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Microwave synthesized chitosan-*graft*-poly(methylmethacrylate): An efficient Zn^{2+} ion binder

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Abstract

Microwave promoted grafting of methylmethacrylate on to the chitosan has been optimized. Chitosan-*graft*-poly(methylmethacrylate) (Ch-*g*-PMMA) could be synthesized with 160% grafting using 80% MW power in 2 min at (MMA) 0.17 M, (Chitosan) 0.1 g/25 ml. While for the same concentration of the methylmethacrylate and the chitosan, 105% grafting was observed when $K_2S_2O_8$/ascorbic acid redox initiator used in presence of Ag^+ (catalyst) and atmospheric oxygen (co-catalyst) at 35 ± 0.2 °C. $K_2S_2O_8$/ascorbic acid redox system is for the first time used for grafting methylmethacrylate on to the chitosan. The representative graft copolymer was characterized by Fourier transform-infrared, thermo gravimetric analysis and X-ray diffraction measurement, taking chitosan as reference. The effect of reaction variables as monomer/chitosan concentration, microwave power and exposure time on the graft co-polymerization was studied. A probable mechanism for grafting under microwave heating has been proposed. Viscosity of the grafted chitosan solutions and water/saline retention for the grafted chitosans were determined and compared with that of the chitosan. The microwave synthesized graft copolymer was found to have efficient adsorption ability for Zn^{2+} ions in aqueous solution. Effect of pH and Zn^{2+} concentration on adsorption was also studied.

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Keywords: Chitosan-*g*-poly(methylmethacrylate); $K_2S_2O_8$/ascorbic acid/microwave radiation; Zn^{2+} adsorption

1. Introduction

Hybridization of natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. One of the natural polymers that attracted great attention recently is chitosan (Sang-Hoon & Samuel, 2003). Chitosan is a high molecular weight polysaccharide composed mainly of β-(1→4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of β-(1→4)-linked 2-deoxy-2-acetamido-D-glucopyranose. It is generally prepared by the partial deacetylation of chitin in a hot alkali solution. Chitosan can be dissolved in an acid solution and becomes a cationic polymer because of the protonation of amino groups on the C-2 position of the pyranose ring. Though chitosan has found potential use in many areas, it is a brittle material and tends to absorb a quantity of moisture and to improve its toughness, solubility and rheological properties, graft copolymerization of a vinyl monomer onto chitosan chains is commonly employed. Conventionally, vinyl monomers are grafted onto chitosan using various redox systems (Don, King, & Chiu, 2002; Kumbar, Soppimath, & Aminabhavi, 2003; Nud'ga et al., 2002; Radhakumary, Divya, Nair, Mathew, & Nair, 2003; Tan & Fu-mei, 2003). Recently structures and thermal properties of chitosan-modified poly(methylmethacrylate) (Trong-Ming, Shih-Chang, & Wen-Yen, 2001) was studied where significant amount of the homopolymer was also formed along with the copolymer. Homogeneous graft copolymerization of chitosan with methyl methacrylate by γ-irradiation via a phthaloylchitosan intermediate has been also studied (Liu, Yu, Wei-an, Guoqing, & Yue-e, 2004). Concurrent homopolymer formation is the main constraint in graft co-polymerization leading to low a grafting yield. Microwave irradiation (Galema, 1997), as efficient thermal energy is becoming standard technique in various fields of chemistry. Grafting of butylacrylate (Zheng, Yan-Bing, Ze-Fang, & Chang-yi, 2000), acrylic acid (Luo, Xiaoxia, Zefang, & Changyi, 1999) and acrylamide (Huang & Chen, 1999) onto the starch and grafting of acrylamide on to LLDPE (low density polyethylene) films (Gupta, Anjum, & Gupta, 2000) has been studied recently using redox initiators under microwave irradiation. Methylmethacrylate has been

