



Preparation and Characterization of Hydrogels from Grafting of Vinyl Pyrrolidone onto Carboxymethyl Cellulose

Ahmad, M. B.^{1*}, Hashim, K. B.², Mohd Yazid, N.¹, and Zainuddin, N.¹

¹Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

²Polymer Technology Division, Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia

ABSTRACT

In this work, hydrogels were prepared from carboxymethyl cellulose (CMC) and 1-vinyl-2-pyrrolidone (VP) by Electron Beam irradiation in the presence of N,N'-methylenebisacrylamide (BIS) as a crosslinking agent. The parameters studied include stirring time and percentage of crosslinking agent. Hydrogels were characterized using Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). VP and BIS were found to be effective as reinforcement materials to improve the properties of CMC. Meanwhile, the optimum conditions were 5% BIS and 3 hours of stirring time. The gel fraction increased when irradiation dose was increased. FTIR confirmed the crosslinking reaction between CMC and VP after the irradiation process by using BIS as the crosslinking agent. TGA thermograms showed changes in the thermal properties of CMC-VP hydrogels in the presence of different amounts of BIS.

Keywords: EB irradiation, crosslinker, carboxymethyl cellulose, vinyl pyrrolidone, hydrogels

INTRODUCTION

Hydrogels are a special class of cross-linked polymers which can be prepared using different polymerization techniques. Using the radiation technology, polymerization

procedure, the crosslinking structure and also cross-linked density of the hydrogels could be easily controlled (Sahiner *et al.*, 2005). Electron beam irradiation has many advantages including a relatively short processing time, in-line processing, high effectiveness, low equipment cost, and increased available energy (Choi *et al.*, 2008). The advantage of hydrogel formation by radiation-induced crosslinking is that the process can be done in water under mild conditions (i.e. room temperature and physiological pH) (Hennink & van

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Email addresses:

mansorahmad@science.upm.edu.my (Ahmad, M. B.),

kbhashim@nuclearmalaysia.gov.my (Hashim, K. B.),

ifahyazid@gmail.com (Mohd Yazid, N.),

hazlin@science.upm.edu.my (Zainuddin, N.)

*Corresponding Author

Nostrum, 2002). Therefore, radiation method is an excellent tool for fabrication of materials for wound dressing, drug delivery and biomedical applications.

Hydrogels are used for a variety of applications such as biomaterials, controlled release devices and superabsorbent materials. Hydrogels derived from natural polymers, such as polysaccharides and poly(amino acids), are desirable from the viewpoint of environmental conscious technology (Zhao *et al.*, 2008).

The use of polysaccharides alone is hampered due to the high solubility in aqueous medium leading to premature release of drug (Nizam El-Din *et al.*, 2010). CMC is similar with other natural cellulosic polymers and a degradable polymer which can be crosslinked to form a hydrogel. However, CMC hydrogels have very poor mechanical strength which limits their applications. The synthetic polymer is used to overcome the disadvantages of CMC. The uncross-linked homopolymers poly(vinyl pyrrolidone) (PVP) is a water-soluble material that has been extensively used as a blood plasma extender, and currently serves as an additive in a variety of pharmaceutical products.

In this work, hydrogels were prepared using carboxymethyl cellulose (CMC), 1-vinyl-2-pyrrolidone (VP) and N,N'-methylenebisacrylamide (BIS). The effects of stirring, irradiation dose and amount of crosslinking agent were also studied. The hydrogels were analyzed using Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM).

MATERIALS AND METHODS

Materials

Sodium salt CMC with a degree of substitution (DS) 1.2 and MW 250 000 were supplied by Acros Organic, New Jersey, US. VP (assay 97%) and BIS, as cross-linking agent were supplied by Fluka Chemicals, Buchs, Belgium. 2,2-dimethoxy-2-phenylacetophenone (DMPA), purity 99% was used as photo initiator agent was purchased from Acros Organic, New Jersey, US. Deionised water was also used throughout the experiment.

