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Studies on the Effect of Crosslinking of Chitosan/PVA Blend Based Hydrogel with Gluteraldehyde to be Used as Thin Membranes

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ABSTRACT

Chitosan (poly-2-amino-2-deoxy-D-glucose) is a nitrogenous-amino based polysaccharide which is produced in large quantities by N-deacetylation of chitin. The major advantage of chitosan is the existence of modifiable positions in its chemical structure. Modification of the chitosan molecule by (i) grafting -inserting functional groups or (ii) crosslinking reactions- uniting the macromolecular chains with each other leads to the formation of chitosan derivatives with superior properties enhancement of adsorption capacity and resistance in extreme medium conditions. Chitosan/ PVA blend was prepared with and without crosslinking agent gluteraldehyde. Films casted out of this was characterized with FTIR, DSC, and water absorption properties. Adsorption of metals was estimated by the UV spectroscope.

1. INTRODUCTION

A hydrogel is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium [1-3]. Hydrogels are highly absorbent (they can contain over 90% water) natural or synthetic polymeric networks. Hydrogels also possess a degree of flexibility very similar to natural tissue, due to their significant water content. The first appearance of the term 'hydrogel' in the literature was in 1894. Common ingredients include polyvinyl alcohol, sodium Polyacrylate, acrylate polymers and copolymers with an abundance of hydrophilic groups[4-6]. Hydrogels are widely used in the area of electrophoresis, bioseparations, proteomic, chromatography, tissue engineering etc. They are well-known in foods and medicines as absorbents in disposable diapers, as filters for water purification and as separation materials for chromatography and electrophoresis. They are also of interest for controlled drug release and for concentration of dilute solutions of macromolecules [8].

Natural hydrogel materials are being investigated for tissue engineering. These materials like polypeptides and other naturally derived polymers. Hydrogels show promise for use in agriculture, as they can release agrochemicals including pesticides and phosphate fertiliser slowly, increasing efficacy and reducing runoff, and at the same time improve the water retention of drier soils such as sandy loams.[7]

Chitin exists in marine media and especially in the exoskeleton of crustaceans, or cartilages of mollusks, cuticles of insects and cell walls of micro-organisms. Chitosan can be easily characterized as a promising material [6–13] not only because of its physical properties (macromolecular structure, non-toxicity, biocompatibility, biodegradability, low cost etc. 2 and applications in many fields like biotechnology, medicine, membranes, cosmetics, food industry etc.[14] but also because of its adsorption potential.

After the primary research work of Muzzarelli and Tubertini, who described the synthesis and adsorption evaluation of chitosan for the removal of metal ions from organic liquids and seawater [15]? The current paper is

focused on removal of dyes from effluents with various chitosan adsorbents, which is a topic of great interest nowadays.

In the case of grafting reactions, the addition of extra functional groups onto chitosan increases the number of adsorption sites and consequently the adsorption capacity. On the other hand, the crosslinking reactions slightly decrease the adsorption capacity because some functional groups of chitosan are bound with the crosslinker and cannot interact with the pollutant. Many researchers have attempted to prepare chitosan-based adsorbent materials by modifying the chitosan molecule.

Hydrogels were prepared using biomaterials. All material used in this tests are biomaterials and completely biodegradable and environmental friendly. Laboratory synthesis was carried out to prepare Chitosan /PVA blend. Swelling behaviour was controlled by crosslinking. Glutaraldehyde was the crosslinking agent for chitosan/PVA beads with low water content and high mechanical strength. It was found that glutaraldehyde reacted with PVA to form crosslinks at acidic conditions (pH 1 and 2). The H^+ ions act as both protection agents of amino groups of chitosan by forming salts and catalyst for the formation of acetal between aldehyde groups and hydroxyl groups of PVA. The blend was characterized using FTIR and all swelling tests were conducted. The Hydrogels prepared with various ratios of chitosan and PVA and optimized. The optimum blend was tested for DSC and TGA and examined using optical microscope.