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reported to polymerize (Cheng, Xiulin, Ming, Jianying, & Lifen, 2003) under microwaves with a very low concentration of the initiators. Recently under MW conditions, grafting of acrylamide and acrylonitrile (Singh, Tiwari, Tripathi, & Sanghi, 2004a–c) on to guar gum and polyacrylonitrile (Singh et al., 2004a–c) on to chitosan could be achieved in a very short reaction time in the absence of any redox initiator/catalyst. In the present work, microwave promoted graft copolymerization of methylmethacrylate (MMA) with chitosan is being communicated where grafting was achieved in good yield for short reaction time in the absence of any radical initiator/catalyst and the results are compared with the $K_2S_2O_8$/ascorbic initiated grafting. Since, chitin and chitosan derivatives are reported to have chelating ability with metal ions and their possible application in metal ion removal from the wastewater has been suggested (Furlan, de Favere, & Laranjerira, 1996; Muzzarelli & Rocchetti, 1986). The grafted co-polymer thus obtained was tested for its binding ability for Zn^{2+} ions. Optimal grafting condition for the microwave method has been studied and the properties of the microwave synthesized copolymer has been compared with the copolymer synthesized using $K_2S_2O_8$/ascorbic acid initiator on thermostatic water bath at 35 ± 0.2 °C. Thus microwaves can be exploited for the poly(methylmethacrylate) grafting on to the chitosan, where both time as well as chemicals can be saved. Moreover samples of chitosan-*graft*-poly(methylmethacrylate) synthesized using microwave irradiation were better metal ion binder than conventionally synthesized copolymer and may find use in the removal of metal ions.

2. Experimental section

A Kenstar (Model no. MOW 9811, 1200W) domestic microwave oven was used for all the experiments. The average bulk temperature at the end of the reaction was measured by inserting a thermometer into the reaction mixture and was less than 100 °C as the all the reactions were performed in aqueous medium. Infra red (IR) spectra were recorded on a Brucker Vector-22 Infra red spectrophotometer using KBr pellets. The sample of pure chitosan (Sigma) from crab shells was used; the degree of deacetylation was 85%. Chitosan was ground to fine powders (>140 mesh) from flats and dried under vacuum at room temperature. Commercial chitosan was purified by dissolving in acetic acid and separating in alkaline solution and then extracting in a soxhlet apparatus by refluxing in alcohol for 24 h and drying at 60 °C in vacuum for 48 h before use. Methylmethacrylate (Merck) was washed with 5% aqueous alkali to remove phenolic inhibitor and then distilled before use. Ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification. Zinc sulphate and ethylenediaminetetraaceticacid disodium solutions were prepared from analytical $ZnSO_4$ (Merck) and EDTA (Sigma). X-ray Diffraction (XRD) was carried out on Isodebeyxlex 2002 X-ray powder diffractometer and TGA was done at Perkin–Elmer TGA-7 at a heating rate of 10 °C per min under nitrogen atmosphere. Brookfield LVDVE viscometer with small sample adapter was used for the viscosity measurements.

The percentage and efficiency of grafting were calculated according to Kojima et al. (Bajpai & Rai, 1988)

$$\%\text{Grafting } (\%G) = \frac{W_1 - W_0}{W_0}100 \qquad (1)$$

$$\%\text{Efficiency } (\%E) = \frac{W_1 - W_0}{W_2}100 \qquad (2)$$

where W_1, W_0 and W_2 denote, respectively, the weight of the grafted chitosan, the weight of original chitosan and weight of the monomer used.

2.1. Graft co-polymerization

2.1.1. Grafting using redox initiator

To a solution of chitosan (0.1 g) in 25 ml of 5% aqueous formic acid, methylmethacrylate (17×10^{-2} M), ascorbic acid (22×10^{-3} M), $AgNO_3$ (8.0×10^{-5} M) were added and thermostated on water bath at 35 ± 0.2 °C. After 30 min $K_2S_2O_8$ (1×10^{-3} M) was added and this time of addition of persulphate was taken as zero time. Graft co-polymerization was allowed for 1 h. Grafted chitosan was separated (Chowdhary, Samul, Kundu, & Nandi, 2001) from polymethylmethacrylate (PMMA) by precipitating the reaction mixture with acetone. Finally, the grafted sample was extracted with acetone in a soxhlet apparatus for 4 h to dissolve all the homopolymer. The colorless product was dried under vacuum at 50 °C for >24 h to a constant weight. $\%G$ and $\%E$ were observed to be 105 and 24.9%, respectively.

