Carbohydrate Polymers 80 (2010) 790–798

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Graft copolymerization of *N*-vinyl-2-pyrrolidone onto chitosan: Synthesis, characterization and study of physicochemical properties

Abhishek Srivastava [a], Dinesh Kumar Mishra [b], Kunj Behari [b,*]

[a] Department of Applied science, LDC Institute of Technical Studies, 22 Km Milesstone, Allahabad 211002, India
[b] Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India

ARTICLE INFO

Article history:
Received 22 November 2009
Received in revised form 12 December 2009
Accepted 15 December 2009
Available online 4 January 2010

Keywords:
Graft copolymer
Swelling capacity
Metal ion uptake
Flocculation

ABSTRACT

The optimum conditions for maximum grafting have been determined by varying the concentrations of *N*-vinyl-2-pyrrolidone, hydrogen ion, potassium bromate, silver nitrate, chitosan along with time and temperature. The grafting ratio increased on increasing *N*-vinyl-2-pyrrolidone concentration and reaches maximum value at 20×10^{-2} mol dm^{-3}. Similarly, the concentration of hydrogen ion increases, the grafting parameters increase and attain maximum value at 1.8×10^{-2} mol dm^{-3}. The grafting parameters increase continuously on increasing the concentration of potassium bromate from 2×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3}. On increasing silver nitrate concentration from 0.4×10^{-2} to 3.6×10^{-2} mol dm^{-3}, grafting ratio is found to be maximum at 2.8×10^{-2} mol dm^{-3}. The grafting parameters decrease continuously on increasing the concentration of chitosan. An attempt has been made to study some of the physicochemical properties in terms of swelling, metal ion sorption and flocculation. The chitosan and chitosan-g-*N*-vinyl-2-pyrrolidone were characterized by infrared spectroscopy and thermogravimetric analysis.

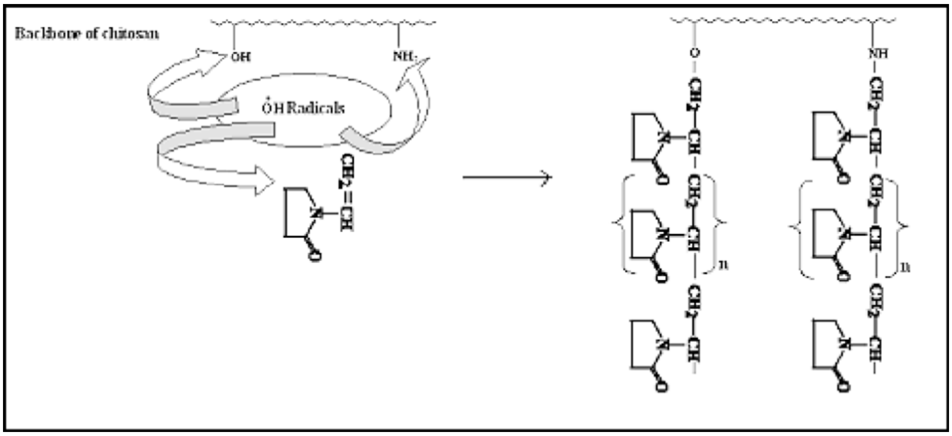
1. Introduction

The synthesis of new hybrid polymer materials of chitosan (El-Tahlawy, El-Rafie, & Aly, 2006; Liu, Xu, Guo, & Han, 2009; Mu & Fang, 2009; Tripathi, Mehrotra, & Dutta, 2008; Xiang, Si, Zhang, Liu, & Guo, 2009; Xu, Yan, Wan, & Li, 2007) has become a rapid expanding field in the area of polymer science using different techniques (Dedinaite, Iruthayaraj, Gorochovceva, Makuska, & Claesson, 2006; Dergunov et al., 2008; Hua, Deng, Tang, Cheng, & Zhu, 2008; Huacai, Wan, & Dengke 2006). So, an attempt has been made to synthesize a new graft copolymer of chitosan using one of the best methods, free radical polymerization of *N*-vinyl-2-pyrrolidone onto itself. Earlier, chitosan has been synthesized in our laboratory with different vinyl monomers and some of the properties that has been investigated (Mishra, Tripathy, & Behari, 2008; Tripathy, Mishra, Yadav, & Behari 2010) to make it more useful in order to increase its possible industrial applications. For the purpose of synthesis of graft copolymer, chitosan is chosen as a backbone which is currently at the focus of increasing scientific and economic interest among all polysaccharides owing to its significance role in nature and technology (Liu et al., 2008; Wang, Cui, & Xu, 2008; Wang, Su, & Chen, 2008). It is a basic polysaccharide of β-(1,4) linked-2-amino-2-deoxy-D-glucopyranose derived by *N*-deacetylation (shown in Scheme 1) of chitin in aqueous alkaline medium (Muzzarelli, 1999). Chitin is abundant naturally occurring polysaccharide with annual production very near the levels of cellulose which consists of mainly β-(1-4)-2-deoxy-D-glucose units (Park, You, Park, Haam, & Kim, 2001; Wongpanit, Sanchavanakit, Supaphol, Tokura, & Rujiravanit, 2005). It occurs in marine invertebrates and shells of marine crustaceans i.e. shrimps and crabs (Hudson & Smith, 1998). Due to its wide availability and unique chemical and biological properties such as biocompatibility, non-toxicity and antimicrobial properties (Lee & Chen, 2001; Park, Park, & Kim, 2006; Pourjavadi & Mahdavinia, 2006) along with the presence of reactive and functional hydroxyl and amino groups, chitosan finds many perspective applications in flocculation for waste water treatment (Hejaji & Amiji, 2003; Jayakumar, Prabahara, Reis, & Mano, 2005; Takayama et al., 1990). It has also found wide applications in a variety of areas such as biomedicine (Berger, Reist, Mayer, Felt, & Gurny, 2004; Jenkins, Samuel, & Hudson, 2001; Pourjavadi, Mahdavinia, Zohuriaan-Mehr, & Omidian, 2003; Yinghai, Zhenghao, Yanzhe, & Kuilin, 2002), pharmaceutical (Jenkins & Hudson, 2002) and food industry (Dutta, Tripathi, Mehrotra, & Dutta, 2009; Tripathi et al., 2008). Inspite of its wide range applications, it is very susceptible to biodegradation (Mi, Tan, Liang, & Sung, 2002; Ravi Kumar, 2000), which limits its uses. By grafting method used, (Mishra, Tripathy, Mishra, & Behari, 2008; Mishra, Tripathy, Srivastava, Mishra, & Behari, 2008; Tripathy, Mishra, & Behari, 2009) not only its stability can be improved but also its physicochemical properties can be increased because of the additional properties of monomer are superimposed onto polymeric

---

* Corresponding author. Tel.: +91 5322545354.
E-mail address: r_dineshmishra@rediffmail.com (K. Behari).

