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Preparation, Characterization and Optical Property of Chitosan-Phenothiazine Derivative by Microwave Assisted Synthesis

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In this article, we have described microwave assisted synthesis of 3-formyl-10H phenothiazine and preparation of chitosan-phenothiazine derivative film with potential for optical properties in biomedical applications, vis-à-vis it is also important to ensure that chemical processes used in converting biopolymer to useful material through green chemistry approach. From optical properties and biomedical application point of views, it is a benign technique. Chitosan-derivative film was prepared from hydrogel by solution casting method. The prepared chitosan-phenothiazine derivative was confirmed by Fourier transform infrared spectroscopy (FTIR). The film was evaluated by XRD, thermal analysis, surface morphology, photoluminescence (PL) spectrscopy and second harmonic generation (SHG) study. Overall, the chitosan-phenothiazine derivative film opens new perspectives to optical material for biomedical applications.

Keywords: Chitosan, formyl phenothiazine, derivative, film, optical properties.

1 Introduction

In the past decade, there has been increasing interest in the organic optical materials for their large optical response and ultra fast signal switching, which are important in future high speed telecommunication, optical storage and optical computing (1–9). A wide variety of materials have been studied for non linear optical (NLO) devices. At first, inorganic materials were mainly studied and they were found to be difficult to process and fabricate, possess only marginal optical nonlinearity and are expensive. Because of these disadvantages of inorganic materials the research efforts in NLO materials have been focused on organic materials. Among them, organic polymeric materials have advantages with regard to the ease of structure modification, good processibility into thin films, large susceptibility, high laser damage threshold, and faster response time etc. (10–13). The crosslinked type of 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 crosslinking reaction. The organic biopolymer containing chromophoric groups towards optical property may be an interesting addition for biomedical applications. From the biomedical applications point of view, chitosan has attracted significant interest in the broad range of scientific research because of its biodegradability, biocompatibility, and bioactivities (14–16). It is not completely deacetylated though; being therefore a copolymer of acetamide and amine groups, with a pK_a between 6.3 and 7.0, it is soluble in acidic media and may be processible as a film, gel or polyelectrolyte. Phenothiazine is a well known bioactive heterocyclic compound (17) with electron-rich sulphur and nitrogen heteroatom. The nonlinear structure of the phenothiazine ring should impede stacking aggregation and intermolecular excimer formation in the polymer main chain. The phenothiazine moieties play the role of photosensitizer (18–23). Because of the presence of phenothiazines chromophores, the polymer absorbs light from the UV-visible spectral region. Electronically excited polymeric chromophores participated in energy and electron transfer processes to the molecule of the suitable acceptors. The incorporation of phenothiazine 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

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of phenothiazines chromophores in the biomolecules, particularly, onto chitosan is not reported so far in the literature as per our knowledge. In this communication, we have reported preparation, characterization and evaluation of optical properties for chitosan-phenothiazine derivative.

2 Experimental

2.1 Material and Reagents

Chitosan with 79% degree of deacetylation (DD) was sponsored by Central Institute of Fisheries Technology (CIFT, Cochin). Phenothiazine (Aldrich) and glacial acetic acid (Merck) were used without further purification. Deionized water of conductivity 20 μS/cm was generated in the laboratory. The purity of all the synthesized compounds has been checked by thin layer chromatography using silica gel with different non-aqueous solvent systems.

2.2 Measurements

Preparation of 3-formyl-10H phenothiazine was carried out in a domestic microwave oven (Samsung, model no. CE113, 900 W, 2450 MHz). The infrared spectra were recorded on Perkin-Elmer RX1 FTIR spectrophotometer. Electronic absorbance spectra (UV) were recorded on Systronics double beam spectrophotometer 2203. The ^{1}H-NMR spectra have been recorded on 400 MHz Brucker NMR spectrometer using TMS as an internal standard in $CDCl_3$. X-ray diffraction study was recorded with a Philips, PW 1729 X-ray diffractometer using Ni-filtered CuK_α radiation at 35 kV-10 mA and a 3°/min scanning speed. Thermogravimetric analysis (TGA) with Perkin Elmer Diamond and Differential Scanning Calorimetry (DSC) with Mettler Toledo DSC 822e were used. Scanning Electron Microscope (SEM) with JEOL Model JSM-6390LV. The Photoluminescent spectra (PL) were recorded on Perkin-Elmer LS55 Fluorescence spectrometer. SHG efficiency of the polymer was measured by Nd–YAG laser using urea as a reference (Fig. 1). SHG activity was measured by spin coating technique. For powder measurement, the sample was ground and graded by standard sieves (75–100 μm) and loaded on a microscope slide with a sample thickness of 1 mm. The laser beam was directed unfocused on to the sample kept at 45° angle to the laser beam, emission was collected from the front face of the sample at 90° angle. The second harmonic signal at 1.06 μm was detected by a photomultiplier and stored on a Philips model PM 3323 digital oscilloscope.

