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MODIFICATION AND CHARACTERIZATION OF CHITOSAN OLIGOSACCHARIDE

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ABSTRACT

The present study was aimed to prepare the novel material, the graft copolymerization of Glycidylmethacrylate onto the glutaraldehyde crosslinked chitosan oligosaccharide has been successfully carried out using ceric ammonium nitrate as a redox initiator in aqueous nitric acid medium. The effect of grafting variables including concentration of initiator, temperature, monomer, and polymer (COS) on the grafting parameters were systematically investigated and optimized for the graft copolymer (COS-g-GMA) to achieve the highest percent grafting. The synthesized graft copolymer was then blended with polypropylene glycol in 1:1 ratio. Furthermore, we were characterized by Fourier transform infra red spectroscopy (FT-IR), X-Ray diffractogram (XRD), Thermo gravimetric analysis (TGA) and Scanning electron microscopic (SEM) studies). Grafting was confirmed by FTIR. X-ray diffraction showed changes in crystallinity pattern. Slightly different mechanisms in side chain substitution for these polymers were envisaged. The thermal properties of prepared graft copolymer blend were obtained by TGA thermal studies. Asymmetric nature and rough surface morphology were confirmed using SEM analysis. From the results, it was concluded that COS-g-GMA/PPG-Glu is an excellent material as a biosorbent for removal heavy metal from waste water.

KEYWORDS:

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Chitosan oligosaccharide, Glycidylmethacrylate, Glutaraldehyde, Ceric ammonium nitrate, Poly propylene glycol.

INTRODUCTION

Heavy metal contamination has becomes a global nuisance. Heavy metals may accumulate in living tissues throughout the food chain, which has humans at its peak, multiplying the danger [1,2]. Heavy metals have received much attention because of their high toxicity, non-biodegradability [3,4] and accumulated in the human body.

In recent times, biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals and is mainly helpful for the removal of contaminants from industrial effluents [5]. Hence, we had chosen Chitosan oligosaccharide (COS), Chitosan oligosaccharide (COS) is a water-soluble polysaccharide mainly obtained from the partial hydrolysis of chitosan, which have better biocompatibility and solubility due to their shorter chain lengths and free amino groups in D-glucosamine units [6]. It cannot be used for water treatment. However, many talented features are linked to the chitosan oligosaccharide-based materials to open for the further development, which can achieve higher adsorption capacity for the removal of heavy metals from aqueous systems.

The grafting and blending of synthetic polymers are improving their adsorption capacity, selectivity and physiochemical properties [7]. Glycidyl methacrylate

(GMA) has a hydrolysable ester group that can be beneficially modified by polymer analogous reactions to get a wide range of functionalized polymers, It also has a reactive epoxy group, which, due to its efficient binding nature [8]. Hence it was selected in this study for grafting process. In this study of blending technique, we had chosen synthetic polymer such as polypropylene glycol (PPG) is a polymer with alternate hydrophobic and hydrophilic groups in molecular chains, and understandable discrepancy in hydrophilicity between the alkyl and ether groups. Chitosan oligosaccharide-g-glycidyl methacrylate copolymer and polypropylene glycol interaction will be improved by adding gluteraldehyde as the crosslinker which may makes the blends stronger for water treatment applications. Based on the literature review, a novel hybrid material COS – g – GMA / PPG-Glu blend was synthesized and characterized by IR, XRD, TGA and SEM analysis.

MATERIALS AND METHODS

Materials

Chitosan oligosaccharide was obtained from India sea foods Cochin, Kerala, India. The monomer Glycidylmethacrylate was purchased from the Sisco research laboratory. Polypropylene glycol, Glutaraldehyde, sodium hydroxide and nitric acid were of analytical grade and used as received.

The graft copolymerization of glycidyl mecharylate onto chitosan oligo saccharide with ceric ammonium nitrate as an initiator. The grafting parameters including the grafting efficiency, grafting percentage and % monomer conversion were systematically evaluated as function of temperature, monomer concentration, chitosan oligo saccharide concentration and reaction time. The percent of grafting, % monomer conversion, grafting efficiency and grafting yield as follows

$$\text{GE (\%)} = \frac{\text{Wt of graft copolymer}}{\text{Wt of graft copolymer} + \text{Wt of homopolymer}} \times 100$$

$$\text{GY (\%)} = \frac{\text{Wt of graft copolymer} - \text{Wt of un grafted polymer}}{\text{Wt of ungrafted polymer}} \times 100$$

$$\text{GP (\%)} = \frac{\text{Wt of graft copolymer}}{\text{Wt of substrate}} \times 100$$

$$\text{\%C} = \frac{\text{Wt of graft copolymer}}{\text{Wt of Monomer}} \times 100$$

From the results illustrated the effect of initiator, monomer and polymer concentration which showed the optimal concentration of Ceric ammonium nitrate, Glycidyl methacrylate and Chitosan oligosaccharide respectively were Ceric ammonium nitrate for 0.9 g, Glycidyl methacrylate for 0.8 mL and Chitosan oligosaccharide for 0.6 g. The optimum value sample was used further applications.

