

Crosslinked Poly(vinyl alcohol)/Carboxymethyl Chitosan Hydrogels for Removal of Metal Ions and Dye from Aqueous Solutions

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ABSTRACT: Hydrogels composed of poly(vinyl alcohol) (PVA) and carboxymethyl chitosan (CMCh) were synthesized via ultraviolet (UV) irradiation that can be used in several industrial fields. Several analysis tools were used to characterize the physical and thermal properties of CMCh/PVA hydrogels namely FT-IR, scanning electron microscope (SEM), XRD, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). TGA results showed that CMCh/PVA hydrogels are thermally more stable than CMCh and their thermal stability increases as PVA content increases in the hydrogel. Also, DSC results showed that CMCh/PVA hydrogels are at least partial miscible blends. Moreover, the swelling

behavior of the CMCh/PVA hydrogels was studied in different buffered solutions and in different salt solutions at various concentrations. CMCh/PVA hydrogels swell much more than CMCh especially at alkaline pH. Both metal and dye uptake were studied for CMCh/PVA hydrogels. The hydrogels adsorb much more dyestuff and metal ions like Cu^{2+} , Cd^{2+} , and Co^{2+} than CMCh itself. Much dyestuff and metal ions are adsorbed by the hydrogels as PVA content increases in the hydrogel. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3459–3469, 2012

Key words: hydrogels; swelling; metal uptake; dye uptake; thermal analysis; physical analysis

INTRODUCTION

Polymer gels have attracted attention as “intelligent materials” because of their peculiar material forms.¹ They consist of an elastic crosslinked network and a fluid filling the interstitial spaces of the network.² Hydrogels are three-dimensional, hydrophilic, polymeric networks capable of imbibing large amounts of water or biological fluids. The networks are composed of homopolymers or copolymers and are insoluble due to the presence of chemical or physical crosslinks, such as entanglements or crystallites.³

Polymer gels have been studied for their applications in a variety of fields, such as chemical engineering, foodstuffs, agriculture, medicine, and pharmaceuticals (e.g., controlled drug delivery systems). They may also have applications as muscle-like soft linear actuators, robotics, sensors, biomimetic energy transducing devices, and separation techniques.⁴

Chitosan (poly- β -(1,4)-D-glucosamine), a cationic polysaccharide, is obtained by alkaline deacetylation of chitin, the principal exoskeletal component in crustaceans. As the combination of properties of chi-

tosan such as water binding capacity, fat binding capacity, bioactivity, biodegradability, nontoxicity, biocompatibility, and antifungal activity, chitosan and its modified analogs like carboxymethyl chitosan have shown many applications in medicine, cosmetics, agriculture, biochemical separation systems, tissue engineering, biomaterials, and drug controlled release systems.^{5–10}

The physicochemical properties of chitosan related to the presence of amine functions (acid–base properties, solubility) make it very efficient for binding metal cations in neutral solutions.^{11–13} This electrostatic attraction mechanism is responsible for the strong interaction existing between chitosan and anionic dyes such as Reactive Black 5 (RB 5).^{14,15}

Because of the good chemical stability, film-forming ability, and high hydrophilicity, the studies on diffusive permeabilities of solutes in poly(vinyl alcohol) (PVA) gel membranes and the application for separation have been reported.^{16–19}

In addition, since PVA is biocompatible and nontoxic, and exhibits minimal cell adhesion and protein absorption, PVA membranes have been developed for biomedical applications.^{20–23}

As the specific intermolecular interactions between PVA and chitosan in the blends, the blend of PVA/chitosan has good mechanical properties and the applications of PVA/chitosan blends have been

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reported.^{24–26} Chemical crosslinking is a highly versatile method to create and modify polymer nanostructure, where properties can be improved, such as mechanical, thermal, and chemical stabilities. In addition degradation is regulated.²⁷ There are several methods reported in literature to prepare hydrogels from PVA/chitosan or carboxymethyl chitosan by using crosslinking agents, and/or initiator.²⁸ Yang et al.²⁹ prepared a blended membranes of chitosan and poly(vinyl alcohol) using formaldehyde as a crosslinker. However, Ezequiel et al.,³⁰ Abdel bary et al.³¹ prepared these hydrogels by adding glutaraldehyde as chemically crosslinking agent.

On the other side, Kim et al.³² used UV irradiation in presence of acryloyl chloride (3 wt %) and 1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPAP), as an initiator, to prepare photocrosslinked hydrogels. A series of excellent hydrogels of (87 wt %) PVA/(3 wt %) CMCh/(10 wt %) H₂O was prepared by electron beam irradiation at room temperature.²⁶ Most of the crosslinkers used to perform covalent crosslinking may induce toxicity if found in free traces before administration. A method to overcome this problem and to avoid a purification and verification step before administration is to prepare hydrogels by photocrosslinking.³³

Therefore, photocrosslinked polymers could provide a clean and convenient biomedical-related applications. Photoinitiation crosslinking is a process that uses light to convert a liquid macromer/prepolymer to a solid gel, with the control of photoinitiating conditions, this process can be carried out under mild and cytocompatible conditions.³⁴

In the present study, the preparation of CMCh/PVA hydrogels with different ratios irradiated with UV radiation is reported. The hydrogels will be characterized by FT-IR, XRD, and SEM. Moreover, the thermal stability of CMCh/PVA hydrogels will be studied with both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Different applications will be done on CMCh/PVA hydrogels like metal ion uptake, dye uptake for different dye types (Congo red, Methylene blue, and Maxilon Blue dye), and swell ability in different buffered and salt solutions.

EXPERIMENTAL

Materials

Chitosan (code KB-002) was purchased from Funakoshi Co. Ltd., Japan. Deacetylation content = 88.2% poly(vinyl alcohol), with a hydrolysis degree of 99.0 to 98.0% (molecular weight = 7.7×10^4 g/mol) and monochloroacetic acid were obtained from Loba chemi Pvt. Ltd., Mumbai, India. Congo red dye (acidic dye), Maxilon Blue dye (cationic dye), and Methylene Blue (basic dye) were purchased from G.T.