0144-8617/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.12.031



Scheme 1. Grafting of ***N*-vi**nyl-2-pyrrolidone onto chitosan.

backbone of chitosan. In the present article, grafting of *N*-vinyl-2-pyrrolidone onto the backbone of chitosan has been reported with the objective of increasing the applications of chitosan. *N*-vinyl-2-pyrrolidone, which is hydrophilic and non-toxic monomer, has various industrial applications (Duan, 1993; Gaenger & Florig, 2007; Suzuki, Fukuda, & Yoneto, 1993). It has been used as a main component of temporary skin covers or wound dressing (Nho & Park, 2002) and also wrapping material (O'Connell et al. 2001) of single-walled carbon nanotubes (SWNTs). Prompted by the applications of chitosan and *N*-vinyl-2-pyrrolidone, the hitherto unreported graft copolymer viz. chitosan-g-*N*-vinyl-2-pyrrolidone was prepared by employing potassium bromate/ silver nitrate redox system. For optimization of grafting conditions, the effect of potassium bromate, silver, hydrogen ion, chitosan and *N*-vinyl-2-pyrrolidone concentration along with the time and temperature has been investigated.

2. Experimental and methods

2.1. Materials

N-vinyl-2-pyrrolidone (Sigma–Aldrich) was freshly distilled at 11 mm Hg and 60 °C and only middle fraction was used. Chitosan was purchased from (Sigma–Aldrich) and to dissolve it acetic acid (Merck, India) was used as such. Potassium bromate solution (Merck, India) is prepared in triple distilled water and used such. For maintaining hydrogen ion concentration sulphuric acid (Merck, India) was used and all the solutions were prepared in triple distilled water. For flocculation studies, coking and non-coking coals used have been were received from steel Plant, Bokaro, India.

2.2. Procedure for graft copolymerization

For each experiment chitosan solution (from 0.4 to 1.8 g dm^{-3}) has been prepared by dissolving it in acetic acid (Gupta & Ravi Kumar, 2000; Singh et al., 2009) as described. This solution is slowly added into reactor containing triple distilled water. The calculated amount of *N*-vinyl-2-pyrrolidone (from 8×10^{-2} to 24×10^{-2} mol dm^{-3}), sulphuric acid (from 1×10^{-2} to 2.2×10^{-2} mol dm^{-3}) and $AgNO_3$ (from 0.4×10^{-3} to 3.6×10^{-3} mol dm^{-3}) were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min at different constant temperature (from 25 °C to 45 °C). A known amount of deoxygenated potassium bromate solution (from 2×10^{-3} to 10×10^{-3} mol dm^{-3}) has been added to initiate the reaction. The reaction was carried out under a continuous flow of oxygen free nitrogen gas. After desired time period (from 60 to 180 min.), the reaction was stopped by letting air into reactor. The reaction mixture was poured in a water–methanol mixture (ratio 1:5). The grafted material was separated out which was filtered, dried and weighed. The poly (*N*-vinyl-2-pyrrolidone) was remained in the filtrate.

2.3. Homopolymer separation

A pinch of hydoquinone has been added into filtrate and then it was concentrated by distillation under reduce pressure. The concentrated solution was precipitate into the pure methanol. The poly (*N*-vinyl-2-pyrrolidone) was separated dried and weighed.

3. Method of characterization of chitosan/chitosan-g-N-vinyl-2-pyrrolidone

3.1. IR Spectroscopy

The IR spectra of chitosan and grafted samples have been recorded with PERKIN ELMER FTIR model in the range 500–4000 cm^{-1} to provide the proof of the grafting.

3.2. Thermogravimetric analysis

The thermograms have been recorded with NETZSCH – Geratebau GmbH thermal analyser in an inert atmosphere.

4. Study of properties

4.1. Swelling

Swelling behaviour of graft copolymer has been studied by taking the different samples of graft copolymer prepared by varying the monomer concentration. The 0.02 g of sample was kept in distilled water for 24 h to study the swelling behaviour. After 24 h the graft copolymer sample was taken out and the surface water on swollen graft copolymer was removed by softly pressing the sample in between the folds of filter paper. After this the sample was weighed and increase in weight was recorded. The behaviour was studied by following relation (EL-Rehim, Hegazy, & Ali, 2000).

$$\text{Swelling ratio}(S_R) = \frac{\text{Weight of swollen sample} - \text{weight of dry sample}}{\text{weight of dry sample}}$$

4.2. Metal ion uptake

Different samples of graft copolymer of chitosan were synthesized by varying the monomer concentration. Graft copolymer samples were immersed for 24 h in 20 mL solution of metal ion of known concentration (All solutions were made in triple distilled water). Filtrates of the solution were analyzed for concentration of unabsorbed ions by titrametrically (Bassett, Denney, Jeffery, & Mendham, 1978). Different relationships were used to express sorption behaviour are as follows (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

$$\text{Percent uptake (Pu)} = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion in feed}} \times 100$$

$$\text{Partition coefficient (Kd)} = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion left in the solution}} \times \frac{\text{volume of solution(ml.)}}{\text{weight of dry polymer(g)}}$$

$$\text{Retention capacity (Qr)} = \frac{\text{amount of metal ion in the polymer(m.Eq)}}{\text{weight of dry polymer(g)}}$$

4.3. Flocculation

In 1.0 litre beaker, 200 cc of 1% wt. coal suspension was taken. The beaker was placed on flocculator dipping the stirrer blade in the suspension. Under a low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for half an hour. Clean supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (DIGITAL NEPHELOMETER MODEL 341 (EI) supplied by ISOTECH SYSTEM) to express the turbidity in nephelometric unit (N.T.U.).

5. Results and discussion

5.1. Estimation of grafting parameters

The graft copolymer has been characterized according to Fanta's definition (Fanta, 1973).

$$\text{Grafting ratio} \quad (\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Add on} \quad (\%A) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion} \quad (\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Grafting efficiency} \quad (\%E) = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Homopolymer} \quad (\%H) = 100 - \%E$$

5.2. Mechanism

In the presence of sulphuric acid, oxidation of silver nitrate by bromate ion produces the number of free radicals like $\dot{O}H$ which abstract hydrogen atom from chitosan molecule producing chitosan macro radical. The monomer molecules, which are in close vicinity of reaction sites, become acceptors of chitosan macro radicals, resulting in chain initiation and thereafter themselves become free radical donors to neighbouring molecules leading to the propagation. These grafted chains are terminated by coupling to give graft copolymer. On the basis of experimental results, a tentative mechanism can be represented as

$$\mathrm{Ag}(I) + \mathrm{BrO_3^-} + \mathrm{H_2O} \rightarrow \mathrm{Ag(II)} + \mathrm{BrO_2^-} + \mathrm{OH^-} + \mathrm{OH^{\cdot}}$$
$$\mathrm{Ag(I)} + \mathrm{BrO_2^-} + \mathrm{H_2O} \rightarrow \mathrm{BrO^-} + \mathrm{OH^-} + \mathrm{OH^{\cdot}} + \mathrm{Ag(II)}$$
$$\mathrm{Ag(I)} + \mathrm{BrO^-} + \mathrm{H_2O} \rightarrow \mathrm{Br^-} + \mathrm{OH^-} + \mathrm{OH^{\cdot}} + \mathrm{Ag(II)}$$
$$\mathrm{Ag(II)} + \mathrm{H_2O} \rightarrow \mathrm{Ag(I)} + \mathrm{OH^{\cdot}} + \mathrm{H^+}$$

