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Study of Chitosan Cross Linked with Glutaraldeyde as Composite Material

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ABSTRACT: Chitosan hydrogels were prepared by cross linking chitosan with glutaraldehyde. The swelling behaviour of the cross-linked and uncross-linked hydrogels was measured by swelling the gels in media of different pH and at different temperatures. The swelling behavior was observed to be dependent on pH, temperature and the degree of crosslinking. The gel films were characterized by Fourier transform Infrared spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). The glass transition temperature (T_g) and the amount of free water in the hydrogels decreased with increasing crosslinking in the hydrogels.

Key words: chitosan, hydrogel, swelling behaviour, thermal properties.

INTRODUCTION

Now days highly swelling polymers are widely used in many fields of industrial, medical and analytical field of chemistry .This is due to their exceptional properties i.e. biocompatibility, biodegrabality, renewability and non-toxicity. Highly swelling polymers, which is, superabsorbent hydrogels are hydrophilic three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight. (1-2) Chitosan hydrogels, like other hydrogels, contain much water. Part of this water is tightly bound to the polymer and rest is present as free water. Water in crosslinked and uncrosslinked chitosan gives rise to a three-dimensional network. Chitosan based hydrogels exhibit good biocompatibility, low degradation and processing ease. The ability of these hydrogels to swell and dehydrate depend on composition and environment which has been exploited to facilitate a range of applications such as drug release, its biodegradability and ability to form hydrogels.

Blending of chitosan with other polymers and crosslinking are both convenient and effective methods of improving the physical and mechanical properties of chitosan for practical applications. Immunization studies carried out on rats using glutaraldehyde crosslinked chitosan spheres showed promising tolerance by the living tissues of the rat muscles.(3)In the present study chitosan was crosslinked with of glutaraldehyde to form hydrogels. The swelling behaviour of the gels in aqueous media at different temperatures and pHs have been examined and the amounts of free water and bound water has been determined. The glass transition temperature and molecular interaction has also been evaluated by DSC and FTIR.

MATERIALS AND METHODS

Chitosan (from Sigma Aldrich Mol wt. 22742 Da and (degree of deacetylation of 75%), 25% glutaraldehyde from sigma aldrich was used as received.

Synthesis of Crosslinked hydrogels

2 gm of Chitosan dissolved into 100 ml of 10 % acetic acid solution and kept for stirring for 24 hors. After that 1% glutaraldehyde solution added into chitosan solution and kept in petry dish for hydrogel formation at room temperature for 2 hours after that it kept in oven for 24 hours.gel get formed .Hard gelled particle were formed which can further washed with water and drying then sieved through mesh 60-80 mesh .

Chitosan crosslinked hydrogel sample (0.10 g) with average particle sizes between 60 to 80 mesh was put into a weighed teabag and immersed in 100 ml distilled water and allowed to soak for 2 h at room temperature (10). The equilibrated

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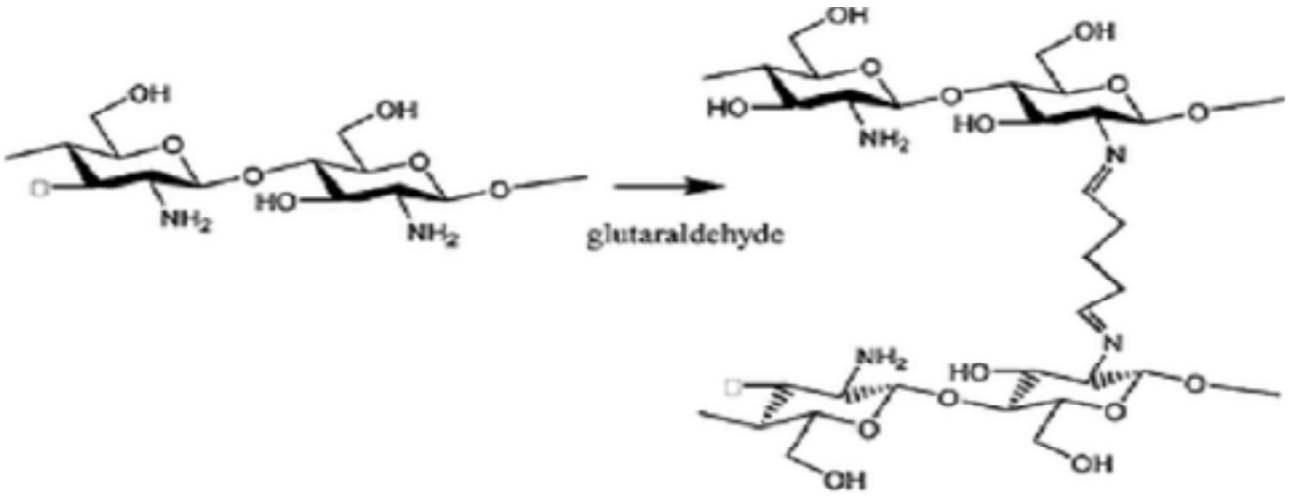

Scheme 1: General Mechanisms for glutaraldehyde cross– Linked chitosan hydrogel

swollen gel was allowed to drain by removing the teabag from water (~20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation:

$$\text{Absorbency} = (W_1 - W_2)/W_2$$

Where, W_1 and W_2 are the weights of the samples swollen in water and in dry state, respectively. So, absorbency was calculated as grams of water per gram of resin (g/g).

