Polym. Bull. (2011) 67:693–707
DOI 10.1007/s00289-011-0461-8

ORIGINAL PAPER

Chemically induced graft copolymerization of 4-vinyl pyridine onto carboxymethyl chitosan

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Received: 10 November 2009 / Revised: 8 February 2011 / Accepted: 14 February 2011 /

Abstract A novel super absorbent polymer was prepared by graft copolymerization of 4-vinyl pyridine (4VP) onto the chains of carboxymethyl chitosan in aqueous solution using potassium persulphate (KPS) as initiator. The effect of monomer and initiator concentration, reaction temperature, and time on the grafting yield has been investigated. The maximum grafting yield was achieved at [KPS] = 4×10^{-2} mol/L, [M] = 2.5 mol/L at reaction temperature = 60 °C within reaction time = 3 h. The molecular structure of the graft copolymer was confirmed by FTIR, surface morphology before and after the polymerization was examined by SEM. Different analyses were done for the graft copolymer such as X-ray diffraction, solubility tests, and thermal analysis. Different applications were done on the graft copolymer such as swell ability in different pH solutions, dye, and metal uptake.

Keywords Carboxymethyl chitosan · 4-Vinylpyridine · Grafting efficiency · Characterization · Dye uptake · Metal uptake · Swell ability

Introduction

Chitosan is a partially deacetylated polymer of acetyl glucosamine obtained by alkaline deacetylation of chitin. It displays interesting properties such as biocompatibility, biodegradability [1, 2] as its degradation products are non-toxic, non-immunogenic, and non-carcinogenic [3]. Therefore, chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membranes, and flocculation. However, chitosan is only soluble in few dilute acid solutions, which limits its applications. Recently, there has been a growing interest

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in chemical modification of chitosan to improve its solubility and widen its applications [4, 5].

Among various methods, graft copolymerization is the most attractive one because it is a useful technique for modifying chemical and physical properties of natural polymers. Chitosan bears two reactive groups that can be modified. First, the free amino groups on deacetylated units at C_2 and secondly, the hydroxyl groups on the C_3 and C_6 carbons on acetylated or deacetylated units.

Grafting chitosan is a common way to improve chitosan properties such as increasing chelation [6] or complexation properties [7], bacteriostatic effect [8] or enhancing adsorption properties [9].

Carboxymethyl chitosan is a very important chitosan derivative showing very good water solubility and biocompatibility. Carboxymethyl chitosan was prepared and characterized by FTIR spectroscopy, elemental analyses, and X-ray diffraction [10].

Preparation of a novel super absorbent polymer by graft copolymerization of sodium acrylate and 1-vinyl-2-pyrrolidone along the chains of *N*,*O*-carboxymethyl chitosan was reported [11]. As 1-vinyl-2 pyrrolidone is a non-ionic monomer, poly(1-vinyl-2-pyrrolidone) (PVPD) segments were introduced to increase the water affinity of the polymers.

Grafting of vinyl imidazole onto carboxymethyl chitosan using persulphate was also studied. Kinetic studies and antibacterial activity were investigated for the graft copolymer [12].

Graft copolymerization onto Carboxy methylchitosan will be the key point, which will introduce many desired properties and enlarge the field of its potential applications by choosing various types of side chains [13]. These modifications were performed with the target to increase CMCh thermal properties and its dye uptake potency. The aim of this study is to modify chitosan structure by etherification process using mono-chloroacetic acid to produce carboxymethyl chitosan (CMCh), the degree of substitution of the latter was determined by elemental analysis [14], followed by graft copolymerization of 4-vinylpyridine (4VP) onto the produced CMCh.

In the present study, the various parameters affecting the grafting of poly(4-vinylpyridine) (P4VP) onto CMCh, characterization of the grafted copolymers by different techniques and their applications are reported.

Experimental

Materials

Chitosan (degree of deacetylation 88%) was purchased from Funakoshi Co. Ltd, Japan. Potassium persulfate (KPS) was supplied from S. D. Fine Chemical, India. 4VP was supplied by Merck (Schuchardt OHG, Hohenbrunn, Germany), it was purified by vacuum distillation before its use. Mono-chloroacetic acid was obtained from LOBA Chemie PVT. Ltd, Bumbai, India.

Congo red dye (Acidic dye) and Maxilon Blue dye (cationic dye) were purchased from G.T.Gurr, London, s.w.6. Other reagents and solvents were of analytical grades and were used as received.

Instrumentals

Infrared spectroscopy

FTIR spectra were recorded on Testcan Shimadzu IR-Spectrophotometer (model 8000) within the wave number range of 4000–600 cm^{-1} at 25 °C.