Initiation

$$\mathrm{M} + \mathrm{R^{\cdot}} \rightarrow \mathrm{RM^{\cdot}}$$
$$\underset{\text{Chitosan}}{\mathrm{ChXH}} + \mathrm{R^{\cdot}} \rightarrow \underset{\text{macroradicals}}{\mathrm{ChX^{\cdot}}} + \mathrm{RH}$$

where X = O or NH
M = monomer

$$\mathrm{ChX^{\cdot}} = \mathrm{ChO^{\cdot}}\,\text{or}\ \mathrm{Ch\dot{N}H}\text{(macro radical)}$$

Propagation

$$\mathrm{ChX^{\cdot}} + \mathrm{M} \rightarrow \mathrm{ChXM^{\cdot}}$$
$$\mathrm{ChXM^{\cdot}} + \mathrm{M} \rightarrow \mathrm{ChXM_1^{\cdot}}$$
$$\mathrm{ChXM_1^{\cdot}} + \mathrm{M} \rightarrow \mathrm{ChXM_2^{\cdot}}$$

....

....

$$\mathrm{ChXM_{\mathit{n}-1}^{\cdot}} + \mathrm{M} \rightarrow \mathrm{ChXM_{\mathit{n}}^{\cdot}}$$
$$\mathrm{RM^{\cdot}} + \mathrm{M} \rightarrow \mathrm{RM_1^{\cdot}}$$
$$\mathrm{RM_1^{\cdot}} + \mathrm{M} \rightarrow \mathrm{RM_2^{\cdot}}$$

....

....

$$\mathrm{RM_{\mathit{n}-1}^{\cdot}} + \mathrm{M} \rightarrow \mathrm{RM_{\mathit{n}}^{\cdot}}$$

Termination

$$\mathrm{ChXM_{\mathit{n}}^{\cdot}} + \mathrm{ChXM_{\mathit{m}}^{\cdot}} \rightarrow \text{Graft copolymer}$$
$$\mathrm{ChXM_{\mathit{n}}^{\cdot}} + \mathrm{RM_{\mathit{n}}^{\cdot}} \rightarrow \text{Graft copolymer}$$
$$\mathrm{RM_{\mathit{n}}^{\cdot}} + \mathrm{RM_{\mathit{m}}^{\cdot}} \rightarrow \text{Homopolymer}$$

5.3. Optimization of grafting conditions

The graft copolymerization reaction (Scheme 1 Grafting of *N*-vinyl-2-pyrrolidone onto chitosan) has been carried out at different concentration of potassium bromate, silver nitrate, chitosan, *N*-vinyl-2-pyrrolidone, sulphuric acid as well as for different temperature and time period.

5.3.1. Effect of bromate ion concentration

The bromate-silver system is an efficient redox initiator for the aqueous polymerization of vinyl monomers. It was tested that neither potassium bromate nor silver nitrate, initiated polymerization. On the other hand, silver ion coupled with bromate ion initiated the polymerization reaction. So the effect of bromate ion concentration on grafting reaction has been studied and observed that grafting ratio (%*G* = 124.0–139.0), efficiency and add on were increased on increasing the bromate concentration from 2×10^{-3} to 8×10^{-3} mol dm^{-3} and thereafter grafting ratio, efficiency and add on were decreased (%*G* = 128.0). The enhancement in grafting parameters within cited range of bromate concentration was due to the progressive reduction of potassium bromate producing greater number of free radicals. These radicals attack on the chitosan molecule creating more macro radical sites onto which monomers addition take place. But beyond the cited range, grafting parameters were decreased because of the presence of large number of free radicals, which may terminate the growing grafted chain by oxidative termination.

5.3.2. Effect of $AgNO_3$ concentration

It has been observed that the grafting parameters were increased on increasing the concentration of $AgNO_3$ from

0.4×10^{-3} to 2.8×10^{-3} mol dm^{-3}, and thereafter the grafting ratio, efficiency, add on were decreased and homopolymer was increased. The increment in grafting parameter within cited range of Ag(I) ion concentration was due to the increment in the concentration of Ag(II) ion which oxidized the BrO_3^- into BrO_2^- and produced more and more free radicals.

5.3.3. *Effect of N-vinyl-2-pyrrolidone (NVP) concentration*

The effect of *N*-vinyl-2-pyrrolidone on graft copolymerization has been studied by varying the concentration of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} mol dm^{-3} (Table 1). It has been found that grafting ratio, add on, efficiency were increased with increasing the concentration of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 20×10^{-2} mol dm^{-3} but beyond 20×10^{-2} mol dm^{-3}, these grafting parameters were decreased. It was evident that homopolymer showed the opposite trend to grafting ratio. The maximum efficiency (%*E*) was 66.34 which showed that maximum *N*-vinyl-2-pyrrolidone was grafted. Increment in grafting parameters was due to the greater availability of monomer molecule at the close proximity of polymer backbone. These monomer molecules, which were at the immediate vicinity of the reaction sites, become acceptor of chitosan radicals (CO$^{\cdot}$) resulting in chain initiation and thereafter themselves become free radical donors to the neighbouring molecules. But beyond the cited range, grafting parameters were decreased which was due to the increase in viscosity of medium to greater solubility of poly (*N*-vinyl-2-pyrrolidone) in reaction mixture.

5.3.4. *Effect of chitosan concentration*

The effect of chitosan concentration on grafting parameters was studied by varying the concentration of chitosan from 0.4 to 1.8 g dm^{-3}. The grafting parameters were decreased (%*G* = 257.0–86.0) continuously on increasing the concentration of chitosan (Table 2). This was due to the increase in viscosity of medium, which restricted the accessibility of monomer onto active sites of growing polymeric chains.

5.3.5. *Effect of hydrogen ion concentration*

The effect of hydrogen ion concentration on grafting parameters has been studied by varying the concentration of sulphuric acid 1×10^{-2} to 2.2×10^{-2} mol dm^{-3}. The grafting ratio, add on, conversion and efficiency were increased (%*G* = 126.0–162.2) continuously with increase in hydrogen ion concentration from 1×10^{-2} to 1.8×10^{-2} mol dm^{-3}.This increment was due to the fact that in the presence of excess hydrogen ion the bromate forms $HBrO_3$ species and thereafter this species further decomposes to give oxygen that acts as scavenger for free radicals so grafting parameters show decreasing trend (%*G* = 160.4).

$$KBrO_3 + H^+ \rightarrow HBrO_3$$

$$4HBrO_3 \rightarrow 2Br_2 + 2H_2O + 5O_2 \uparrow$$

5.3.6. *Effect of time period*

The graft copolymerization has been studied by increasing the time period of the reaction from 60 to 180 min. Grafting ratio, efficiency and add on were increased on increasing the time period from 60 to 150 min, whereas maximum grafting efficiency was found at 150 min. On further increment in time period, grafting parameters shows decreasing trend. The increment (%*G* = 126.0–142.8) in grafting parameters was due to the more availability of more active species which give more formation graft copolymer whereas decrement (%*G* = 125.2) was attributed due to termination of growing grafted chains.

