

## Preparation of Carboxymethyl Sago Pulp Hydrogel from Sago Waste by Electron Beam Irradiation and Swelling Behavior in Water and Various pH Media

Vengidesh Pushpamalar,<sup>1</sup> Steven James Langford,<sup>2</sup> Mansor Ahmad,<sup>3</sup> Kamaruddin Hashim,<sup>4</sup> Yau Yan Lim<sup>1</sup>

<sup>1</sup>School of Science, Monash University Sunway Campus, Jalan Lagoon Selatan, 46150 Bandar Sunway, Petaling Jaya, Selangor, Malaysia

<sup>2</sup>School of Chemistry, Monash University, Clayton, VIC 3800, Australia

<sup>3</sup>Department of Chemistry, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>4</sup>Radiation Modification of Polymer Group, Radiation Processing Technology Division, Malaysian Nuclear Agency, Bangi 43000 Kajang, Selangor, Malaysia

Correspondence to: V. Pushpamalar (E-mail: Pushpa.Janarthanan@monash.edu)

**ABSTRACT:** Solutions of carboxymethyl sago pulp (CMSP) of various degree of substitution were irradiated with electron beam of various radiation doses. The gelation dose ( $D_g$ ) and  $p_o/q_o$  ratio ( $p_o$  is degradation density,  $q_o$  is crosslinking density) is dependent on CMSP concentration and degree of substitution. In the range of concentrations of 10% to 80% (w/v) CMSP with degree of substitutions of 0.4, 0.6, and 0.8, the  $p_o/q_o$  ratio decreases with increasing %CMSP showing that crosslinking processes are dominating and increasing the gel network of the CMSP hydrogel. The fourier transform infrared spectra of CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 with percentage of gel fractions 25, 35, and  $\geq 40$  show differences in the intensity of the absorption bands at 1020–1100, 1326, and 1422  $\text{cm}^{-1}$  with different degree of substitutions and percentage of gel fraction (%GF) that correspond to different extents of chain scission and crosslinking. The swelling behavior in water shows that CMSP hydrogels could absorb 3500–5300% of water by 1 g of CMSP hydrogel. The ability to absorb water increases with the decrease of degree of substitution and %GF of the CMSP hydrogels. It is also observed that the optimum pH for swelling CMSP hydrogel is at pH 7. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** CMSP hydrogel; electron beam irradiation; crosslinking; sago pulp; FTIR

Received 18 January 2012; accepted 11 June 2012; published online

**DOI:** 10.1002/app.38192

### INTRODUCTION

Polysaccharides have been intensively researched due to their sustainability, biodegradability, and biosafety.<sup>1</sup> Modified polysaccharides such as carboxymethyl starch,<sup>2</sup> carboxymethyl cellulose (CMC),<sup>3,4</sup> carboxymethyl chitosan,<sup>5</sup> carboxymethyl chitin,<sup>6</sup> sodium alginate,<sup>7</sup> carrageenan,<sup>8</sup> and other agricultural wastes can be modified by irradiation for the production of biodegradable hydrogels. Hydrogels of natural polysaccharides are nontoxic, biodegradable, and biocompatible. This hydrogels are of great interest because of their applications in biomedicine and pharmaceutical,<sup>3,9,10</sup> bioengineering,<sup>11</sup> food industry,<sup>12</sup> biotechnology,<sup>13</sup> agriculture<sup>6,14</sup> and other fields.<sup>15</sup> Naturally occurring biomaterials such as collagens, gelatin, alginate, chitosan, and fibrins are used as biomaterials which are capable of adjusting to targeted *in vivo* microenvironment and may also have an advantage of inducing mild inflammatory responses *in vivo*. The composition of natural biomaterials exhibits batch-to-batch var-

iations. The variations and the mechanical properties have not been completely characterized and potential immunogenic properties of such materials may pose additional problems. Thus, there is important to develop and design novel modified biomaterial with optimized physical properties and desirable performance for use as polymeric scaffolds.<sup>16</sup> Biomaterial prepared using radiation technique where immobilization of biologically active species in hydrogel matrices, their use as drug delivery systems and enzyme traps and modification of material surfaces to improve their biocompatibility and ability to bond antigens and antibodies have been the subject of their researches.<sup>9</sup> Hydrogels have been widely used as intelligent carriers in controlled drug delivery systems where the researchers have optimized their properties such as permeability, environmental responsive nature, surface functionality, biodegradability, and surface bio recognition sites.<sup>11</sup> Hydrogel for wound dressings prepared by radiation crosslinking have been used on patients in

the Navy 411 Hospital. From 60 case studies of the clinical effects, the result showed that slow drug releasing relieves the pain effectively for prolonged period of application. The dressing can reduce wound oozing, make the wound heal faster, and reduce number of dressing changes required.<sup>17</sup>

