophene derivative film through a green chemistry approach by using solution casting method. The prepared chitosan derivative was confirmed by Fourier transform infrared spectroscopy (FTIR) and Ultraviolet–visible (UV) spectroscopy. The film was evaluated by XRD which confirms the crystalline morphology, thermal analysis shows thermally stable up to 275 °C, surface morphology indicates the film is relatively smooth and homogeneous, photoluminescence (PL) spectroscopy shows red-shifted emission and Z-scan measurement shows nonlinear absorption results. It is assumed that the chitosan derivative film as an optical material may open new perspectives in practical applications in the field of optical, biomedical and biosensing.

1. Introduction

Polymeric materials having the optical properties, particularly, the ability to participate in energy or electron transfer processes are becoming increasingly important in the recent years (Konishi et al., 2003; Manjuatha, Adhikari, & Hegde, 2009). Most of the studies have been carried out with synthetic polymers (Komarova, Ren, & Neckers, 2003). The good optical and mechanical properties of Schiff based polymers can be controlled optically, which aroused considerably the interest of people (Iwan & Sek, 2008). At the outset, inorganic materials were mainly studied and these were found to be not only difficult to process and fabricate but also possess only marginal optical nonlinearity. On the other hand, these are too expensive. Because of these disadvantages of the inorganic materials, the research efforts in NLO materials have been focused on organic materials. The organic polymeric materials are more advantageous over inorganic polymeric materials as a consequence of ease of structure modification, good processibility into thin films, large susceptibility, high laser damage threshold, faster response time, etc. (Cai, Zhou, & Gao, 2009; Cui, Qian, Chen, Wang, & Wang, 2008; Geethakrishnan & Palanisamy, 2007; Hao et al., 2007, 2008; Issam, 2007; Salafsky, 2007). The cross-linked polymers exhibits even greater stability of optical activity than the host–guest system, but a significant optical loss occurred as a result of limited uniformity of the cross-linking reaction. The organic biopolymer containing chromophoric groups towards optical property may be an interesting addition for biomedical applications. Furthermore, there is a growing interest in natural polymers for practical applications, especially in biotechnology and environmental protection (Jayakumar, Nwe, Tokura, & Tamura, 2007; Jayakumar, Prabaharan, Reis, & Mano, 2005; Jayakumar, Selvamurugan, Nair, Tokura, & Tamura, 2008; Krupka et al., 2008; Kwon, Park, Chung, Kwon, & Jeong, 2003). A unique feature of natural polymers in comparison with synthetic ones is the ability to undergo biodegradation (Morimoto et al., 2001). Among various natural polymers, one of the most obvious choices for these applications is polysaccharide, the most abundant polymer in biosphere.

Chitosan, a linear β-(1,4)-D-glucosamine, is a biocompatible, nontoxic compound mainly obtained by deacetylation of chitin, a natural structural component present for instance in crustaceans. Due to its special biological, chemical and physical properties, namely, biodegradability, biocompatibility, and bioactivities; chitosan and its derivatives have found applications in many industrial, biomedical, optical, agriculture, and environmental protection fields (Dutta & Dutta, 2005; Ding, Lian, Samuels, & Polk, 2003; Dutta, Tripathi, Mehrotra, & Dutta, 2009; Kumar & Dutta, 2008; Kumar, Dutta, & Dutta, 2009a, 2009b; Jayakumar et al., 2010a; Jayakumar, Prabaharan, Nair, & Tamura, 2010b; Wu, Zeng, Zhu, & Tong, 2005). It is not completely deacetylated and is consequently a copolymer of acetamide and amine groups, with a pK_a between 6.3 and 7.0. It is soluble in acidic media such as glacial acetic acid and may be processible as a film, gel or polyelectrolyte complex. The most accepted approach for the improvement of thermal stability of chitosan is a chemical modification in the structure by introducing thermally stable heterocyclic polymers

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like polyazomethine (Gandini, Hariri, & Nest Le, 2003; Park, Kim, Zin, & Jung, 1993). So the incorporation of thiophene moiety onto chitosan may provide the photosensitive chitosan and it would be the combination of optical property into biomolecules which may lead to the application of the visible light to conduct an efficient degradation of a wide range of unwanted human tissue cells. The presence of thiophene chromophores in the biomolecules, particularly, onto chitosan is not reported so far in the literature as per our knowledge. In this article, we have reported preparation and characterization of optical cross-linked film of chitosan with 2-thiophenecarboxaldehyde.