Table 1
Effect of *N*-vinyl-2-pyrrolidone concentration.

[NVP] × 10^2 mol dm^{-3}	%*G*	%*E*	%*A*	%*C*	%*H*
8	113	58.7	53.2	22	41.3
12	116	60.0	53.7	14.4	40.0
16	134	61.4	57.3	12.3	38.6
20	152.2	53.9	60.3	12.7	46.1
24	135.4	53.0	57.5	9.9	46.9

[ChXH] = 1 g dm^{-3}, [BrO_3^-] = 6×10^{-3} mol dm^{-3}, [Ag^+] = 20×10^{-4} mol dm^{-3}, [H^+] = 1.4×10^{-2} mol dm^{-3}, Temp. = 35 °C, Time = 120 min.

Table 2
Effect of chitosan concentration.

[ChXH] g dm^{-3}	%*G*	%*E*	%*A*	%*C*	%*H*
0.4	257	63.1	71.9	9.2	36.9
0.6	225	65.9	69.3	11.5	34.1
1.0	134	61.4	57.3	12.3	38.6
1.4	100	58.8	50.0	13.4	41.2
1.8	86	58.0	46.2	12.5	41.9

[NVP] = 16×10^{-2} mol dm^{-3}, [BrO_3^-] = 6×10^{-3} mol dm^{-3}, [Ag^+] = 20×10^{-4} mol dm^{-3}, [H^+] = 1.4×10^{-2} mol dm^{-3}, Temp. = 35 °C, Time = 120 min.

5.3.7. *Effect of temperature*

The grafting ratio, add on, conversion and efficiency were increased as temperature was increased from 25 °C to 40 °C, but thereafter the values of these parameters were found to decrease. The increase in the values of grafting parameters (%*G* = 104.0–154.0) was due to the increasing rate of diffusion of monomer molecules onto backbone and increasing rate of production of primary free radicals. The decrement (%*G* = 120.0) in grafting parameters was due destruction of primary free radicals at the initial stage due to higher temperature.

5.4. *Evidence of grafting*

5.4.1. *IR spectroscopy*

On comparing the IR spectra of chitosan (Mishra, Tripathy, Srivastava, Pandey, & Behari, 2009a) and chitosan-g-*N*-vinyl-2pyrrolidone (presented in Fig. 1), following additional peaks appeared in the spectra of chitosan-g- *N*-vinyl-2-pyrrolidone. Infra red spectrum of chitosan showed two strong peaks at 3388.3 cm^{-1} and at 1593.4 cm^{-1} due to OH stretching vibration and NH bending vibration respectively. On comparing the IR spectra of chitosan and chitosan-*N*-vinyl-2pyrrolidone, Chitosan-g-*N*-vinyl-2-pyrrolidone showed variations in intensity of OH stretching and NH bending vibrations. The shifting of peak from 3388.3 to 3416.8 cm^{-1} appeared due to OH stretching vibration and disappearance of peak appeared at 1593.4 cm^{-1} due to NH bending vibration from the spectrum of chitosan indicating the participation of hydroxyl and amino groups in chemical reaction. The grafting of monomer is further confirmed by characteristic absorption band at 1632.8 cm^{-1} due to >C=O stretching vibration, and at 1402.9 cm^{-1} due to –C≡N stretching vibration of monomer molecule respectively (Mishra et al., 2008). The appearance of additional peaks in spectrum of graft copolymer and shifting of >NH bending vibration from the spectrum of chitosan-g-*N*-vinyl-2-pyrrolidone showed that grafting might have been taken place on –OH and –NH_2 sites of chitosan backbone.

5.4.2. *Thermogravimetric analysis*

Thermogravimetric analysis curve of chitosan (Mishra, Tripathy, Srivastava, Pandey, & Behari, 2009b) shows that degradation of chitosan starts at 180.0 °C. The polymer decomposition temperature (PDT) has been 243.8 °C. It is a single step degradation process and T_{max}, temperature at which maximum degradation occurs, has been found at 297.4 °C which is also confirmed by an endothermic peak at about 290.0 °C present in DTA curve of chitosan. The

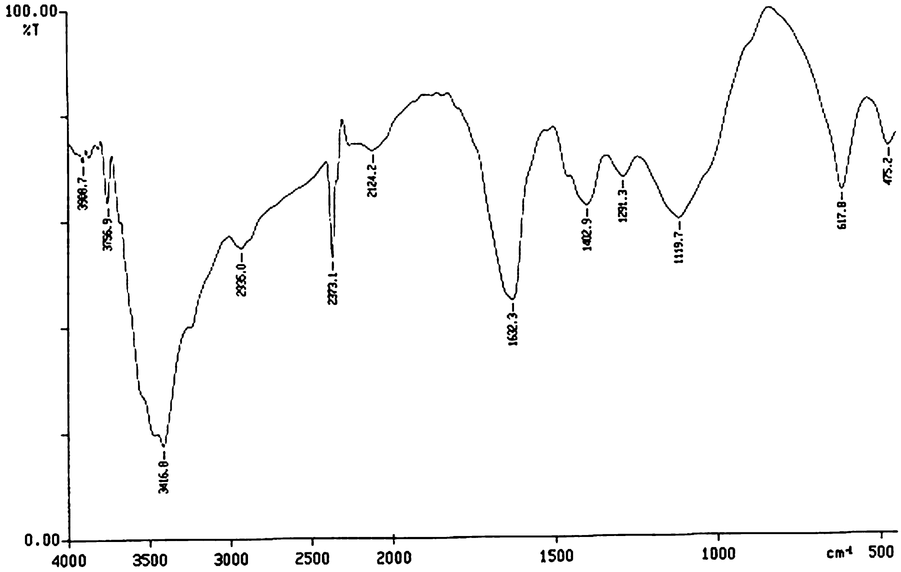


Fig. 1. IR spectrum of chitosan-g-*N*-vinyl-2-pyrrolidone.

integral procedural decomposition temperature (IPDT) has been observed at 314.5 °C. The rate of weight loss increases on increasing the temperature up to 400.0 °C thereafter decreases. Nearly 55% weight loss of chitosan has been observed at about 700 °C. The final decomposition temperature (FDT) has been found 1031.25 °C. On comparing the TGA curve of graft copolymer with, the rate of weight loss occurs at 95 °C is due to loss of water molecule. The graft copolymer (chitosan-g-*N*-vinyl-2-pyrrolidone) starts to degrade at about 150.0 °C. The rate of weight increases maximum with increase in temperature from 150.0 °C to 200.0 °C and thereafter decreases gradually. It is two steps degradation processes because two $T_{\max,}$ shown in thermogravimetric analysis curve of chitosan-g-*N*-vinyl-2-pyrrolidone (Fig. 2) are at 203.3 and 1191.0 °C respectively. The first $T_{\max}$ i.e. at 203.3 °C has been found due to loss of functional group -OH or -NH_2 which is confirmed by endothermic peak at 205.0 °C presents in DTA curve of chitosan-g-*N*-vinyl-2-pyrrolidone. While second $T_{\max}$ at 1191.0 °C has been observed due to loss of pyridine ring of poly (*N*-vinyl-2-pyrrolidone) attached to chitosan and confirmed by endothermic peak at 1200.0 °C. The final decomposition temperature (FDT) value and integral procedural decomposition temperature (IPDT) value have been found nearly at about 1300.0 °C and at 325.0 °C respectively (Table 3). Two steps degradation and high value of IPDT overall favour that the graft copolymer chitosan-g-*N*-vinyl-2-pyrrolidone is thermally more stable than chitosan backbone. The degradations steps are shown in Scheme 2.