2.3 Preparation of Microwave Assisted 3-formyl-10H Phenothiazine.

A mixture of phenothiazine 1 g (5 mmol), urotropine 1.4 g (10 mmol) and glacial acetic acid 50 ml was subjected to microwave irradiation for preparation of 3-formyl-10H Phenothiazine. Yellow powder, m.p. = 194°C was obtained according to procedure as described elsewhere (24). OH (ppm): 6.70 (d, 1H), 6.75 (dd, 1H), 6.80 (t, 1H), 7.35 (s, 1H), 7.50 (dd, 1H), 7.90 (d, 1H), 9.64 (s, 1H).

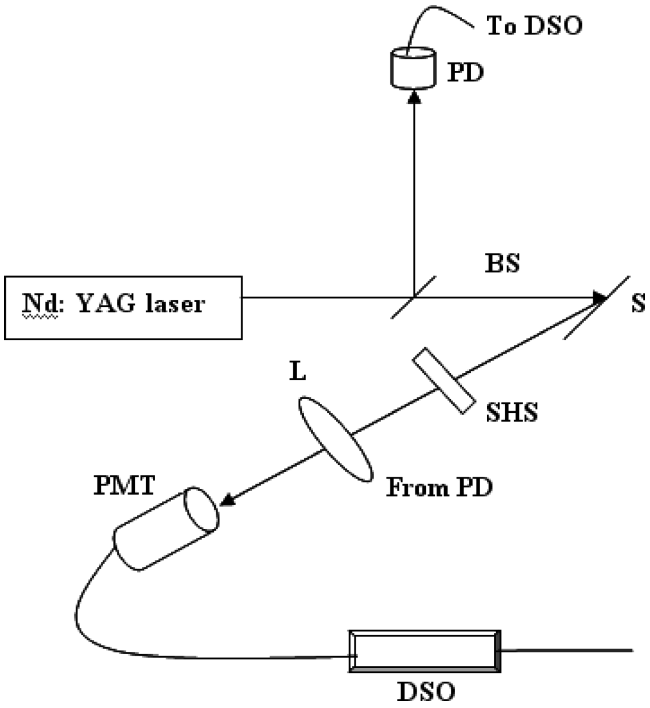
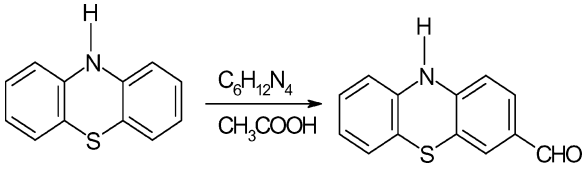


Fig. 1. Experimental set up of powder method. **Laser**: Q switched Nd:YAG laser, **DSO**: Digital storage oscilloscope, **PD**: Photodetector, **BS**: Beam splitter, **S**: Sample, **L**: Lens, **PMT**: Photo multiplier tube, **SHS**: Second harmonic separator.

2.4 Preparation of Chitosan Derivative Films:

Chitosan derivative films were prepared by solution casting method. In a 100 ml of beaker 0.200 g chitosan in 14 ml of 1% (v/v) aqueous acetic acid was prepared, stirred and filtered to remove the undissolved matter. A crosslinker of 0.025 g 3-formyl 10H phenothiazine in 1 ml glacial acetic acid was prepared and added dropwise in a 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 crosslinked chitosan derivative films were carefully detached from the glass plates.



Sch. 1. Preparation of microwave assisted 3-formyl-10H Phenothiazine.