Gurr, London, s.w.6. Cobalt, copper, and cadmium chloride salts were purchased from Aldrich.

Experimental studies

Preparation of carboxymethyl chitosan

Carboxymethyl chitosan (CMCh) was prepared according to the methods reported in literature^{25,35} by stirring 5 g chitosan in 100 mL 20% NaOH (w/v) for 15 min. Fifteen grams of monochloroacetic acid was added drop wisely to the reaction medium and the reaction continued for 2 h at 40°C with continuous stirring. Then the reaction mixture was then neutralized with 10% acetic acid, poured into an excess of 70% methanol, filtered using a G₂ sintered funnel, and washed with methanol. The produced carboxymethyl chitosan was dried in a vacuum oven at 55°C for 8 h to give 6.5 g dried carboxymethyl chitosan. IR analysis proved the carboxymethylation process done on chitosan. The degree of substitution (0.75) was determined according to the method described in literature.³⁶

Preparation of the blend hydrogels

CMCh solution was prepared in a 500-mL reactor equipped with mechanical stirrer. CMCh was dissolved in degassed distilled water containing 1 wt % acetic acid and then added to PVA solution with continuous stirring to form homogeneous mixture accompanied with heating at 60 to 70°C for 1 h. CMCh/PVA in the final solution was made up to weight ratio 1 : 1, 1 : 3, 3 : 1. This gel-like solution was poured into a petridish and exposed to UV-irradiation for 1 h at a fixed distance of 20 cm height under N₂ atmosphere. Before characterization, the photocopolymerized hydrogels were washed with excess water to remove unreacted materials then dried in a vacuum oven till constant weight was reached.

Gel fraction

After irradiation, the soluble part from the gel was extracted by using the following method: the hydrogel samples were extracted using soxhlet in hot distilled water for 72 h. The remained gel was filtered on a sintered glass, dried to constant weight at 70°C. Gel fraction was measured gravimetrically:

$$\text{Gel fraction (\%)} = W_d/W_o \times 100$$

where W_d is the weight of dry gel after extraction and W_o is the initial weight of dry gel.

Instrumentation

Photoirradiation was provided by 450 W UV lamp (Ace Glass) placed 20 cm above the samples. The

surrounding temperature was $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The wavelength was 254 to 313 nm.

FT-IR spectra were recorded in KBr discs on (FT-IR model 8000) Testcan Shimadzu IR-Spectrometer under dry air at room temperature within the wave number range of 4000 to 600 cm^{-1} .

The dry sample, spread on a double-sided conducting adhesive tape, pasted on a metallic stub, was coated ($100\ \mu$) with gold in an ion sputter coating unit (JEOL S150A) for 2 min. and observed in a JEOL-JXA-840A Electron probe microanalyzer at 20 KV.

Atomic absorption was done on A Analyst 100 win lab-Perkin-Elmer to determine the amount of metal ions remaining in the hydrogel liquor.

Colorimetric spectrophotometry was done on Unico 1200 Spectrophotometer at λ_{max} 480 nm for Congo red dye, λ_{max} 580 nm for Maxilon blue dye, and λ_{max} 660 nm for Methylene blue dye.

Thermal analysis was done on TGA-50H Shimadzu thermogravimetric analyzer. Samples were heated from 0°C to 500°C in a platinum pan with a heating rate $10^{\circ}\text{C}/\text{min}$, in N_2 atmosphere at a flow rate of $25\text{ mL}/\text{min}$.

Thermal behavior of CMCh/PVA blends was investigated by using Conventional DSC TA Q100-TA instrument. It was used to characterize T_g , T_m , T_c of CMCh/PVA blends. DSC cycle runs were done. The first heating run was from -10 till 250°C with heating rate $20\text{ K}/\text{min}$, the cooling run begins from 250° till -10°C with cooling rate $20\text{ K}/\text{min}$. The second heating run was from -10°C till 250°C with heating rate $20\text{ K}/\text{min}$. Glass transition temperature, melting temperature, and melting enthalpy were evaluated from the second heating run.

Applications for CMCh/PVA blend hydrogels

Swelling studies

Water uptake of hydrogels was studied at 30°C in doubly distilled water (pH 7) and in buffered solutions of different pH values 4 and 9. A known weight of predried sample was placed into a flask with 25 mL water or buffer solution of the given pH and kept undisturbed in a thermostated water bath (30°C) until equilibrium swelling was reached (~ 72 h). After wiping off the excessive water on the surface with filter paper, the weight of the swollen samples was determined.

The swelling ratio was calculated according to the following equation:

$$\text{Water uptake percentage (\%)} = [(W_s - W_o)/W_o] \times 100$$

where W_s = weight of wet sample, W_o = weight of dry sample.

The results obtained represent the average of three comparable experiments for each sample.

Dye uptake

Three types of dyes were used: Congo red (acidic dye), Maxilon Blue (Cationic dye), and Methylene blue (basic dye). First 25 mL of the dye solution of a known concentration was added to 0.1 g of the hydrogel in 100 mL flat bottomed flask and stirred continuously at room temperature for 24 h to reach equilibrium. After filtration, the concentration of the remained dye in the filtrate was determined colorimetrically at 480 nm, 580 nm, and 660 nm, respectively. The quantity of the adsorbed dye was calculated according to the following equation²⁷:

$$Q = (N_a - N_s)/W$$

Q = fixed quantity of dye (mg)/hydrogel (g), N_a = quantity of original dye (mg); N_s = quantity of remaining dye after adsorption (mg). W = mass of hydrogel (g).