2.1.2. Grafting under microwave irradiation

Chitosan (0.1 g) dissolved in 25 ml of 5% aqueous formic acid and methylmethacrylate (17×10^{-2} M) was irradiated in a domestic microwave oven in a 150 ml flask. Chitosan-*graft*-poly(methylmethacrylate) (Ch-*g*-PMMA) was separated from poly(methymethacrylate) (PMMA) as described above. Percentage of grafting and efficiency of grafting were calculated ($\%G$ 160, $\%E$ 37.9). Reaction was repeated for different monomer concentration in the range of 4–17×10^{-2} M, microwave power and exposure time. Optimal grafting was observed at 17×10^{-2} M methyl(methacrylate) concentration, 80% microwave power at 90 °C in 2.0 min (Figs. 1–3).

2.1.3. Viscosity measurements

Weighed quantity of the chitosan samples were dissolved in 5% HCOOH and samples of the graft copolymer were dissolved in water (adjusted to pH 6.5) and made up to a desired concentration and agitated vigorously for about 15 min till the solutions became viscous and homogeneous. The measurements were made using small sample adapter (spindle no S-18) of Brookfield LVDVE viscometer at 30 °C and results are listed in Table 1.

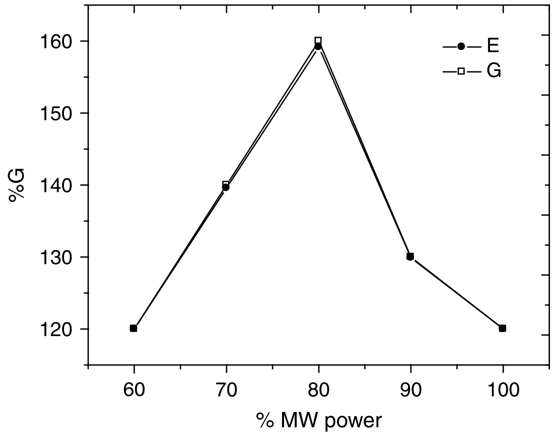


Fig. 1. %*G* and %*E* with changing MW power at fixed concentration of MMA (16.8×10^{-2}), (chitosan) (0.1 g/25 ml), exposure time, 2 min.

2.2. Determination of water and saline retention

An accurately weighed amount of the dried polymer was placed in a previously dried and weighed sintered glass crucible (G-4), which was then filled with 50 ml of water and after 30 min, suction from a vacuum pump was applied. The glass crucible was then weighed to determine (Bajpai, Mishra, & Sandeep, 1993) the amount of water retention per gram of the dried material and this was taken as water retention capacity. Similarly saline retention capacity was determined by using 1% aqueous sodium chloride solution. Results are summarized in Table 1.

2.3. Study of Zn^{2+} ions adsorption

To reaction flasks thermostatically maintained at 40±0.5 °C were added 100 mg of chitosan/grafted chitosan and 50 ml of aqueous solution of 1 mM zinc ions. The reaction mixtures were adjusted to different pH ranges (Fig. 4) and the systems were maintained under magnetic stirring. After 1 h, the mixtures were filtered and the amounts of the adsorbed metal ions (mM) were determined by titration with 0.01 M EDTA using Eriochrome Black-T as indicator. The amount of metal ions adsorbed per gram of the polymer was calculated by difference between the initial and final numbers of *m* mol in the solutions. The same procedure was repeated at different Zn^{2+} ions concentrations and the results are summarized in Fig. 5.

