
Synthesis and Characterization of Natural Graft Co Polymer of Chitosan

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ABSTRACT:

Graft co polymerization of chitosan (CS) onto Methyl methacrylate (MMA) was carried out through simple free radical initiation polymerization using redox initiation. Grafting percentage (%G), grafting efficiency (%GE) and conversion (%C) were calculated and it is noticed that all the above values are dependent of concentrations of initiator, monomer and temperature. Prepared co polymer was analyzed by Fourier transfer infrared spectroscopy (FTIR), proton nuclear magnetic spectroscopy (¹H-NMR Spectrum) and X-ray diffraction (XRD) to conform grafting of MMA on chitosan. The Proposed possible reaction mechanism was illustrated for Graft co polymerization.

KEYWORDS: Chitosan, methyl methacrylate, graft copolymer and radical polymerization.

1. INTRODUCTION:

Grafting is a simple and novel polymerization technique for the development of new natural and bio degradable polymeric devices in various applications like bone tissue engineering [1], drug delivery [2], bio medical and ion removal etc. Graft co polymerization of chitosan with vinyl monomers gained more impotence and this creates more interest for many research groups in this area from three decades. This method will provide new polymeric devices with excellent properties chitosan n is a derivative of 1(4)-2-amino-2-deoxy-D-glucon) chitin and it was prepared by N-deacetylation of chitin using strong alkaline medium[3]. Chitin is a polysaccharide and it occurs naturally in the shells of Crustacea, insects and bacterial cell walls.

Sugar based polymers gained much importance in various fields because of their compositions, complex architecture, and well defined molecular weights were become more popular and provide a wide range of applications in biomedical and pharmaceutical area [4]. Sugar based natural polymers have great advantages over synthetic polymers like biodegradability, bio compatibility and non-immunogenic properties makes them promotable goods and which are particularly suitable for in-vivo, in vitro therapeutic applications including drug, gene, protein and antigen delivery as well as diagnostic devices.

Chitin and chitosan have several applications in pharmacology, bone tissue engineering, bio medicine, flocculants and agriculture [4-5] because of their hydrophilic surface good bio compatibility, host response and bio degradable by lysozyme and other enzymes, bactericidal/bacteriostatic activity and the capacity to maintain a predefined shape after cross linking[samaneh saber samadari et al.,2017][6-9].

Grafting can be done by different techniques such as microwave, irradiation -radiation and chemical initiators. Several studies have been investigated on graft co polymerization of vinyl monomers like methyl methacrylate on starch, -cyclo dextrin on to chitosan and acrylic acid on to chitosan [10-12].graft co polymerization of corboxy methyl chitosan with acryl amide was done using ceric ammonium nitrate to prepare ultra -adsorbent materials which are more thermally stable than parent polymer [13]. Grafting of natural polymers with vinyl monomers and synthetic polymers with defined grating ratios were studied with possibility of persulphate radicals [14-15]. From this it is noticed that the polymer and the persulphate radical could react to form radicals directly on polymer back bone, this technique can also be used to prepare desired properties polymer matrix with grafting of chitosan with water soluble vinyl monomers [16-17]. The improved water retention, thermal stability, solubility and binding strength properties were observed in graft copolymers of cellulose/chitosan with acrylamide [18].