5.5. Studies of proprties

5.5.1. Swelling measurement

The swelling study for graft copolymer samples, prepared at different concentrations of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} mol dm^{-3}, is investigated and results are presented in Fig. 3. A marked increment in water absorbency is observed with increasing the concentrations of *N*-vinyl-2-pyrrolidone from 8×10^{-2} to 20×10^{-2} mol dm^{-3} and then, decreases with further increase in concentration of *N*-vinyl-2-pyrrolidone up to 24×10^{-2} mol dm^{-3} (Results are presented in Fig. 3). The initial increment in swelling ratio is attributed to the higher hydrophilicity and greater availability of monomer molecules in the close vicinity of the macro radicals of polymeric backbone. But beyond cited range i.e. from 8×10^{-2} to 24×10^{-2} mol dm^{-3}, the decrement in swelling ratio may be originated from the increase in viscosity of the reaction which restricts the movement of reactants

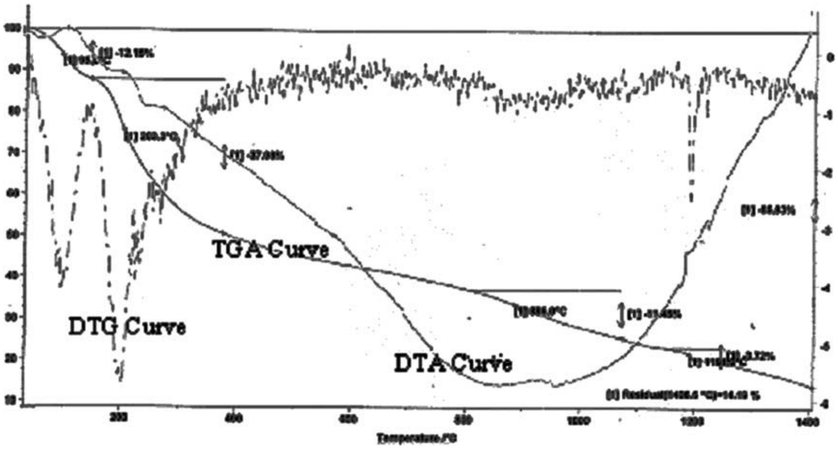


Fig. 2. Thermogravimetric curve.

Table 3
Thermogravimetric analysis.

Sample	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)	Endo (°C)
Chitosan	243.7	1031.2	297.4	314.5	339.0
Chitosan-g-NVP	150.0	1300.0	203.3 1191.0	325.0	205.3 1200.0

and deactivates the macroradical growing chains resulted enhancement in homopolymerization.

5.5.2. Metal ion sorption studies

Hydrophilic-hydrophobic balance and nature of monomer are major factors those effect the metal ion uptake (Lehto, Vaaramaa, Vesterinen, & Tenhu, 1998). These functionalities can be tailored and incorporated by grafting to retain ion by polymer analogous reaction or by simple chelation absorption due to opening of polymer matrix or pores created. Out of these possibilities, all may contribute in the metal ion sorption, though extent of contribution of any factor may be different (Inou, Baba, & Yoshizuka, 1993). However functional group incorporated with the help of grafting by its ability to interact with metal ions may play more important role in determination of selectivity and quantum of metal ion uptake (Sheng, Ting, Chen, & Hong, 2004). Five metal ions have been choosen (Cu^{+2}, Zn^{+2}, Ni^{2+}, Pb^{2+} and Hg^{2+}) for the study of metal ions sorption and the amount of metal uptake was calculated by titrating the unabsorbed metal ions (all the solutions were made in triple distilled water). The increment in all these parameters might be due to grafting of *N*-vinyl-2-pyrrolidone which accounts for the higher sorption of these divalent cations through a chelating reaction (Onsoyen & Skaugrud, 1990) as shown (Scheme 3 metal ion uptake) and the results are given in Table 4.

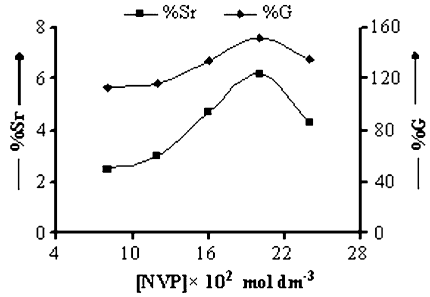
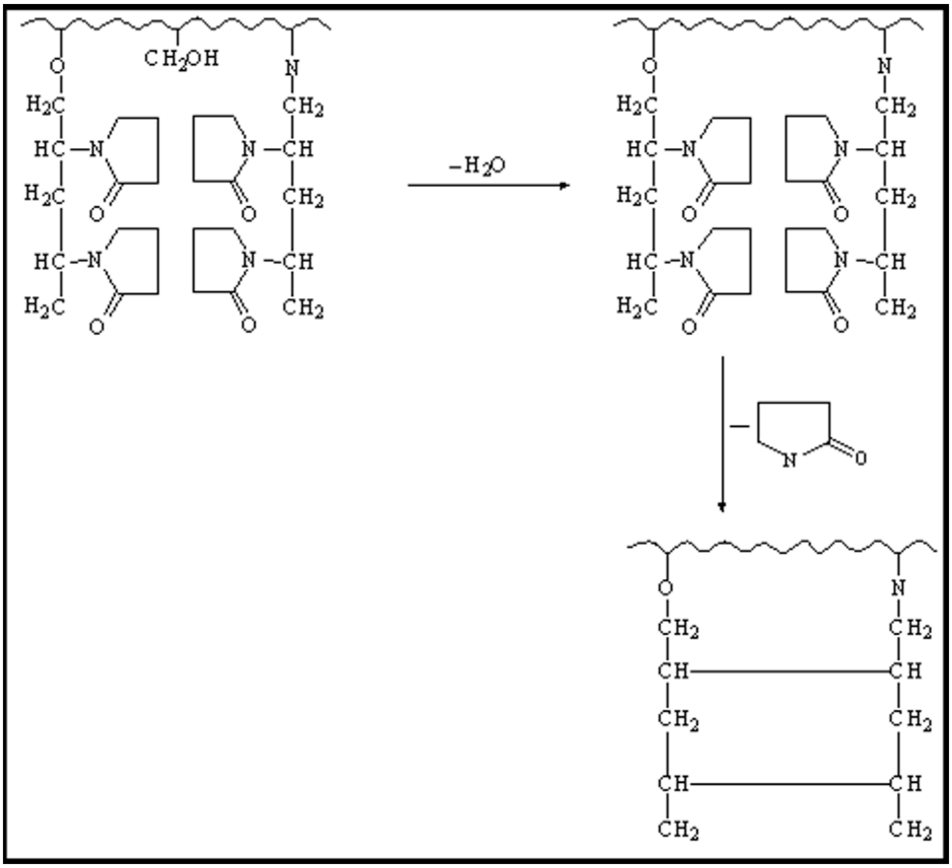