Table 1. Preparation of microwave assisted 3-formyl-10H phenothiazine: Comparison between the results obtained by microwave assisted synthesis versus conventional heating method

Temperature (°C)		*Time (min.)*		*Yields*		
Δ	*mw*	Δ	*mw*	Δ	*mw*	*Procedure Supporting*
120	94	1060	30	40	50	Ethanol

3 Results and Discussion

The microwave assisted duff formulation of phenothiazine with urotropine in glacial acetic acid gave good yields of 3-formyl-10H phenothiazine (Sch. 1) in a significantly shorter reaction time as compared to classical reaction protocol (Table 1). Duff formylation reaction was applied for the first time to a phenothiazine compound. The processing techniques employed were simultaneous cooling method in the presence of an ethanol. The microwave assisted synthesis of phenothiazine derivatives are described by the chemical equations presented in Scheme 1. Table 1 presents a comparison between the results obtained by microwave assisted synthesis versus conventional heating method (25).

The choice of chitosan as the film promoting macromolecular structure stemmed from two consideration, namely, on the one hand, the fact that previous work had shown the very good aptitude of this modified polysaccharide to give strong thin membrane (26) and, on the other hand, the presence of primary amino groups in most of its repeat units. The latter feature seemed to be particularly appropriate to achieve the grafting of the phenothiazine chromophores through the same type of hydrogel as prepared. The chitosan derivative was confirmed by UV and FT-IR.

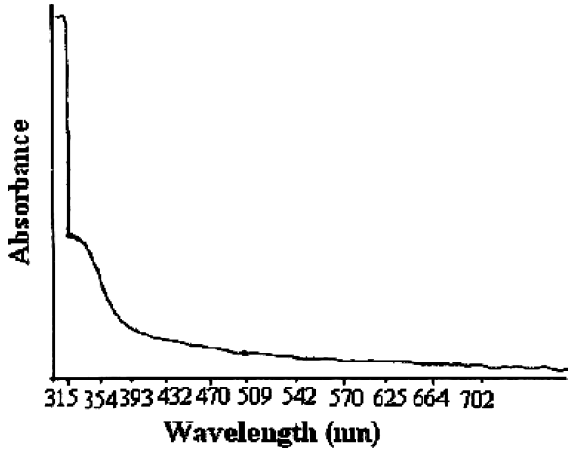
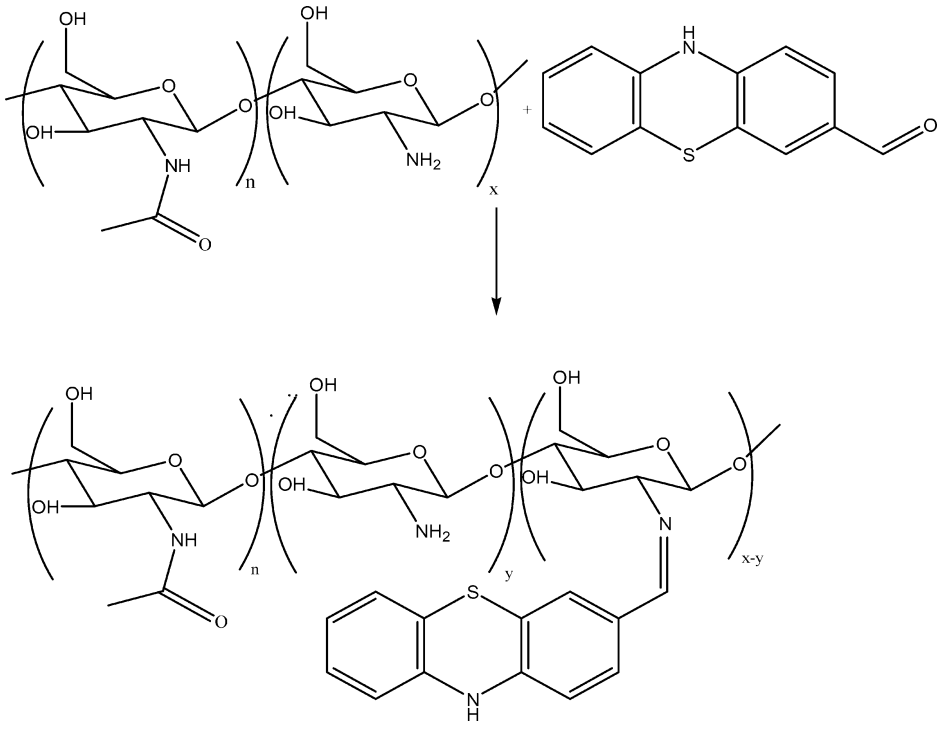


Fig. 2. UV spectrum of chitosan derivative.