Scanning electron microscopy (SEM)

The dry sample, spread on a double sided conducting adhesive tape, pasted on a metallic stub, was coated with a gold layer of 100-μm thickness using an ion sputter coating unit (JEOL S150A) for 2 min and observed in a JEOL-JXA-840A Electron probe micro analyzer at 20 kV.

Atomic absorption

Atomic absorption was done on AAnalyst 100 Winlab-Perkin Elmer to determine the amount of metal ions remaining in the soaking liquor.

Colorimetric spectrophotometry

Colorimetric spectrophotometry was done on Unico 1200 Spectrophotometer at λ_{max} 480 nm for Congo red dye and λ_{max} 580 nm for Maxilon Blue dye.

Thermogravimetric analyses

Thermogravimetric analyses were done on TGA-50H Shimadzu Thermogravimetric Analyzer. Samples were heated from 0 to 500 °C in a platinum pan with a heating rate of 10 °C/min under N_2 atmosphere with flow rate of 25 mL/min.

X-ray diffraction

X-ray diffraction was done using Brukur D_8 Advance, at 40 kV, 40 mA using target Cu K_α with secondary monochromator, Germany.

Experimental techniques

Preparation of carboxymethyl chitosan (CMCh)

Carboxymethyl chitosan (CMCh) was prepared according to the method described by Chen and Park [15] via stirring 5 g of chitosan in 100 mL of 20% NaOH (w/v) for 15 min. Then, 15 g of mono-chloroacetic acid was added portion wisely to the reaction medium and stirring was continued for 2 h at 40 °C. The reaction mixture was then neutralized with 10% acetic acid, poured into excess of 70% methanol, filtered using G_2 sintered glass funnel and washed with methanol. The produced sodium salt of carboxymethyl chitosan was then acidified with methanol solution containing few drops of nitric acid; the excess acid was then removed by washing with methanol–water solution till acid free. The produced CMCh was dried in vacuum oven at 55 °C for 8 h. The degree of substitution (0.75) was determined according to the method described by Wu et al. [16].

Graft copolymerization

CMCh (0.5 g) dissolved in 25 mL distilled water was stirred for an hour followed by 30 min purging with nitrogen gas. A predetermined amount of 4VP was charged under nitrogen atmosphere and heated at 60 °C with continuous stirring for 15 min. After that, the required amount of initiator (KPS) dissolved in distilled water was added portion wisely to the flask to initiate graft copolymerization. The reaction was continued for a predetermined temperature and time.

The grafting mixture was filtered and washed with distilled water to remove the unreacted monomer and dried at 60 °C until constant weight was reached. Exhaustive extraction (using soxhlet apparatus) for 10 h of the product with methanol was done to get rid of any homopolymer (PVP) formed during the grafting reaction. The grafted samples were dried in an air oven at 60 °C till constant weight.

The grafting parameters were calculated according to the following equations [17]:

$$\text{Graft yield } (G\%) = [(W_1 - W_0)/W_0] \times 100$$

$$\text{Homopolymer } (H\%) = [(W_2 - W_1)/W_3] \times 100$$

$$\text{Grafting efficiency } (\text{GE\%}) = [(W_1 - W_0)/(W_2 - W_0)] \times 100$$

where W_0 and W_1 are the weights of the initial matrix and grafted matrix (i.e., weight of grafted product after extraction), respectively, W_2 the crude product before extraction, and W_3 the weight of monomer.

Swell ability

The swelling capacity of CMCh and different graft copolymers CMCh-g-P4VP was studied. The preweighed samples were immersed in different buffer solutions (pH = 4, 7, and 9) and kept undisturbed at room temperature until equilibrium swelling was reached.

The swollen samples were then removed from buffer solutions, quickly wiped with filter paper to remove droplets on their surfaces and reweighed. The percent swelling (P_s) was calculated using the following expression [18]. Swelling measurements were made in triplicate, and the error was estimated to be within 10%.

$$(P_s) = [(W_1 - W_0) / W_0] \times 100$$

where W_0 is the weight of dry polymer and W_1 the weight of swollen polymer

Metal ion uptake

A definite weight of either CMCh or CMCh-g-P4VP of different graft yield (G%) was soaked in the aqueous solutions of various heavy metal chlorides (Ni^{2+}, Co^{2+}, Cd^{2+}, and Cu^{2+}) of known concentrations (2 M) and kept undisturbed till equilibrium. The strength of unabsorbed metal salt solutions was determined by atomic absorption technique.