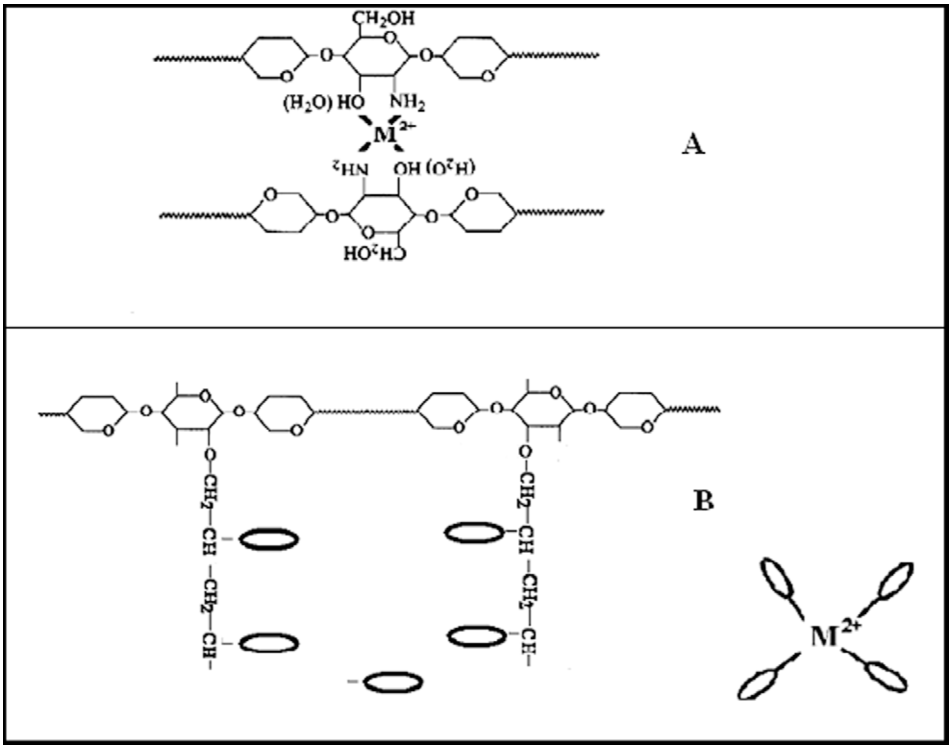
Fig. 3. Effect of *N*-vinyl-2-pyrrolidone on swelling.

5.5.3. Flocculation performance

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone chitosan and graft copolymer of methacrylic acid with chitosan. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are presented in (Fig. 4). It is obvious that grafted copolymer (chitosan-g-*N*-vinyl-2-pyrrolidone) shows better performance with low turbidity than chitosan itself. This phenomenon could be explained by considering bridging mechanism (Deshmukh, Singh, & Chaturvedi, 1985; Gregory, 1983). In grafted copolymer, the dangling of poly (*N*-vinyl-2-pyrrolidone) chains has better approachability as acrylamide (Bratby, 1980) to the contaminant coal particles hence



Scheme 2. Tentative representation of degradation steps of graft copolymer.



Scheme 3. Chelating of the divalent metal ion with chitosan (A) and graft copolymer chitosan-g-*N*-vinyl-2-pyrrolidone (B).

Table 4
Metal ion uptake behaviour.

Sample code	[NVP] × 10^2 mol dm^{-3}	%*G*	Percent uptake (Pu)					Partition coefficient (Kd)					Retention capacity (Qr)				
			Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}
C	–	–	6.6	6.3	5.5	2.1	1.0	35.7	33.9	29.1	10.5	5.1	3.3	3.2	3.2	0.9	0.5
C_{P1}	8	113.0	19.0	16.7	15.8	5.4	2.8	117.7	100.5	93.5	28.4	14.4	9.3	8.4	9.0	2.5	1.4
C_{P2}	12	116.0	20.4	16.9	16.9	6.2	2.9	128.0	101.6	101.4	33.0	14.7	9.9	8.5	9.7	2.8	1.4
C_{P3}	16	134.0	21.8	17.1	18.0	6.6	3.4	139.2	103.0	109.8	35.4	17.8	10.6	8.6	10.3	3.0	1.7
C_{P4}	20	152.2	22.4	17.8	18.5	7.0	3.5	144.4	108.6	113.7	37.8	18.1	10.9	8.9	10.6	3.2	1.7
C_{P5}	24	135.4	21.9	17.2	18.2	6.3	3.5	140.8	103.6	110.9	33.4	17.9	10.7	8.6	10.4	2.9	1.7

[ChXH] = 1 g dm^{-3}, [Ag^+] = 20 × 10^{-4} mol dm^{-3}, [H^+] = 1.4 × 10^{-2} mol dm^{-3}, [BrO_3^-] = 6 × 10^{-3} mol dm^{-3}, Time = 120 min, Temp. = 35 °C.

increasing its flocculation capability (Erciyes, Erim, Hazer, & Yagci, 1992). By grafting of poly (*N*-vinyl-2-pyrrolidone) onto chitosan, efficient flocculant has been obtained and it may be used for the treatment of coal mine waste water.

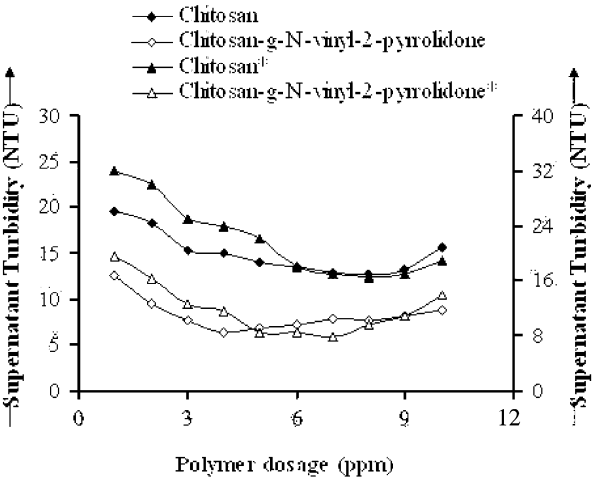


Fig. 4. Effect of polymer dosage on turbidity for coking and non-coking coal*.

6. Conclusion

In this work, a graft copolymer was synthesized, by free radical polymerization of *N*-vinyl-2-pyrrolidone onto chitosan. The spectroscopic data confirm that the grafting of *N*-vinyl-2-pyrrolidone might have taken place at hydroxyl and amino groups, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data also show that the grafted polymer is thermally more stable than pure chitosan. So, swelling capacity of graft copolymer was recognized to be affected by grafting. The synthesized graft copolymer i.e. chitosan-g-*N*-vinyl-2-pyrrolidone shows better results for metal ion sorption and flocculation in comparison to chitosan. It is concluded that synthesized graft copolymer could be exploited very well industrially.