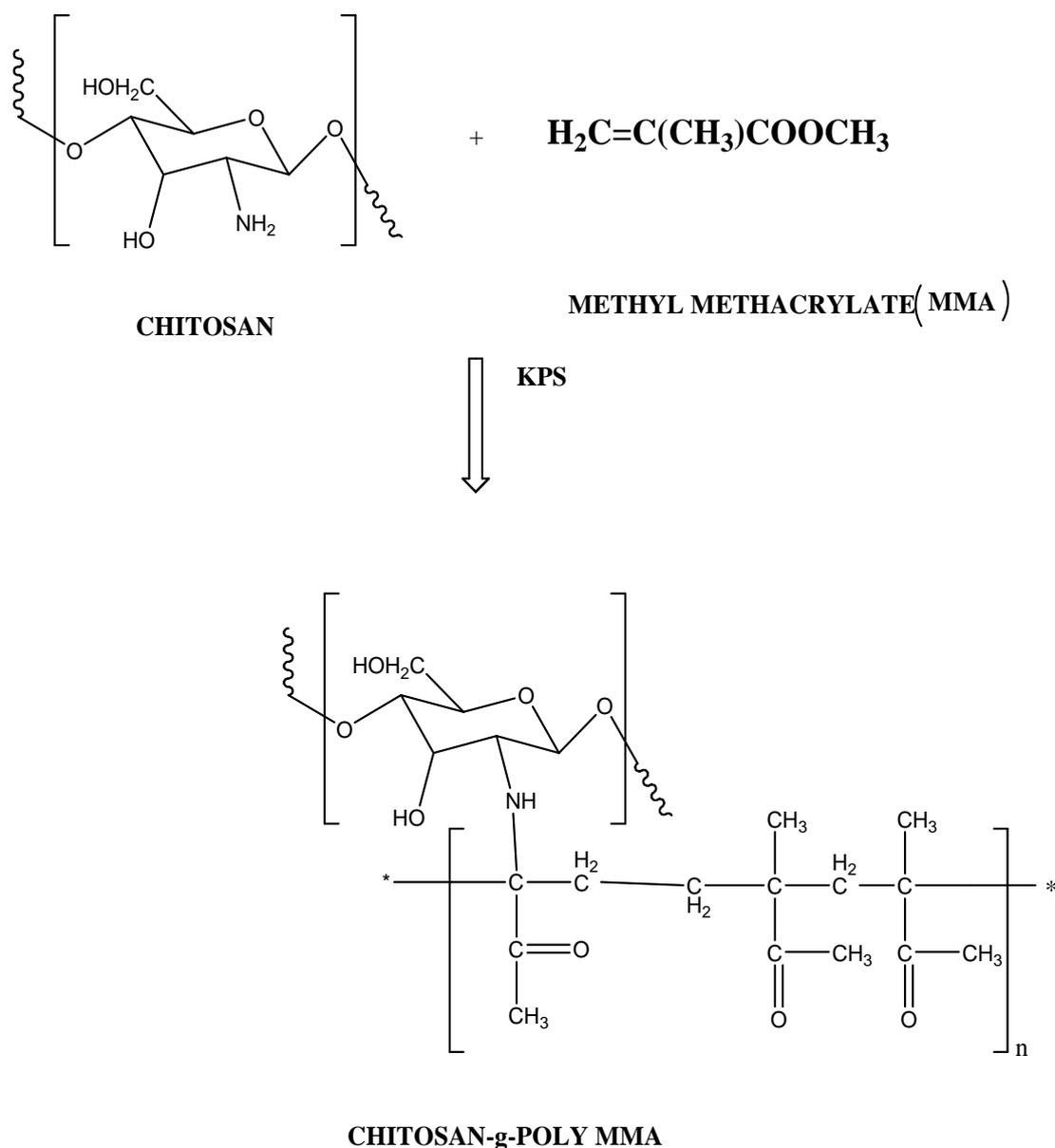
The past studies were revealing that the co polymerization of chitosan with vinyl monomers will provide promising graft copolymers with desired properties. In our work we prepared graft copolymer of methyl methacrylate grafted in to chitosan and characterization was done, it was confirmed the formation of product. Effect of monomer, initiator and temperature was studied.

2. EXPERIMENTAL

2.1 MATERIALS AND METHODS

Chitosan medium molecular weight was purchased from sigma Aldrich USA, methyl methacrylate, sodium sulphate and potassium persulphate were purchased from Sd fine chem Mumbai, India. Acetone and acetic acid were purchased from SRL Scientifics Mumbai India. And were all used without further purification. Double distilled water was used in all experiments.

2.2 GRAFT COPOLYMERIZATION



Scheme-I: proposed reaction mechanism for graft copolymerization

Chitosan and methyl methacrylate co polymer was fabricated by simple free radical polymerization. Chitosan (0.5) was dissolved in acetic acid (50ml) and solution was stirred overnight. To this solution known amount of methyl methacrylate (1ml) was added directly and stirred for 60min at 60^oc followed by the addition of known amount of initiator (10% K₂ S₂O₈). Polymerization was carried for 3hours in thermo stated water bath at 60^oc with constant stirring and continuous purging of nitrogen gas. When polymerization completed the product was cooled at room temperature and poured into excess hot acetone for precipitation. Then the product was washed with acetone /water (50:50) to remove unreacted material then vacuum dried at 40^oc until the weight was constant. The percentage of grafting (%G), grafting efficiency (%GE) and conversion (%C) were calculated [19-21] using

$$\text{Percentage of Grafting (\%G)} = \frac{W_1 - W_0}{W_0} \times 100 \quad \text{----- (1)}$$

$$\text{Grafting efficiency (\%GE)} = \frac{W_1 - W_0}{W_2} \times 100 \quad \text{----- (2)}$$

$$\text{Percentage of conversion (\%C)} = \frac{W_1}{W_2} \times 100 \quad \text{----- (3)}$$

Where W₀, W₁ and W₂ are the weights of CS, graft copolymer and monomer respectively.

