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Synthesis and characterisation of chitosan/sodium alginate/carboxymethyl cellulose beads

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ABSTRACT

The biopolymer chitosan, sodium alginate and carboxymethyl cellulose is widely used in many industrial applications and also in laboratory due to its good biocompatibility. In the present work the chitosan/sodium alginate/carboxymethyl cellulose beads were prepared in 1:2:1 ratio in the presence and absence of the glutaraldehyde crosslinker. The prepared polymeric bead samples were characterized by Fourier transform infra red spectroscopy (FT-IR), X-ray diffraction (XRD) and Thermo gravimetric analysis (TGA) studies. FT-IR result suggests that the interactions are taking place between added polymers and also the presence of crosslinking between the polymers and glutaraldehyde. The XRD studies were carried to find the reduction in crystallinity of prepared samples and through TGA studies the enhancement in the thermal stability of polymer beads were identified. The results confirms the formation and compatibility of the prepared beads.

Key words: chitosan, sodium alginate, carboxymethyl cellulose, glutaraldehyde, thermal stability.

INTRODUCTION

The products of a natural carbon-capture process, photosynthesis, followed by further biosynthetic modifications were actually termed as polysaccharides. Certain polysaccharides either in their native or chemically modified forms was produced on a very large scale in nature which has industrial relevance with, for example, materials and food applications [1]. The chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers and to use this renewable resource in the content of sustainable development. Chitosan is a natural biopolymer, derived from chitin which is made up of the exoskeleton of crustaceans (crabs and shrimp) and cell walls of fungi [2]. Certain chemical modifications which affords a wide range of derivatives were mainly done to improve chitosan's performance especially for specific applications in biomedical and biotechnological fields [3]. Due to this modification the fundamental skeleton of chitosan does not change but brings only the new or improved properties [4].

In the 80-ties of XX century, spherical chitosan structures (CS) have been started to produce [5,6] which find applications in medicine as the active substances carriers [7,8] and as well as sorbents in the processes of water purification from heavy metal ions or the decolourisation of textile sewages [9]. Alginate a linear biopolymer

consisting of alternating blocks of 1–4 linked α -L-guluronic acid (G) and β -D-mannuronic acid (M) residues with randomly alternating composition and sequence isolated mainly from brown seaweed [10,11].

Specifically, the M-blocks possess a shape proposed to be an extended ribbon whereas the G-blocks were found to be clasped. A diamond shaped hole results from the side by side alignment of the two G-block regions. The dimensions of so-called hole are ideal for the collective binding of calcium ions. Because of its capacity for gelatinization, the sodium alginate (NaAlg) which is a renewable and biodegradable natural polymer was used in a variety of commercial applications [12]. The ability of alginate sodium salt, to rapidly form viscous solutions and gels on contact with aqueous media has been exploited by the various industries.

Many carbohydrates pose advantages for tissue engineering applications due to their hydrophilicity, degradability, and availability of chemical groups for modification [13]. Sodium carboxymethyl cellulose is one of the most important cellulose derivatives which is an anionic polyelectrolyte derived from cellulose [14]. CMC has high transparency [15], low cost and environmentally friendly [16] and so when used as a capping material it will help to reduce the potential for toxicity. The presence of both carboxylated and hydroxyl groups makes CMC to readily form complexation with divalent alkaline metals.

In the present work, effort has been made to prepare ternary beads by mixing chitosan, sodium alginate and carboxymethyl cellulose with and without the cross linking agent glutaraldehyde. The main objective of this paper is to find out the change in crystalline behavior and also the enhancement in thermal stability by the addition of crosslinking agents to the chitosan/sodium alginate/carboxymethyl cellulose beads. The results were investigated.

MATERIALS AND METHODS

MATERIALS

Chitosan was obtained from Indian Sea foods, Cochin, Kerala. Sodium alginate was obtained from Nice Chemicals Private Ltd. Carboxymethyl cellulose was provided by Thermo Fisher Scientific private Ltd India. The crosslinking agent glutaraldehyde was obtained from SD-fine-chemicals Limited, India. All the reagents used to prepare the solutions were of analytical reagent grade.