Acknowledgement

The financial support from UGC is acknowledged with thanks for awarding Emeritus Fellowship to K. Behari.

References

Bassett, J., Denney, R. C., Jeffery, G. H., & Mendham, J. (1978). *Vogel's textbook of quantitative inorganic analysis* (4th ed.). London: Longman. p. 370.

Berger, J., Reist, M., Mayer, J. M., Felt, O., & Gurny, R. (2004). Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications. *European Journal of Pharmaceutics and Biopharmaceutics, 57*, 35–52.

Bratby, J. (1980). *Coagulation and flocculation*. UK: Uplands Press Ltd, Croydon, Cambridge.

Dedinaite, A., Iruthayaraj, J., Gorochovceva, N., Makuska, R., & Claesson, P. M. (2006). Interfacial properties of chitosan-PEO graft oligomers: Surface competition with unmodified chitosan oligomers. *Progress in Colloid and Polymer Science, 132*, 124–130.

Dergunov, S. A., Nam, I. K., Maimakov, T. P., Nurkeeva, Z. S., Shaikhutdinov, E. M., & Mun, G. A. (2008). Study on radiation-induced grafting of hydrophilic monomers onto Chitosan. *Journal of Applied Polymer Science, 110*, 558–563.

Deshmukh, S. R., Singh, R. P., & Chaturvedi, P. N. (1985). The turbulent drag reduction by graft copolymers of guar gum and polyacrylamide. *Journal of Applied Polymer Science, 1985*, 4013–4018.

Duan, D. C. (1993). Pressure-sensitive adhesives, U.S. Patent 5225473.

Dutta, P. K., Tripathi, S., Mehrotra, G. K., & Dutta, J. (2009). Perspectives for chitosan based antimicrobial films in food applications. *Food Chemistry, 114*, 1173–1182.

EL-Rehim, H. A. A., Hegazy, E. S. A., & Ali, A. M. (2000). Selective separation of some heavy metals by poly (vinyl alcohol)-grafted membranes. *Journal Applied Polymer Science, 76*, 125–132.

El-Tahlawy, K. F., El-Rafie, Safaa. M., & Aly, A. S. (2006). Preparation and application of chitosan/poly (methacrylic acid) graft copolymer. *Carbohydrate Polymers, 66*, 176–183.

Erciyes, T. A., Erim, M., Hazer, B., & Yagci, Y. (1992). Synthesis of polyacrylamide flocculants with poly (ethylene glycol) segments by redox polymerization. *Angewandte Makromolekulare Chemie, 200*, 163–171.

Fanta, G. F. (1973). Block and graft copolymerization. In R. J. Ceresa (Ed.). *Synthesis of graft and block copolymers of starch* (Vol. 1, pp. 1–27). New York: Wiley-Interscience.

Gaenger, K., & Florig, E. (2007). Hair treatment composition containing a combination of three different film-forming hair-fixing polymers. U.S. Patent, 7279153.

Gregory, J. (1983). Polymeric flocculants. In C. A. Finch (Ed.), *Chemistry and technology of water soluble polymers* (pp. 307–320). New York and London: Plenum Press.

Gupta, K. C., & Ravi Kumar, M. N. V. (2000). Preparation, characterization and release profiles of pH-sensitive chitosan beads. *Polymer International, 49*, 141–146.

Hejaji, R., & Amiji, M. (2003). Chitosan-based gastrointestinal delivery systems. *Journal of Controlled Release, 89*, 151–165.

Hua, D., Deng, W., Tang, J., Cheng, J., & Zhu, X. (2008). A new method of controlled grafting modification of chitosan via nitroxide-mediated polymerization using chitosan-TEMPO macroinitiator. *International Journal of Biological Macromolecules, 43*, 43–47.

Huacai, G., Wan, P., & Dengke, L. (2006). Graft copolymerization of chitosan with acrylic acid under microwave irradiation and its water absorbency. *Carbohydrate Polymers, 66*, 372–378.

Hudson, S. M., & Smith, C. (1998). Polysaccharides: Chitin & Chitosan chemistry and technology of their use as structural materials. In D. L. Kaplan (Ed.), *Biopolymers from renewable resources* (pp. 115). Berlin, Heidelberg, New York: Springer-verlag.

Inou, K., Baba, Y., & Yoshizuka, K. (1993). Adsorption of metal ions on chitosan and crosslinked copper (II)-complex chitosan. *Bulletin of the Chemical Society of Japan, 66*, 2915–2921.

Jayakumar, R., Prabahara, M., Reis, R. L., & Mano, J. F. (2005). Graft copolymerized chitosan—present status and applications. *Carbohydrate Polymers, 62*, 142–158.

Jenkins, D. W., & Hudson, S. M. (2002). Heterogeneous graft copolymerization of chitosan powder with methyl acrylate using trichloroacetyl-manganese carbonyl co-initiation. *Macromolecules, 35*, 3413.

Jenkins, D. W., Samuel, M., & Hudson, S. M. (2001). Review of vinyl graft copolymerization featuring recent advances toward controlled radical-based reactions and illustrated with chitin/chitosan trunk polymers. *Chemical Review, 101*, 3245–3274.

Lee, W. F., & Chen, Y. J. (2001). Studies on preparation and swelling properties of the *N*-isopropylacrylamide/chitosan semi-IPN and IPN hydrogels. *Journal of Applied Polymer Science, 82*, 2487–2496.

Lehto, J., Vaaramaa, K., Vesterinen, E., & Tenhu, H. (1998). Uptake of zinc, nickel, and chromium by *N*-isopropyl acrylamide polymer jells. *Journal of Applied Polymer Science, 68*, 355–362.

Liu, L., Xu, X., Guo, S., & Han, W. (2009). Synthesis and self-assembly of chitosan-based copolymer with a pair of hydrophobic/hydrophilic grafts of polycaprolactone and poly (ethylene glycol). *Carbohydrate Polymers, 75*, 401–407.

Liu, G. Y., Zhai, Y. L., Wang, X. L., Wang, W. T., Pan, Y. B., Dong, X. T., et al. (2008). Preparation, characterization, and in vitro drug release behavior of biodegradable chitosan-graft-poly (1,4-dioxan-2-one) copolymer. *Carbohydrate Polymers, 74*, 862–867.

Mi, F. L., Tan, Y. C., Liang, H. F., & Sung, H. W. (2002). In vivo biocompatibility and degradability of a novel injectable-chitosan-based implant. *Biomaterials, 23*, 181–191.

Mishra, D. K., Tripathy, J., & Behari, K. (2008). Synthesis of graft copolymer (k-carrageenan-g-*N,N*-dimethylacrylamaide) and studies of metal ion uptake swelling capacity and flocculation properties. *Carbohydrate Polymers, 71*, 524–534.

Mishra, D. K., Tripathy, J., Mishra, M. M., & Behari, K. (2008). Modification of dextran through the grafting of *N*-vinyl-2-pyrrolidone and studies of physicochemical phenomena in terms of metal-ion uptake, swelling capacity, and flocculation. *Journal of Applied Polymer Science, 110*, 3455–3463.