The radiation technique is used to prepare hydrogels because polymer solution undergoes crosslinking on radiation and forms gel like material. This technique has advantages of relatively low costs and not requiring chemicals such as initiators or crosslinker.<sup>15</sup> The gel-sol analysis of irradiated polymers allows the estimation of important radiation parameters such as yield of crosslinking and degradation, gelation dose, and the correlation of these with some physicochemical properties. The sols are dispersions of colloidal particles in the liquid and the gel is an interconnected rigid network with pores and polymeric chains with average lengths greater than micrometer. These crosslinked polymers with high equilibrium swelling in water or aqueous solutions can be based on macromolecules with high hydrophilicity and flexibility, often in combination with the polyelectrolyte nature of chains. Great attention has been given to the application of superabsorbent hydrogels in agriculture for soil improvement and plant growth. Superabsorbent hydrogel particles distributed in soil are capable of absorbing water and as a result, this should efficiently improve the water holding capacity of the soil and promote optimal plant growth.<sup>13</sup>

The cellulose derivative, CMC when exposed to high-energy radiation would undergo ionization which eliminates electrons creating excited fragments of CMC polymers called CMC macroradicals. Macroradicals are formed on main or side chains of CMC. The formation of radicals on the main chain occurs on C1-C6 atoms of the anhydroglucose repeating unit of cellulose. The macroradicals placed on main chain initialized a random cleavage of glycoside bonds in the main chain which leads to chain scission. The macroradicals formed on the side chains are responsible for intermolecular crosslinking.<sup>18–20</sup>

In Sarawak, Malaysia, sago palms (*Metroxylon sago*) are inexpensive and grow well in swampy areas that are in urgent need of economic development. Sago pulp (57% w/w) isolated from sago waste was converted to carboxymethyl sago pulp (CMSP) by etherification using sodium monochloroacetate and sodium hydroxide.<sup>21,22</sup> The objectives of this article are to report on the preparation of CMSP hydrogel from sago waste by electron beam irradiation and investigate the swelling behavior of formed CMSP hydrogel in water and various pH medium with respect to the degree of substitution and crosslinking density of CMSP hydrogel. The intention is to produce pure CMSP hydrogel without adding other polymer or crosslinker.

## EXPERIMENTAL

### Materials

Sago waste was supplied by PPES Sago Industries (Mukah) Sdn Bhd., Sarawak. All the chemicals being used for this research study were analytical grade. General solvents were obtained from John Kollin Corporation, United Kingdom and industrial grade ethanol was obtained from HmbG Chemicals, Germany. Distilled water was used for all aqueous solution preparations.

### Isolation of Sago Pulp from Sago Waste

Sago waste was oven dried for 3 h, ground using a stainless steel blender and sieved through a 0.5 mm<sup>2</sup> test sieve. The ground sago waste was predried in the oven at 60°C for 1 h. About 5 g of sago waste was added into a 500 mL Erlenmeyer flask and suspended in hot distilled water (160 mL) together with glacial acetic acid (1 mL). Technical grade sodium chlorite (1.5 g) was then added. The conical flask was stoppered and heated in a water bath maintained at 70°C over a period of 3 h. The final residue was an almost white solid that retained the woody structure of the original sample. The mixture was filtered using a Buchner funnel and washed with cold distilled water until the pH of the filtrate was 7.0. The residue was dried in an oven at 60°C to constant weight.<sup>21,22</sup>

### Preparation of CMSP from Sago Pulp

CMSP was prepared by etherification of sago pulp with NaOH, sodium monochloroacetate and the solvent used in this study was 2-propanol.<sup>21,22</sup>

**Preparation of CMSP of Degree of Substitution 0.4.** Dried sago pulp (5.0 g, 30.9 mmol cellulose) was added into 2-propanol (100 mL) and sodium hydroxide (30% w/v, 10 mL) was added in a drop-wise fashion. After stirring for 1 h, sodium monochloroacetate (3.0 g, 0.026 mol) was added and the reaction mixture placed in thermostated water bath with horizontal shaker. The reaction mixture was heated to 45°C and shaken for 3 h. Once complete, the mixture was filtered and the residue was suspended in methanol (300 mL) overnight. The suspended methanol solution was then neutralized using glacial acetic acid and the resultant residue was washed with 300 mL ethanol, filtered and dried to constant weight.

**Preparation of CMSP of Degree of Substitution 0.6.** The same procedure as for DS 0.4 except the quantity of sodium monochloroacetate was 6.0 g (0.052 mol) with a reaction time of 2 h.