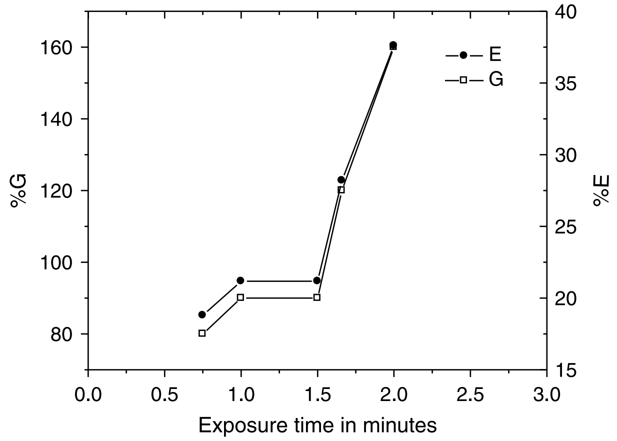


Fig. 2. %*G* and %*E* with exposure time at the fixed concentration of MMA (16.8×10^{-2}), chitosan (0.1 g/25 ml) at 80% MW power.

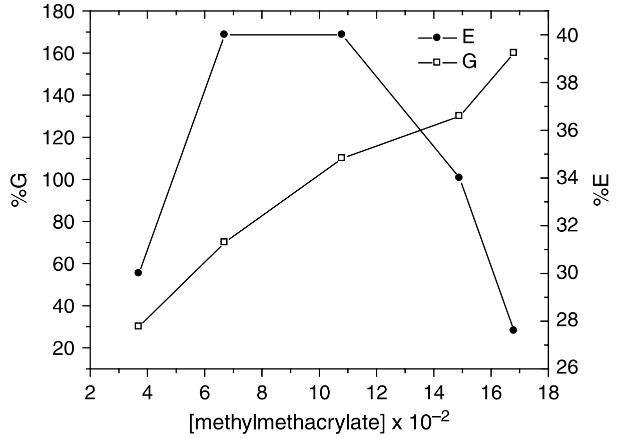


Fig. 3. %*G* and %*E* with changing monomer concentration at fixed concentration of chitosan (1 g/25 ml), exposure time, 2 min.

3. Results and discussion

3.1. Characterization of the grafted gum

3.1.1. FTIR spectra

The IR spectrum of the chitosan showed strong peaks at 1030, 1076, and 1261 cm^{-1}, characteristic peaks of a saccharide structure (due to O–H bending, C–O stretching, and C–N stretching). The strong peak around 3400 cm^{-1} could be assigned to the stretching vibration of O–H, the extension vibration of N–H, and inter hydrogen bonds of the polysaccharide (Fig. 6). The IR spectrum of a representative MW synthesized Ch-*g*-PMMA (Fig. 7) has additional sharp absorption peaks at 1731 and 2966 cm^{-1} (due to carbonyl stretching and symmetrical stretching of the methyl group, respectively). IR spectrum of Ch-*g*-PMMA synthesized by conventional method (Fig. 8) has also the same peaks but at a relatively lower intensity. This result provides a substantial evidence of grafting on to the chitosan. To separate the grafted side chain from the chitosan backbone, the graft copolymer was subjected to acid hydrolysis. The FTIR spectra of the dried product had an identical spectrum to that reported for the PMMA, which confirmed the formation of Ch-*g*-PMMA.

3.1.2. XRD spectra

XRD spectra of the Ch-*g*-PMMA show more crystalline areas with respect to the pure chitosan due to grafted PMMA chains in 2θ 35–50° region. (Figs. 9 and 10)

3.1.3. TGA spectra

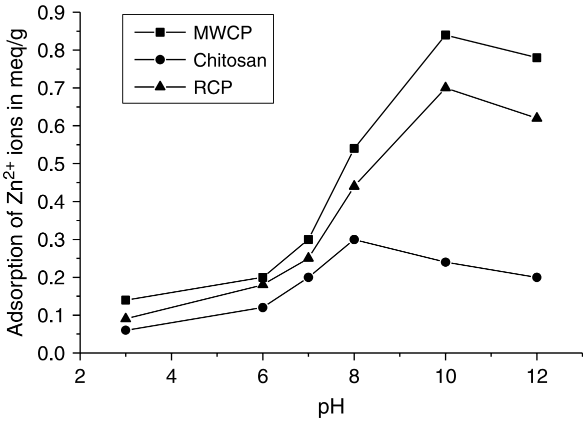
DTA curve (Fig. 11) for the Ch-*g*-PMMA shows two distinct endothermic peaks at 163 and 282 °C, respectively.