2. EXPERIMENTAL

Materials used

Shrimp source chitosan (CS) was purchased from a local company with a deacetylation percentage (DD) of 88.1%.This chitosan is acid-soluble and white colored flakes. PVA Fluka (98-99) with an average molecular weight of 14,000g/ mol was supplied by Research lab fine chemical industries. Acetic acid (glacial 99.5%) was purchased from nice chemicals (p) ltd. Glutaraldehyde (GLA) solution (25%, w/w) was supplied by Merck. Ultra pure water was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were used in all experiments.

Chitosan was dried in an oven until a constant weight was observed. Chitosan was dissolved in acetic acid (0.1 M) followed by mild stirring and heating at about 60^0C for 1 hr to form a chitosan solution. Air bubbles were eliminated by keeping the solutions at room temperature for 30min. A similar solution of PVA was prepared by dissolving in preheated ultrapure water. The solution was then stirred and kept at about 80^0C for 1 h.

Blended solutions were prepared by adding the aqueous PVA solution drop by drop to a chitosan solution, which was kept on a magnetic stirrer, at about 94^0C and the mixture was stirred at a moderate speed for 30 min. The aqueous PVA solution was added drop by drop to the chitosan solution, under stirring at 90^oC in various proportions by volume. Glutaraldehyde is added and stirred well. The films of the solutions were obtained by casting prescribed amounts of the solution onto two different polystyrene Petri dishes followed by drying at 60^oC

for 48 h. The films were peeled off and stored. All films obtained were transparent and free of air bubbles. The film thicknesses of two samples were measured with a digital micrometer (Mitutoyo, Japan) with 0.001 mm resolution. Several thickness measurements were taken at various positions on each specimen and the average value was recorded and compared.

Water absorption of CS/PVA-GLA and CS/PVA films has been tested by the dissolution experiment. For the water absorption test, the specimens are dried in an oven for a specified time and temperature and then placed in desiccators to cool. Immediately upon cooling the specimens are weighed. The material is then emerged in water at agreed upon conditions, often 23°C for 24 hours or until equilibrium. Specimens are removed, patted dry with a cloth, and weighed.

A Differential Scanning Calorimetry was used for thermal analysis. The scanning temperature range and the heating rate were -20 to 300 at 10^{O}C/min respectively. The measurements were performed by taking 10mg of the sample film using model TA Q.20 DSC. The samples were scanned under a N_2 atmosphere with a flow of 50ml/min.

UV analysis was conducted using RIGOL ULTRA 3600 model up spectrophotometer. Fourier transformation was taken in the range of wavelengths that can be used in the calculation is limited by the separation of the data points in the interferogram.

Using TGA technique the thermal degradation of the sample is analysed between the room temperature and 600^{0}C.For this TGA Q50 model is used. The scanning temperature range and the heating temperature rate are 600^{0}C and 10^{0}C/min.

3. RESULTS AND DISCUSSION

3.1 Physical properties

Table 1 shows the physical properties of the chitosan /PVA blend hydrogel film

Sl.No	Properties	Uncrosslinked	Crosslinked
1	Water absorption, %	2621	3149
2	Water Intake in grams	3.249	2.721
3	Film thickness, mm	0.05	0.07
4	Density, g/cm^3	0.002	0.013

All the tests were carried out for crosslinked and uncrosslinked specimens made out of chitosan /PVA blend hydrogels membranes. The results give clear evidence that crosslinked hydrogels are more stable and give better physical properties compared to uncrosslinked hydrogels. As per the basic nature of Hydrogels stable structures are obtained by controlled crosslinks. The hydrophilic nature of hydrogel materials from chitosan and PVA are

restricted by the crosslinks. The materials are having tendency to dissolve in water or similar medium. Water absorption percentage is found to be more crosslinked hydrogel. This is due to the water holding capacity of the crosslinked structure. Uncrosslinked structure can take water but cannot hold in as much as crosslinked structure. The values clearly give the indication of super absorption capacity of chitosan /PVA hydorgels. Amount of water absorbed in the structure is also higher. Crosslinked hydrogels can be obtained with slightly higher thickness and much higher density ranges.