2. Experimental section

2.1. Materials

Chitosan with 79% degree of deacetylation (DD) was obtained as a gift sample from Central Institute of Fisheries Technology (CIFT, Cochin). 2-Thiophenecarboxaldehyde (Merck), methanol (Merck), and glacial acetic acid (Merck) were used as received. Deionized water of conductivity 20 μS/cm was generated in the laboratory.

2.2. Measurements

UV–Visible spectrum was measured on a Systronics double beam spectrophotometer 2203. FTIR spectra were recorded on Perkin Elmer RX1 FT-IR spectrophotometer. XRD pattern of the hydrogel film was recorded on X-ray diffractometer (D/Max2500VB2+/Pc, Rigaku, Japan) with Cu $K\alpha$ characteristic radiation (wavelength $\lambda = 0.154$ nm) at a voltage of 40 kV and a current of 50 mA. The scanning rate was 3°/min and the scanning scope of 2θ was from 2° to 50° at room temperature (25 °C). TGA was carried out with a Perkin Elmer Diamond analyzer from 0 to 800 °C at a heating rate of 10 °C/min. Differential Scanning Calorimetry (DSC) with Pyris-6 heating and cooling rates of 10 °C was used. The morphology of chitosan derivative film was analysed by using a Leica Cambridge S360 SEM at an accelerating voltage of 15 kV. The Photoluminescence spectra (PL) were recorded on Perkin Elmer LS55 fluorescence spectrometer.

2.3. Preparation of chitosan-thiophene derivative film

Chitosan derivative film was prepared by solution casting method. In a 100 mL of beaker 500 mg chitosan in 25 mL of 1% (v/v) aqueous acetic acid was prepared, stirred and filtered to remove any undissolved matters. Then we added the crosslinker 2-thiophenecarboxaldehyde solution dropwise in chitosan solution with vigorous stirring. A bubble-free solution was spread over a clean glass plate to the desired thickness and dried in atmospheric conditions at room temperature about 24 h. Finally, the resulting cross-linked chitosan derivative film was carefully detached from the glass plate.

2.4. Z-scan measurements

The third-order nonlinear optical properties were measured using a Z-scan technique. The Z-scan technique is based on the principles of spatial beam distortion, and offers simplicity as well as very high sensitivity for measuring both the nonlinear refractive index and nonlinear absorption coefficient. In our experiment, we used an Nd:YAG laser operating at 1064 nm with pulse duration of 40 ps and a repetition of 10 Hz to eliminate the accumulative thermal effect. The light intensities transmitted across the sample was measured as a function of the sample position in the Z-direction with respect to the focal plane either through a small aperture (closed-aperture) or without an aperture (open-aperture), in order to resolve the nonlinear refraction and absorption coefficients.

3. Results and discussion

3.1. Preparation and characterization

The choice of chitosan as the film-promoting macromolecular structure stemmed from two considerations: namely, on the one hand, the fact that previous work had shown (i) the very good aptitude of this modified polysaccharide to give strong thin membranes (Kumar et al., 2009a, 2009b) and (ii) the presence of primary amino groups in most of its repeat units. The latter's feature seemed mainly appropriate to achieve the grafting of the poly-