Dye uptake

Two examples for dyes were used in this study; Congo red (acidic dye) and Maxilon Blue (Cationic dye). Twenty five milliliter of the dye solution of a known concentration was added to 100 mg of CMCh, CMCh-g-P4VP with different graft percentages in 100 mL flat bottomed flask with a ground joint stopper and stirred continuously at room temperature for 24 h to reach equilibrium. After filtration, the concentration of the dye in the filtrate was determined colorimetrically at wavelength 480 and 580 nm for Congo red and Maxilon Blue dyes, respectively. The quantity of adsorbed dye (Q) was calculated according to the following equation [19]:

$$Q = (\mathrm{Na} - \mathrm{Ns})/W,$$

where Q fixed quantity of dye (mg)/weight of the substrate (g), Na quantity of original dye (mg), Ns quantity of remaining dye in the solution after adsorption (mg), and W mass of the substrate (g).

Solubility tests

The grafted products were tested for solubility in water, 1% acetic acid, acetic acid (1%): ethanol mixture (1:1), DMF, 1,4-Dioxane, and THF. In each case, 1% (w/v) solution was examined.

Results and discussion

Parameters controlling the grafting process

The effect of initiator concentration on the extent of grafting is represented in Fig. 1. The initiator concentration was varied from 2×10^{-2} till 8×10^{-2} mol/L keeping all the other parameters constant; monomer concentration is kept at 1.5 mol/L, the temperature at 60 °C and the reaction was conducted for 2 h.

Both G% and GE% increase with increasing the initiator concentration reaching its maximum value at 4×10^{-2} mol/L. A further increase in KPS concentration is accompanied by a considerable decrease in the grafting yield. This could be due to

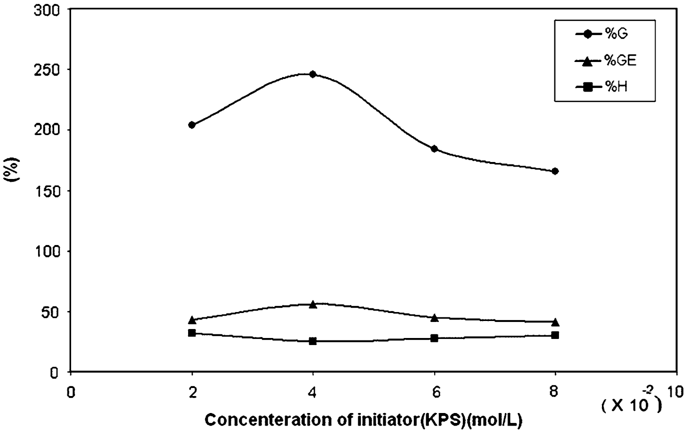


Fig. 1 Variations of G%, GE%, and H% of carboxymethyl chitosan with initiator concentration (KPS) [Time = 2 h, Temp. = 60 °C, [M] = 1.5 mol/L]

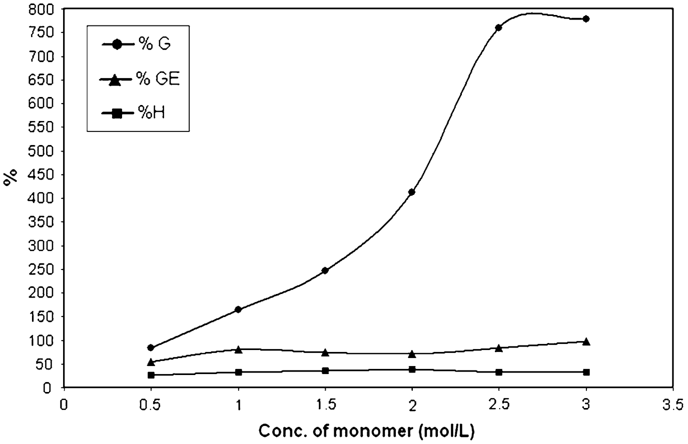


Fig. 2 Variations of G%, GE%, and H% of carboxymethyl chitosan with monomer concentration [Time = 2 h, Temp. = 60 °C, [KPS] = 4 × 10^{-2} mol/L]

several known reasons such as the competition between initiation and termination reactions through chain-transfer reactions to initiator or due to the coupling between initiator radicals.

The effect of 4VP concentration on the grafting process is illustrated in Fig. 2. The monomer concentration was studied within the range 0.5–3 mol/L, while the initiator concentration was kept constant at 4 × 10^{-2} mol/L, the temperature at 60 °C and the reaction time was conducted for 2 h. The data revealed that the increase in both the graft yield (G%) and graft efficiency (GE%) reaching its maximum value at 2.5 mol/L monomer concentration. The increase in the monomer concentration more than 2.5 mol/L does not lead to a remarkable increase in the

G%. Whereas, at very high monomer concentration and especially at the later stages of polymerization, the medium becomes highly viscous and the diffusion of monomer into the growing chains become so difficult and consequently the G% will start to level off. The increase in the G%, which takes place on the expense of the homopolymer formation, is probably attributed to the sequence of addition of the reactants in the reaction vessel which gives much more chance for the grafting process to occur.

