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# Crosslinking Parameter on the Preparation of Cellulose Based Hydrogel with Divynilsulfone

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## Abstract

Polymeric hydrogels are crosslinked polymers which display high sorption capacity in water and water solution. In this work, cellulose based hydrogel was prepared with divinylsulfone as crosslinking agent. Cellulose based hydrogel was synthesized as a mixture of sodium salt of carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC). The effect of chemical composition, temperature and reaction time during crosslinking processes was investigated both the value of equilibrium water uptake and swelling ratio. Infrared spectra of the synthesized polymeric networks were studied to investigate the chemical structure of crosslinking reaction qualitatively. The thermal properties and morphology of the obtained cellulose based hydrogels were observed by means of TGA (thermo-gravimetry analysis) and SEM (scanning electron microscopy), respectively. Crosslinking of CMCNa/HEC polymeric network results in a decrease in thermal stability. Hydrogel with weight ratio of CMCNa/HEC 5 to 1 at reaction temperature of 60 °C gave the highest absorption capacity in distilled water.

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## 1. Introduction

Hydrogels are three-dimensional polymeric networks that are able to absorb and retain large volumes of water. Chemical or physical crosslinking is required to avoid dissolution of the hydrophilic polymer chains into the aqueous phase [1–3]. Because of their sorption capacity, superabsorbent hydrogels have been extensively used as water retaining devices, mainly the field of personal hygiene products and in agriculture pharmaceutical, biomedical and catalysis [4–9]. Usually, polymer-based superabsorbent materials are made of synthetic polyelectrolytes such as crosslinked poly(sodium acrylate). Due to environmental issues, growing efforts have been put forward in developing natural polymer-based

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superabsorbent materials that guarantee biodegradability [10].

As reported in the previous studies, a high degree of swelling ratio in water can be achieved using polyelectrolyte gel [11-12]. In fact, the presence of fixed charges on macromolecular chains determines a large swelling capacity of the polymer due to a Donnan equilibrium established between gel and the external solution, whose ionic strength strongly affects the swelling degree [13-15].

In this work, we utilized a linear biodegradable water-soluble material which, properly crosslinked, turns into a biodegradable hydrogel. Carboxymethyl-cellulose (CMC) which is a biodegradable polymer easily available on the market could be thought of as a possible candidate. However, CMC cannot be used as itself because it tends to form intramolecular rather than intermolecular crosslinking. For this reason a mixture of CMC, in its sodium salt form (CMCNa), with hydroxyethylcellulose (HEC) was crosslinked using divinylsulfone. The introduction of HEC avoids the formation of intramolecular crosslinking [16].

Several factors are expected to affect the swelling properties of the obtained hydrogels in distilled water, such as chemical composition, temperature and reaction time. Swelling properties of various samples differing for the CMCNa/HEC ratio and reaction temperature as well as for the adopted preparation protocols were evaluated.

## 2. Experiment

### 2.1. Materials

HEC was purchased from Fluka Biochemica. Sodium carboxymethylcellulose (CMCNa,  $2.43 \times 10^4$ ) was analytical-grade reagent purchased from Kanto Chemical, Co. Inc. The degree of carboxymethyl substitution (DS) is 0.7, which is the number of substituents per sugar ring. Divinylsulfone was purchased from Kanto Chemical, Co. Inc. Potassium hydroxide (KOH) and acetone were purchased from E-Merck and used as received. The chemical structures of CMCNa and HEC are presented in Figure 1.