PREPARATION OF CHITOSAN/SODIUM ALGINATE/CARBOXYMETHYL CELLULOSE BEADS

Chitosan /sodium alginate/ carboxymethyl cellulose beads were prepared in 1:2:1 ratio with and without the crosslinking agent glutaraldehyde using ionic crosslinking method. Initially the chitosan solution was prepared by dissolving 1 g of chitosan in 30 mL of 2% acetic acid solution. Chitosan solution was blended with sodium alginate (2 g in 30 mL water) and carboxymethyl cellulose (1 g in 30 mL water) under stirring over a period of 15 min. The stirring process was continued until a uniform dispersion was obtained. The resultant homogeneous bubble free slurry dispersion obtained above was then dropped through a syringe needle into 100 mL of 2% calcium chloride. The beads of CS/SA/CMC were allowed to stand in calcium chloride solution for 24 h and after 24 h, it was then washed and dried. The crosslinked CS/SA/CMC bead was prepared by dipping the dried beads in glutaraldehyde solution for 24 h. It was then finally washed with distilled water and dried.

CHARACTERIZATION

FTIR

The prepared chitosan/sodium alginate/carboxymethyl cellulose beads was characterized by FTIR spectroscopy. Measurements were performed on these samples with a Perkin Elmer 200 FT-IR spectrophotometer using potassium bromide pellets. The FTIR spectra were obtained in the wave number range from 4000 to 450 cm^{-1} .

X-RAY DIFFRACTION (XRD)

The X-ray diffraction patterns of the samples were tested by an X-ray scattering SHIMADUZ XD- diffractometer using in filter $\text{Cu K}\alpha$ radiation source (LAMDA = 0.154 nm), set a scan rate = 10/min, using a voltage of 40kv and a current of 30mA.

TGA

The prepared chitosan/sodium alginate/carboxy methyl cellulose beads were tested in a SDT Q600 V80 build 95 instrument. The temperature range was varied from room temperature to 850°C with the heating rate of 20°C /min

RESULTS AND DISCUSSION

Fourier transform infra red spectroscopy (FTIR)

Figure-1 shows the FTIR spectra of chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead. The broad peak which was obtained at 3428.26 cm^{-1} indicates the presence of OH stretching and NH stretching [17]. The peaks observed at 2967.11 cm^{-1} , 2861.14 cm^{-1} and 1634.95 cm^{-1} proves that the presence of aliphatic asymmetric CH stretching, symmetric CH stretching in CH_2 group and $\text{C}=\text{O}$ stretching in carboxylate ion respectively. Furthermore, the peak obtained at 1464.78 cm^{-1} , 1406.54 cm^{-1} , 1258.52 cm^{-1} , 799.18 cm^{-1} and 487.06 cm^{-1} may be due to C-H bending in alkanes, OH plane bending in alcohols, C-O stretching in alcohols, N-H wagging and C-C bending respectively.