Preparation of Chitosan oligosaccharide – g- Glycidyl methacrylate (COS – g – GMA)

Chitosan oligosaccharide (0.6 g) was dissolved in 30 mL of water and the monomer glycidyl methacrylate (0.8 mL) was dissolved in minimum amount of ethanol. The above prepared solutions were mixed well and stirred continuously in magnetic stirrer to attain 80 °C. In order to initiate the polymerization process in the above mixture, about 10 mL of ceric ammonium nitrate (0.9 g CAN dissolved in10 mL of Nitric acid) was added. This mixture was stirred constantly at 80 °C for a period of 30 minutes. The resultant solution was cooled to room temperature and then it was poured into 2N NaOH to precipitate the product. The obtained graft copolymer was then filtered, washed with water for several times and then dried at room temperature.

Preparation of Chitosan oligosaccharide -g- Glycidyl methacrylate / Polypropylene glycol blend (COS – g – GMA / PPG-Glu)

About 1 g of Chitosan oligosaccharide -g- Glycidyl methacrylate copolymer was dispersed in a minimum amount of water and 1 g of polypropylene glycol was dissolved in a minimum amount of ethanol separately. The above solutions and 6mL of glutaraldehyde were then mixed thoroughly at room temperature in magnetic stirrer for 30 minutes. After stirring, COS – g – GMA / PPG-Glu blend formed was then poured into petri plates and dried at room temperature.

CHARACTERISATION

FT-IR

A thermo nicolet AVATAR 330 IR spectrophotometer was used to record the IR spectra within the range of 4000–400 cm^{-1}. The IR spectrum was recorded in a solid state using a KBr pellet method.

XRD

The molecular packing of the blend membranes was analyzed with X-ray powder diffractometer (XRD-SHIMADZU XD-D1) using a Ni-filtered Cu Kα X-ray radiation source.

Thermo gravimetric analysis

The thermogravimetric analysis was carried out as follows: About 2.0 mg of this sample was heated from 30 to 870 °C at a heating rate of 10 °C/min at N_2 atmosphere and corresponding weight losses were measured as a function of temperature in a Perkin Elmer thermal analyzer.

Scanning electron microscopy (SEM)

The surface morphology of the COS – g – GMA / PPG-Glu blend were observed with scanning electron microscopy to verify the compatibility of the mixtures. For the analysis, the samples were cut into pieces of various sizes and wiped with a thin gold-palladium layer by a sputter coater unit (SEM, Leica, Cambridge, UK).

Result and discussion

3.1 FT-IR Analysis

FT-IR spectrum is an essential tool for predicting the reaction progress. It gives details about the covalent bond and the hydrogen bonding present in the system. Hence this blend has been analyzed using FT-IR and the possible interactions between the functional groups in a polymer blend was studied.