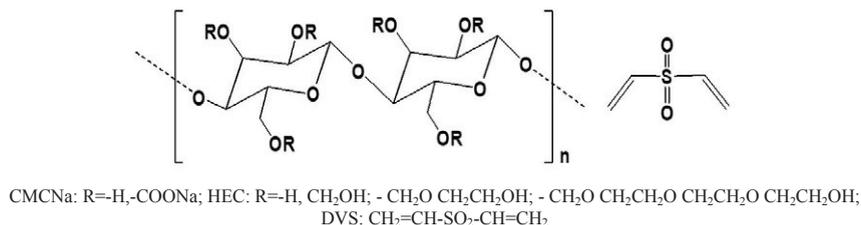


Fig. 1. The cellulose derivatives repeating unit and DVS

### 2.2. Sample preparation

Crosslinking reaction was performed according to procedures reported in the literature [17]. First, liquid divinylsulfone was added to the distilled water, stirring gently at room temperature until complete dissolution for 5 minutes. Batches with divinylsulfone concentration of 0.04 M were prepared in order to obtain samples with various degree of crosslinking. A mixture of CMCNa and HEC has been added to divinylsulfone water solution until a concentration of 2% by weight. Four different CMCNa/HEC weight ratios (1/1, 3/1, 5/1 and 10/1) have been investigated. A mixture of CMCNa and HEC was dissolved in a divinylsulfone aqueous solution by vigorous stirring at room temperature until a transparent solution was obtained. After stirring, an aqueous solution of KOH (1 M) was then added to catalyze the polymer reaction. In a few hours, a partially swollen hydrogel was obtained. To remove unreacted divinylsulfone,

excess amount of KOH and other impurities, the obtained hydrogel was cut in small pieces and then soaked several times in fresh distilled water until equilibrium swelling was reached under continuous stirring. Microporous xerogel was finally prepared by desiccating swollen hydrogel samples by phase inversion with acetone, as reported for different cellulose-based hydrogels [10,18]. A further desiccation stage in an air atmosphere at room conditions allows the elimination of the residual acetone.

### 2.3. Characterization

Infrared spectra samples were taken as KBr pellets using IR Prestige-21 Shimadzu spectrophotometer. The thermal properties were measured by using Seiko SSC 5200H TG/DTA 200 system. The samples were heated from room temperature to 550 °C at a heating rate of 10 °C/min using nitrogen gas at a flow rate of 260 mL/min. The micrographs of samples were taken using scanning electron microscope (SEM JSM-6360LA, JEOL, Ltd) after coating the sample with gold film.

### 2.4. Swelling analysis

The water absorption capability of hydrogel was measured by tea bag method using nylon fabric [19]. The hydrogel (approximately 100 mg) was weighed and poured in the nylon bag. The open side of the nylon bag was closed. The nylon bag was then immersed into the distilled water to swell. After the suitable period, the nylon bag was taken out from the water. The nylon bag was hanged for 15 min to remove the excess water and then weighed to determine the amount of distilled water absorbed into the hydrogel. Equilibrium swelling measurements in distilled water were carried out for all the samples using an electronic microbalance (Adam AAA 250L) with an accuracy of  $\pm 10^{-4}$  g. Reported values of equilibrium water uptakes for each different samples have been averaged over 3 independent measurement after about 24 h. The water uptake is expressed in terms of swelling ratio ( $Q$ , g/g) and defined as follow:

$$Q = (W_t - W_o - W_n) / W_o \quad (1)$$

Where  $W_n$  is the weight of nylon cloth,  $W_o$  is the weight of the dry hydrogel, and  $W_t$  is the weight of the swollen hydrogel.

## 3. Results and Discussion

### 3.1. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of polymeric networks synthesized were studied to investigate the crosslinking reaction qualitatively. The infrared spectroscopy was used to determine the type of bonds or functional groups present in the hydrogel. Infrared spectra indicated that the crosslinking process resulted the hydrogel contained sulfone group ( $-\text{SO}_2$ ). New absorption peaks at 1016 and 1098  $\text{cm}^{-1}$  arises from S=O symmetric stretching vibration. Absorption peaks at 755 and 826  $\text{cm}^{-1}$  are attributed to S-C stretching vibration [20].