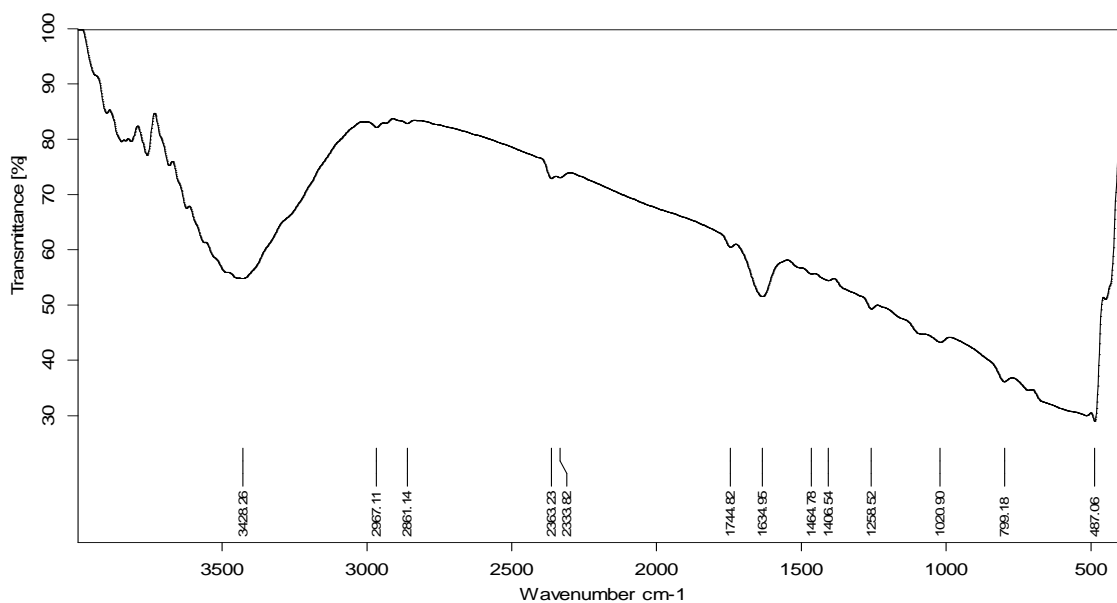


Fig: 1- CS/SA/CMC (1:2:1) bead

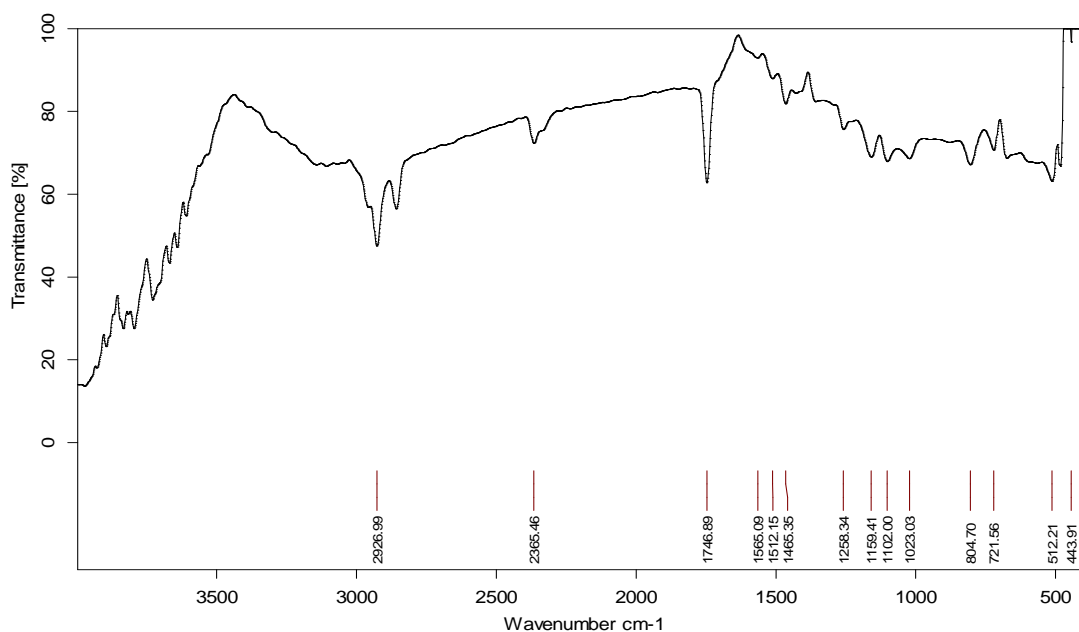


Fig: 2 - CS/SA/CMC (1:2:1) bead- glutaraldehyde

The FT-IR spectral details of chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead prepared with crosslinking agent glutaraldehyde was represented in figure-2. The prominent peaks observed at 2926.99 cm^{-1} , 1746.89 cm^{-1} , 1565.09 cm^{-1} and 1465.35 cm^{-1} was assigned to aliphatic C-H stretching in CH_2 [18], C=O stretching in ester, C=N stretching and OH bending respectively. Furthermore, the peaks observed at 1258.34 cm^{-1} , 1159.41 cm^{-1} , 1102.00 cm^{-1} corresponds to C-O stretching in alcohol, C-N stretching, C-O-C linkage. The peaks at 1023.03 cm^{-1} , 721.56 cm^{-1} , 443.91 cm^{-1} were attributed to C-C stretching, N-H wagging, C-C bending respectively.

