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Optical Studies on H_2SO_4 Crosslinked Chitosan Membranes

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Abstract

Crosslinking and protonation of Chitosan membranes (prepared by solution casting technique) with sulfuric acid and systematic study on its variation of optical band gap, type of transition and the shape of the absorption edge for different concentration (0.1M – ch-1, 0.5M – ch-5 and 0.9M – ch-9) of sulfuric acid through UV-Visible Spectroscopy have been investigated. The synthesized Chitosan membranes of 25 μm thickness were subjected to XRD (X-Ray Diffraction) analysis to determine the structure. From the results it is proved to be amorphous in nature exhibiting some crystalline peaks (2θ) around 10°, 15° and 20°.

Keywords: Chitosan – Crosslinking – UV-Vis and XRD Analysis.

Introduction

Chitosan is a natural polysaccharide comprising copolymers of glucosamine and N-acetylglucosamine, and can be obtained by the partial deacetylation of chitin obtained from the exoskeleton of industrially processed crustaceans, the second most abundant natural polymer after cellulose. (Illum, L. 1998, Nunthanid, J.et al. 2001, No, H.K and Meyers, S.P 1995) Chitin made up of a linear chain of acetyl glucosamine groups when dissolved in weak acids becomes Chitosan . It can also be formed when Chitin is heated in a strong solution of NaOH (>40%) at high temperature (90-120°C). It is known from literature that atleast 65% of the acetylic groups should be removed on each monomeric chitin to obtain the ability of being put in solution (Roberts, G.A.F 1992). The most striking feature of Chitosan is the high content of primary amino groups which confers two important characteristics on this biopolymer. Firstly, since the amino groups are basic it can be protonated at moderately low pH (6.3) and the resulting cationic polyelectrolyte is water-soluble. Secondly, the amino group

nucleophilicity means that, at higher pH values (7.0) they are deprotonated and the unshared electron pair can undergo a variety of reactions. The reactivity of these amino groups allows chemical modification of Chitosan under mild conditions. (Koyama, Y. and Taniguchi, A. 1986,Yalpani,M. and Hall,J.D. 1984). This proclaims that there is good potential for controlled modification of the functional properties of Chitosan. Chemically modified and crosslinked Chitosan have been used as a host polymer to study Solid Polymer Electrolytes (SPE) for batteries (Mohamed, N.S.et al., 1995, Morni, N.M. and. Arof, A.K 1999, Morni, N.M et al., 1997, Subban, R.H.Y. et al.,1996) and the Proton Exchange Membranes (PEM) for Fuel Cells.

In order to study the optical properties of chemically modified and crosslinked Chitosan, UV-Visible spectroscopy a most simple and elegant method is adopted. The absorption of light by polymer in the UV-visible range depends on the nature of chemical and functional groups present in the structure. Polymers containing saturated hydrocarbon chains or saturated alkyl, alcohol and ether groups are transparent in the region 200 - 1000 nm. Colored polymers usually have attached chromophores - functional groups exhibiting absorption of the characteristic nature in the ultraviolet or visible region. The optical absorption and transmittance studies are useful to understand the effect of chemical and functional groups on band gap, refractive index, extinction coefficient, nature of transitions, either direct or indirect etc (H. K. Pulker, 1979). The objective of the present work is to cross link and protonate the Chitosan with sulfuric acid and study the variation of optical band gap, type of transition and the shape of the absorption edge for different concentrations (0.1M – ch- 1, 0.5M – ch-5 and 0.9M – ch-9) of sulfuric acid and then to analyze its structure by XRD.

Methodology

Preparation of crosslinked Chitosan membranes

The Chitosan solutions were prepared by mixing 0.1 g finely grinded Chitosan powder with 5 ml of acetic acid in a glass beaker and stirred for about 1 hour continuously using a Teflon pellet, which was rotated with a help of a magnetic stirrer maintained at room temperature to form a 2 wt % solution. Minor insoluble solids were removed using a syringe filter with a pore size of 1 micron. The prepared solution is poured in optically plane, smooth glass moulds and the biopolymer membrane is thus casted. The membranes were then kept in an oven at a temperature of 60°C and dried for 24 hours. The dried membranes were neutralized in 2M NaOH for 15 minutes and thoroughly washed with de-mineralized (DM) water.