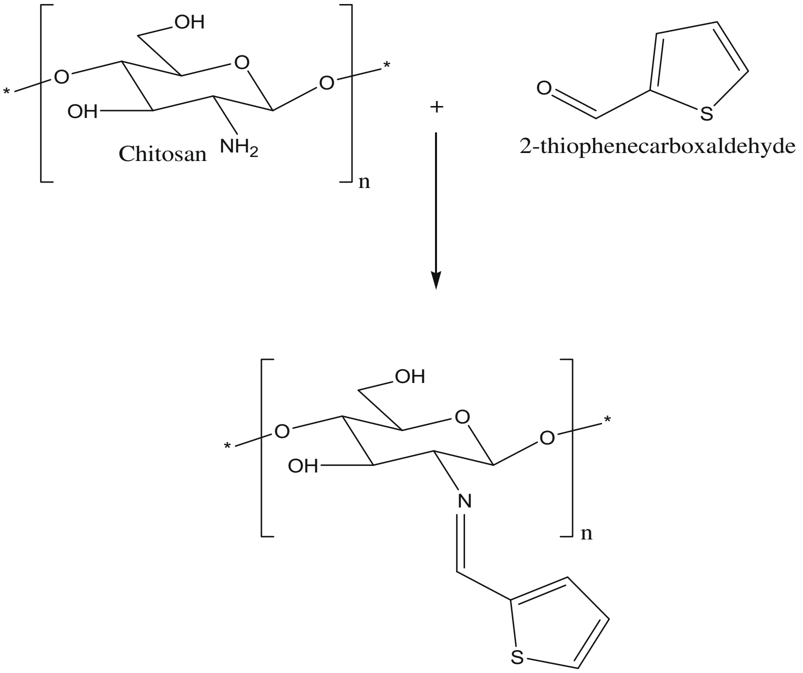

Fig. 1. Preparation of chitosan-thiophene derivative.

saccharide chains and the thiophene chromophores through the cross-linking reaction i.e., the formation of Schiff bases between the NH_2 functions of chitosan and the aldehyde function borne by the thiophene-chitosan derivative hydrogel (Fig. 1). The film is drawn in solution casting method. The chitosan derivative was confirmed by UV and FT-IR.

Chitosan itself is transparent in the UV and visible region, and so its conformation is hard to characterize by spectroscopy methods. However, we can overcome this natural handicap by borrowing chromophores from extrinsic molecule. UV of chitosan derivative showed a broad band between the 320 and 350 nm due to the presence of aromatic ring. The FT-IR spectrum of chitosan (Fig. 2a) shows a broad –OH stretching absorption band between 3500 and 3100 cm^{-1} and the aliphatic C–H stretching between 2990 and 2850 cm^{-1}. As the –OH stretching band and the aliphatic C–H stretching band are aligned, they appear as a broad band from 3500 to 2850 cm^{-1} in the spectrum. The other major absorption band between 1220 and 1020 cm^{-1} represents the free primary amino group ($-NH_2$) at C_2 position. The peak at 1647 cm^{-1} represents acetylated amino group of chitin, which indicates that the sample is not fully deacetylated. The peak at 1384 cm^{-1} represents the –C–O stretching of primary alcoholic group ($-CH_2-OH$). In the chitosan derivative (Fig. 2b) the stretching bands of OH, CH=N, and C–O are observed at 3109, 1558 and 1020 cm^{-1}, respectively. As a result of the cross-linking reaction significant changes are observed in the FT-IR spectrum of the chitosan derivative film. The FT-IR spectrum of cross-linked chitosan film displayed a distinct change in the carbonyl-amide region.

The weak diffraction peaks centered at 12°, 20° and sharp diffraction peaks at 30°, 36°, 39°, 44°, 48° and 49° are indicative of the crystalline morphology of chitosan-thiophene derivative film in Fig. 3(b), while for pure chitosan film in Fig. 3(a) no diffraction peaks could be observed at 12°, 20°,30°, 36°, 39°, 44°, 48° and 49° but some weak diffraction peaks centered at 20° appeared; this could be attributed to the generally amorphous state of pure chitosan film. The XRD analysis confirmed that chitosan-thiophene derivative film may participate into nonlinear optical properties.