Adsorption of metal ions

Chloride salts of the heavy metal ions (Co^{2+} , Cd^{2+} , Cu^{2+}) solutions of known concentrations were prepared (0.05 mol/L), then 0.1g of the hydrogel was added to 25 mL solution, stirred for 24 h at room temperature till equilibrium is attained. After filtration, hydrogel was estimated by using atomic absorption technique for the remaining metal ion solution after soaking to determine the amount of metal ions remaining and consequently the amount of adsorbed metal ions can be calculated by difference.

q (mg/g wet weight), was calculated using the following relation:

$$q = V(C_o - C_A)/1000 W$$

where V (L) is the volume of metal solutions, W (g) is the weight of the dry hydrogel, C_o (mg/L) is the initial metal ions concentration, and C_A (mg/L) is the metal ions concentration at definite time.^{34,37}

The total uncertainty for all experiments ranged from 3 to 5%.

RESULTS AND DISCUSSION

IR analyses of gel portion

After extraction, the gel (insoluble) portion was freeze dried and pulverized to elucidate the mechanism of formation of the crosslinked CMCh/PVA hydrogels, FT-IR spectra of the formed gels were studied.

For comparison, FT-IR spectra of CMCh and PVA were also shown in Figure 1, as seen in the PVA

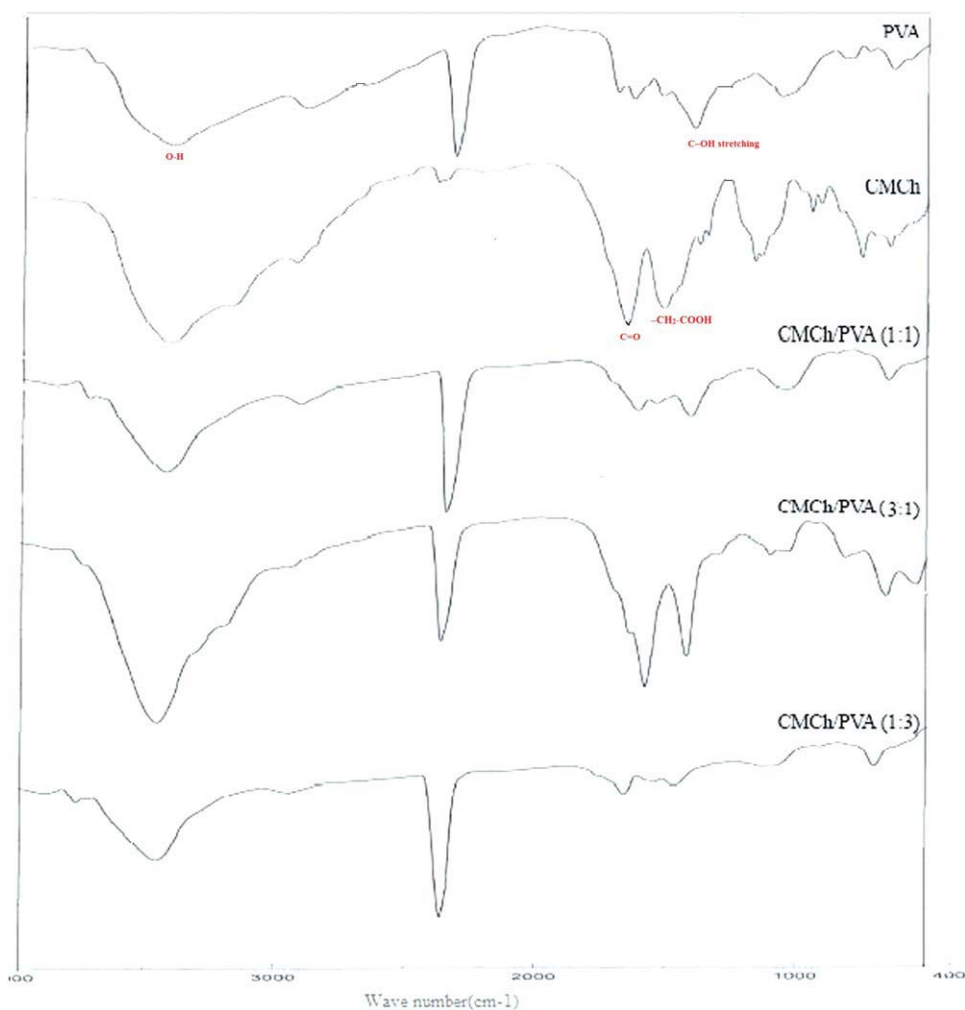


Figure 1 IR Spectrum for PVA, CMCh, and CMCh/PVA hydrogels with different ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectrum, the following peaks were recorded: 2800 to 3000 cm^{-1} which corresponds to the stretching -CH groups in alkanes, 1100 cm^{-1} characteristic for C-OH stretching, and a wide-strong absorption peak at 3200 to 3550 cm^{-1} is associated with the stretching O-H from the intermolecular and intramolecular hydrogen bonds and the peaks between 1750 and 1735 cm^{-1} are due to the stretching C=O and C-O of acetate groups remaining in PVA.³⁸ However for pure CMCh, the band at 1587 to 1625 cm^{-1} corresponds to -COOH and the -NH₂ group makes the peak broad in the spectrum. The spectrum of CMCh also shows a peak at 1414 cm^{-1} which contributes to -CH₂-COOH group. In FT-IR spectrum of hydrogels with different ratios, absorption peaks belonging to the two components; CMCh and PVA exist, such as at 2800 to 3000 cm^{-1} due to -CH stretching and 1100 cm^{-1} due to C-OH stretching in PVA and also the bands at 1587 to 1625 cm^{-1} which correspond to the -COOH group in CMCh, which gave an evidence on the hydrogel formation.