The effect of reaction temperature on grafting percentage as well as grafting efficiency and homopolymer formation is shown in Fig. 3. The reaction temperature varies from 55 to 70 °C keeping the initiator concentration constant at 4×10^{-2} mol/L, the monomer concentration at 2.5 mol/L, and the reaction time was conducted for 2 h. It is apparent that the optimum temperature for maximum grafting is 60 °C beyond which the grafting percentage starts to decline, while % homopolymer formation increases thus GE% decreases consequently.

The effect of reaction time on the grafting process is illustrated in Fig. 4. Increasing the reaction time from 1 to 4 h increases grafting, while keeping the reaction temperature constant at 60 °C, the initiator concentration at 4×10^{-2} mol/L and the monomer concentration at 2.5 mol/L. At longer reaction times, the grafting percentage begins to level off. The grafting percentage (G%) starts to decrease after 2 h due to the depletion of the monomer, initiator, and available grafting sites as the reaction proceeds. Grafting efficiency also shows a similar trend. However, the increase in the % homopolymer as a function of reaction time may be attributed to the possible coupling of the macro radicals formed in the medium especially at the later stages of polymerization.

FTIR characterization of CMCh and CMCh-g-P4VP

FTIR spectra of chitosan (Fig. 5a) shows two bands at 3445 and 3422 cm^{-1} corresponding to the –NH_2 group, while the spectra of CMCh (Fig. 5b) shows a

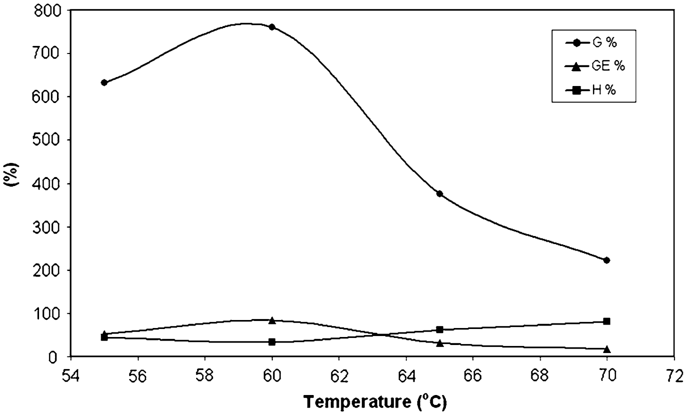


Fig. 3 Variations of G%, GE%, and H% of carboxymethyl chitosan with reaction temperature. [Time = 2 h, [I] = 4×10^{-2} mol/L, [M] = 2.5 mol/L]

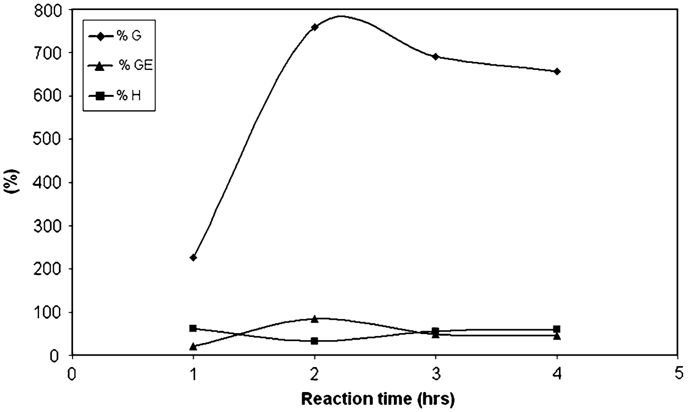


Fig. 4 Variations of G%, GE%, and H% of carboxymethyl chitosan with reaction time. [Temp. = 60 °C, [I] = 4 × 10^{-2}, [M] = 2.5 mol/L]