TGA study of the chitosan derivative film indicates two weight loss processes in Fig. 4. It shows an initial decomposition at about 40–100 °C due to the loss of water and solvent. The second weight loss starts at 255 °C due to thermal decomposition of chitosan derivative. The decomposition peak of chitosan derivative observed at 274 °C as obtained from derivative of thermogravimetric analysis (DTGA) (figure not shown). The DSC thermogram of chitosan derivative (Fig. 5) observed as the endothermic peak at 85 °C associated with loss of water and solvent from the chitosan derivative and the exothermic peak at 275 °C corresponds to thermal degradation of chitosan derivative.

The "native chitosan" presented in Fig. 6(a and b) showed very rough morphology, flat and compact with very sparsely distributed

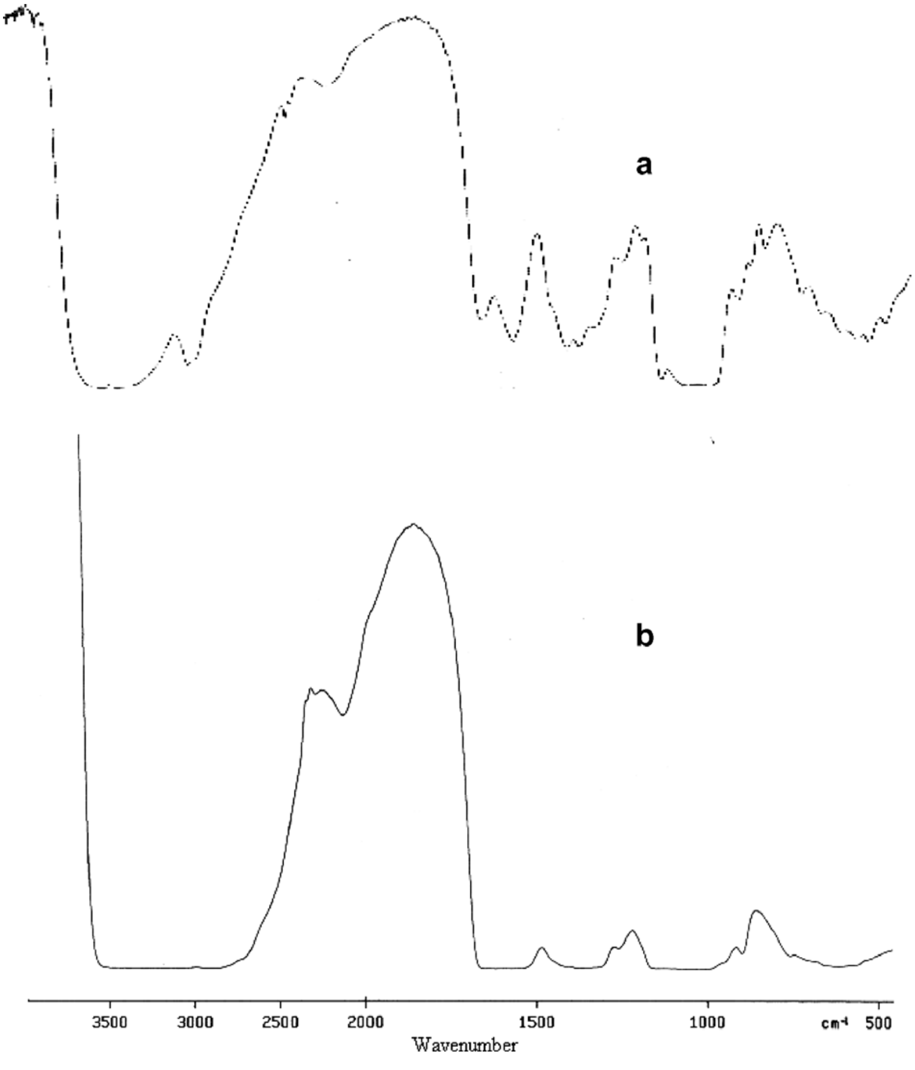

Fig. 2. FT-IR spectra of pure chitosan film (a) and chitosan derivative film (b).