Mishra, D. K., Tripathy, J., Srivastava, A., Mishra, M. M., & Behari, K. (2008). Graft copolymer (chitosan-g-*N*-vinyl formamide): Synthesis and study of its properties like swelling, metal ion uptake and flocculation. *Carbohydrate Polymers, 74*, 632–639.

Mishra, D. K., Tripathy, J., Srivastava, A., Pandey, P. K., & Behari, K. (2009a). Synthesis and characterization of chitosan-g-methacrylic acid and studies of its additional physicochemical properties, such as swelling, metal-ion sorption, and flocculation behavior. *Journal of Applied Polymer Science, 113*, 2429–2439.

Mishra, D. K., Tripathy, J., Srivastava, A., Pandey, P. K., & Behari, K. (2009b). Synthesis and characterization of chitosan-g-methacrylic acid and studies of its additional physicochemical properties, such as swelling, metal-ion sorption, and flocculation behavior. *Journal of Applied Polymer Science, 113*, 2429–2439.

Mu, Q., & Fang, Y. (2009). Preparation of thermosensitive chitosan with poly (*N*-isopropylacrylamide) side at hydroxyl group via O-maleoyl-*N*-phthaloyl-chitosan (MPCS). *Carbohydrate Polymers, 72*, 308–314.

Muzzarelli, R. A. A. (1999). Native, industrial and fossil chitin. In P. Jollès & R. A. A. Muzzarelli (Eds.), *Chitin and chitinases*. Switzerland: Birkhauser Verlag, Basel.

Nho, Y. C., & Park, K. R. (2002). Preparation of properties of PVA/PVP hydrogel containing chitosan by radiation. *Journal of Applied Polymer Science, 85*, 1787–1794.

O'Connell, M. J., Boul, P., Ericson, L. M., Huffman, C., Wang, Y., Haroz, E., et al. (2001). Reversible water-solublization of single-walled carbon nanotubes by polymer wrapping. *Chemical Physics Letter, 342*, 265–271.

Onsoyen, E., & Skaugrud, Q. (1990). *Journal of Chemical Technology & Biotechnology, 49*, 395–404.

Park, H., Park, K., & Kim, D. (2006). Preparation and swelling behavior of chitosan based superporous hydrogels for gastric retention application. *Journal of Biomedical Material Research Part A, 76*, 144–150.

Park, S. B., You, J. O., Park, H. Y., Haam, S. J., & Kim, W. S. (2001). A novel pH-sensitive membrane from chitosan TEOS IPN; preparation and its drug permeation characteristics. *Biomaterials, 22*, 323–330.

Pourjavadi, A., & Mahdavinia, G. R. (2006). Superabsorbency P^{H}-senstivity and swelling kinetics of partially hydrolyzed chitosan-g-Poly (acrylamide) hydrogels. *Turkish Journal of Chemistry, 30*, 595–608.

Pourjavadi, A., Mahdavinia, G. R., Zohuriaan-Mehr, M. J., & Omidian, H. (2003). Modified chitosan. I. Optimized cerium ammonium nitrate-induced synthesis of chitosan-graft-polyacrylonitrile. *Journal of Applied Polymer Science, 88*, 2048–2054.

Ravi Kumar, M. N. V. (2000). A review of chitin and chitosan applications. *Reactive and functional polymers, 46*, 1–27.

Rivas, B. L., Maturana, H. A., Molina, M. J., Gomez-Anton, M. R., & Pierola, I. F. (1998). Metal ion binding properties of poly (*N*-vinylimidazole) hydrogels. *Journal Applied Polymer Science, 67*, 1109–1118.

Sheng, P. X., Ting, Y. P., Chen, J. P., & Hong, L. (2004). Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms. *Journal of Colloid and Interface Science, 275*, 131–141.

Singh, J., Dutta, P. K., Dutta, J., Hunt, A. J., Macquarrie, D. J., & Clark, J. H. (2009). Preparation and properties of highly soluble chitosan–L-glutamic acid aerogel derivative. *Carbohydrate Polymers, 76*, 188–195.

Suzuki, T., Fukuda, M., & Yoneto, K. (1993). Pharmaceutical preparation for percutaneous absorption, E.P. 0529123.

Takayama, K., Hirata, M., Machida, Y., Masada, T., Sannan, T., & Nagai, T. (1990). Effect of interpolymer complex formation on bioadhesive property and drug release phenomenon of compressed tablet consisting of chitosan and sodium hyaluronate. *Chemical & Pharmaceutical Bulletin, 38*, 1993–1997.

Tripathi, S., Mehrotra, G. K., & Dutta, P. K. (2008). Chitosan based antimicrobial films for food packaging applications. *E-Polymers, 093*, 1–7.

Tripathi, S., Mehrotra, G. K., Tripathi, C. K. M., Banerjee, B., Joshi, A. K., & Dutta, P. K. (2008). Chitosan based bioactive film: Functional properties towards biotechnological needs. *Asian Chitin Journal, 4*, 29–36.

Tripathy, J., Mishra, D. K., & Behari, K. (2009). Graft copolymerization of *N*-vinylformamide onto sodium carboxymethylcellulose and study of its swelling, metal ion sorption and flocculation behaviour. *Carbohydrate Polymers, 75*, 604–611.

Tripathy, J., Mishra, D. K., Yadav, M., & Behari, K. (2010). Synthesis, characterization and applications of graft copolymer (Chitosan-g-*N,N*-dimethylacrylamide). *Carbohydrate Polymers, 79*, 40–46.

Wang, Y. N., Cui, L., & Xu, T. K. (2008). Applications of modified chitosan flocculant to dyeing wastewater. *Wool Textile Journal, 5*, 18–20.

Wang, C. C., Su, C. H., & Chen, C. C. (2008). Water absorbing and antibacterial properties of *N*-isopropyl acrylamide grafted and collagen/chitosan immobilized polypropylene nonwoven fabric and its application on wound healing enhancement. *Journal of Biomedical Materials Research – Part A, 84*, 1006–1017.

Wongpanit, P., Sanchavanakit, N., Supaphol, P., Tokura, S., & Rujiravanit, R. (2005). Preparation and characterization of microwave-treated carboxymethyl chitin and carboxymethyl chitosan films for potential use in wound care application. *Macromolecular Bioscience*, *5*, 1001–1012.

Xiang, Y., Si, J., Zhang, Q., Liu, Y., & Guo, H. (2009). Homogeneous graft copolymerization and characterization of novel artificial glycoprotein: Chitosan-poly(L-tryptophan) copolymers with secondary structural side chains. *Journal of Polymer Science, Part A: Polymer Chemistry*, *47*, 925–934.

Xu, H. X., Yan, Y. H., Wan, T., & Li, S. P. (2007). Preparation and characterization of chitosan-poly (acrylic-acid) bilayer membrane. *Wuhan Ligong Daxue Xuebao/Journal of Wuhan University of Technology*, *29*, 51–54.

Yinghai, L., Zhenghao, L., Yanzhe, Z., & Kuilin, D. (2002). Graft copolymerization of methyl acrylate onto chitosan initiated by potassium diperiodatonickelate (IV). *Journal of Macromolecular Science, Pure and Applied Chemistry*, *A39*(1 & 2), 129–143.