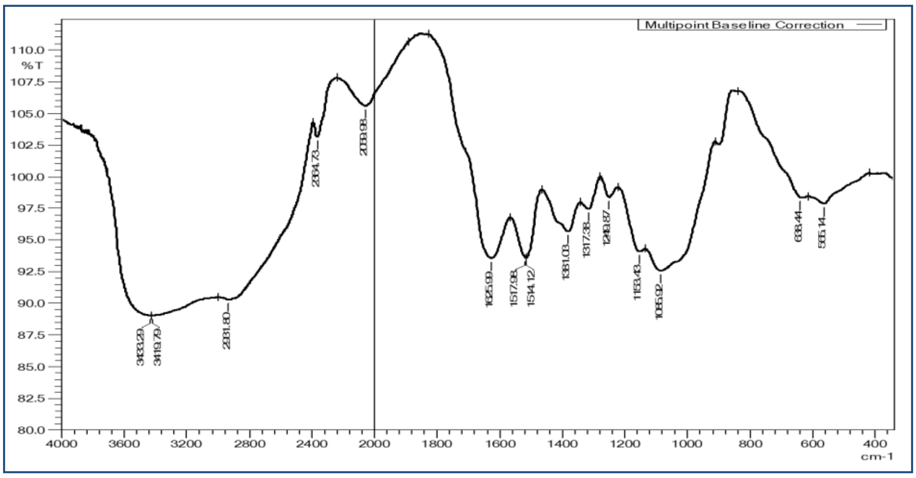

Figure -1a: FTIR spectrum of pure Chitosan oligosaccharide

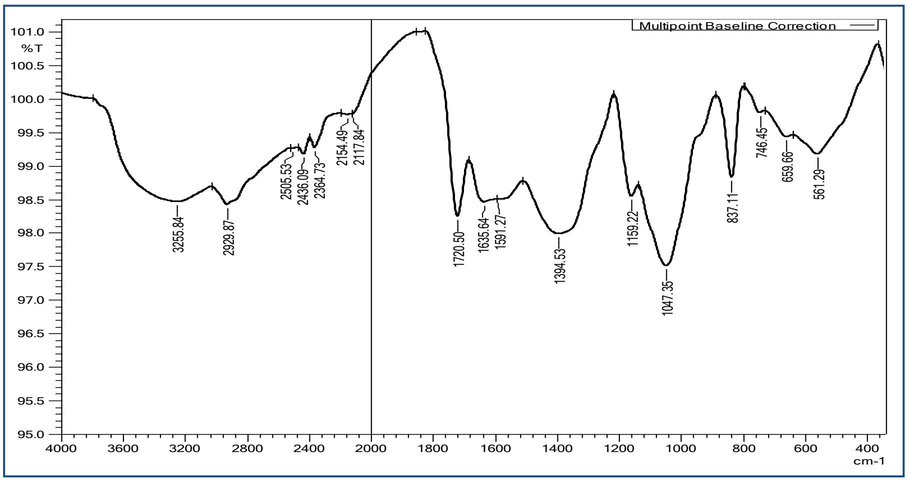

Figure -1b: FTIR spectrum of COS – g – GMA copolymer

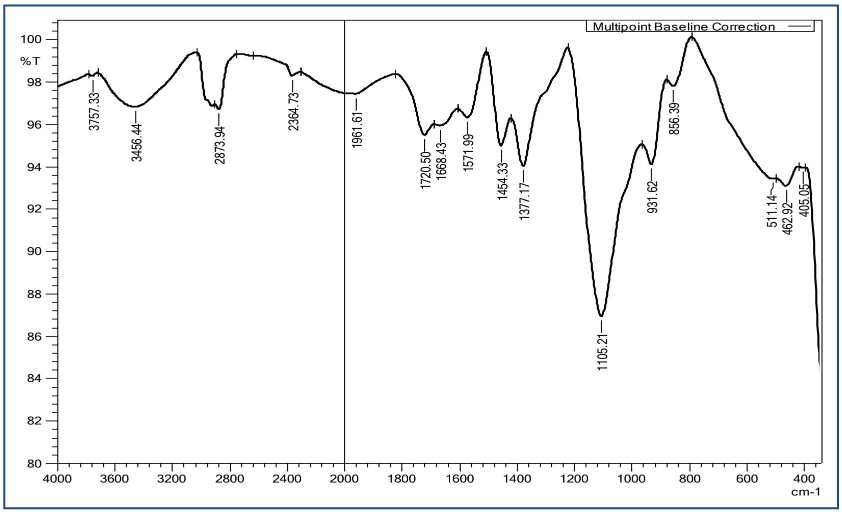

Figure -1c: FTIR spectrum of COS – g – GMA/PPG-Glu blend

FT-IR spectrum of pure chitosan oligosaccharide (Figure-1a) shows a band around 3419.19 cm^{-1} due to OH stretching and NH stretching. The absorption band around 2931.80cm^{-1},1625.99cm^{-1} and 1517.98cm^{-1} due to CH stretching, amide I and amide II group. The characteristic absorption band at1317.38cm^{-1}, 1153.43cm^{-1} were assigned to the C-O stretching in secondary alcohol and asymmetric stretching of the C-O-C in skeletal linkage of chitosan oligosaccharide [9]. From the COS-g-GMA spectrum (Figure -1b), the strong new band appears at 1720.50cm^{-1} and at 837.11 cm^{-1} which indicate carbonyl group and the double bond of methacrylate group [10] respectively. Thus, confirmed the grafting of GMA group onto COS.