In this work, the membranes were crosslinked and protonated by submersion in different concentrations such as 0.1M, 0.5 M and 0.9M H_2SO_4 for 30 minutes. Then they were washed thoroughly with DM water and again kept in an oven at a temperature at 60°C for 24 hours. The synthesized samples were removed from the oven and kept under dry condition.

Results and discussion

UV-Vis Analysis

The spectral distribution of transmittance (T) data in the spectral region of 200-800 nm was analyzed for pure Chitosan (ch-u) and sulfuric acid crosslinked (0.1M – ch-1, 0.5M – ch-5 and 0.9M – ch-9) Chitosan membranes. Higher transmission in the higher wavelength region and its decline at absorption edge was observed for all the membranes (Fig. 1.)From the optical transmission data of pure and crosslinked Chitosan membranes, analysis of the absorption coefficient (α) has been carried out to evaluate the optical band gap and also to study the shape of the absorption edge. The frequency dependence of the absorption coefficient described by an empirical relation $\alpha = A\ (h\nu - E_g)_p$ is used to evaluate the optical band gap. and the value obtained reasonably fits with the above equation at p= 2 for pure and cross linked Chitosan membranes. The plots $(\alpha h\nu)^{1/2}$ versus $h\nu$ are linear functions, indicating the existence of indirect and allowed transitions in both pure and cross linked Chitosan membranes as shown in the Fig. 2(a-d). Extrapolations of linear dependence to zero absorption coefficient yields the corresponding optical band gaps E_g as shown in Table.1.

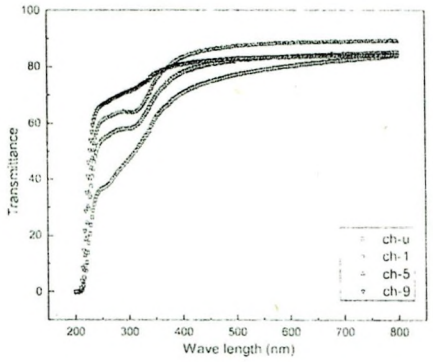
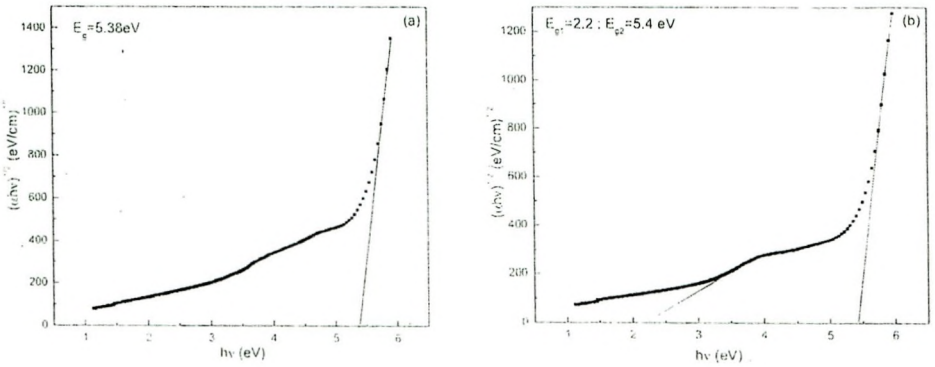


Figure 1: Transmittance spectra of pure and cross linked Chitosan membranes.



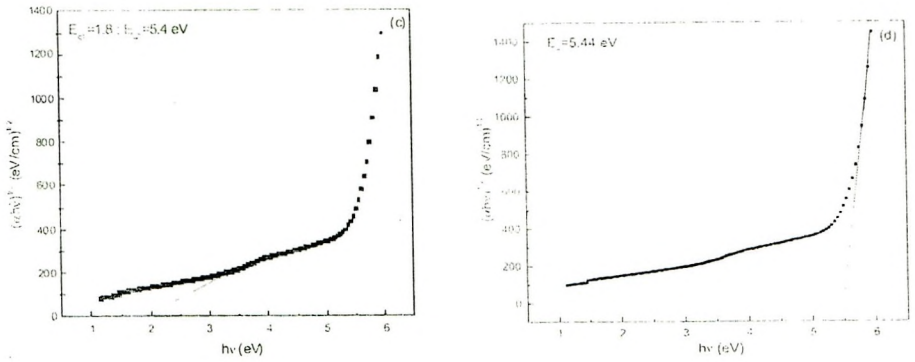
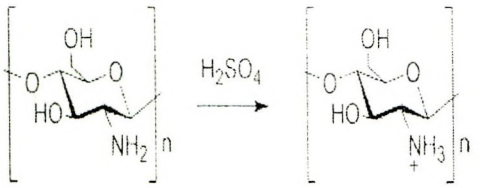


Figure 2(a-d): Plots of $(\alpha h\nu)^{1/2}$ versus hν show indirect transition in pure and sulfuric acid cross linked Chitosan membranes.