Preparation of the Hydrogels

The samples were prepared according to previous study (Ibrahim *et al.*, 2007) by dissolving the CMC in 100 ml deionised water and leave it overnight. Then VP and BIS were added into the solution and stirred to form homogeneous pastes. The total polymer weight was 20 g. The homogeneous pastes were then transferred into a plastic mould which was then inserted into a plastic bag. The plastic bag, together with the plastic mould and paste, was vacuum-sealed to remove air. The irradiation of the paste-like mixture was carried out via electron beam irradiation. An electron beam accelerator EPS 3000 with beam current of 10 mA and acceleration energy of 2 MeV was used for irradiation of the sample from 5 to 25 kGy. The effect of stirring time was studied on the samples with ratio CMC:VP 50:50 and 5% BIS. The samples were stirred for about 1 to 5 hours to form a homogeneous mixture, and irradiated at 10 kGy and 20 kGy. The effect of the crosslinking agent on the mixture was studied by varying the percentages of BIS, i.e. between 3 to 7% of the total weight of monomer at the optimum stirring time.

Determination of Gel Fraction and Swelling Behaviour of the Hydrogels

The percentage of the gel content was determined using the method used by Yoshii *et al.* (2003). The irradiated hydrogels were first weighed, loaded in a tea bag and soaked in distilled water for 48 hours. The soluble parts, namely uncross-linked CMC and VP, were extracted into the water during this period and the cross-linked hydrogels remained inside the tea bag. The samples were then dried at 60°C until a constant weight was obtained. The percentage of the gel content was calculated using the following equation:

$$\text{Percentage of the gel content (\%)} = (W_d/W_i) \times 100 \quad (1)$$

where W_d and W_i are the weight of the insoluble parts after extraction with water and the weight of the initial dried hydrogels after irradiation, respectively.

Meanwhile, swelling ratio was measured by swelling the hydrogels in deionised water at room temperature. The amount of the water absorbed was reported as a function of soaking period.

Characterization of the Hydrogels

The characterization of the hydrogels was carried out using Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

The Effect of Stirring Time on Gel Fraction

Fig.1 shows the effect of stirring time on the gel fraction of CMC: VP (50:50) at 10 and 20 kGy with 5% BIS. It shows that the gel fraction for both doses increases with stirring time. This means prolonging the stirring time gives higher homogeneity of CMC and VP mixture. The optimum gel fraction was obtained at 3 hours stirring time and remained constant. On the contrary, extending the stirring time does not contribute to higher gel fraction since it may cause oxidation process towards VP.

The Effect of Crosslinking Agent on Gel Fraction

The effect of crosslinking agent, BIS, on the composition CMC:VP (50:50) at 10 and 20 kGy with 3 hour stirring time is shown in Fig.2. The gel fraction for 10 and 20 kGy increases with the increase in the amount of the crosslinking agent and reaches the maximum value at 5% of BIS. The preliminary result showed that there was no formation of hydrogels obtained at 1 and 2% of BIS. Meanwhile, the gel fraction increases rapidly from 3 to 5% of BIS where the maximum crosslink is at 5% of BIS, but with no significant increase at 6% and 7% of BIS. In addition, the gel fraction at 20 kGy is higher than 10 kGy due to the increase in the degree of crosslinking. The use of the crosslinking agents *in situ* with electron beam radiation in the preparation of hydrogels has been discussed in a previous study (Ibrahim *et al.*, 2007).

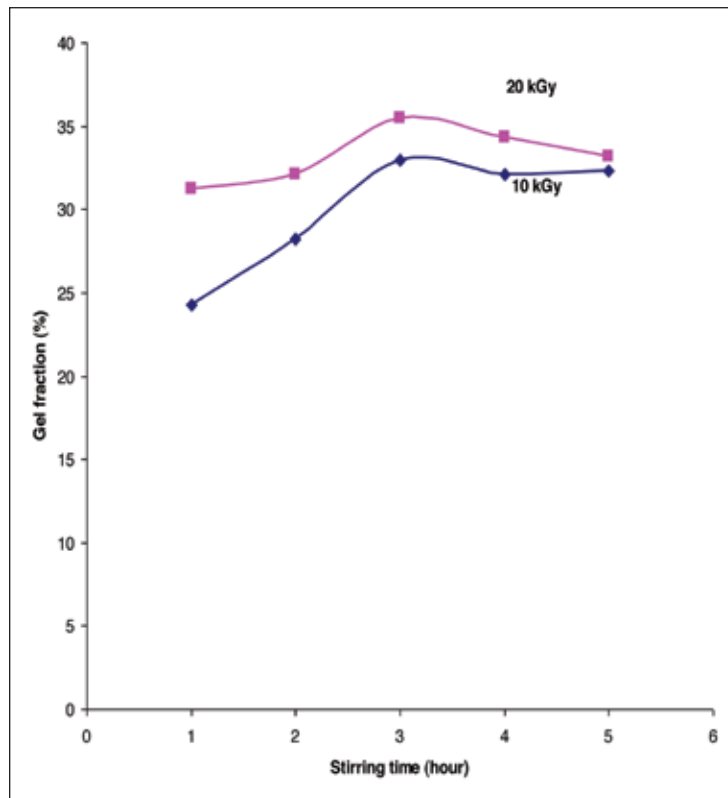


Fig.1: The effect of stirring time on gel fraction at composition CMC:VP (50:50) at 10 and 20 kGy