3.2 UV absorbance study

Figure 1 shows the effect of contact time of absorbance of the sample under UV spectrometer. It is clear that crosslinked can have more absorption of Cu ++ ions when compared with uncrosslinked hydrogels. Whereas uncrosslinked hydrogels the absorbance values remains without much changes even after more exposure time. In crosslinked hydrogels the absorbance decreases as the hydrogels take up the Cu ++ ions make the solution lighter. The value decreases and reaches a steady state after which there are not many changes in absorbance as the system comes to equilibrium. Hence it is very evident that chitosan /PVA blend Hydrogels with controlled amount of crosslinks can make a good absorbing medium for water solutions. This can be a good water purifier for the removal of heavy metals like Cu++.

3.3 DSC analysis

Figure 2. DSC Analysis of CS/PVA Film crosslinked with glutaraldehyde was examined. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample which is chitosan/PVA blend hydrogel crosslinked with gluteraldehyde. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures T_G. The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample are shown with a positive or negative peak.

Peaks obtained are a broad endothermic peak at 119.14 ^{0} C and a small peak at 185 to 70 ^{0} C. DSC curve of chitosan film shows a broad endothermic peak at about 79 ^{c}o while PVA film shows a smaller endothermic peak at 89^{o}C. All compositions exhibited broad endothermic peaks at lower positions than the pure components in the range of 70.3 to 77.3 ^{o} C. Figure 2 reveals that there is a difference in the endothermic peak area of all films, they vary in their water-holding capacity in a way showing that pure chitosan film has the highest water content while pure PVA one has the lowest water content unlike the blend films which their TD shows lower values and stands in between those of their pure components and is a function of the composition.

The variation in TD of blended film is believed to be due to the physical and molecular changes caused by the molecular chains interaction between chitosan and PVA, which suggests the formation of more stable films. Since chitosan tends to absorb moisture, a second heating run of the DSC, after heating to 150 ^{c}o, hold for a minute and then cooling to 40 ^{c}o, was performed to eliminate the effect of moisture. The first point to note is the absence of the

endothermic peak, confirmed that this peak is attributed to the water content in the sample. Also, pure PVA film exhibited a sharp endothermic melting transition at about 222 °C [4-6] while pure chitosan film did not show any melting transition due to the fact that most polysaccharides do not melt but degrade upon heating above a certain temperature. The melting point of PVA is close to the value reported in the literature. This shows that there is a little shift in the endothermic melting transition to lower temperature with increasing chitosan content in the blends. The melting depression in CS/PVA blends may be due to some interaction between the two polymers [7].

3.4 FTIR analysis

Figure 3: FTIR analysis was conducted for CS/PVA film crosslinked with glutaraldehyde. The spectrum of chitosan/PVA film shows a broad band at 3367 cm^{-1}which is due to the OH stretching. The band at 1560 cm^{-1} is due to the NH bending (amide II) (NH_2) the small peak at 1647 cm^{-1} is attributed to the C=O stretching (amide I) O=C-NHR. The bands at 2927, 2884, 1411, 1321 and 1260 cm^{-1} are designated to CH_2 bending due to pyranose ring [7]. The band at 1380 cm^{-1} is due to CH_3 group. All the characteristic features of chitosan spectrum in this study are similar to that of previous reports [8-10]. The spectrum shows an absorption peak at 3368 cm^{-1} which refers to the intermolecular hydrogen bonding and –OH stretch vibration [11]. The vibration band observed at 2941 cm^{-1} is associated with the C-H stretching from alkyl groups. The absorption corresponding to the C-O stretching occurs at 1096 cm^{-1}.