Table 1: Optical Parameters.

Sample	Type of Transition	E_g (eV)
Pure Chitosan	Indirect allowed	5.388
0.1M H_2SO_4 cross linked Chitosan	Indirect allowed	2.2; 5.4
0.5M H_2SO_4 cross linked Chitosan	Indirect allowed	1.8 ; 5.4
0.9M H_2SO_4 cross linked Chitosan	Indirect allowed	5.44

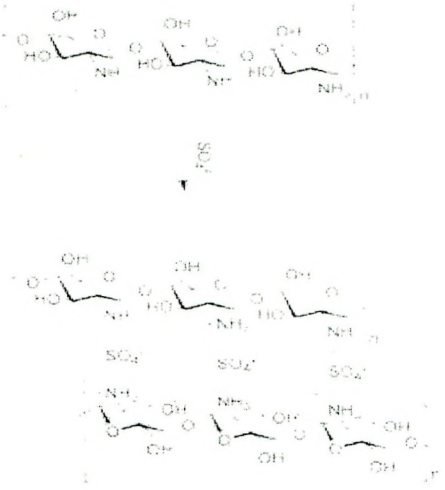
The value of the optical energy gap obtained from the graph for pure Chitosan membrane is 5.38eV. However, as the concentration of sulfuric acid increases from 0.1 – 0.5M, the NH_2 groups in the Chitosan chains were protonated by the H^+ supplied by sulfuric acid and converted to NH_3^+ groups,as described by Scheme 1. The protonation results in formation of the impurity states at 2.2 and 1.8eV found for 0.1M and 0.5M sulfuric acid doped Chitosan respectively.



Scheme 1: Protonation of Chitosan membrane.

However, beyond 0.5M doping level, there is no formation of impurity states and band gap almost remains the same. This is due to the fact that as the concentration of

sulfuric acid beyond 0.5M more SO_4^{2-} ions diffused to locations bridging two NH_3^+ groups, increasing the degree of ionic crosslinking (Scheme 2) (Zheng Cui et al.,2008) drops the availability of the free carriers. Since Chitosan is a low dielectric constant material (Mukoma,P et al., 2004) it may encourage ion-pair formation which results in a very low proton conductivity or wide optical band gap.



Scheme 2: Ionic crosslinking of Chitosan membrane.

Study of absorption edges

Urbach formula is verified by plotting ln α versus hν for pure and cross linked Chitosan membranes near the absorption edge as shown in Figs. 3 (a-c).

The inset of Figs. 3 (a-c) shows the slope of the straight line of these curves yields the value of band tails (E_u) whose magnitude is 0.45, 0.33 and 0.30 for pure, 0.1M and 0.9M sulfuric acid cross linked Chitosan respectively. The relatively lower value of E_u obtained in the case of crossed linked Chitosan sample indicates that the amorphous nature of crosslinked Chitosan. This result is better demonstrated from the XRD Pattern

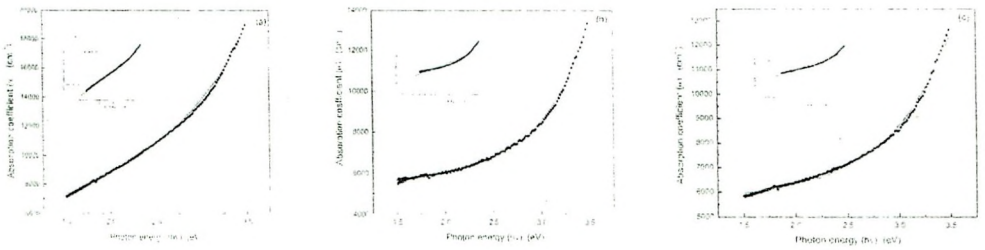


Figure 3(a-c): Plots of α versus hν for pure, 0.1M and 0.9 M sulfuric acid crosslinked Chitosan membrane respectively.