Scanning electron microscopy: (magnification $\times 1000$)

The scanning electron micrographs of carboxymethyl chitosan (CMCh), PVA, CMCh/PVA hydrogels are shown in Figure 2. It is shown that carboxymethylation process to chitosan, followed by hydrogel formation, completely modified the surface morphology of chitosan. The flaky nature of chitosan was totally modified due to the formation of carboxymethyl chitosan (CMCh) as there appear more lumps on the smooth surface of chitosan due to the formation of the bulky-COOH groups on the surface.

Study of the scanning electron microscopy (SEM) verified that the addition of PVA indeed made the hydrogel beads surface become quite porous and dense in nature, thus may provide maximum surface area for the adsorption of metals,³⁰ as shown in Figure 2. CMCh/PVA hydrogels showed a homogeneous and smooth morphology, suggesting that blend homogeneity between CMCh and PVA took place.

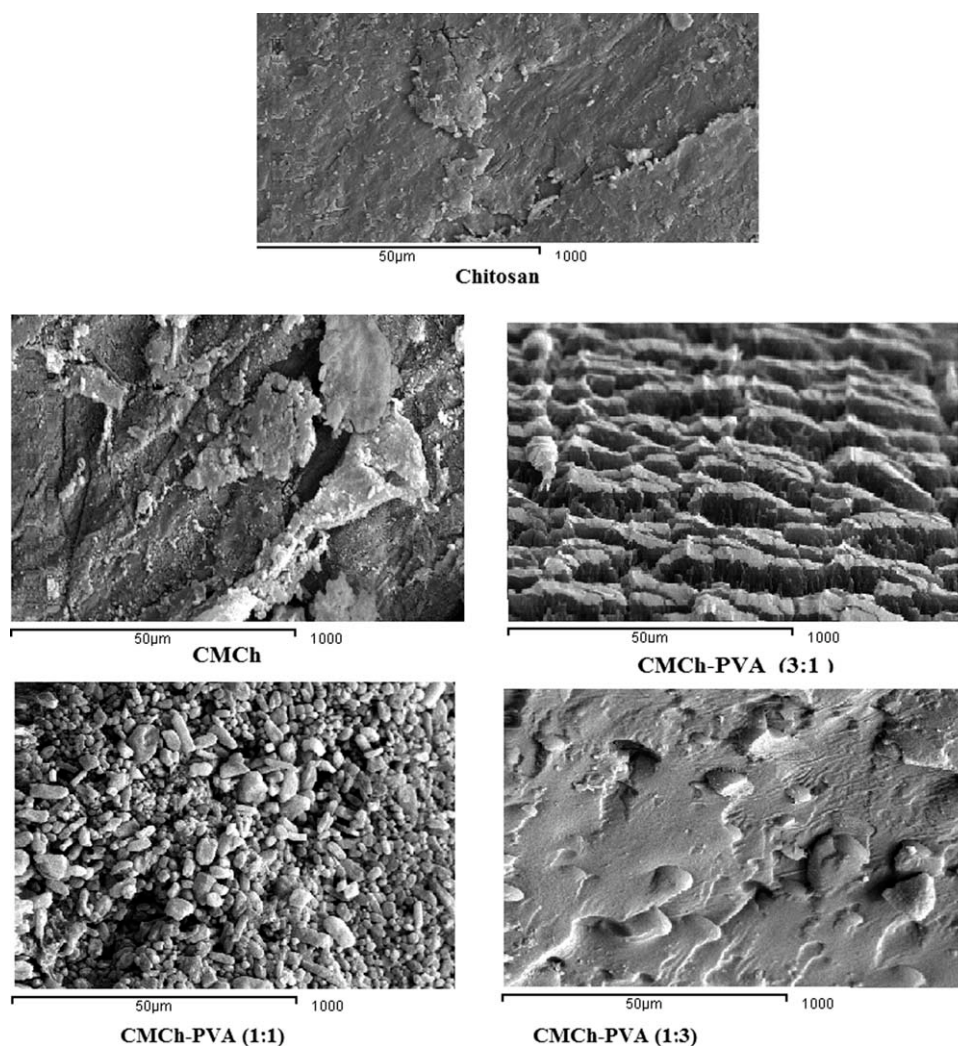


Figure 2 SEM micrographs for CMCh and CMCh/PVA with different ratios.

Furthermore, the results of *SEM* demonstrate that the good compatibility was sustained by the hydrogen bonds and the intermolecular interaction between CMCh and PVA. As the content of PVA increases in the hydrogels,³⁰ the smooth nature of the surface increases.

X-ray diffraction

X-ray patterns of CMCh and CMCh/PVA blend hydrogels are shown in Figure 3. The diffraction peaks of carboxymethyl chitosan are at around 16.5° , 20° , and 36° . The diffraction peaks associated with CMCh are very weak indicating low crystallinity. This was in good agreement with literature.³⁹ However, diffraction peaks of pure PVA are found at 20° and 40° . These peaks are more strong and intense indicating the high crystalline structure of PVA. On the other hand, X-ray investigations showed that hydrogels based on CMCh/PVA contained two diffraction peaks occur at $2\theta \sim 20^\circ$ and 40° . Their intensities decreased with increasing CMCh content.

Therefore, addition of CMCh suppresses the capacity of PVA to crystallize in blends. In PVA blends, this may imply an interaction between the

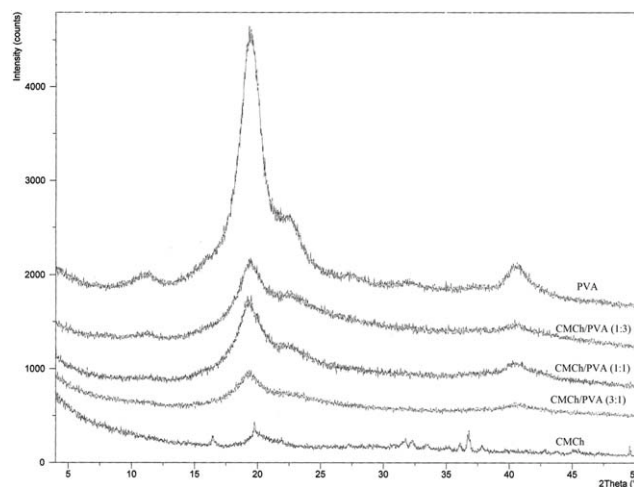


Figure 3 XRD for PVA, CMCh, and CMCh/PVA hydrogels with different ratios.