On comparing the FTIR spectral details of chitosan/sodium alginate/carboxy methyl cellulose (1:2:1) prepared with and without the crosslinking agent agent glutaraldehyde it was observed that an additional peak was obtained in Figure (2) at 1565.09 cm^{-1} corresponding to the presence of C=N stretching. This observed peak confirms the strong binding of chitosan, sodium alginate and carboxymethyl cellulose with the crosslinking agent glutaraldehyde.

X-RAY DIFFRACTION STUDIES

The XRD study facilitates to realize the crystalline or amorphous nature of core material in the polymeric matrix. Figure-(3) and Figure-(4) represents the X-ray diffraction patterns of chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead prepared in the absence and presence of the crosslinking agent glutaraldehyde. In the XRD pattern of chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead, a short broad peak was obtained at $2\theta = 30.5^\circ$ whereas in the case of the XRD pattern of chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead prepared in the presence of crosslinking agent glutaraldehyde a long broad peak was obtained at around $2\theta = 41.5^\circ$. On comparing the XRD patterns, it was found that the degree of crystallinity was found to be decreased in case of bead prepared in the presence of glutaraldehyde. The crystallinity parameter of chitosan is a key parameter in the accessibility to internal sites for both water and metal ions [19]. Many of the studies have shown that decreasing the crystallinity results in an improvement in metal ions sorption properties. From the observed results it is evident that the chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead prepared with glutaraldehyde crosslinker has more amorphous nature which will be suitable for the adsorption process.

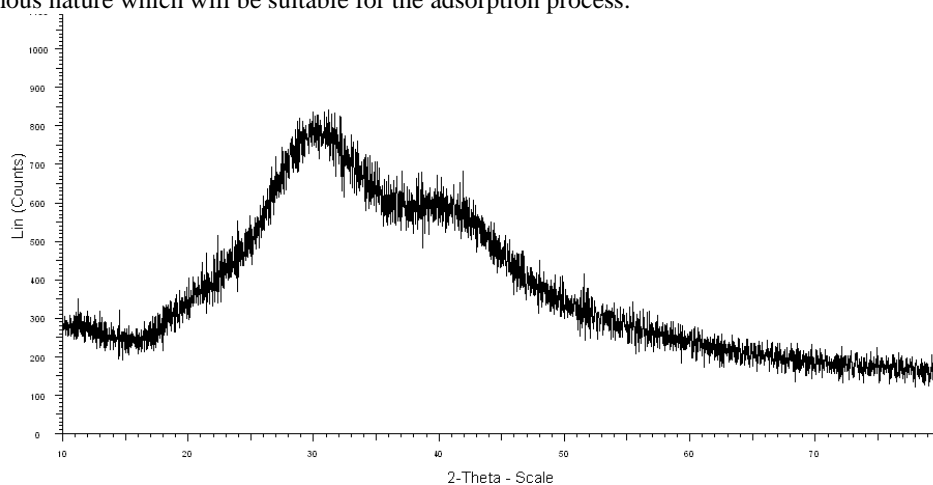


Fig:3- CS/SA/CMC (1:2:1) bead

THERMAL ANALYSIS

THERMO GRAVIMETRIC ANALYSIS

The TGA thermogram details of chitosan/sodium alginate/carboxymethyl cellulose bead prepared in (1:2:1) ratio (Table-1 and Figure-5) shows that the residual temperature at 787°C . The first decomposition peak was due to the evaporation of water both on the surface and in the pores of the sample [20]. Figure-5 showed a weight loss of water of about 19.83% (30°C to 100°C) and degraded in the temperature range of 212.50°C to 346.40°C with 45% weight loss. Around 65% of the sample is disintegrated at around 400°C and at the end of the experiment i.e., at 780°C only 0.5950% of the blend remained as a residue.