Table 1
Viscosity, water and saline retention and Zn^{2+} ion adsorption of chitosan and grafted chitosan

S. no	Polymer	Viscosity (P)	RPM	%*T*	Water retention	Saline retention	Zn^{2+} ion adsorption in meq/g at 1 mM conc of Zn^{2+} solution
1.	Chitosan	400.20	0.6	8.0	16.1	8.6	0.24
2.	RCP	335.40	0.6	6.7	13.7	7.2	0.70
3.	MWCP	285.32	0.6	6.4	11.8	6.1	0.84

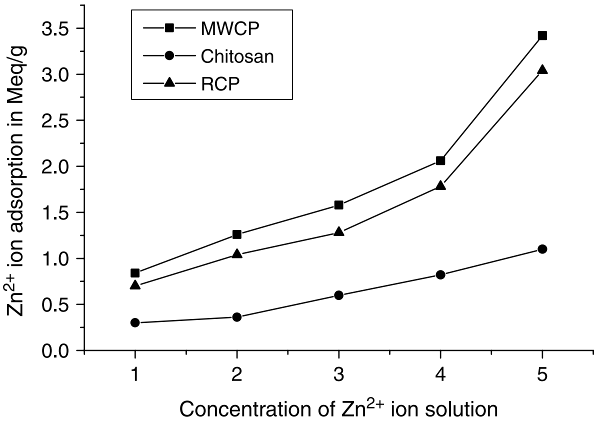
RCP is graft co-polymer synthesized using redox initiator; MWCP is graft co-polymer synthesized using microwave irradiation.

The first peak may be attributed to the loss of adhered and bound water molecules and second due to the decomposition of the grafted chitosan. TGA indicates that the decomposition of the graft copolymer onsets at 258 °C and 31% weight is lost up to 282 °C when the graft co-polymer slowly degrades.



where RCP: Graft copolymer synthesized using redox initiators
MWCP : Graft copolymer synthesized using microwave

Fig. 4. Zn^{2+} ion adsorption by chitosan and grafted chitosan at 1 mM of Zn^{2+} ion concentration at different pH.



where RCP: Graft copolymer synthesized using redox initiators
MWCP : Graft copolymer synthesized using microwave

Fig. 5. Adsorption of the Zn^{2+} ions by chitosan and grafted chitosan at different concentrations of Zn^{2+} ions.

3.2. Optimization of the grafting conditions

3.2.1. Effect of MW power

%*G* and %*E* both increases initially with the increasing microwave power up to 1720 GHz (80%) power, this may be due to more availability microwave energy at high microwave power, causing more monomer and macro radical generation and hence grafting (Fig. 1). After 80% power, decrease in %*G* and %*E* both may be attributed to more homopolymer formation at high microwave powers or to some decomposition of the graft copolymer at high power**.**

3.2.2. Effect of microwave exposure time

It was observed that %*G* and %*E* initially increase up to 1 min exposure and then is constant nearly up to 1.5 min

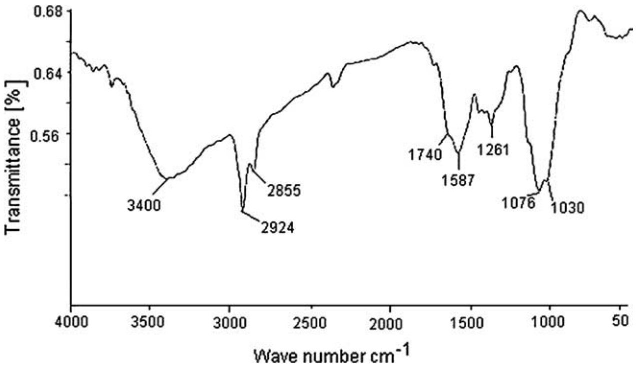


Fig. 6. IR spectra of pure chitosan.