3.1 UV and FTIR Spectra of Chitosan Derivative

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. Electronic absorbance spectrum (UV) of chitosan derivative shows in Figure 2 a broad band



Sch. 2. Preparation of chitosan-3-formyl phenothiazine derivative (Schiff base).

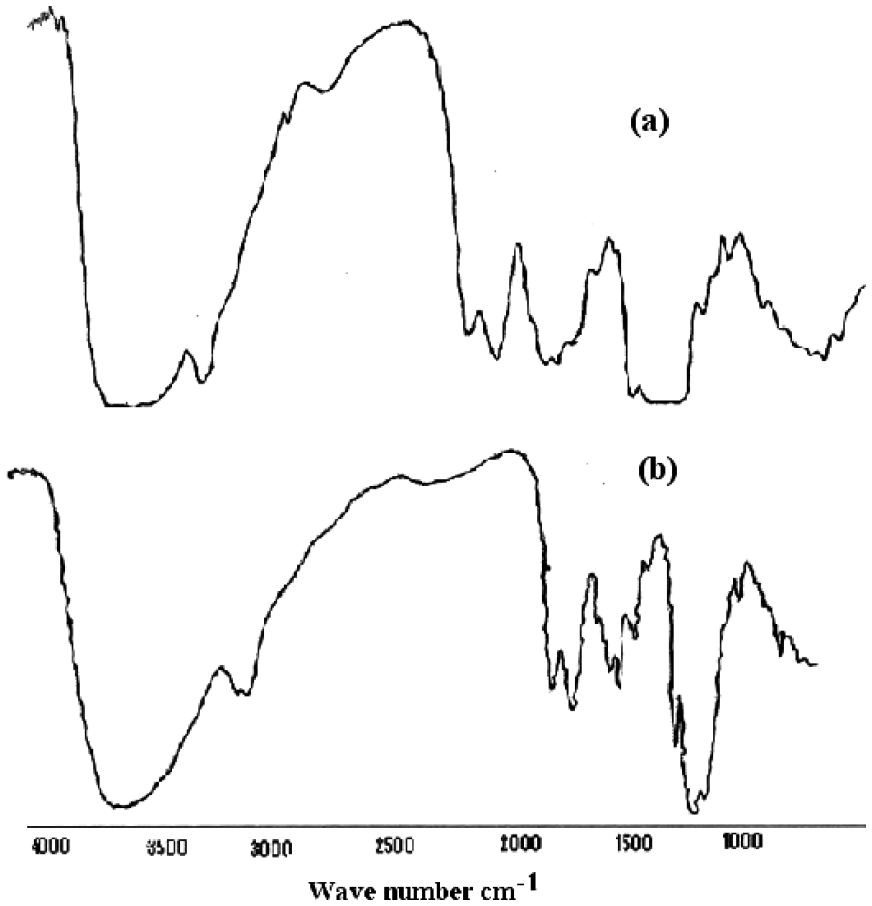


Fig. 3. FT-IR spectrum of chitosan (a) and chitosan derivative (b).

between the 320–347 nm due to the presence of aromatic ring. The infrared spectrum of chitosan and chitosan derivative has been shown in Figure 3. The significant peak at 1557 cm^{-1} due to the presence of the imine bond (CH=N) formed by crosslinking reaction between the amino groups in the aldehyde group in 3-formyl-10H phenothiazine. The peak 2921 cm^{-1} corresponds to CH_2 stretching, whereas that of free hydroxyl group is observed at 3425 cm^{-1}. The wavenumber of 1072 cm^{-1} indicates ether linkage, C-O-C band stretching.

The FTIR results suggest that the CHO group of 3-formyl 10H phenothiazine have been successfully bonded to the NH_2 group of chitosan main chain. The intensity of these bands depends on the amount and bulkiness of the 3-formyl 10H phenothiazine. Degree of deacetylation (DD) also affects the intensity band, OH stretching which becomes broader and moves to a lower frequency with increasing DD up to ~50%, indicating an increase in the disordered structure. The bands then become narrow and move back to higher frequency (~3550 cm^{-1}) with the increase of DD up to 96%, indicating a more ordered structure.