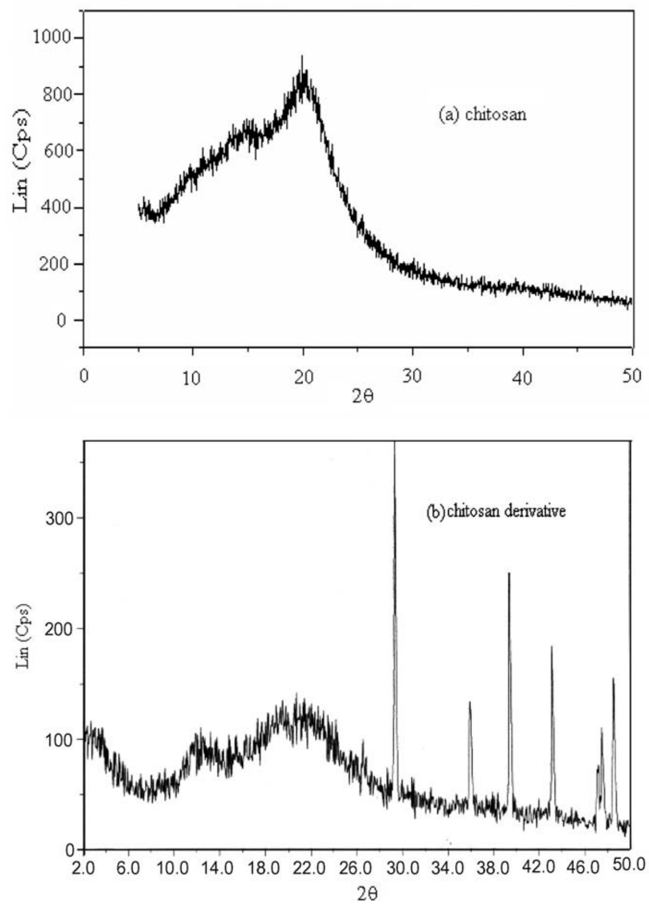

Fig. 3. X-ray diffractogram of chitosan (a) and chitosan-thiophene derivative (b).

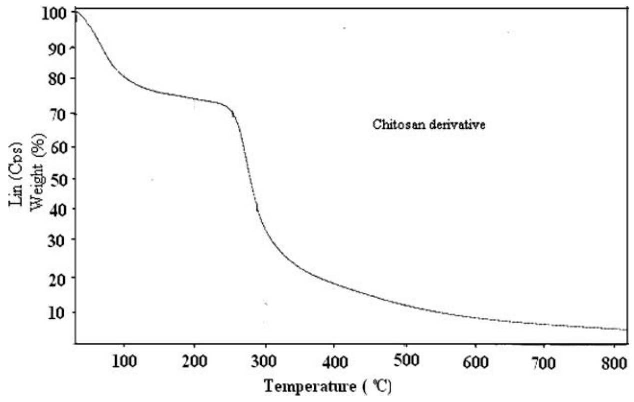

Fig. 4. Thermogravimetric analysis of chitosan derivative.

small particles without any phase separation. However, Fig. 6(c and d) show the surface of chitosan derivative film, which is relatively smooth and homogeneous and thus resulting a continuous matrix without any pores or cracks with good structural integrity.

3.2. Photoluminescence properties

As shown in Fig. 7, the emission spectra and fluorescent intensity of chitosan and chitosan derivative are performed at their own excitation wavelength. The emission spectra (λem) of pure chitosan and chitosan derivative observed at 525 and 580 nm respectively, at excitation wavelength of 430 nm. Chitosan derivative showed red-shifted emission maximum due to the electron rich polymer main chain. The fluorescent intensity was also controlled by the conjugation length and variation of the substituents.