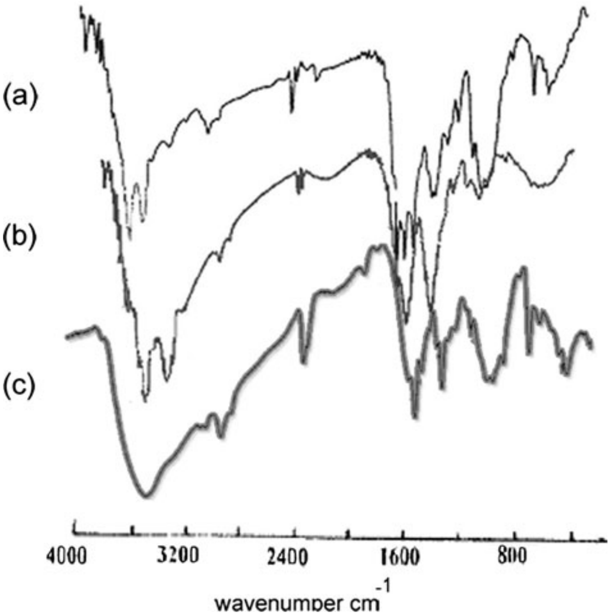


Fig. 5 IR spectra of Chitosan, CMCh, and CMCh-g-P4VP copolymer. (*a*) Chitosan, (*b*) CMCh, and (*c*) CMCh-g-P4VP (*G* = 176%)

strong peak at 1412 cm^{-1} which could be assigned to the symmetrical stretching vibration of COO^{-} group [20]. The asymmetrical stretching vibrating of COO^{-} group near 1550 cm^{-1} is overlapped with the deforming vibration of NH_2 at 1600 cm^{-1} to obtain a very strong peak. The C–O absorption peak of the secondary hydroxyl group became stronger and was shifted to 1074 cm^{-1}. The results indicated that the carboxymethylation process had occurred at C_6 position.

FTIR spectrum of the grafted CMCh (Fig. 5c) has proved that the initiation step for grafting was done onto the amino group at C_2. This is well illustrated by the disappearance of the two bands at 3445 and 3422 cm^{-1} corresponding to the $–NH_2$ group and the appearance of only one band at 3400 cm^{-1} for –NH group which indicates the abstraction of a H-atom by the $KS\overset{\bullet}{O}_4$ radical derived from the decomposition of the potassium persulphate initiator.

$$\mathrm{Ch-NH_2 + KS\overset{\bullet}{O}_4 \rightarrow Ch-\overset{\bullet}{N}H + KHSO_4}$$

The absorption band of the –OH of the –COOH group in CMCh is observed at 3000–2700 cm^{-1}, and the –OH groups of the CMCh have also an absorption band at 3400–3200 cm^{-1}, so there is an overlap between many bands in this area screening the absorption band of –NH group.

Whereas in Fig. 5c, the IR spectrum of the grafted copolymer (CMCh-g-PNVI) shows some characteristic bands for –CH bending of the aromatic ring of the vinyl pyridine that appear around 750, 823, and 1605 cm^{-1} which are very indicative of the presence of the vinyl pyridine moiety in the grafted copolymer [21].

X-ray diffraction

X-ray diffraction analyses for CMCh, P4VP, and their copolymer ($G = 84\%$) (Fig. 6a) showed that CMCh has one peak at $2\theta = 20°$ indicating its crystalline

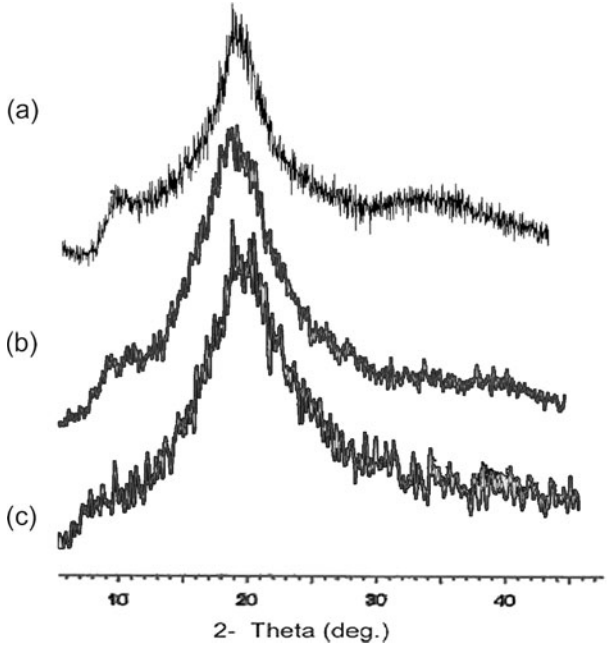


Fig. 6 X-ray diffraction patterns of CMCh, P4VP homopolymer, and CMCh-g-P4VP copolymer. (*a*) CMCh, (*b*) P4VP, and (*c*) CMCh-g-PVP ($G = 84\%$)