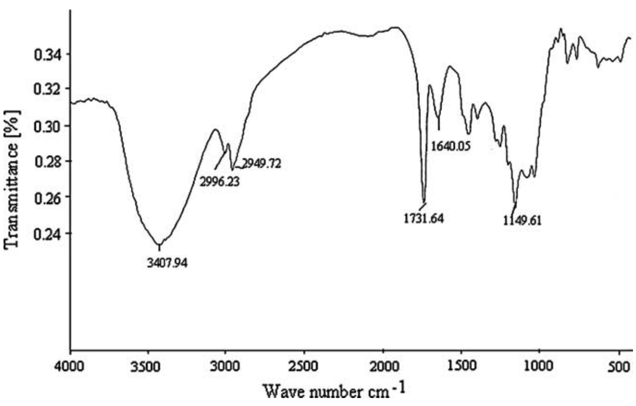


Fig. 7. IR spectra of microwave synthesized Ch-*g*-PMMA (MWCP).

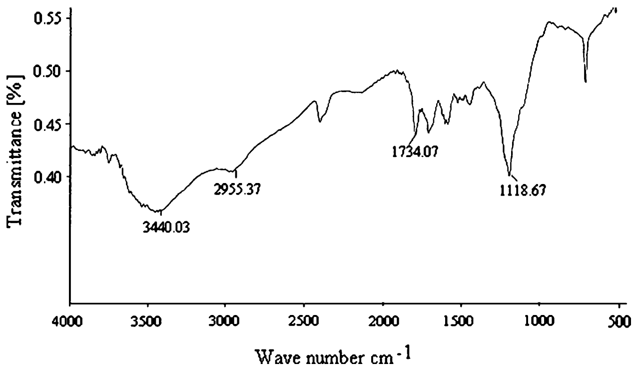


Fig. 8. IR spectra of redox synthesized Ch-*g*-PMMA (RCP).

exposure to 80% microwave power, thereafter both %*G* and %*E* increases sharply with the exposure duration at the fixed concentration of MMA (16.8×10^{-2} M) and chitosan (0.1 g/25 ml) (Fig. 2). More microwave energy is taken when the reaction mixture is exposed to longer duration thus increasing %*G* and %*E*.

3.2.3. Effect of monomer concentration

%*G* increases with the monomer concentration, while the efficiency of grafting increases initially with monomer concentration but then decreases after 10.8×10^{-2} M. (Fig. 3). The initial increase in %*E* could be due to the greater availability of the monomer molecules in the proximity of the chitosan increasing the chance of the molecular collision and hence grafting. The decrease in the %*E* after certain level of the MMA concentration (10.8×10^{2}) is probably due to homopolymerization of methylmethacrylate.

3.3. Mechanism of grafting under MW irradiation

Chitosan is a large molecule with many pendent –OH and –NH_2 groups and these groups attached to large chitosan molecule may behave as if were anchored to an immobile raft and its localized rotations (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998) therefore, will be observed in the microwave region and resulting dielectric heating of the chitosan molecule may result in an enhancement of reaction rates specifically at these groups. The dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (MMA and water), since it is not possible to store the energy in a specific part of the molecule. The dielectric heating results in bond breaking creating radical sites at oxygen and nitrogen atoms. However, there will be a greater possibility of the free radical at nitrogen as bond energy of N–H bond is reported to be lower than O–H bond energy. Further microwaves are also reported to have special effects (Galema, 1997) of lowering of Gibbs energy of activation of the reactions and in view of the above two affects a plausible free radicals mechanism for the grafting under the microwave irradiation has been proposed. N–H bonds at chitosan absorb microwave energy and will cleave generating monomer free radical and macro radical (Scheme 1).