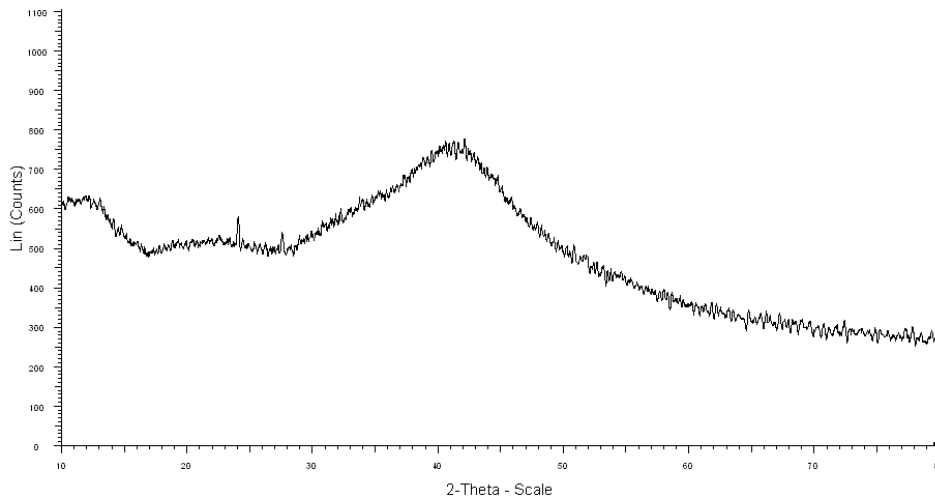


Fig:4- CS/SA/CMC (1:2:1) bead- glutaraldehyde

Table-1 and Figure-6 represents the TGA thermogram details of chitosan/sodium alginate/carboxymethyl cellulose bead (1:2:1) prepared in the presence of crosslinking agent glutaraldehyde. The residual temperature of the sample is 780°C. From 300°C there is only linear shallow decrease in weight with increase in temperature. Around 70% of the sample was disintegrated within 600°C. Maximum weight loss occurs at the temperature range of 100°C-300°C. At the end of the experiment i.e., at 787°C only 24.63% of the bead remained as a residue. The crosslinking of chitosan macromolecules resulted in the destruction of amino groups [21]. Due to the thermal degradation of a new crosslinked material formed by thermal crosslinking reactions occurring in the first stage of degradation process, the second decomposition step appears at high temperature. In the beginning, mass loss is faster but after 300 °C it is noticed to be slow, may be due to crosslinking of chitosan in the earlier stage [22].