Structural analysis

X-ray diffractograms of Chitosan membranes cross linked with different concentration of sulfuric acid is shown in Fig. 4. The diffractograms exhibit two major crystalline peaks (2θ) around 10°, 15° and 20° in agreement with previously reported results (Wan, Y. et al.,,2003). The characteristic peaks of Chitosan disappear for the concentrationof 0.1M sulfuric acid and an amorphous hump is seen around 25°. The same observation is seenin all the concentration of sulfuric acid.

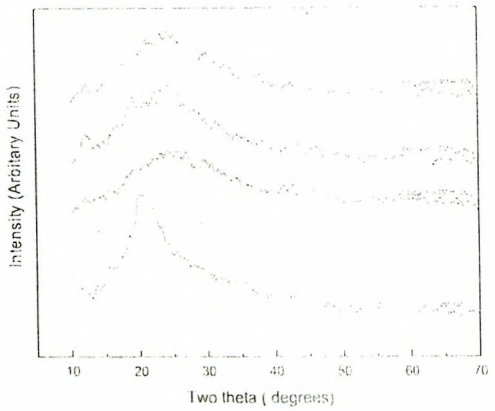


Figure 4: X-ray diffractograms of pure andcross linked Chitosan membrane.

From XRD spectroscopy measurements, change in crystallinity even for the small (0.1M) concentration of sulfuric acid is observed. This suggests that 0.1M is sufficient for complete ionic crosslinking of 25μm thick membranes treated for 30min.

Conclusion

The Optical absorption and X-ray diffraction studies were utilized to understand the chemical modification, crosslinking process and also to measure the optical parameters. The rigid crystalline structure of pure chitosan is stabilized mainly by intra and intermolecular hydrogen bonds. When glucosamine units in chitosan membranes are protonated, hydrogen bonding involving the NH_2 groups is disrupted, so the rigid crystalline structure weakens. Further, ionic crosslinking, which increases packing of the chitosan chains, deform the crystalline regions. Thus the interaction detected in this work decreases the membrane crystallinity. The changes in crystallinity and the optical parameters can be used to monitor the progress of the cross linking reaction.

References

[1] Illum, L., Chitosan and Its use as a Pharmaceutical Excipient. Pharm Res., 15:1326-1331, 1998.

[2] Nunthanid, J., Puttipipatkhachorn, S., Yamamoto, K. and Peck, G.E., Physical Properties and Molecular Behavior of Chitosan Films. Drug Dev Ind Pharm., 27 (2): 143- 157, 2001.

[3] No, H.K and Meyers, S.P (1995).Preparation and Characterization of Chitin and Chitosan. Journal of Aquatic food product techonology.,Vol.4, Pp.27-52.

[4] Roberts, G.A.F (1992).Chitin Chemistry .Macmillan, London.

[5] Koyama, Y. and Taniguchi, A. (1986) Journal of Applied Polymer Science, Vol.31.Pp1986.:

[6] Yalpani,M. and Hall,L.D.(1984) Macromolecules, Vol. 17, Pp.:272.

[7] Mohamed, N.S., Subban, R.H.Y. and Arof, A.K. (1995) J. Power Sources Vol.56 ,Pp.153.:

[8] Morni, N.M. and. Arof, A.K (1999).J. Power Sources, Vol.77, Pp. 42-48.:

[9] Morni, N.M., Mohamed, N.S.and Arof,A.K. (1997). Mater. Sci. Eng. B,Vol. 45, Pp.140.;

[10] Subban, R.H.Y.,. Arof, A.K.and Radhakrishna, S. (1996) Mater. Sci.Eng.B Vol.38, Pp. 156.

[11] H. K. Pulker, Appl. Opt., 18 (1979) 1969.

[12] Zheng Cui, Yan Xiang, Jiangju Si, Meng Yang, Qi Zhang, Tao Zhang, (2008) Ionic interaction between sulfuric acid and chitosan membranes Carbohydrate Polymer 73 111-116.

[13] Mukoma,P., Jooste, B.R.and Vosloo, H.C.M. (2004) J. Power SourcesVol. 136,Pp. 16.

[14] Wan, Y., Creber, K. A. M., Pepply, B., & Bui, V. T. (2003). Ionic conductivity of chitosan membranes. Polymer, 44, 1057–1065.