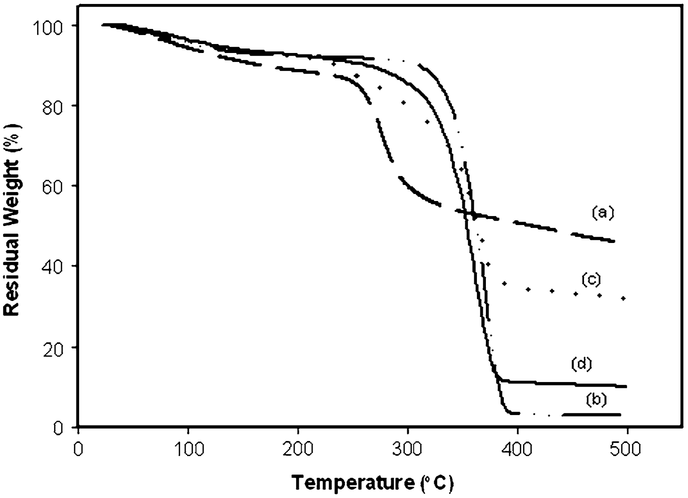


Fig. 7 TGA curves of CMCh, P4VP homopolymer, and different CMCh-g-P4VP copolymers. (*a*) CMCh, (*b*) P4VP, (*c*) CMCh-g-P4VP ($G = 84\%$), and (*d*) CMCh-g-P4VP ($G = 176\%$)]

nature, while P4VP itself has a peak at $2\theta = 18°$ (Fig. 6b). Whereas the grafted copolymer (G = 84%) showed two distinct peaks related to both CMCh and PVP which is considered to be an additional proof for the grafting process.

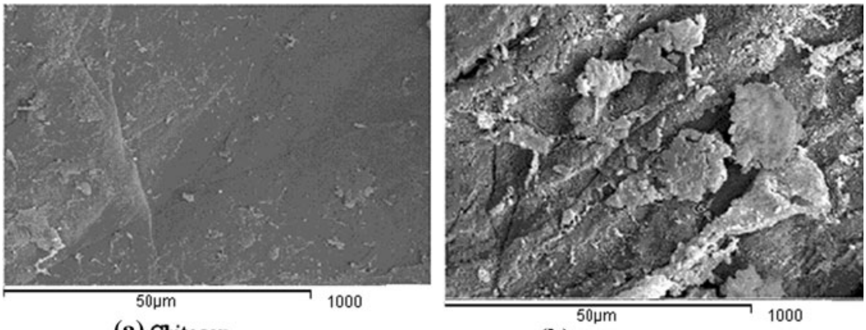
Thermogravimetric analyses of CMCh, P4VP, and CMCh -g-P4VP

CMCh-g-P4VP copolymers (G = 84%) and (G = 176%) showed a higher thermal stability than that of CMCh below 400 °C in terms of both initial decomposition temperature (IDT) and the residual weight below 500 °C (Fig. 7). The thermal stability of the copolymers is increased with increasing the content of P4VP in the graft copolymers. This may be attributed to the higher thermal stability of P4VP due to the presence of the aromatic ring and also the thermal instability of CMCh is due to the loss of CO_2 upon gradual heating.

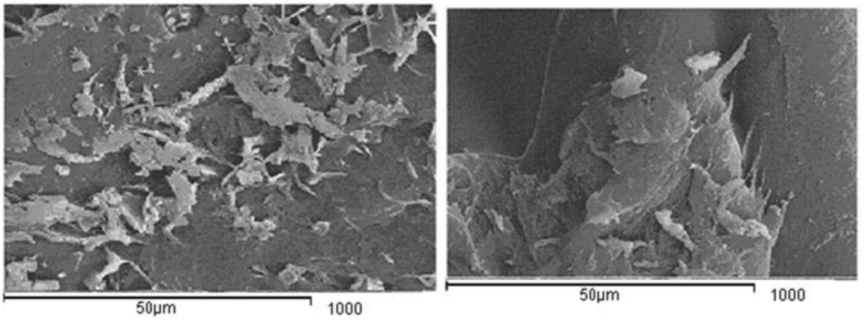
However, at 500 °C, the weight loss of the copolymers is higher than that of CMCh and is increased with the increase in P4VP content onto the copolymers (Table 1).