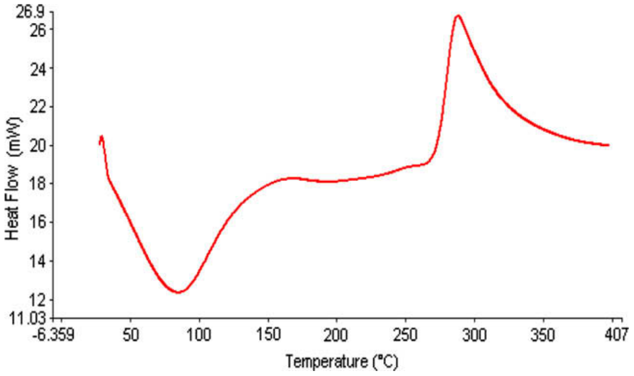

Fig. 5. DSC thermogram of chitosan derivative.

In order to investigate the effect of side chain introduction and the electronic effect of the substituent on the side chain, fluorescence spectra of the polymers at the same excitation wavelength of 430 nm are compared in Fig. 7, chitosan derivative shows red-shifted emission maximum because the attachment of the conjugate side group to the backbone will enlarge the degree of delocalized π-bond on the whole molecular chain. The emission intensity was greatly influenced by the electronic effect of substituents. The π–π conjugated side chain can make the emission maximum of chitosan derivative red shift. The shifting wave number was decided by electronic effect. The side chain containing the electron-withdrawing group will decrease the emission intensity, while the electron donating group will increase it (Kumar et al., 2009a, 2009b).

3.3. Nonlinear optical measurement

The Z-scan technique is a single-beam method for measuring the optical nonlinearities through detecting the far-field sample transmittance of a focused Gaussian beam as a function of sample position (z). This method provides a direct measurement of nonlinear absorption and refraction along with the sign of nonlinearity. The sign of the nonlinearity is an important parameter for practical application of optical signal processing devices. This information cannot be obtained by the other commonly techniques such as degenerate four-wave mixing and third harmonic generation. In Z-scan measurement, the intensity-dependent transmission of the sample measured without an aperture (open-aperture scan) gives information on purely absorptive nonlinearity whereas the aperture scan (closed-aperture) contains the information of both the absorptive and dispersive nonlinearities. The ratio of the normalized closed-aperture and open-aperture scans generates a Z-scan due to the purely dispersive nonlinearity. We first performed a Z-scan measurement on a standard sample carbon disulfide (CS_2) in a quartz cell with 1 mm thickness (shown in Fig. 8a).

The positive nonlinearity is confirmed by the valley–peak configuration of the data. The vacant quartz substrates and quartz cells used in our experiments exhibit very weak optical nonlinearities and their effects on the experimental results can be neglected. The NLO properties of the film of 2-thiophene-chitosan were investigated with 532 nm laser pulses of 8 ns duration using Nd:YAG laser. The nonlinear absorption component of the ultra thin film is evaluated under an open-aperture configuration.

The open-aperture Z-scan curve of the film on the quartz substrate is shown in Fig. 8b. According to the open-aperture Z-scan curve. The NLO refractive effects are assessed by dividing the nor-