### 3.2. Thermal analysis (TGA)

Thermogravimetry analysis (TGA) is a process in which materials are decomposed by heat, which causes bonds within the molecule to be broken. TGA plays an important role in determining thermal

stability of the materials. TGA curves are presented in Figure 3. The TGA curves show that the thermal stability of the blend samples changes within the reaction of crosslinking. The thermal degradation is completed in two steps. These steps are distinguishable in the diagram of weight loss during heating. All the thermogravimetric analysis (TGA) of CMCNa and crosslinked CMCNa/HEC hydrogel were studied by comparing their thermogram curves as shown in Figure 3. As the temperature increased from 100 °C to 170 °C the weight loss of CMCNa and crosslinked CMCNa/HEC hydrogel indicating the loss of moisture present in these samples [21]. From the curves the temperature of decomposition ( $T_D$ ) were found to be 285.5 °C (weight loss 68.2%) for CMCNa and 276.6 °C (weight loss 56.8%) for crosslinked CMCNa/HEC (5/1) hydrogel. It is to be noted that the peak temperature of the main degradation step was shifted to lower temperature compared to pure CMCNa. This is an indication that CMCNa is more stable than crosslinked CMCNa/HEC and the crosslinking structure plays an important role in the thermal decomposition process.

The initial decomposition temperature and the temperature at the maximum decomposition rate of step were obviously lower than those corresponding to CMCNa. The temperature for 10% weight loss of CMCNa/HEC crosslinked hydrogel was also lower than that of CMCNa. The results indicated that the introduction of HEC to polymer network resulted in a decrease in thermal stability. It could be concluded that the thermal stability of the CMCNa/HEC crosslinked hydrogel was lower than that of CMCNa.

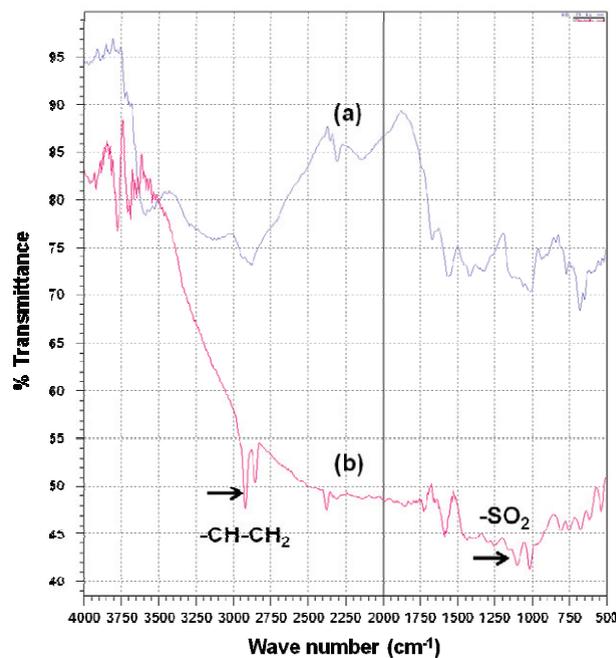


Fig. 2. Infrared spectra of the CMCNa/HEC mixture before (a) and after crosslinking (b)

### 3.3. Swelling studies

With the aim of investigating the effect of different degrees of crosslinking on the material's sorption properties, equilibrium swelling measurements in distilled water were performed on hydrogel samples. The measurements obtained on four different weight ratio CMCNa/HEC (1/1; 3/1; 5/1 and 10/1) in the 2% polymer solution and 0.04 mol/L divinylsulfone. The resulting swelling ratios were displayed in

Figure 4. Figure 4a showed how the water uptake capability for hydrogel increased with increased content of CMCNa, due to the presence of ionic group on CMCNa. However, the highest water uptake capability cannot be obtained by as high as CMCNa concentration. This was because over a critical CMCNa concentration intramolecular crosslinking sets in gelation was not attained [10]. That it took about 10 minutes to reach the steady state of absorption for all samples, but the maximum water uptake capability was obtained from sample with CMCNa/HEC 5/1 ratio.