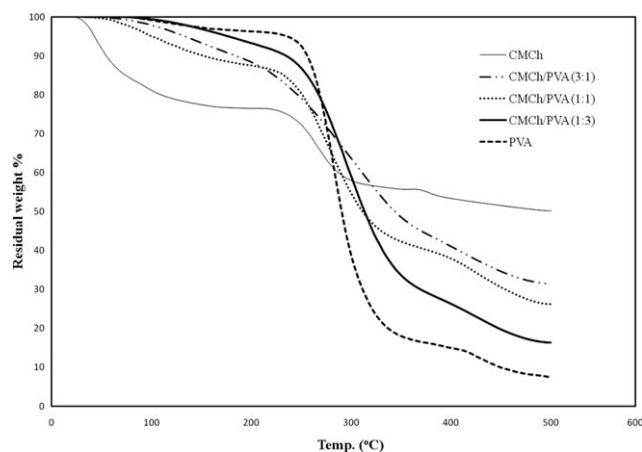


Figure 4 TGA Curves for PVA, CMCh, and CMCh/PVA hydrogels with different ratios.

components. Similar results are reported for both PVA/chitosan hydrogels and CMCh/PVA.^{39,40}

Thermogravimetric analyses

Thermogravimetric analyses of CMCh, PVA, and CMCh/PVA hydrogels of different weight ratios are represented in Figure 4. The initial decomposition temperature (IDT) of CMCh is found to be 240°C, while that of PVA is 260°C. The relatively low IDT of the parent CMCh is mainly attributed to the presence of -COOH groups which may decompose giving up CO₂ gas. The same behavior was reported by Biswal and Singh for carboxymethyl cellulose.⁴¹

The initial decomposition temperatures of CMCh/PVA hydrogels (3 : 1) (1 : 1) (1 : 3) were 241, 245, and 253°C, respectively. This indicates that as PVA content increases, the thermal stability of the hydrogel increases. Moreover, the TGA curve indicates the decrease in the thermal degradation rate of the CMCh hydrogels as the PVA content increases in the hydrogels. At 300°C, CMCh loses about 40% of its initial weight, while CMCh/PVA (1 : 3) hydrogel loses about 25% of its original weight, CMCh/PVA (1 : 1) hydrogel loses 29% of its weight and CMCh/PVA (3 : 1) hydrogel loses 35% of its initial weight.

DSC analyses

DSC cycle runs were done for CMCh/PVA blends with heating and cooling rate 20 K/min in temperature range from -10 to 250°C. The first heating scan of cast films ends at 250°C, it is performed to eliminate and remove all the prehistory of the sample and excess water. Polysaccharides have a strong affinity for water, and in the solid state these molecules may have disordered structure which can be easily hydrated.^{42,43} Therefore, in the first DSC run broad irregular endothermic peaks are observed due to the release of water.

Figure 5 represents DSC cooling curves of pure PVA, pure CMCh, and their blends, which crystallized from molten state at a cooling rate 20 K/min. The maximum exothermic crystallization temperature of pure PVA occurs at 190°C. It is clearly seen that with the increase in CMCh content, the maximum exothermic crystallization temperature, and crystallization enthalpy shift to lower values. For example, the maximum exothermic crystallization temperature of CMCh/PVA (3 : 1) is 130°C and ΔH for CMCh/PVA (3 : 1) is 7 J/g. Therefore, it can be concluded that the addition of CMCh retards the crystallization of PVA (see Fig. 5). This may be attributed to the following reasons: (i) dilution effect that diminishes the probability of formation of a critical nucleus on the front of the growing spherulite, (ii) entropic factors that produce an increase in the free energy related to the formation of a nucleus of critical size, and/or (iii) reduction of the driving force for crystallization due to changes in the equilibrium melting, or (iv) interactions of both macromolecules probably by hydrogen bonds (see IR results).

DSC second heating curves of pure PVA and CMCh/PVA till 250°C with a heating rate of 20 K/min were observed in Figure 5. In the temperature range from -10 to 100°C a step change in heat flow is observed. This is attributed to glass transition temperature. The glass transition temperature of pure PVA is 70°C. This is in a good agreement with literature.⁴²⁻⁴⁴ For pure CMCh, a weak and wide step change in the heat flow is observed in the vicinity of 100 to 200°C. The accurate evaluation of T_g was difficult, equals 164°C, because it is followed by degradation of CMCh. This observation is in a good agreement with Kacurakova et al.⁴² For CMCh/PVA, the glass transition temperatures are getting broader for rich CMCh content. The values of glass transition temperature are almost 70°C, independent

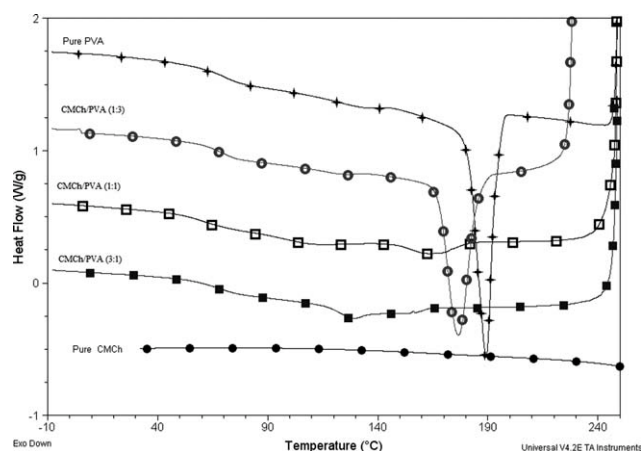


Figure 5 DSC curves (cooling curve) for PVA, CMCh, and CMCh/PVA hydrogels with different ratios.