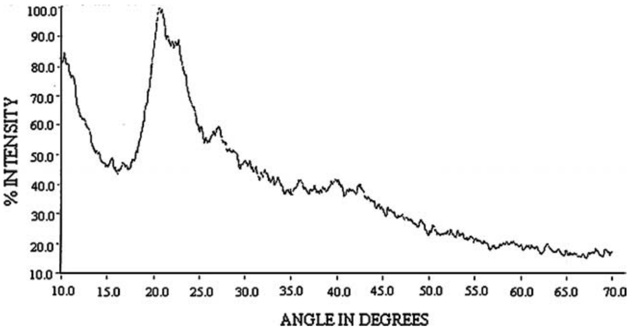


Fig. 9. XRD of pure chitosan.

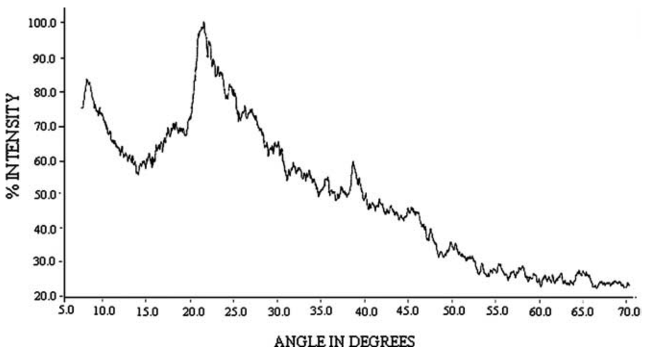


Fig. 10. XRD of Ch-*g*-PMMA (MWCP).

3.4. Solubility

Solubility of chitosan on grafting with methylmethacrylate shifts more towards the neutral pH, this confirms the grafting at the NH_2. Chitosan dissolves at acidic pH around pH 3.5 while Ch-*g*-PMMA dissolves at pH 6–6.5.

3.5. Adsorption of Zn^{2+} ions on to Ch-g-PMMA

The influence of pH on zinc metal ion binding ability of chitosan and Ch-*g*-PMMA was investigated (Muzzarelli, 1973) and was observed to be higher at alkaline pH (pH 8 for chitosan and pH 10 for Ch-*g*-PMMA). Results are summarized in Fig. 4. Adsorption variation with respect to changing Zn^{2+} ion concentration is shown in Fig. 5. Metal binding capacity of chitosan is markedly increased by the presence of poly(methylmethacrylate) grafts, which provide additional metal binding sites. Since, hydroxyl groups of chitosan are highly hydrated and are known not to be adsorption sites, the amino groups of chitosan and ester groups at grafted chains are the sites responsible for metal ion adsorption. Since at the acidic pH the amino groups remain protonated and are not free for binding, better adsorption is observed at alkaline pH. However at $\mathrm{pH}>8$