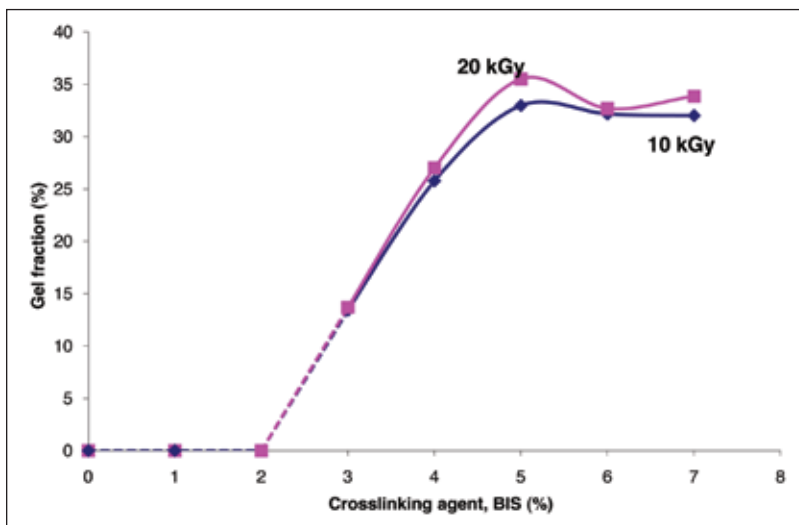


Fig.2: The effect of crosslinking agent on gel fraction at composition CMC:VP (50:50) at 10 and 20 kGy with 3 hours of stirring time

The Effect of Stirring Time on Swelling Behaviour

The effect of stirring time on the swelling behaviour of composition CMC:VP (50:50) at 10 and 20 kGy with 5% BIS is illustrated in Fig.3. The degree of swelling decreases with the increase in the stirring time up to 3 hours before levelling off. The degree of swelling for hydrogels irradiated at 10 kGy is higher than for those at 20 kGy, which is related to the degree of crosslinking.

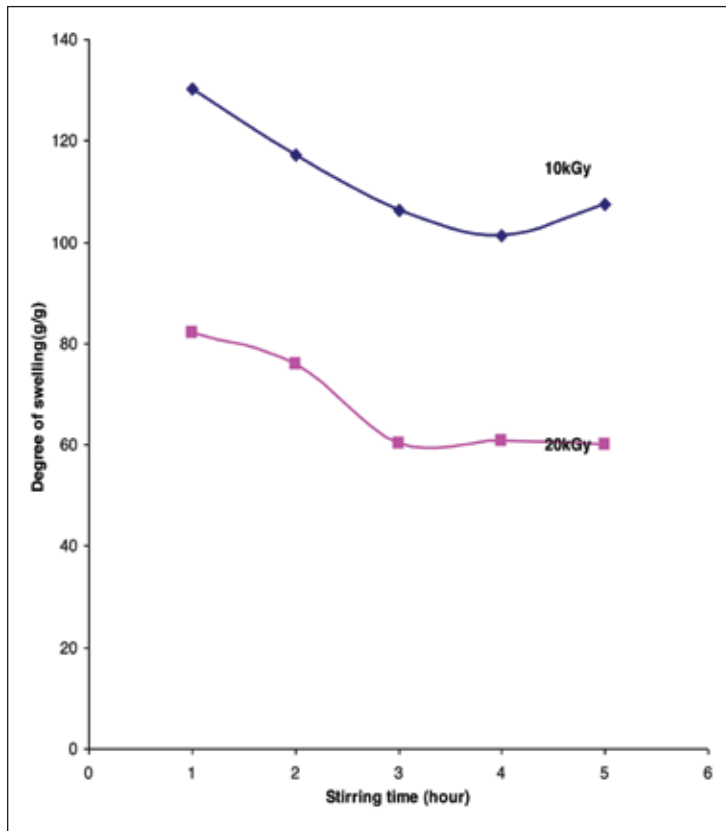


Fig.3: The effect of stirring time on swelling behaviour at composition CMC:VP (50:50) at 10 and 20 kGy with 5% BIS