It is evident from the graph that by the addition of PVA in the blended films caused a decrease in the intensity of the band arising from the NH bending (amide II) at 1561 cm^{-1} of chitosan. There is also an increase in the intensity of CH group at around 2928 cm^{-1} was observed as the presence of PVA. There was a remarkable shift for the peak at 1077 cm^{-1} to a higher wave number with the increase of PVA content in the blend. The band at 850 cm^{-1} disappeared in the spectra of the pure chitosan film compared to the chitosan/PVA blend film containing PVA concentration of 50%, crosslinked with gluteraldehyde.

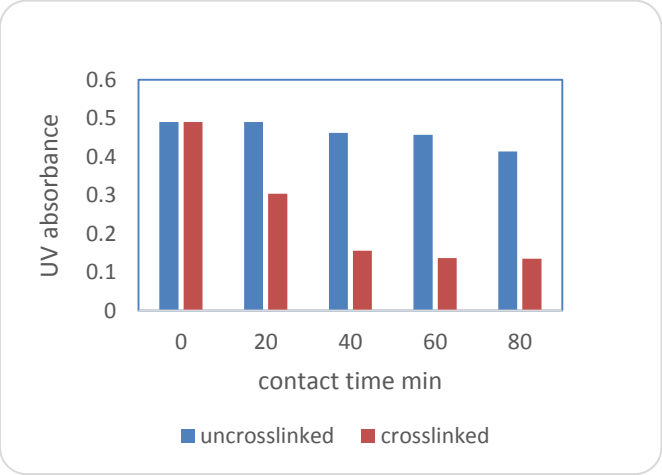

Figure 1 UV absorbance Vs Contact time

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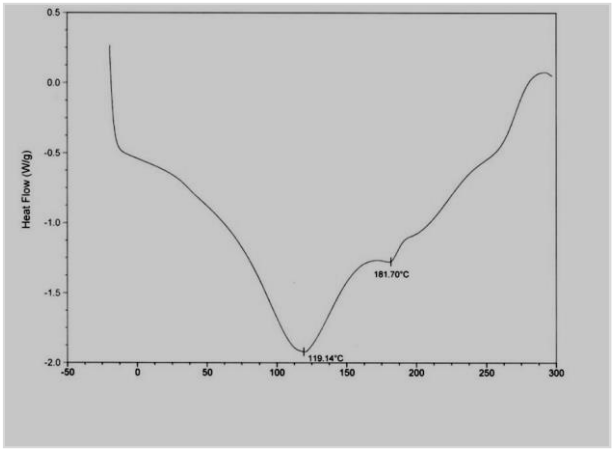

Figure 2 DSC graph of Chitosan /PVA blend crosslinked with gluteraldehyde

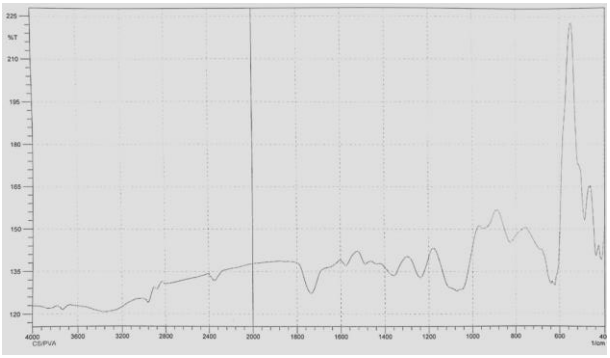

Figure 3 FTIR spectrum of CS/PVA film crosslinked with glutaraldehyde

4. CONCLUSIONS

Chitosan derivatives are in their peak nowadays regarding their adsorption abilities and it is notable that many researches are going worldwide focus on their preparation. This paper presents, which clearly demonstrate that the adsorption capacity of chitosan which is very high up to 1300 mg/ g depending on the dye molecule. The potential of these materials is very great regarding the decolourization of waste waters and in the next few years they are expected to be used even more for adsorption applications.

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