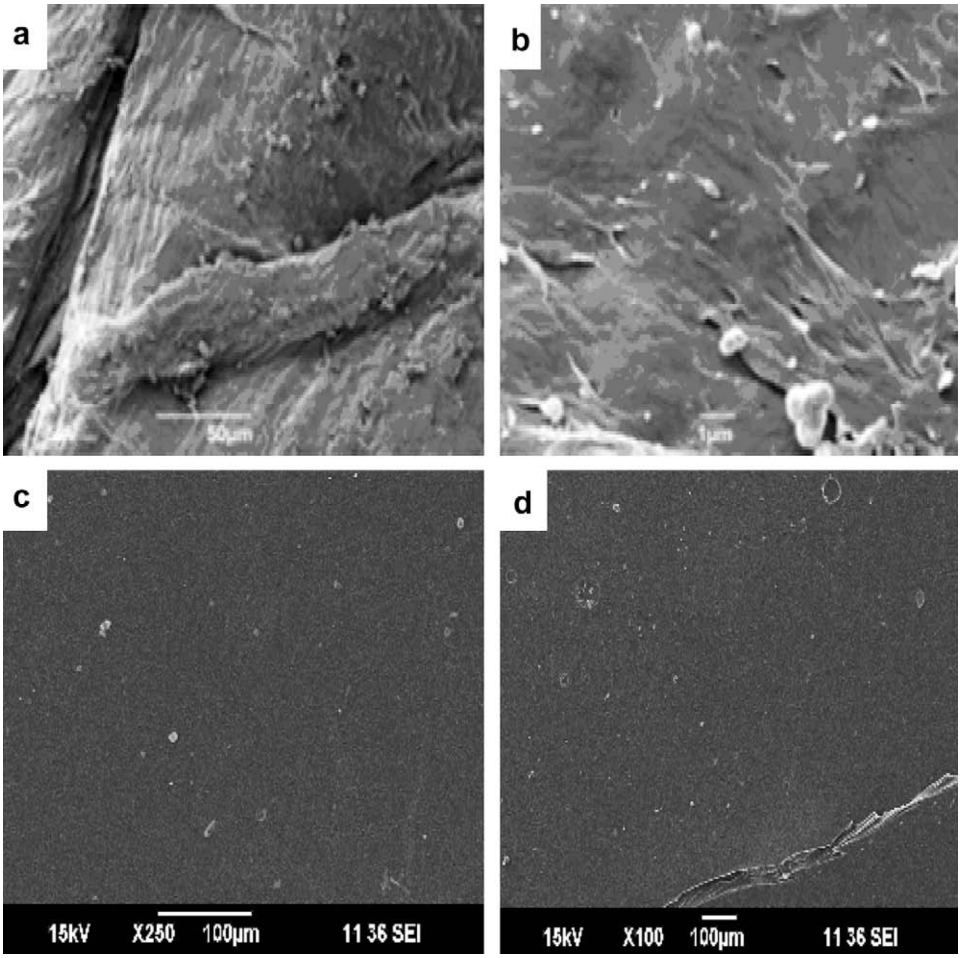

Fig. 6. SEM image of the native chitosan (a, b) and chitosan derivative (c, d).

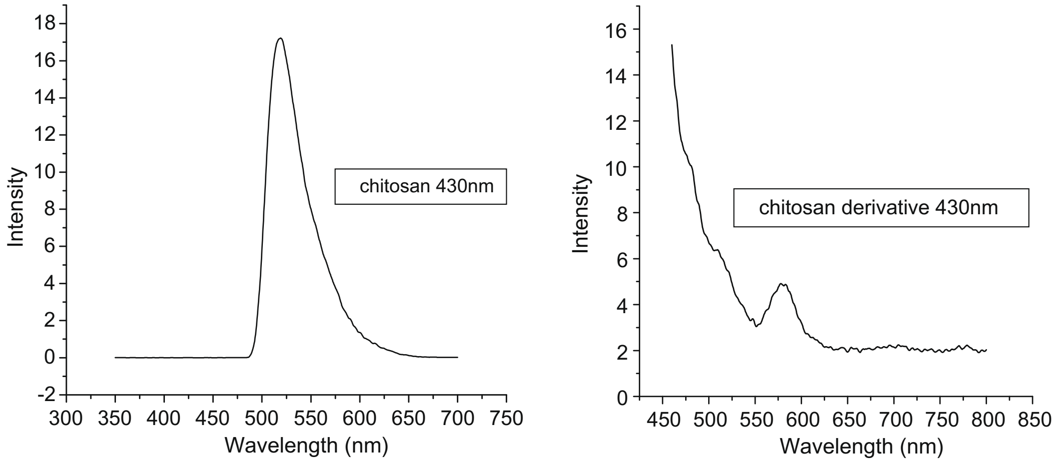

Fig. 7. Photoluminescence (PL) spectra of chitosan and derivative at excitation wavelength 430 nm.

malized Z-scan data obtained under the closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration. An effective third-order NLO refractive index n_2 can be derived from the difference between the normalized transmittance values at valley and peak positions. Fig. 8c presents the typical NLO refractive data for the film sample. The peak–valley pattern of the normalized transmittance curve obtained under the closed-aperture configuration indicates that the chitosan-thiophene film has a negative sign for the nonlinear refraction and exhibits strong self-defocusing behavior. In order to validate the above results, repeated Z-scan experiments were carried out. Repeated Z-scan experiments on the same place of the film may obtain very parallel nonlinear absorption results (He et al., 2009; Poornesh et al., 2009; Sun, Ren, Wang, Zhang, & Xu, 2009).