2.3. FOURIER TRANSFORM INFRARED SPECTRO SCOPY (FT-IR)

FTIR Spectrum was recorded for grafted product using (Perkin Elmer spectrum two model, Singapore) spectrometer by KBr pellet method. The spectra were scanned in the range between 4000 cm⁻¹ to 400 cm⁻¹.

2.4. ¹H-NMR SPECTRUM:

For synthesized product ¹H-NMR spectrum was scanned for analysis using Burker analytic GMBH D-76287 Rheinstetten Germany spectrum.

2.5.X-RAY DIFFERATION (XRD)

XRD studies were performed for CS-g-MMA graft co polymer on a Rigaku diffractometer (Rigaku, Japan) with Cu-K radiation at 30Kv and 40 mA (=1.5418 A⁰) and scans were recorded in the angle range of 0-70^o at 5^o/min.

3. RESULTS AND DISSCUSSIONS

3.1. FT-IR STUDIES:

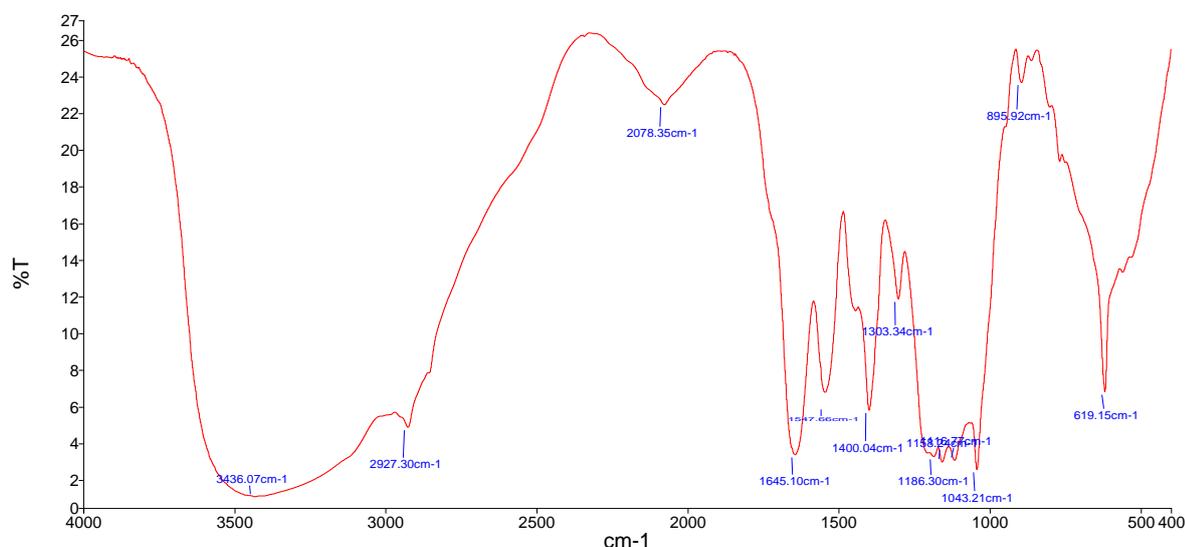


Figure.1: FT-IR spectrum of CS-g-MMA co polymer

The graft co polymer of methyl methacrylate grafted on to chitosan using redox initiator was confirmed by infrared spectrum shown in fig(1). A broad peak at 3438cm^{-1} was observed and assigned for the stretching vibrations of O-H and N-H formation of inter-hydrogen bonds of poly saccharide chitosan. An intense peak at 1645cm^{-1} and 2927cm^{-1} were referred for carbonyl stretching and symmetrical stretching of methyl group, a significant peak at 1148cm^{-1} assigned to C-N stretching vibrations. From this it is conformed that the formation MMA was grafted on chitosan.