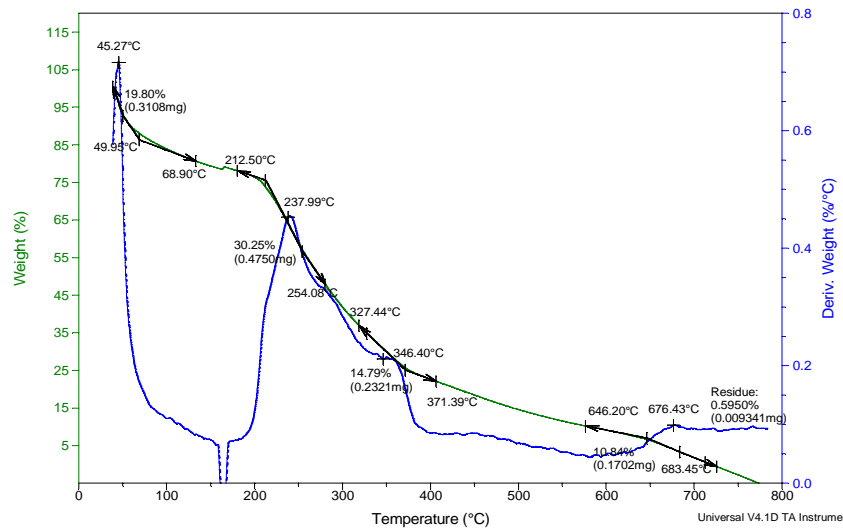


Fig:5(a)- TGA thermogram of CS/SA/CMC (1:2:1) bead

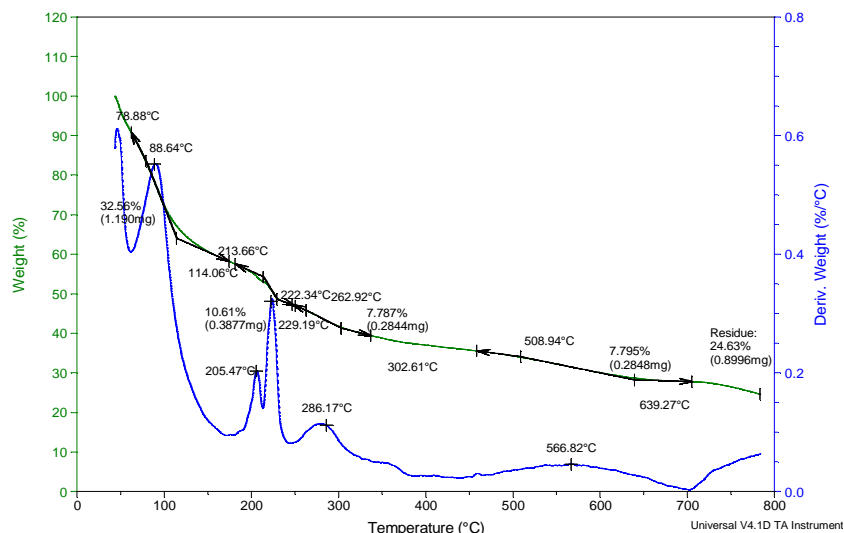


Fig-6: TGA thermal studies of CS/SA/CMC (1:2:1) –glutaraldehyde bead

Table-1: TGA Thermal studies of CS/SA/CMC (1:2:1) bead

Percentage Decomposition	Decomposition Temperature in °C	
	CS/SA/CMC (1:2:1) bead	CS/SA/CMC bead (1:2:1) –glutaraldehyde bead
10	60	75
20	140	93
30	215	113
40	248	166
50	270	233
60	300	312
70	350	633
80	430	
90	570	

The TGA curves revealed that chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead (Figure-5) decomposed at 60°C, whereas the glutaraldehyde crosslinked chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead (Figure-6) decomposed at 75 °C, respectively. From the comparison of all the decomposition temperatures and amount of bead remained as residue at the end of the experiment it was observed that the prepared crosslinked bead were found to be highly thermally stable than that of the chitosan/sodium alginate/carboxymethyl cellulose (1:2:1) bead prepared without the crosslinking agent. The higher thermal stability of crosslinked beads might be due to the lower chance of elimination of many small molecules which acted as an infusible support and provided thermal resistance to the bead [23].

CONCLUSION

The observed results suggest that there is strong interaction between the molecular chains of chitosan, sodium alginate and carboxymethyl cellulose which may lead to the miscibility at specific ratios of the three components. From the FTIR results, it was found that the C=N type of linkage were observed in the crosslinked polymer bead. This confirms the crosslinking had taken place between the polymer and the crosslinking agents. The XRD studies elucidate the reduction in the crystallinity of the chitosan, sodium alginate and carboxymethyl cellulose bead prepared in the presence of glutaraldehyde and the observed TGA results indicate that the addition of glutaraldehyde enhanced the thermal stability of the polymer bead when compared to the bead prepared without glutaraldehyde crosslinker.

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