Grafted chitosan oligosaccharide was blended with poly propylene glycol to form COS – g – GMA / PPG-Glu blend. From the figure-1c, the observed shift in band position are due to the inclusion of poly propylene glycol and glutaraldehyde crosslinker for copolymer modification into blend. When the poly propylene glycol was incorporated into graft copolymer, the number of hydroxyl groups increased which result in the increased hydrogen bond interaction between copolymer and poly propylene glycol [11]. This reveals that COS-g-GMA (copolymer) and polypropylene glycol (PPG) get blended successfully.

3.2. XRD analysis

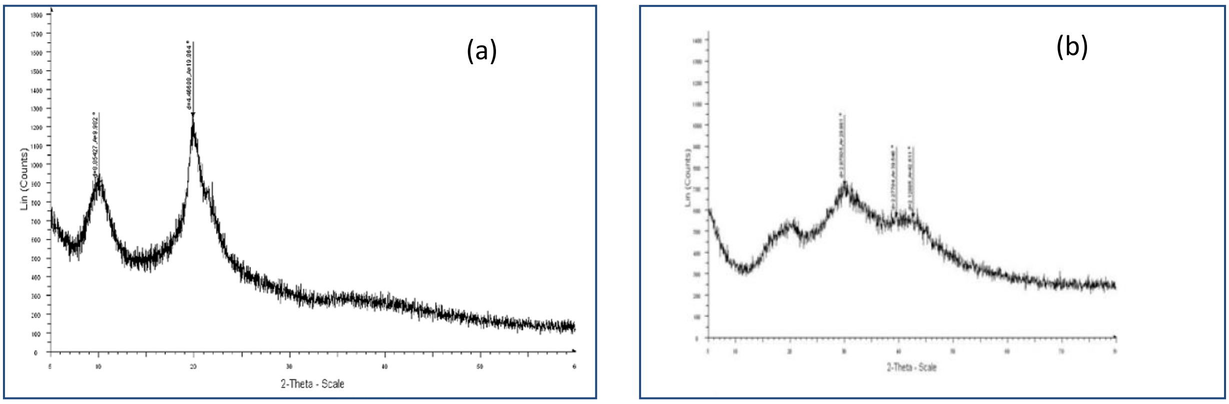

Figure -2: X-ray diffractogram of (a) pure chitosan oligosaccharide and (b) COS-g-GMA/PPG-Glu Blend

On comparing XRD pattern of COS and COS-g-GMA/PPG-Glu showed peaks at 10° 20° and 29°,39°, 42° respectively. From the observed broad nature of the diffractogram, it was detected that there was a decrease in crystallinity in the COS-g-GMA/PPG-Glu blend. Therefore, the metal ion could more easily penetrate through the blend surface, which can be useful for the waste water remediation.

3.3 Thermo gravimetric analysis

The TGA thermogram of details of COS and COS-g-GMA/PPG-Glu samples were represented in the figure 3a and 3b. On comparing with pure COS, the change in thermal behavior was seen in the case of the copolymer blend. In the prepared blend there were four stages of weight loss, whereas in pure COS three stages were observed. The first weight loss in COS-g-GMA/PPG – Glu blends was observed in the temperature range of 35^{0}C to 215^{0}C, due to disruption of absorbed water molecules. Second stage of weight loss from 215^{0}C to 355^{0}C was due to the decomposition of glycidyl methacrylate (245^{0}C-290^{0}C) and polypropylene glycol (265^{0}C-363^{0}C). These results are in good agreement with other GMA-based copolymers reports presented in the literature [12]. Major weight loss of 34.40% was taken place in the third stage which was observed between 355^{0}C to 520^{0}C. This corresponds to the degradation of formed covalent bond between the polymers and crosslinking agents. In last stage, there is only linear shallow decrease in weight with increase in temperature range between 520^{0}C to 790^{0}C, due to the degradation of backbone of chitosan molecule. Thus, the addition of glycidyl methacrylate and polypropylene glycol to the chitosan oligosaccharide, the change in thermal behavior was observed, confirming the complete miscibility of two polymer during blending.