3.2 X-ray Diffraction (XRD) Study of Chitosan Derivative

The X-ray diffraction of pure chitosan film and chitosan derivatives film shows in Figure 4a and 4b. The diffraction peaks centered at 2θ, 9° and 12° are indicative of the crystalline morphology of chitosan derivative film in Figure 4(b), while for pure chitosan film in Figure 4(a) no diffraction peaks could be observed at 2θ, 9°and12° but some weak diffraction peaks centered at 2θ, 20° appeared; this could be attributed to the generally amorphous state of pure chitosan film. The XRD analysis confirmed that chitosan derivative film may participate into NLO properties.

3.3 Thermal Analysis

The thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) thermograms of chitosan derivative are shown in Figures 5 and 6. TGA and DSC were done at a heating rate of 10°C/min in nitrogen atmosphere. In Figure 5, observed TGA thermogram studies indicate the onset of thermal decomposition of chitosan derivative is 261°C. The DSC thermogram of chitosan

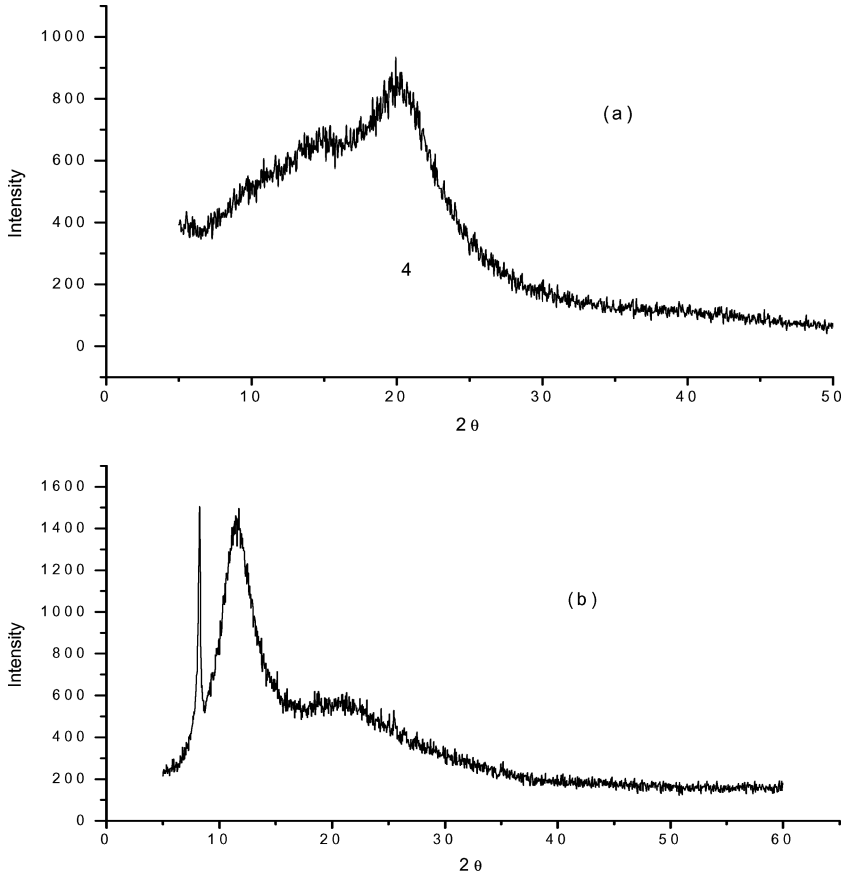


Fig. 4. (a) X-ray diffractogram of chitosan. (b) X-ray diffractogram of chitosan derivative.

derivative (Figure 6) shows multiple endothermic onset at 113°C, 214°C and 262°C, respectively which may be due to change of crystallization and or self arrangement among themselves.