Table 1 Thermogravimetric analyses for P4VP homopolymer, CMCh, CMCh-g-P4VP ($G = 84\%$), and CMCh-g-P4VP ($G = 176\%$)

Type of polymer	Initial decomposition temp. (IDT) (°C)	Temp. at 10% wt. loss	Temp. at 20% wt. loss	Temp. at 30% wt. loss	Wt. loss % at 500 °C
CMCh	258	168	275	282	55
P4VP	332	312	340	352	86
CMCh-g-P4VP (84%)	310	250	318	340	62
CMCh-g-P4VP (176%)	320	278	322	342	88



(a) Chitosan **(b)** CMCh



(c) CMCh-g-P4VP (G 84 %) **(d)** CMCh-P4 VP (G 176 %)

Fig. 8 SEM micrographs of chitosan, CMCh, and different CMCh-g-P4VP copolymers. **a** Chitosan, **b** CMCh, **c** CMCh-g-P4VP ($G = 84\%$), and **d** CMCh-g-P4VP ($G = 176\%$)

Scanning electron microscopy: (magnification ×1000)

The scanning electron micrographs of Chitosan, CMCh, CMCh-g-P4VP (G = 84%), and CMCh-g-P4VP (G = 176%) are shown in Fig. 8. The fibrous nature of chitosan was totally modified due to the preparation of carboxymethyl chitosan (CMCh) as more lumps were covering the smooth surface of chitosan due to the presence of the bulky –COOH groups. On the other hand, scanning electron microscopy of CMCh-g-P4VP showed a complete modification of the morphology of the surface of CMCh as it has more grooves on it, which increase by increasing the percentage of grafting.

Solubility

Solubility tests for two samples of CMCh-g-P4VP of different graft yield representing a moderate and a high G% together with the parent CMCh and P4VP homopolymer were done in different solvents like; water, 1% acetic acid, acetic acid (1%): ethanol mixture (1:1), DMF, 1,4-dioxane, and THF. The results revealed that the grafted copolymers were insoluble in all solvents used, irrespective to the G% and the solvent type.

Applications of the CMCh-g-P4VP

Two grafted samples representing the lowest (G = 84%) and the highest (G = 176%) grafting values were chosen for this study.

Swell ability

The results of swelling of CMCh and CMCh-g-P4VP in different buffered solutions have been summarized in Table 2. These results represent the average of three comparable experiments for each sample. The data showed that CMCh swelled much more than its grafted copolymers in all investigated pH values, as it is much hydrophilic in nature due to its high polarity. Grafted copolymers swell much more in acidic pH solutions due to the basicity of the pyridine groups of P4VP. Swellability is minimum at neutral pH due to the presence of acidic groups –COOH and basic groups (pyridine rings) in the CMCh-g-P4VP. On increasing the grafting percentage, the swellability increases. This is well illustrated from the data reported for the water uptake % in case of CMCh-g-P4VP (G = 176%) as compared with that of (G = 84%) irrespective to the pH value of the medium.

This experimental finding may be attributed to the fact that increasing the G% lowered the total attractive forces between the neighboring chains of CMCh thus permitting more diffusion of the solvents between the chains and consequently increases its swellability.

As for literature [21], the swelling of chitosan increases with the increase in the grafting percent using PVP, in this way the hydrophilicity of the graft copolymer is higher than the original chitosan, which could have important consequence in biomedical applications. The pH has a strong effect on the extent of swelling increasing in the following order in pH value: 3 > 10 > 6.5.

Metal ion sorption

Table 3 represents the metal ion uptake of CMCh and CMCh-g-P4VP copolymers. CMCh adsorbs much more metal ions which is due to the presence of the two chelating functional groups –NH_2 and –COOH, while the PVP has very low chelating ability. For this, CMCh adsorbs more metal ions (Ni^{2+}, Co^{2+}, Cd^{2+}, and Cu^{2+}) than the grafted copolymers due to the hydrophobicity of the grafted copolymer and the decrease in the content of the CMCh in the grafted samples.

Table 2 Water uptake (%) of CMCh, CMCh-g-P4VP (*G* = 84%), and CMCh-g-P4VP (*G* = 176%) in different buffer solutions

pH	Water uptake (%)		
	CMCh	CMCh-g-P4VP (G 84%)	CMCh-g-P4VP (G 176%)
4	809	525	683
7	994	383	479
9	814	472	597

Table 3 Metal uptake (%) of CMCh, CMCh-g-P4VP ($G = 84\%$), and CMCh-g-P4VP ($G = 176\%$) for different metal ions

Types of metal ions	Metal ion uptake (wt%)		
	CMCh	CMCh-g-PVP ($G = 84\%$)	CMCh-g-PVP ($G = 176\%$)
Co^{2+}	83	87	86
Ni^{2+}	88	83	82
Cd^{2+}	75	63	61
Cu^{2+}	90	73	68