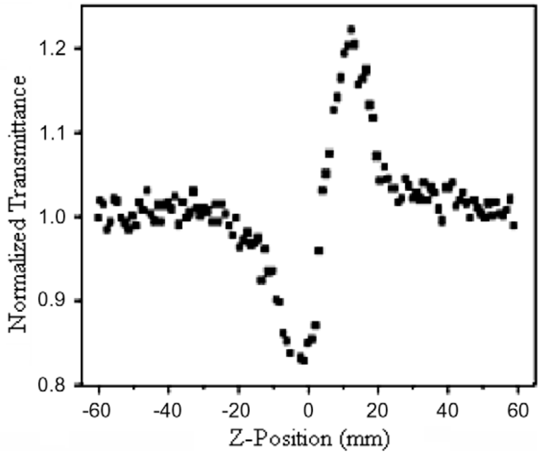

Fig. 8a. Z-scan curve of a standard sample of CS_2 under the closed-aperture configuration.

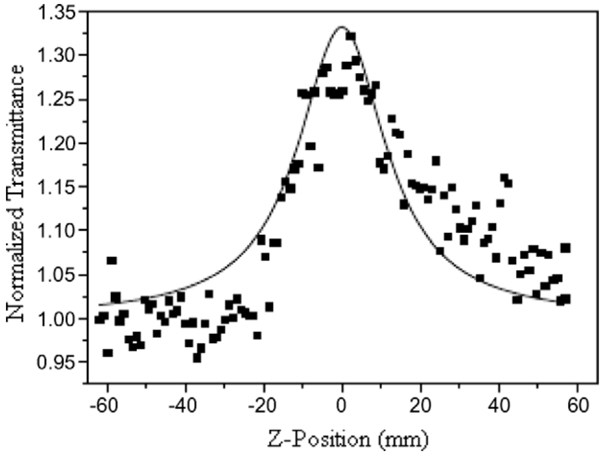

Fig. 8b. Z-scan curve for chitosan-thiophene film on a quartz substrate under the open-aperture configuration.

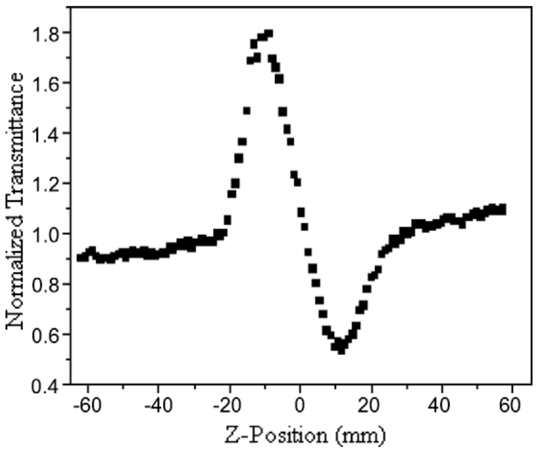

Fig. 8c. Normalized closed-aperture Z-scan curve of chitosan-thiophene film under the closed-aperture configuration.

4. Conclusions

In summary, we describe a novel chitosan-thiophene derivative hydrogel film as drawn in solution casting method. The chitosan derivative is confirmed by FT-IR and characterized by X-ray diffraction study. The TGA and DSC studies show that the films are thermally stable. The morphological study of the chitosan derivative have shown smooth and homogeneous surface. The photoluminescence spectra of chitosan derivative shows red-shifted emission maximum. Z-scan technique shows the optical nonlinearity. The results showed that the chitosan-thiophene derivative might be a very promising candidate for practical applications in the field of optical, biomedical and biosensing.

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