Swelling studies is carried out at different pH Solution 1 to 14.It is very interesting to note that every gel have specific pH range in which absorption become maximum .pH range for maximum activity is between pH - 6 to pH- 8,this observation can be correlated with pKa value of Chitosan. In this pH range carboxylic acid groups and proton of amide group gets ionized and electrostatic repulsive forces between charge groups (COO^-) increases the swelling capacity of gels, whereas at pH 6 ionic interaction of $NH3^+$ and COO^- ions from cross linking may give low swelling.(4)As prepared gel showing changes in surrounding stimuli, so gels shows large several thousand times change in their physical properties.(5-6)

The product obtained is characterized by IR, DSC and SEM analysis.

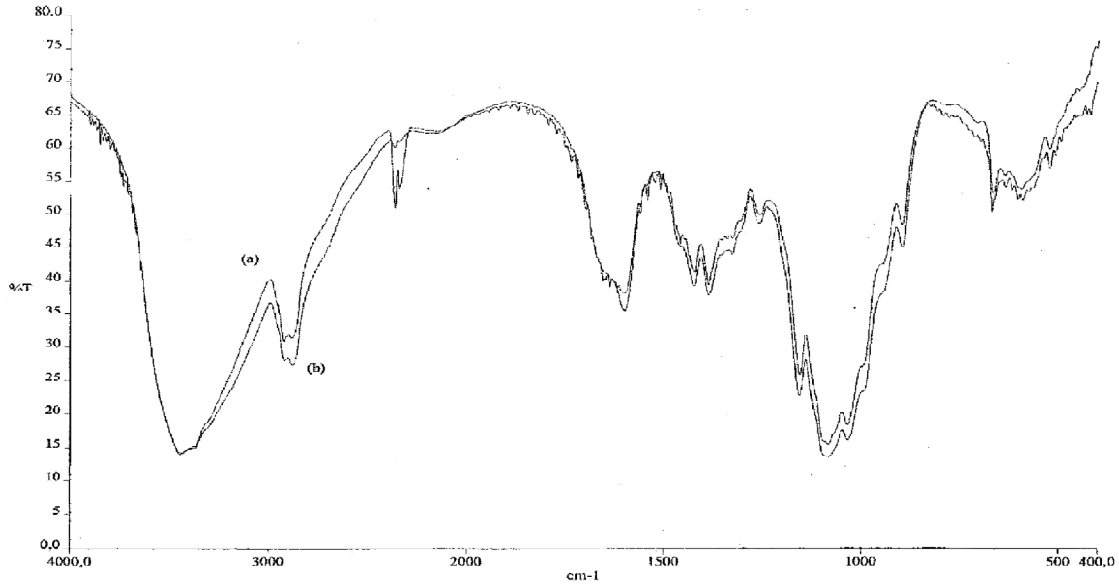

Figure 1: IR of (a) Pure Chitosan (b) Chitosan crosslinked with glutaraldehyde

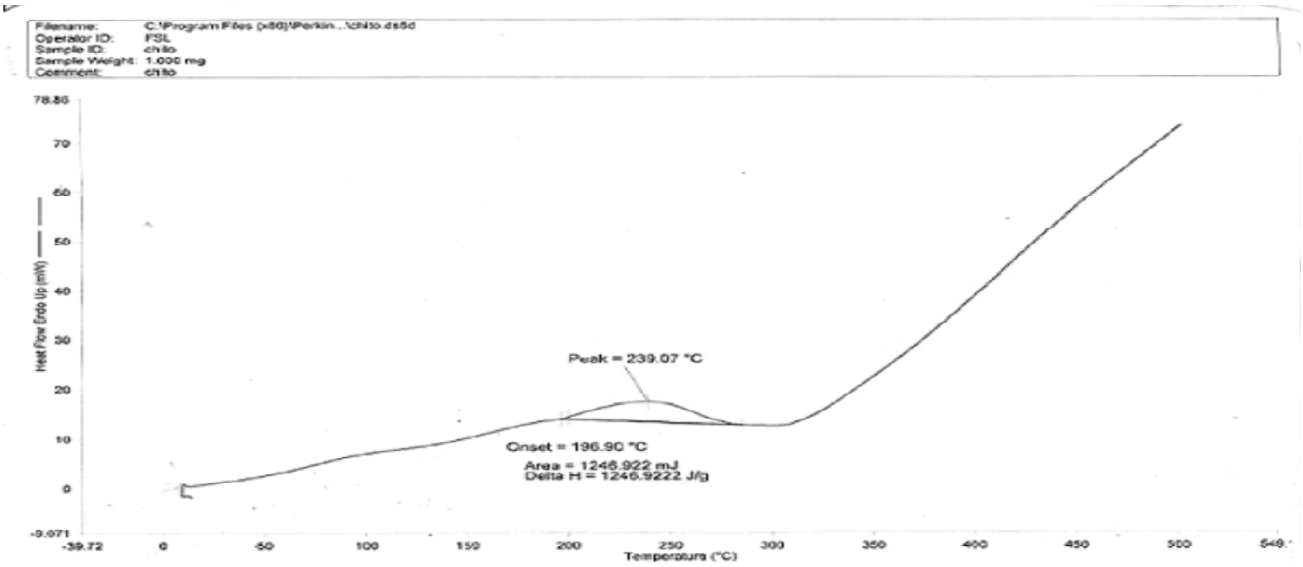

Figure 2: DSC of P(Chito)

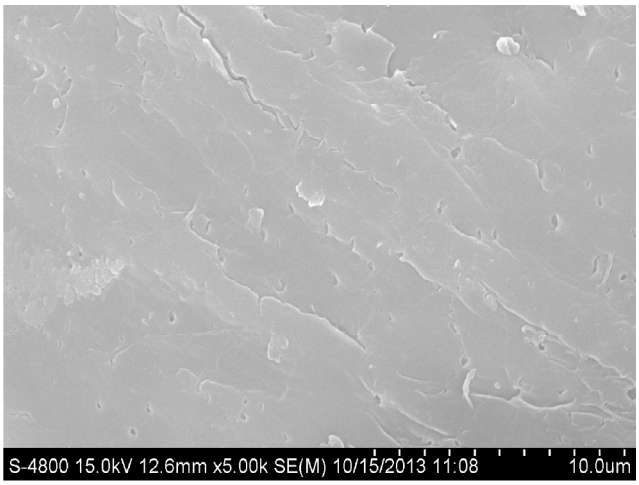

Figure 3: SEM image of Chitosan

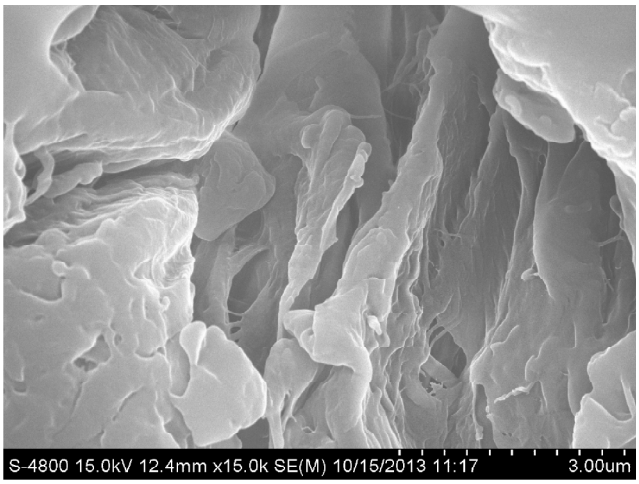

Figure 4: SEM Image of Chitosan hydrogel crosslinked with glutardehyade

RESULTS AND DISCUSSION

IR spectral characterization

For identification of the hydrogel, infrared spectroscopy and SEM were used. The FTIR spectra of pure chitosan (a) and superabsorbent hydrogel cross linked with glutaraldeyde (b) are shown in Figure 1. In Figure 1a, a broad band at 3342 cm^{-1}corresponds to the associated -OH stretching vibrations of the hydroxyl groups and the peak at 1658 cm^{-1}corresponds to the N-H deformation bending of chitosan. The superabsorbent hydrogel product comprises a chitosan backbone with side chains that carry carboxylate and amide functional groups that are evidenced by new peaks at 1550 and 2097 cm^{-1}corresponds,respectively. The very intense characteristic band at 1665 $cm^{-1}$is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1449 cm-1 which is related to the symmetric stretching mode of the carboxylate anion.(7) Decreasing in percentage transmittance of crosslinked hydrogel indicates involvement of hydroxyl group and other functional moieties in crosslinking with glutaraldehyde.