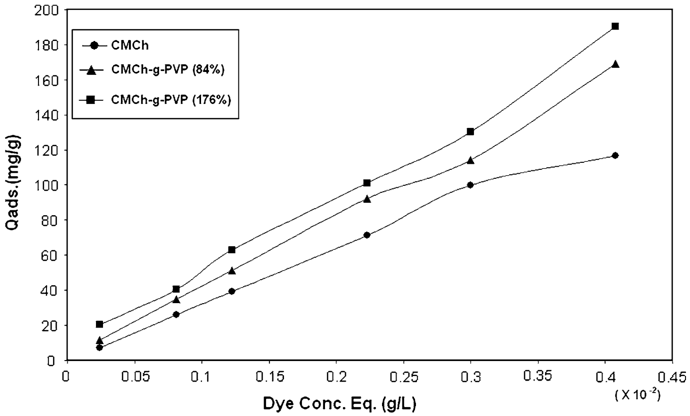


Fig. 9 Variations of the concentration of Congo red dye adsorbed by CMCh, CMCh-g-P4VP ($G = 84\%$), and CMCh-g-P4VP ($G = 176\%$)

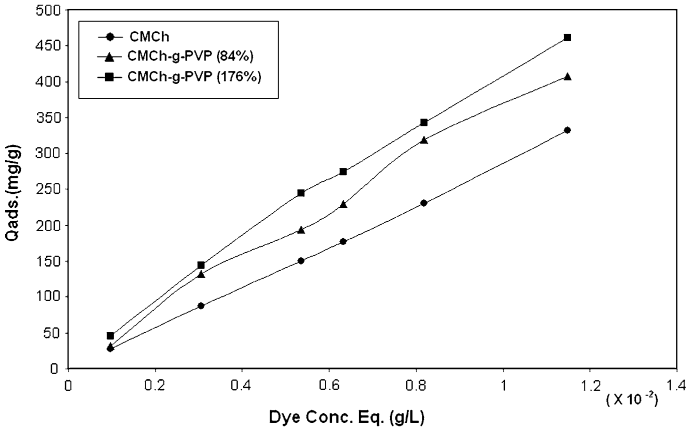


Fig. 10 Variations of the concentration of Maxilon Blue dye adsorbed by CMCh, CMCh-g-P4VP ($G = 84\%$), and CMCh-g-P4VP ($G = 176\%$)

Moreover, the results also reveal that the sequence of metal ions adsorption is as follows: $Cu^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$ for CMCh, while for the grafted copolymers is $Co^{2+} > Ni^{2+} > Cu^{2+} > Cd^{2+}$.

Dye uptake

Adsorption of different dyes by CMCh was reported in literature [22]. In the present work, results of adsorption of Congo red and Maxilon Blue dyes by CMCh and CMCh-g-P4VP copolymers are illustrated in Figs. 9 and 10. For both dyes, as the G% increases, the ability of CMCh-g-P4VP copolymers to adsorb dye increases which may be attributed to the presence of more pyridine groups together with the –COOH groups of the CMCh units. The ability of CMCh and grafted copolymers to adsorb the cationic Maxilon Blue dye more than acidic Congo red dye is attributed to the attraction force between the –COOH groups in the grafted matrix and the basic group of Maxilon Blue dye.

Conclusions

In the present work, carboxymethyl chitosan was prepared, characterized by various analysis tools such as FTIR, SEM, XRD, and TGA, then it was modified by grafting technique via introducing some desired properties on CMCh to enlarge the field of its applications in industry by using 4VP. TGA studies showed the increase in the thermal stability of the copolymers CMCh-g-P4VP than the parent CMCh and that the thermal stability increases with the increase in G%. Moreover, it was obvious from SEM results that carboxymethylation of chitosan and its graft copolymerization by PVP modified the fibrous nature of CMCh surface morphology. Grafting technique was confirmed by various analyses, and the effects of different reaction parameters onto the grafting yield were investigated. Optimum grafting conditions were reported as follows: $[I] = 4 \times 10^{-2}$ mol/L, $[M] = 2.5$ mol/L, reaction temperature = 60 °C, and reaction time = 3 h.

Grafted copolymers swell much more in acidic pH solutions due to the basicity of the pyridine group of PVP. Swellability is found to be minimum at neutral pH due to the presence of both acidic groups –COOH and basic groups (pyridine rings) in the CMCh-g-P4VP. On increasing the percentage of grafting, the swell ability increases. Also as G% increases, the ability of the grafted copolymers to adsorb much more dye increases which may be attributed to the presence of more pyridine groups. The ability of CMCh and grafted copolymers to adsorb Maxilon Blue dye more than Congo red dye is attributed to the presence of–COOH groups in the main chains of CMCh.

Acknowledgments The authors are much thankful to GRCF (Graduate research challenge fund) of Faculty of Science-Cairo University for facilitating the purchase of chemicals and for making the required analyses of the present work.

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