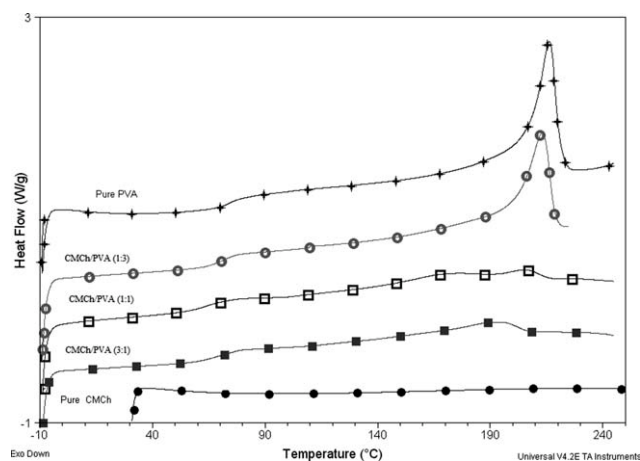


Figure 6 DSC curves (heating curve) for PVA, CMCh, and CMCh/PVA hydrogels with different ratios.

on wt % of CMCh. This may be attributed to that CMCh can act as solid filler. Similar behavior was observed in rubber with carbon black.⁴⁵ However, the T_g (II) of CMCh in the CMCh/PVA is not detected, as no step change was observed at temperature range 150 to 200°C.

In the temperature range of 150 to 230°C, melting peak of PVA is detected, thus prevents determination of glass transition of CMCh. A strong endothermic peak in the range of 150 to 230°C resulting from melting of PVA crystalline phase is seen in Figure 6. The maximum melting temperature of pure PVA is 216°C, and melting enthalpy is 71 J/g. The maximum melting temperature moves to lower temperature value, i.e., from 216°C for pure PVA to 195 for CMCh/PVA (3 : 1). Moreover, the melting enthalpy decreases with decreasing PVA content in the blends, ΔH for CMCh/PVA (3 : 1) is 7 J/g (see Table I). This means that addition of CMCh depresses the crystallinity of PVA. These results are in a good agreement with X-ray results. These results prove that CMCh/PVA is at least partially miscible blend. Similar results were reported for PVA/chitosan.^{44,46,47}

Gel fraction

CMCh/PVA blend systems were irradiated; PVA radicals reacted easily with the other PVA molecules

to form crosslinked PVA network.⁴⁸ CMCh macroradicals are considered to be separated by water and PVA molecules. However, CMCh macroradicals were capable to contact with PVA chains around and then grafted onto PVA network. Blend hydrogels of polysaccharides and synthesized polymer have been prepared and studied widely. Some researchers proposed that the chemical reaction between polysaccharide and synthesized polymer molecules occurred to bond polymers of the two types. Polysaccharide repeating units contain reactive groups at C₂, C₃, and C₆ positions.⁴⁹

Grafting reaction between chitosan and PVA was widely reported in literature⁵⁰ and it was found that C₂-C₃ bond of chitosan molecules was easily cleaved to yield an aldehyde and a free radical.⁵¹

In this study, the gel fraction (%) was calculated for CMCh irradiated alone as CMCh is one of the polysaccharides which are able to form hydrogels by irradiation crosslinking in so-called “paste-like” status. It was found that the gel fraction (%) increased with the increase in PVA content in the blend hydrogels—Table II—due to the higher affinity of PVA to crosslink formation through the intra- and/or intermolecular hydrogen bonding via -OH groups.

Swelling behavior

All swelling behavior was plotted on the average of three trials. All hydrogels swelled rapidly and reached equilibrium within 72 h. CMCh is an amphoteric macromolecule containing both carboxyl and amino groups. CMCh gel swelled at low pH 4 and also at high pH 9; however, deswelling occurred in the range of pH 7 : 0 because CMCh gel contains both carboxyl and amino groups, thus forms a network with oppositely charged structures which change the charge state of the ionic groups varying with pH.

In case of low pH, the dominant charges in the gel are the protonated amino group. In case of high pH, the dominant charges in the gel are the unprotonated carboxyl group. The hydrogel CMCh/PVA (3 : 1) had the highest swelling ratio in time-dependent swelling behavior, while the swelling ratio of

TABLE I
DSC Analysis of CMCh/PVA Hydrogels

Materials	Cooling scan		2nd Heating scan			
	T_c (°C)	ΔH_c	T_g (°C)	T_c	T_{mmax} (°C)	ΔH_m
Pure PVA	190	55	72	Not detected	216	71
CMCh/ PVA (1 : 3)	177	47	71	Not detected	214	49
CMCh/PVA (1 : 1)	164	6	65	Not detected	206	10
CMCh/PVA (3 : 1)	130	7	70	Not detected	195	7
Pure CMCh	Not detected	Not detected	165	Not detected	Not detected	Not detected

TABLE II
Gel Formation in CMCh /PVA Blend Hydrogels

Sample	Gel fraction (%)
CMCh	62
CMCh/PVA (3 : 1)	91
CMCh/PVA (1 : 1)	95
CMCh/PVA (1 : 3)	98

CMCh/PVA (1 : 3) had the lowest (Table III). The swelling ratio increased with increasing the molar ratio of hydrophilic groups of CMCh in the hydrogel. This behavior might be shown due to the formation of more loosely crosslinked network with the increase in CMCh content. Results revealed that swelling ratio decreases with increasing PVA content in the hydrogel due to enhancing the crosslinking by intramolecular H-bonding between PVA chains in the hydrogel network structure, while with increasing the content of CMCh, crosslinking density of CMCh/PVA hydrogel decreased and molecular entanglement between CMCh and PVA was weakened, which resulted in improvement of its water absorbing ability.