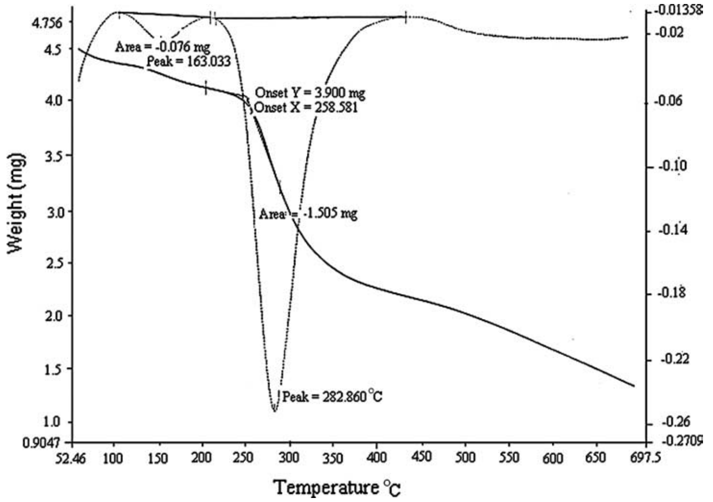
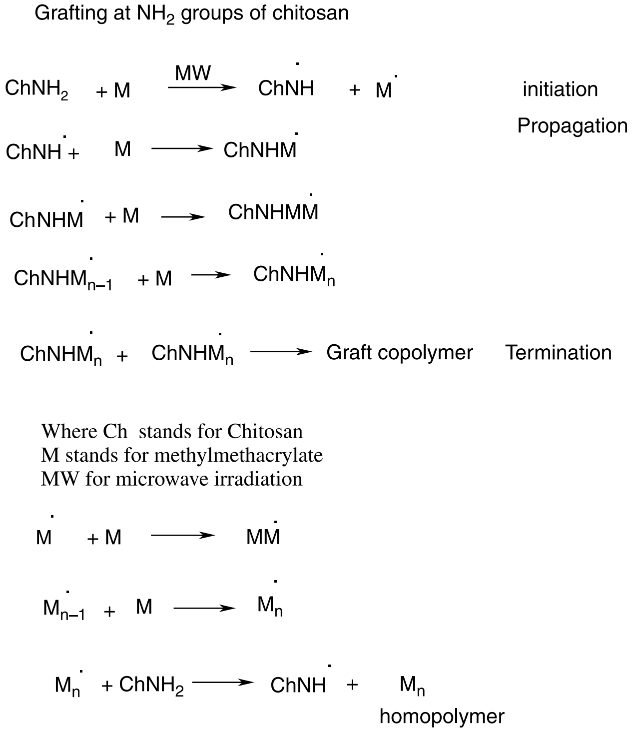


Fig. 11. TGA of Ch-*g*-PMMA (MWCP).


Grafting at NH_2 groups of chitosan

$\mathrm{ChNH_2} + \mathrm{M} \xrightarrow{\mathrm{MW}} \mathrm{ChN\dot{H}} + \dot{\mathrm{M}}$ initiation

Propagation

$\mathrm{ChN\dot{H}} + \mathrm{M} \longrightarrow \mathrm{ChNH\dot{M}}$

$\mathrm{ChNH\dot{M}} + \mathrm{M} \longrightarrow \mathrm{ChNHM\dot{M}}$

$\mathrm{ChNH\dot{M}_{n-1}} + \mathrm{M} \longrightarrow \mathrm{ChNH\dot{M}_n}$

$\mathrm{ChNH\dot{M}_n} + \mathrm{ChNH\dot{M}_n} \longrightarrow$ Graft copolymer Termination

Where Ch stands for Chitosan
M stands for methylmethacrylate
MW for microwave irradiation

$\dot{\mathrm{M}} + \mathrm{M} \longrightarrow \mathrm{M\dot{M}}$

$\dot{\mathrm{M}}_{n-1} + \mathrm{M} \longrightarrow \dot{\mathrm{M}}_n$

$\dot{\mathrm{M}}_n + \mathrm{ChNH_2} \longrightarrow \mathrm{ChN\dot{H}} + \mathrm{M_n}$
homopolymer

Scheme 1.

for chitosan and >10 for graft co-polymer the adsorption decreases.

4. Conclusions

Graft co-polymer of chitosan and methylmethacrylate was successfully synthesized using $K_2S_2O_8$/ascorbic acid as redox initiator with the advantage that reaction can be done in presence of oxygen at 35 °C. The same could be synthesized in a very short reaction time and in much better yield under microwave irradiation where no redox initiator or catalyst was required. Further the grafted chitosan so obtained using microwave irradiation was found to be an efficient adsorbent for Zn^{2+} ions thus showing its potential in removal of these ions from waste and natural water. Moreover, the solubility of chitosan is improved on grafting with methylmethacrylate solubility shifted towards neutral from acidic pH.

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