The Effect of Crosslinking Agent on Swelling Behaviour

The effects of crosslinking agent on the swelling behaviour of 50:50 (CMC:VP) hydrogels at 10 and 20 kGy with the optimum stirring time (3 hours) are shown in Fig.4. There is no hydrogel formed at 1- 2% BIS and the maximum degree of swelling is obtained at 3% of BIS. When the amount of the crosslinking agent increases, the crosslink density also increases, and this leads to a more compact polymeric network, reduces the pore size and consequently decreases the amount of water uptake (Pourjavadi *et al.*, 2006; Singh *et al.*, 2007).

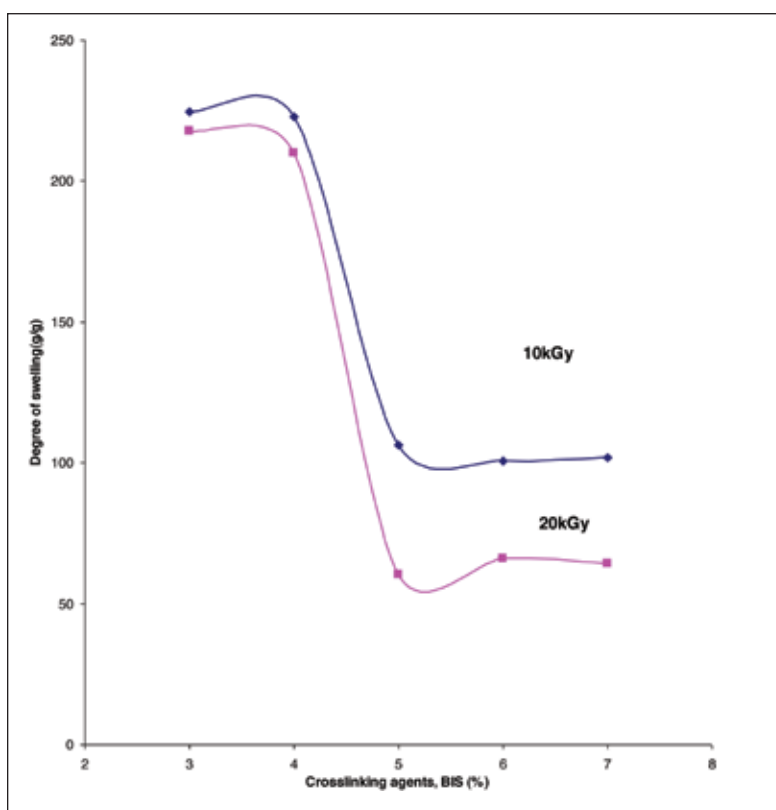


Fig.4: The effect of the crosslinking agent on swelling behaviour at composition CMC:VP (50:50) at 10 and 20 kGy with 3 hours of stirring time

Fourier Transform Infrared Spectroscopy

Fig.5 shows the FT-IR spectra of CMC hydrogels at 10 kGy, CMC, VP, CMC:VP (50:50) without BIS at 10 kGy and CMC:VP (50:50) with BIS at 10 kGy. For all the spectra, a broad band occurs at 3000-3500 cm^{-1} and it corresponds to the O-H stretching vibration of hydroxyl group and molecules of water in all the samples. The characteristic absorption band of CMC hydrogels is similar to pure CMC, which is at 1587 cm^{-1} , due to the peak assigned by C=O stretching vibration of the carbonyl group (COO-) group. The intensity of the hydrogen bonding of CMC increases as a result of the polymerization of PVP, as indicated by the very wide broad absorption band at 3000-3500 cm^{-1} . The formation of the hydrogen bonding between the carboxylic and with the non-substituted hydroxyl group of cellulose molecule has been shown to be directly due to the crosslinking reaction between CMC and VP (Taleb *et al.*, 2009).

Morphology Study

Fig.6 shows the SEM micrographs of the fracture surface cross-section of (a) CMC hydrogels at 10 kGy, (b) CMC:VP (50:50) at 10 kGy, and (c) CMC:VP (50:50) at 20 kGy for 400x magnification at the optimum condition. The morphology of the hydrogels confirms the higher swelling behaviour of the hydrogels at 10 kGy as compared to hydrogels at 20 kGy, as shown

previously. The average pore sizes for CMC hydrogels (a) and (b) are $64.77 \mu\text{m}$, $65.18 \mu\text{m}$ and (c) $49.01 \mu\text{m}$, respectively. The decrease in the pores size may be due to the higher degree of crosslinking at a higher irradiation dose.