Also CMCh is more hydrophilic than PVA—Table III—the swelling ratio increased with increasing the molar ratio of the hydrophilic groups of CMCh in the hydrogel.⁵²

This pH-responsive swelling behavior was demonstrated in Table III. The hydrogels show a lower swelling ability in pH 7 as compared with pH 4 and 9. It is known that a high concentration of charged ionic groups in the hydrogel increases swelling due to osmosis and charge repulsion. Thus, when the degree of ionization of the hydrogel bound groups decreased, swelling also decreased.⁵²

Since the swelling process of hydrogels involves the ionization of amino groups in acidic buffer solution, the acid would be attached to the hydrogels by ionic bonds. Therefore, the weight of the hydrogels increased in the acidic buffer. Also at high pH, the swell ability of the hydrogel increased due to the presence of -COOH groups in the hydrogel. This

could be attributed to the electrostatic attraction or repulsion between ionic groups of the CMCh in different pH environments.⁵³

The driving force for the swelling and shrinking of polyelectrolyte gel is the difference between the concentration of free ions inside and outside of the gel.⁵⁴

For the swelling of CMCh/PVA hydrogels in NaCl concentrations of 0.1M, the swelling ratios increases as CMCh content increases in the hydrogel. Swelling in NaCl may lead to salting-in of the polymer at appreciable salt concentration.⁵⁴ This is in agreement with the behavior in KCl solution, as the CMCh content increased the swelling ability increased.

The swelling ability in CaCl₂ solution increases as the CMCh content also increases in CMCh/PVA hydrogels. It is assumed that formation of Ca (II) crosslinked bridges between COO⁻ groups makes a dense architectural structure of the polymer gels. Furthermore, the chelating ability of COO⁻ groups to Ca(II) plays an important role, which increased with increasing Ca(II).⁵⁴ Same behavior for swelling in KNO₃ was also noticed, swelling ability increases with the increase in CMCh content in the hydrogels.

Swelling of CMCh/PVA hydrogels in Na₂SO₄ (0.1M) solution showed an increase also with the increase in CMCh content. This may be attributed to the fact that as CMCh content increases, the amount of amino and -COOH groups was also increased leading to an increase in the amount of crosslinking centers and a decrease in the dimensions of the crosslinked network.⁵⁵

Metal uptake

For the CMCh/PVA hydrogels used in this study, it may be expected that adsorption might be due to many available chelating sites on the CMCh/PVA hydrogels. The adsorption sites for cations of Cd²⁺, Cu²⁺, and Co²⁺ are at the nitrogen atoms of the amino groups in CMCh and the oxygen atoms of the hydroxyl groups in both CMCh and PVA.

TABLE III
Swelling Behavior of CMCh/PVA Hydrogels in Different pH Values and Different Electrolytes

pH	CMCh (wt. %)	CMCh/PVA (3 : 1) (wt %)	CMCh/PVA (1 : 1) (wt %)	CMCh/PVA (1 : 3) (wt %)
4	154	395	261	167
7	122	195	174	129
9	591	411	346	205
NaCl (1M)	87	157	127	95
KCl (1M)	95	197	141	112
CaCl ₂ (1M)	114	258	161	117
KNO ₃ (1M)	120	226	201	124
Na ₂ SO ₄ (0.5M)	76	75	59	53

TABLE IV
Adsorption of Cu^{2+} , Co^{2+} , and Cd^{2+} by
CMCh/PVA Hydrogels

Sample	Cu^{2+} (ppm)	Co^{2+} (ppm)	Cd^{2+} (ppm)
CMCh	3000	3290	2600
CMCh/PVA (3 : 1)	3500	5264	11,689
CMCh/PVA (1 : 1)	3549	5297	9698
CMCh/PVA (1 : 3)	3822	5305	9241

Table IV represents the equilibrium adsorption amounts of metal ions at 24 h under various equilibrium concentrations. It was found that the adsorption of Co (II) and Cu (II) increased with the increase in concentration of PVA as the chelating centers increase, for example the adsorption of CMCh/PVA (3 : 1) hydrogel for Co (II) and Cu (II) cations is less than CMCh/PVA (1 : 1) hydrogel which is in turn less than CMCh/PVA (1 : 3) hydrogel.

These results are in good agreement with the work of Kumar et al.²³ which reported that crosslinked chitosan/PVA beads with ratio (1 : 2) were an effective adsorbent over a wide range of adsorbate (Cd(II)) concentration at pH 6.0. However, for the adsorption of Cd(II) ions, it decreased with the increase in the concentration of PVA in the blend. Similar results were observed in case of chitosan-PVA microspheres which were used as a potential carrier for drugs.²³ The low adsorption of Cd^{2+} relative to the Co(II) and Cu(II) ions may be a consequence of their lack of affinity to the alcohol groups present in the CMCh/PVA hydrogels. Apart from the contribution of the charge density and hydration energy of the CMCh/PVA hydrogels in ion uptake, the hydration sphere of these ions also contributes significantly to the selectivity in the observed results.⁵³

Dye uptake

The chemical structures of the dyes shown below are quite different and allow these substrates to

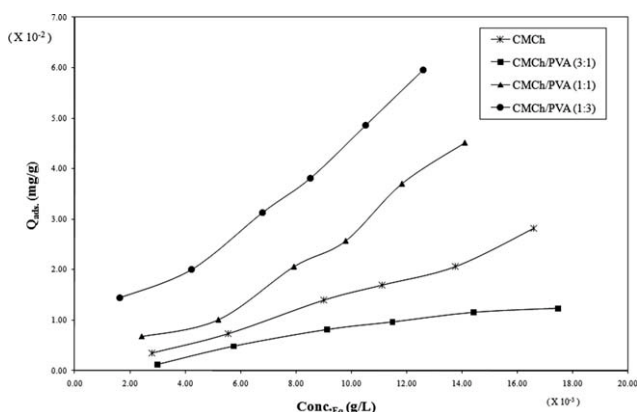


Figure 7 Variation of Congo red concentration adsorbed by CMCh/PVA hydrogels.