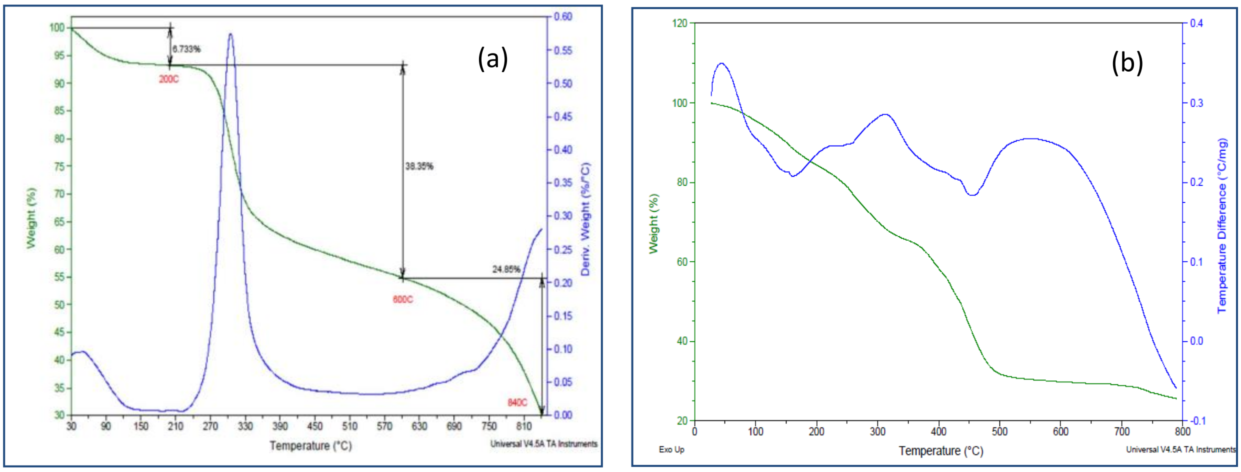

Figure-3: TGA thermogram of (a) pure chitosan oligosaccharide and (b) COS-g-GMA/PPG-Glu Blend

3.4 Scanning electron microscopy Analysis

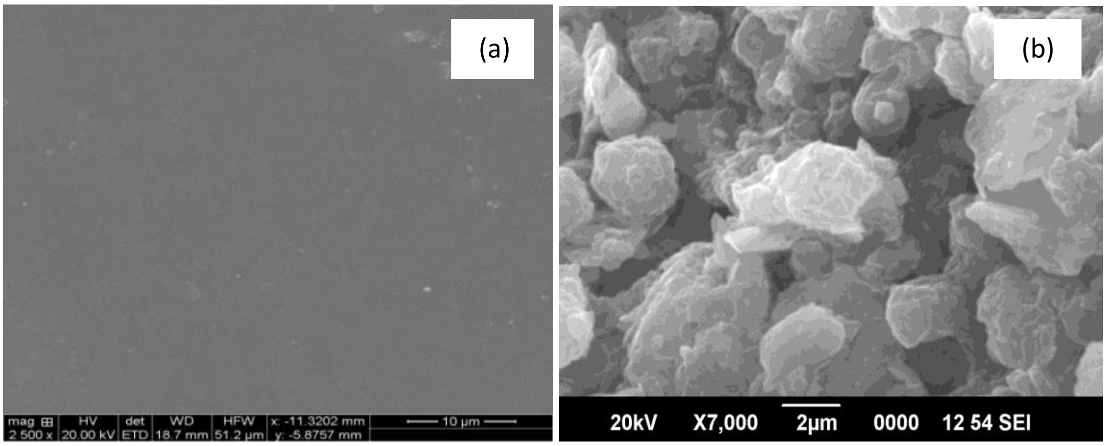

Figure-4: SEM image of (a) pure chitosan oligosaccharide and (b) COS-g-GMA/PPG-Glu Blend- Glu

The surface morphology of COS and COS-g-GMA/PPG-Glu samples were characterized by SEM indicated porous and rough surface for the sample structure. COS has smooth and regular structure whereas COS-g-

GMA/PPG – Glu blend displays a rough surface with porous structure and number of caves with void. It can be seen without a doubt that particles possessed a non-uniform aggregation, some smaller particles were adhered together to form a big one, which could prove the multiple relationship particle size [13]. These observations confirm that COS-g-GMA/PPG – Glu blend shows rough surface morphology, which is important useful for the removal of metal ions.

CONCLUSION

A novel hybrid material of COS-g-GMA/PPG – Glu blend was synthesized through graft co-polymerization in aqueous solution using ceric ammonium nitrate as initiator. FTIR spectroscopy confirmed the introduction of glycidyl methacrylate side chain onto the chitosan oligosaccharide backbone by graft co-polymerization. The XRD results provide supporting evidence to the FTIR result that some specific chemical interaction between COS-g-GMA copolymer and PPG. SEM images show a rough surface morphology for the COS-g-GMA/PPG – Glu blend with many pores and imperfections. TGA analysis was carried out to study the thermal behavior of the prepared blend. Hence, it was concluded that COS-g-GMA/PPG – Glu blend as an inexpensive absorbent for the removal of heavy metal ion from aqueous solution and industrial effluents.

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