3.2. $^1\text{H-NMR}$ STUDIES

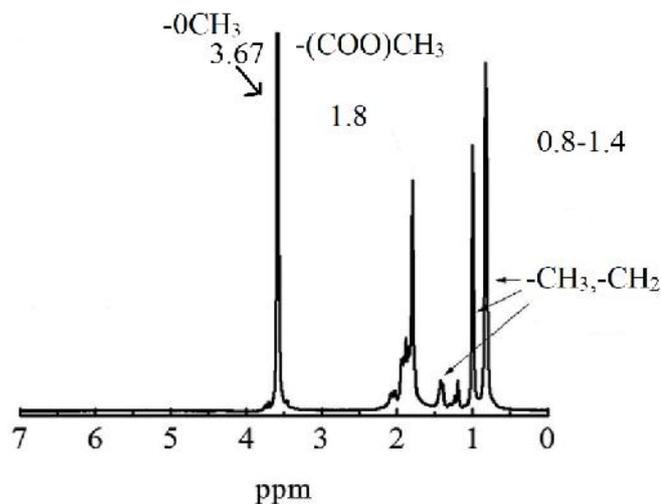


Figure 2: $^1\text{H-NMR}$ spectrum of CS-g-MMA

From fig 2 it was analyzed that the peaks in the range of 0.8 to 1.4 were assigned to $-\text{CH}_3$, $-\text{CH}_2$ and peak at 1.8 ppm was referred to $(-\text{COO})\text{CH}_3$ group of co polymerization of CS-g-MMA. From past studies it is observed that the $^1\text{H-NMR}$ pure chitosan had peaks at 5.4 and 6.1 ppm were present but in the spectrum of CS-g-MMA peaks at 5.4 and 6.1 ppm are disappeared Which suggests that the group of $\text{C}=\text{C}$ of MMA had been involved in grafting and it confirms that MMA was grafted on to chitosan (CS).

3.3. X-RAY DIFFRACTION STUDIES

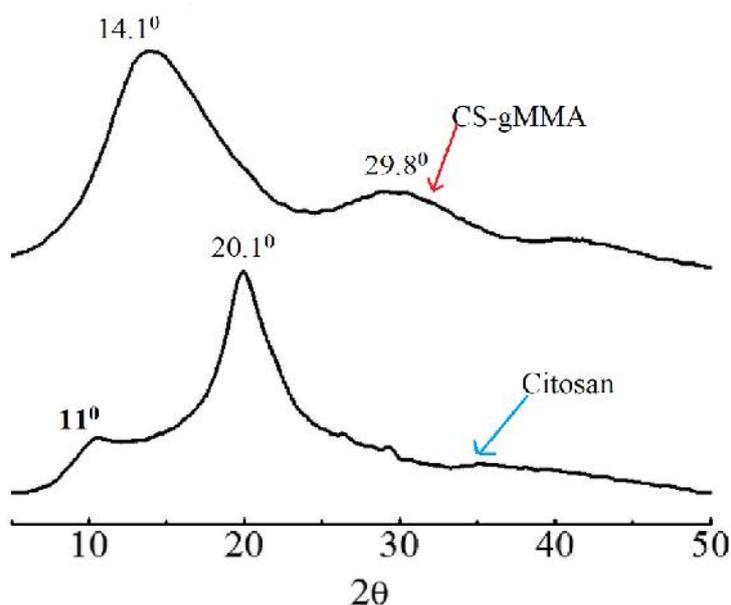


Figure 3: X-ray diffractograms of chitosan and CS-g-MMA

The X-ray diffraction data shows crystalline peaks at $2\theta = 11^\circ$ and 20.1° were assigned to chitosan, these are significant peaks for chitosan [Krishna rao et al]. The peak at $2\theta = 11^\circ$ anhydrous crystal form I and the strong peak at $2\theta = 20.1^\circ$ was observed in chitosan prepared by dissolved in acetic acid [22-24]. After grafting reaction crystalline area of CS was around $2\theta = 14.1^\circ$ and $2\theta = 29.8^\circ$ in co polymerization. This was because many hydrogen bonds are formed to disrupt the original crystalline structure of the chitosan throughout preparation. These suggests that MMA had grafted on to chitosan successfully [25].

3.4. EFFECT OF POLYMER, INITIATOR AND TEMPERATURE ON GRAFTING

Effect of polymer was observed that as the concentration of chitosan is increasing percentage of grafting (%G) and percentage of efficiency (%E) were increased. This was because of as increasing the content of chitosan number of $-NH_2$ groups in reaction mixture were increase and it will provide more reactive sites for grafting MMA. Increase the concentration of initiator on grafting results increase in percentage of grafting (%G) and efficiency (%E). As the concentration of initiator increase it will increase the production of chitosan radicals in reaction mixture which leads to the formation of more product as co polymer. Temperature plays a vital role on graft copolymerization. In this case when temperature increases it will accelerates the reaction towards graft copolymerization and homo polymerization caused for formation of more product.

4. CONCLUSION:

In this study methyl methacrylate has been successfully grafted on to chitosan via free radical polymerization. The synthesized product was a natural co polymer with effective properties as biodegradable, bio compatible which could be better devices for biomedical applications. Synthesis was confirmed by FT-IR spectroscopy and structure of graft co polymer has been illustrated by 1H -NMR spectrum. XRD studies reveled changes in the crystallinity of product.

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