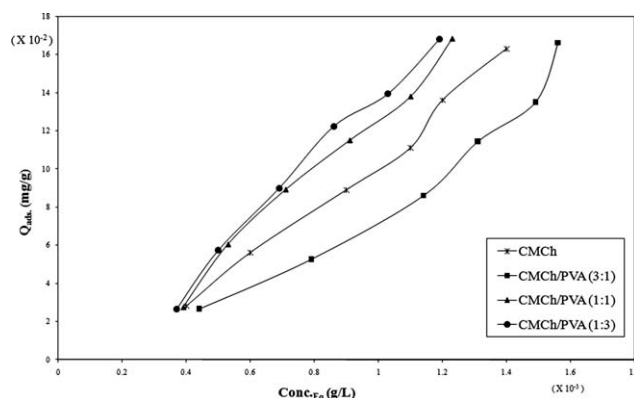
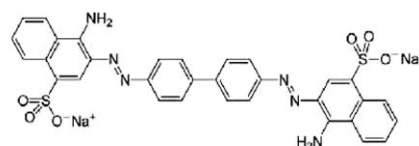


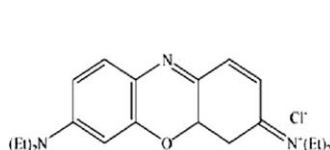
Figure 8 Variation of Maxilon blue dye concentration adsorbed by CMCh/PVA hydrogels.

induce interactions of various natures with their surroundings. Among these dyes, Congo Red Dye is an acidic dye; it bears two cationic sites (amino groups) and two anionic sites (sulfonate groups).

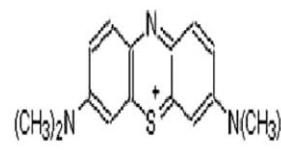
The adsorption of this dye increases by the decrease of CMCh content in the hydrogel due to the acidic character of the dye, so CMCh/PVA (1 : 1) hydrogel adsorbs much more Congo red dye than pure CMCh—which is more acidic in character, while CMCh/PVA (1 : 3) hydrogel adsorbs much more dye than all other hydrogels as it has less CMCh content than other gels, as shown in Figure 7.



Congo Red Dye



Maxilon Blue Dye



Methylene Blue Dye

The same behavior was noticed for Maxilon Blue dye (cationic dye) which is electrostatically attracted by the alcohol groups in PVA (Fig. 8). This reaction allows neutralizing of the cationic charges of dyes that can bind together and settle. When the amount of negatively charged alcohol groups reached the complete neutralization of cationic charges, the removal of the dye reached a maximum.⁵³

However, the adsorption of Methylene blue dye (basic dye) (Fig. 9) increases with the increase of CMCh content in CMCh/PVA hydrogel due to the

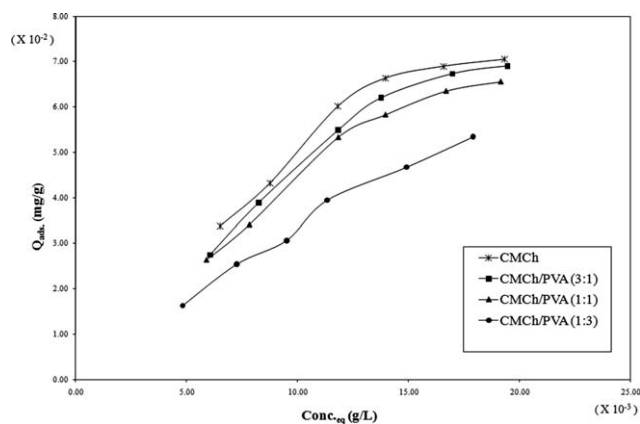


Figure 9 Variation of Methylene blue dye concentration adsorbed by CMCh/PVA hydrogels.

basic nature of the dye, being attracted to -COOH groups in CMCh.

CONCLUSIONS

CMCh/PVA crosslinked hydrogels were prepared in different ratios via UV-irradiation. These blend hydrogels were used as adsorbents for different metal ions and dyes from their aqueous solutions, so these hydrogels can be used industrially for water treatment purpose. These hydrogels also swell greatly in different pH solutions and electrolytes, so they can be also used in irrigation hydrogels applications.

Several analysis tools were used to characterize the physical and thermal properties of the prepared hydrogels namely FT-IR, scanning electron microscope (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Some important obtained results could be summarized as follows:

1. In case of high pH, the CMCh/PVA (3 : 1) hydrogel had the highest swelling ratio, while the swelling ratio of CMCh/PVA (1 : 3) had the lowest. The swelling ratio increased with increasing the molar ratio of carboxymethyl chitosan in the hydrogel. The hydrogels show a lower swelling ability in pH 7 as compared with pH 4 and 9. Swelling of CMCh/PVA hydrogels in different salt solutions showed an increase also with the increase in CMCh content.
2. The adsorption of Co(II) and Cu(II) ions increased with the increase in PVA concentration as the chelating centers increase. However, for the adsorption of Cd(II) ions, it decreased with the increase in PVA concentration, thus these hydrogels can be used to be selective to metal ions.

3. The adsorption of Congo Red dye increases with the increase in PVA content in the hydrogel. The same behavior was noticed for Maxilon Blue dye (cationic dye). However, the adsorption of Methylene blue (basic dye) decreases with increase of PVA content in CMCh/PVA hydrogel.
4. Thermogravimetric analysis indicates that the thermal stability of the hydrogel increases as PVA content increases in the hydrogel.

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