Differnationl scanning colourimentry

Differential scanning calorimetry (DSC) is the best analytical technique to find the polymer crystalinity, which measures the physical nature of the sample, i.e. Whether it is heated, cooled or

under isothermal conditions. In this technique a sample would heat or cool at linear intervals of temperature and measure the particular temperature and energy accompanied with any one of the range of thermal events. DSC studies reavels that crosslinked hydrogel are more thermally stable as compared to pure chitosan stable. (fig 2) The glass transition temperature of pure chitosan is observed at 200°C, when it is cross linked with aa-am the glass transition temperature is observed at 168 °C.(8)

SEM Analysis

One of the most important properties that must be considered is hydrogel microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Fig. 3 shows as SEM images of pure chitosan where as Fig. 4 shows an SEM image of the polymeric hydrogels obtained from the fracture surface. The hydrogel has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the crosslinked hydrogel. SEM Micrograph of Polymeric hydrogel obtained in fig. 4 from the hydrogel shows that it is compact structure as compare to pure chitosan in fig. 3, pure chitosan sample have uniform but fracture surface whereas hydrogel has porous structure which may be due to presences of water molecule in this rigion or beneath region. Porous structure support permeation and interfere site of external stimuli which hydrophilic group of grafted hydrogels. (9-11).

CONCLUSION

IR analysis indicates enviourment of –OH from chitosan backbone in the cross liking which is indicating by brond band 3342 cm^{-1}. Decreasing in percentage transmittance of crosslinked hydrogel indicates involvement of hydroxyl group and other functional moieties in crosslinking with glutaraldehyde. DSC indicates crystalline nature of cross linked hydrogel.SEM indicates porous structure & support permeation of water molecule in hydrogel, inversion supports the applicability of such smart hydrogel material in drug delivery, Biomedical material and analytical Chemistry. Also the swelling study of gels reveals that the gels are have variable swelling behavior at different pH solutions. The gels used in present investigation have polyamphophilic network which intelligently gives response to pH change. Thus these gels may be considered as excellent advanced material for sustainable development in field of Analytical chemistry.

Abbreviations

P(Chito), Crosslinked Chitosan**, SEM,** scanning electron microscopy; **DSC** Differential Scanning Colourimentry**, FTIR,** Fouirer transfer infra red spectroscopy

References

[1] Chen Y, Liu YF, Tan HM, Jiang JX. Synthesis and characterization of a novel superabsorbent polymer of N,Ocarboxymethyl chitosan graft copolymerized with vinyl monomers. *Carbohyd. Polym.* 75: 287-292, **(2011)**.

[2] Dengshan Bao, Preparation and characterization of double crosslinked hydrogel films from carboxymethylchitosan and carboxymethylcellulose, Carbohydrate Polymers, Volume 110, 22 September **2014**, Pages 113-120.

[3] V. R. Sinha, A. K. Singla,Chitosan microspheres as a potential carrier for drugs, *International Journal of Pharmaceutics* 274, **(2004)**, 1–33.

[4] Lin H., Zhou J., Yingde C., Gunasekaran S. Synthesis and Characterization of pH- and Salt-Responsive Hydrogels Based on Etherificated Sodium *Alginate J. Appl. Polym. Sci.* 115: 3161-3167, **(2010)**.

[5] Jia Liu, Qian Li, Yuan Su, Qinyan Yue, Bao yu Gao Characterization and swelling–deswelling properties of wheat straw cellulose based semi-IPNs hydrogel Carbohydrate Polymers, Volume 107, 17 July 2014, Pages 232-240.

[6] Pourjavadi A, Farhadpour B, Seidi F. Synthesis and Investigation of Swelling Behavior of New Agar Based Superabsorbent Hydrogel as a Candidate for Agrochemical Delivery. *J. Polym. Res.* 16: 655-665, **(2009)**.

[7] Zohuriaan-Mehr MJ, Pourjavadi A. Superabsorbent Hydrogels from Starch-g-PAN: Effect of Some Reaction Variables on Swelling *Behavior. J. Polym. Mater.* 20, 113-120, **(2003)**.

[8] Mohammad Sadeghi and Mojgan Yarahmadi, Synthesis and characterization of superabsorbent hydrogel based on chitosan-g-poly (acrylic acid-co-acrylonitrile) *African Journal of Biotechnology*, Vol. 10(57), pp. 12265-12275, 28.

[9] J. Brugnerottoa, J. Lizardib, An infrared investigation in relation with chitin and chitosan Characterization, Polymer 42, **(2001),** 3569- 3580.

[10] Chin-San Wu, A comparison of the structure, thermal properties, and b iodegradabilit of polycaprolactone/ chitosan and acrylic acid grafted polycaprolactone/ chitosan, PolymerVolume 46, Issue 1, 6 January **2005**, Pages 147–155.

[11] Prerna P. Dhawade and Ramanand N. Jagtap, Characterization of the glass transition temperature of chitosan and itsoligomers by temperature modulated differential scanning calorimetry, Advances in Applied Science Research, **2012**, 3 (3): 1372-1382.