When the pores in contact with water molecules are small, the water-uptake capacity will be reduced. This finding also confirms the result of gel fraction, whereby the gel fraction increases with the increase of irradiation dose. It was also found that CMC:VP hydrogels

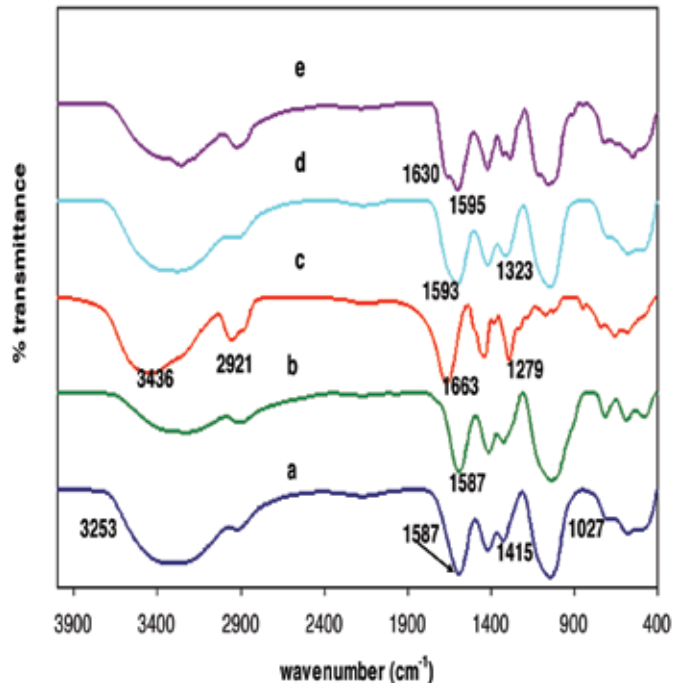


Fig.5: The FT-IR spectra of (a) CMC hydrogels at 10 kGy, (b) CMC, (c) VP, (d) CMC:VP (50:50) without BIS at 10 kGy and (e) CMC:VP (50:50) with BIS at 10 kGy

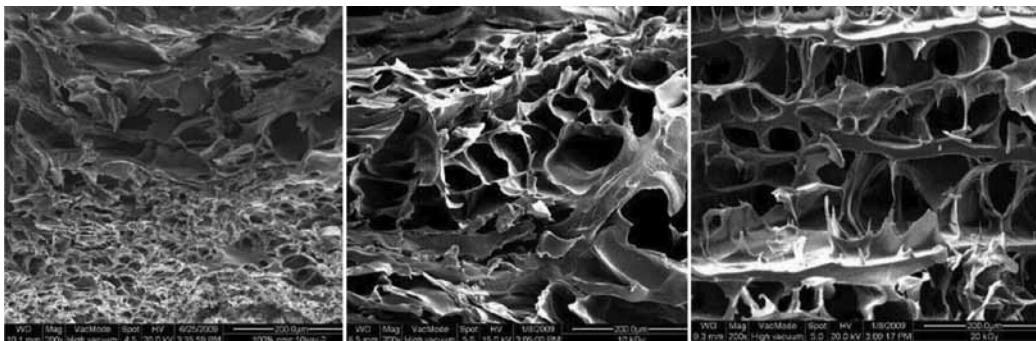


Fig.6: The SEM micrographs of the fracture surface cross-section of (a) CMC hydrogels at 10 kGy, (b) CMC:VP (50:50) at 10 kGy and (c) CMC:VP (50:50) at 20 kGy with 3 hours of stirring and 5% of BIS, 200x magnification

have more homogeneous distribution of pores and uniform pore size than CMC hydrogels. It is also assumed that the presence of VP in the formulation contributes to the homogeneity and uniformity of the morphology of the hydrogels.

CONCLUSIONS

This study revealed the potential for VP and BIS as reinforcement materials to increase the properties of CMC. The optimum amount of BIS as a crosslinking agent to increase the gel fraction was 5%. Meanwhile, the optimum stirring time was 3 hours. The gel fraction was found to increase with irradiation dose. FTIR confirmed the crosslinking reaction between CMC and VP via irradiation technique and BIS as the crosslinking agent.

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