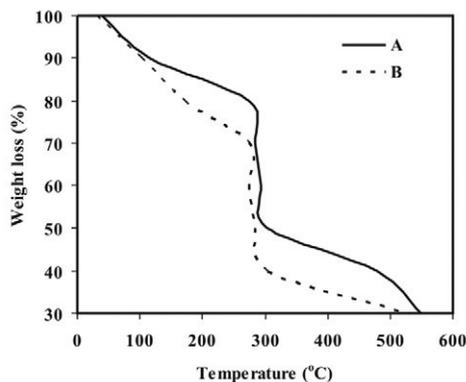


Fig. 3. TGA thermograms of (A) CMCNa and (B) CMCNa/HEC hydrogels

It can be seen from Figure 4b that it took about 10 min to reach the steady state of absorption at both of reaction temperatures, i.e. room temperature and 60 °C. For the polymer obtained at the reaction temperature of 60 °C the water absorption was greater than the degree of swelling. This phenomena indicated that there were interactions during the crosslinked reaction at 60 °C between polymer and the crosslinking agent divinylsulfone.

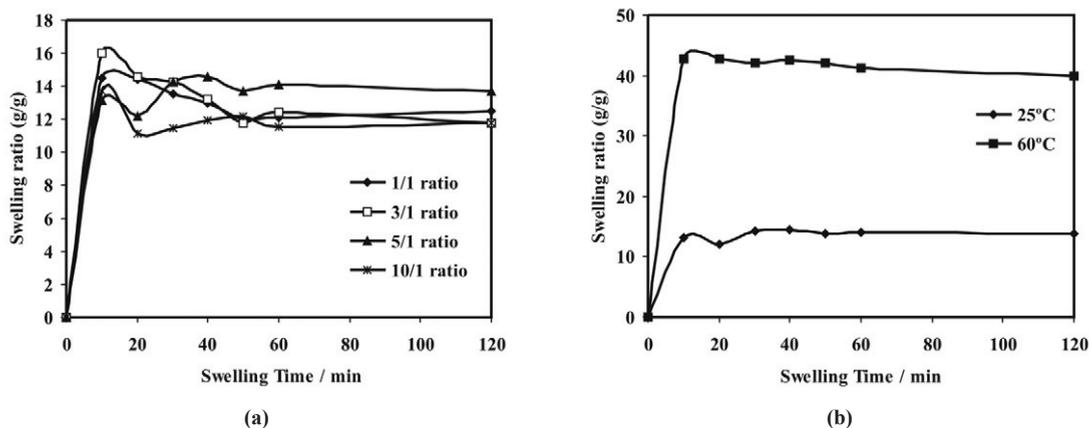


Fig. 4. (a) Water absorption rate of a sample obtained starting from equal reaction condition at room temperature for 6 h for different CMCNa/HEC ratio; (b) Effect of reaction temperature on the swelling ratio at the ratio CMCNa/HEC of (5/1).

The effect of the chemical composition and reaction temperature on the equilibrium water uptakes swelling capacity is showed in Figure 5a. Reaction temperature affected the equilibrium water uptake, since the crosslinking reaction at 60 °C occurred effectively compared with the same reaction at room

temperature. Examining further Figure 5b, it is shown that equilibrium water uptake of sample after crosslinking at different polymer composition, i.e. at CMCNa/HEC ratio 3/1 and 5/1 for 3, 6 and 8 h, respectively. It can be seen that increasing of reaction time for 8 h has resulted more increase of the hydrogel swelling capacity until more than 90 g/g for sample with CMCNa/HEC ratio 5/1.