3.4 Morphology Study

The scanning electron micrographs (SEMs) of the native chitosan and derivative are shown in Figure 7. The native chitosan (Figure 7a and b) exhibited a nonporous, smooth

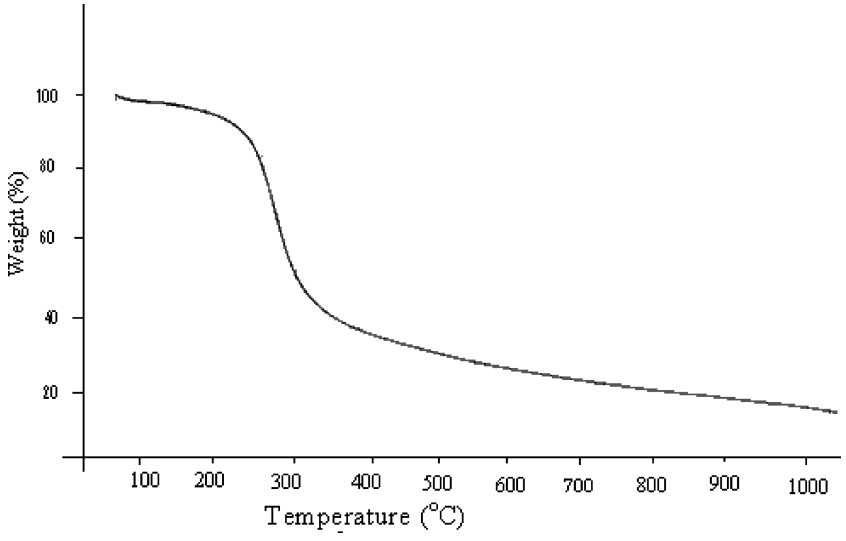


Fig. 5. TGA curve of chitosan derivative.

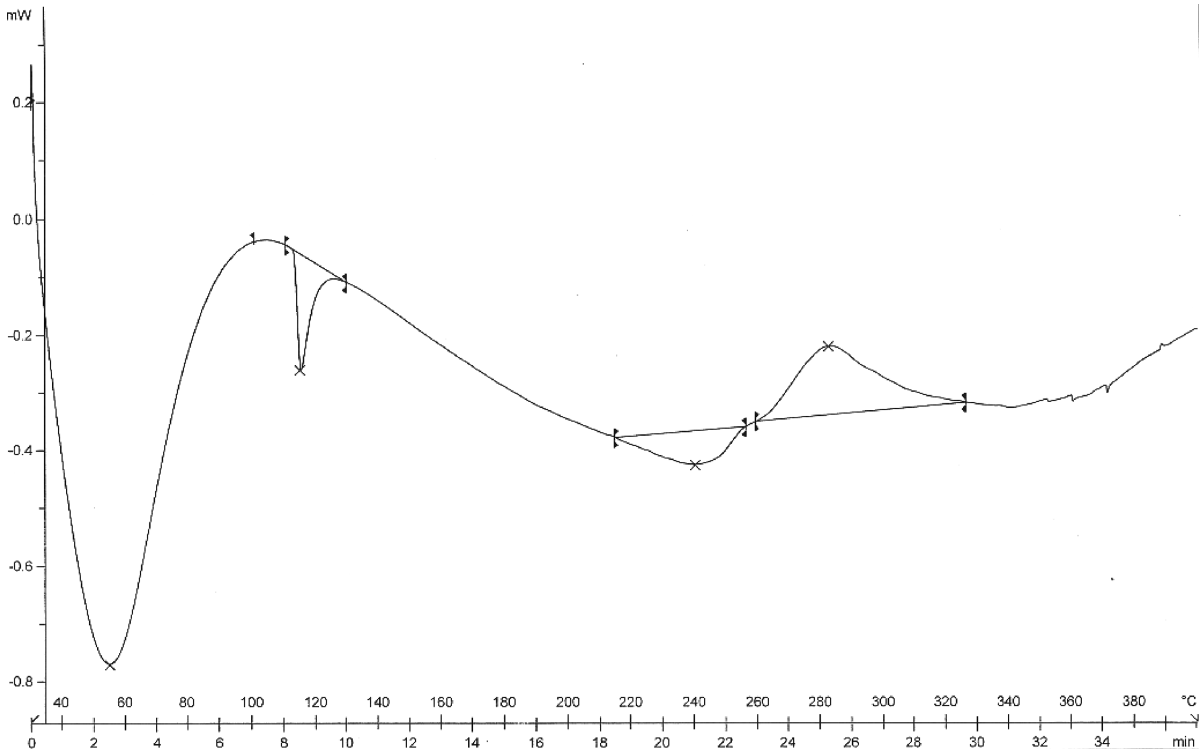


Fig. 6. DSC curves of chitosan derivative.