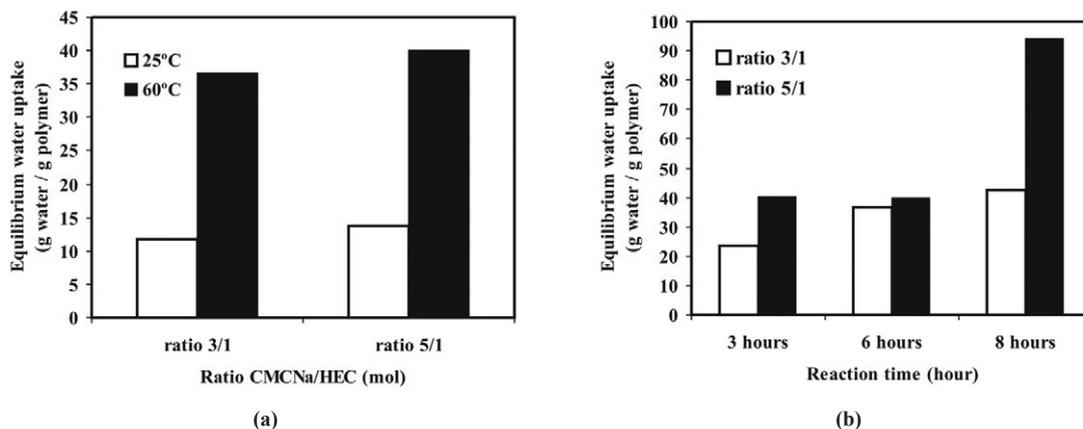


Fig. 5. Equilibrium water uptake as a function of (a) CMCNa/HEC ratio for a sample obtained starting from equal reaction time (6 h) and divinylsulfone concentration at different reaction temperatures; (b) reaction time for a sample obtained starting from equal temperature (60 °C) and divinylsulfone concentration at different CMCNa/HEC ratios.

### 3. 4. Morphological analysis

The micrographs of crosslinked CMCNa/HEC before and after swollen in distilled water are showed in Figures 6a and b, respectively. Dry crosslinked polymer showed a microporous structure with some long microtubes. This unique structure enhances its swelling capability due to capillarity effects as well as to the fact that part of the water condensates in the microvoids whose dimension further increases after polymer swelling [10]. The micrograph of swollen polymer was measured after frozen in the liquid nitrogen, Figure 6b. The swollen polymer showed dense and compacted structure and the pores in the CMCNa/HEC polymer was covered by water.

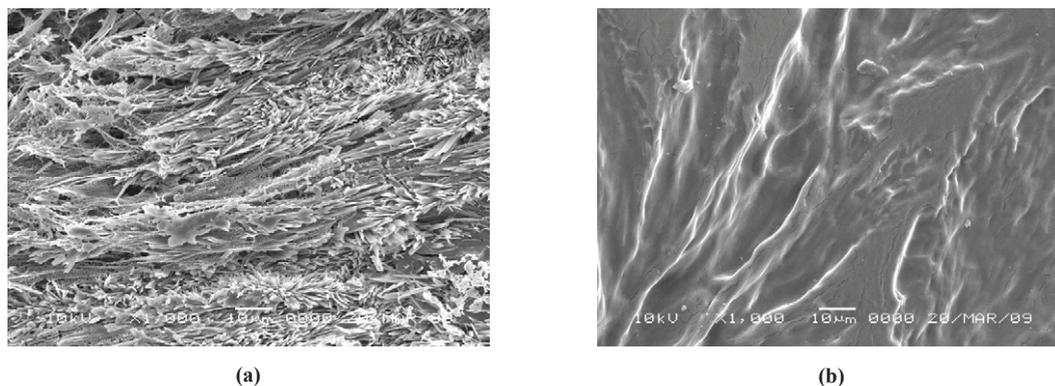


Fig. 6. SEM pictures of the polymer (a) before swelling and (b) after swelling

#### 4. Conclusion

Reaction parameters such as temperature, reaction composition of CMCNa/HEC ratio and reaction time affected the hydrogel water uptake. Water uptake capability was increased by increasing the temperature and reaction time. The CMCNa/HEC hydrogel exhibit lower thermal stability than the pure CMCNa polymer.

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