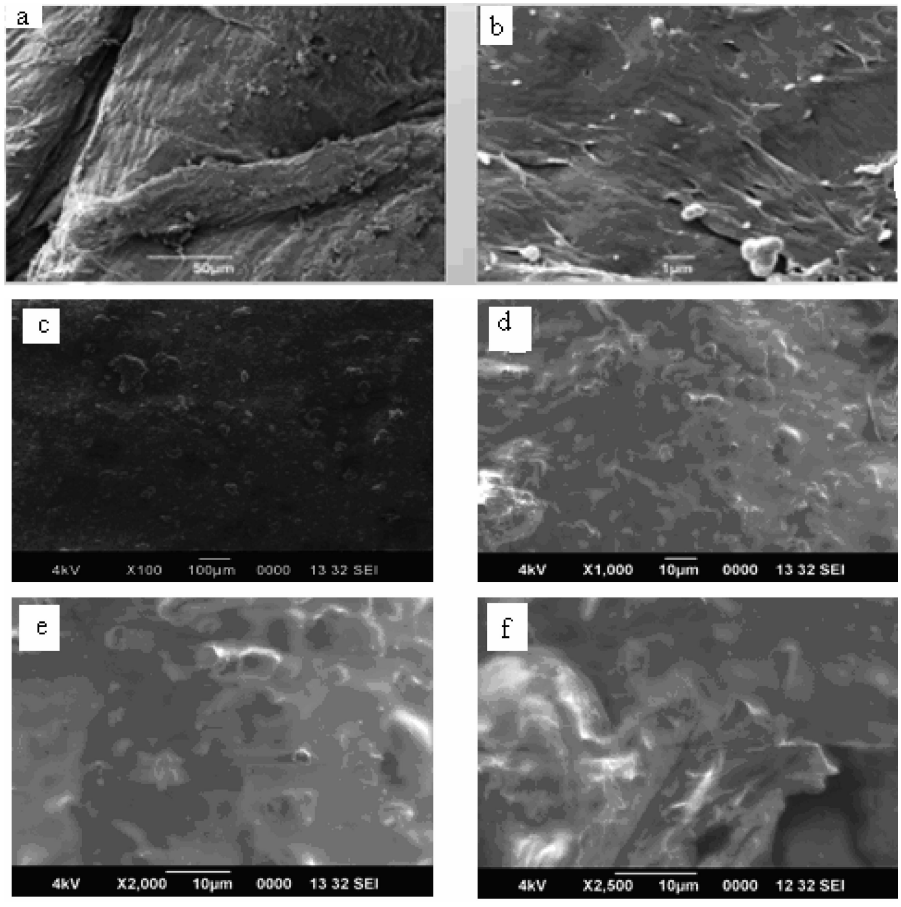


Fig. 7. Scanning electron micrographs of (a) and (b): native chitosan (c),(d),(e) and (f): chitosan derivative.

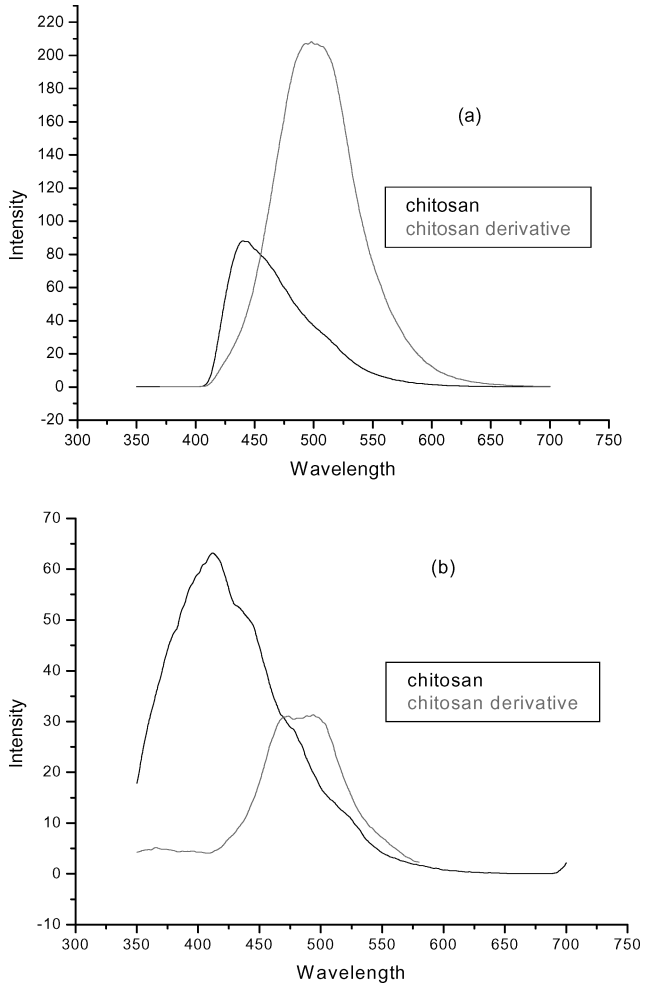


Fig. 8. Photoluminescence (PL) spectra of chitosan and derivative at excitation wavelength 380 nm (a) and 320 nm (b).

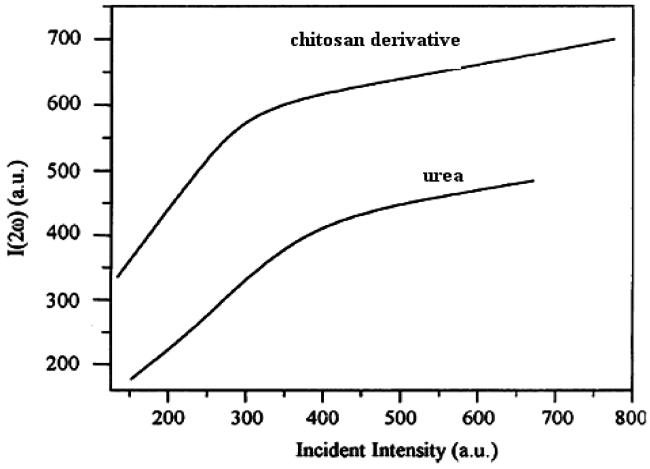


Fig. 9. Comparison of output intensities of polymer with urea.

membranous phases consisting of dome shaped orifices, microfibrils and crystallites. It also exhibited flat lamellar phases on which a large number of protruding microfibrils are evident.

The photomicrograph of chitosan derivative has shown porous nature (Figure 7c–f with different resolution). This property may be an added advantage for the biomedical applications of the optical material.

3.5 Photoluminescence Properties

The photoluminescence spectra (Figure 8a and b) of chitosan and derivative film are performed at their excitation wavelength 380 nm and 320 nm, respectively. The derivative showed red-shifted emission maxima due to the phenothiazine electron rich resulting in a better π-electron delocalization. The phenothiazine ring works in a p-π conjugated system. The photoluminescence intensity was also controlled by the conjugation length and variation of the substituents.

3.6 Second Harmonic Generation (SHG) Study

The SHG efficiency of the polymer was examined by the powder reflection technique of Kurtz and Perry (27). Laser beam from Nd–YAG pulsed laser (1.06 lm, 11 ns) was used. The measurement was recorded as a comparison of the second harmonic signal observed at 1.06 μm. No reabsorption of the second harmonic signal as well as no resonance enhancements were noticed during SHG study which indicate chitosan derivative possesses excellent SHG ability (Fig. 9). It is assumed that the semicrystalline grains of the polymer exhibit greater degree of alignment along one particular direction. The directional orientation of the polymer molecule is greatly enhanced by the donor-acceptor group of π electron system. The centrosymmetry is necessarily broken when the preferred helicity is achieved in the supra molecular and or self organization and hence, there is preference to one sense of the helix which leads to high SHG stability (28).

4 Conclusions

Chitosan-phenothiazine derivative has successfully been synthesized by microwave assisted technique and the film was prepared from hydrogel by solution casting method. The characterization of prepared material justifies the crystallinity, good thermal and surface morphological behavior. The optical property in terms of photoluminescence spectra and second harmonic generation (SHG) results indicates its potentiality in biomedical applications, vis-à-vis it is also important to ensure that the entire chemical processes used in converting biopolymer to useful material through green chemistry approach. From optical properties and biomedical application point of views, it is a benign

technique. Overall, the chitosan-phenothiazine derivative film opens new perspectives to optical material for biomedical applications.

Acknowledgments

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