**Preparation of CMSP of Degree of Substitution 0.8.** The procedure was the same as preparation of CMSP of degree of substitution 0.4 except for the basification process where NaOH was added (25% w/v, 10 mL) and the quantity of sodium monochloroacetate was 6.0 g (0.052 mol). The absolute values of DS were determined by potentiometric titration.<sup>21,22</sup>

### Preparation of CMSP hydrogels from CMSP

**CMSP Solutions Preparation and Irradiation Procedures.** Distilled water was added to CMSPs with degree of substitutions of 0.4, 0.6, and 0.8, which were then mixed until homogenous using a glass rod. For preparing high concentrations of CMSP solutions (above 20% (w/v) CMSP), CMSP were kneaded well and left for 24 h for complete dissolution. The CMSP mixtures were degassed before irradiation using a Henkovac vacuum. For free air irradiation, the CMSP mixtures were placed into polyethylene bags to make the process impermeable to air. After evacuation 15 mL of the mixture is spread evenly in a plastic mold and covered with a plastic sheet. Then the covered plastic mold was placed in polyethylene plastic bag and sealed using sealer machine.

In the CMSP hydrogel preparation, the irradiation of the CMSP mixture was carried out by electron beam generated from an

electron beam machine (2 MeV; model EPS-3000, 10 mA current) and various doses of irradiation were used.<sup>23</sup>

**Determination of Gel Content in CMSP Hydrogel with Various Degrees of Substitutions.** After electron beam irradiation, the CMSP hydrogels were accurately weighed ( $W_0$ ) and immersed in distilled water for 48 h and then dried in oven at 60°C to a constant weight ( $W_1$ ). The percentages of soluble fraction and gel fraction were calculated according to the following equations, respectively.<sup>24</sup>

$$\text{Sol fraction (\%)} = [W_0 - W_1] / W_0 \times 100 \quad (1)$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction} \quad (2)$$

The yield  $p_0/q_0$  ratio and gelation dose ( $D_g$ ) which is the minimum energy required to start the gelation process were estimated by gel-sol analysis on the basis of the Charlesby-Pinner equation.<sup>25</sup> Estimation of  $p_0/q_0$  and gelation dose  $D_g$  were performed with the computer tool GelSol95 (<http://mitr.p.lodz.pl/gelsol.html>) using the eq. (3) which allows plotting the relation between sol and dose in a form of straight line:

$$s + \sqrt{s} = p_0/q_0 + (2 - p_0/q_0)(D_g + D_v)/(D_v + D) \quad (3)$$

Here,  $s$  is the sol fraction,  $p_0$  is degradation density, average number of main chain scissions per monomer unit and per unit dose,  $q_0$  is the crosslinking density, proportion of monomer units crosslinked per unit dose,  $D_g$  is the gelation dose,  $D_v$  is the virtual dose, a dose required for changing the distribution of the molecular weight of the polymer in such a way that the relation between weight-average and number-average molecular weight would be equal to 2 and  $D$  is radiation dose.

#### Fourier transform infrared Analyses

The CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 with percentage of gel fractions of  $\geq 40$ , 35, and 25% were freeze-dried for two days. Upon completion, samples were ground together with KBr and a pellet was formed. FTIR analysis spectra with a range of 4000–360  $\text{cm}^{-1}$  were recorded by Perkin Elmer FTIR spectrophotometer (model Spectrum RX) in absorbance mode.

#### Swelling Behavior

**Swelling of the CMSP Hydrogel in Water.** From optimization of the conditions on preparing the CMSP hydrogel, Table I shows the conditions for preparing selected CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 and percentage gel fractions of 25%, 35%, and  $\geq 40\%$ . CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 with percentage of gel fractions of 25, 35, and  $\geq 40$  were subjected to swelling in distilled water. The swelling of the CMSP increases with time but reaches a limiting value which is proposed as the equilibrium value. It was found that all the CMSP hydrogels attained the equilibrium within 48 h.

The degree of swelling was determined by gravimetric method where the dried hydrogel was immersed in excess distilled water at room temperature. The hydrogels were periodically weighed after the excess surface water was removed by dabbing dry with

**Table I.** Preparation Conditions of CMSP Hydrogels with Various %GFs from CMSP Solutions with Degree of Substitutions of 0.4, 0.6, and 0.8.

CMSP	% CMSP	Radiation Dose (kGy)	% Gel fraction (%GF)
CMSP with DS 0.4	60	30	25
	70	25	35
	80	30	40
CMSP with DS 0.6	50	25	25
	70	30	35
	80	40	46
CMSP with DS 0.8	50	40	25
	70	30	35
	80	40	48

a filter paper. The swelling ratio was calculated according to the equation:

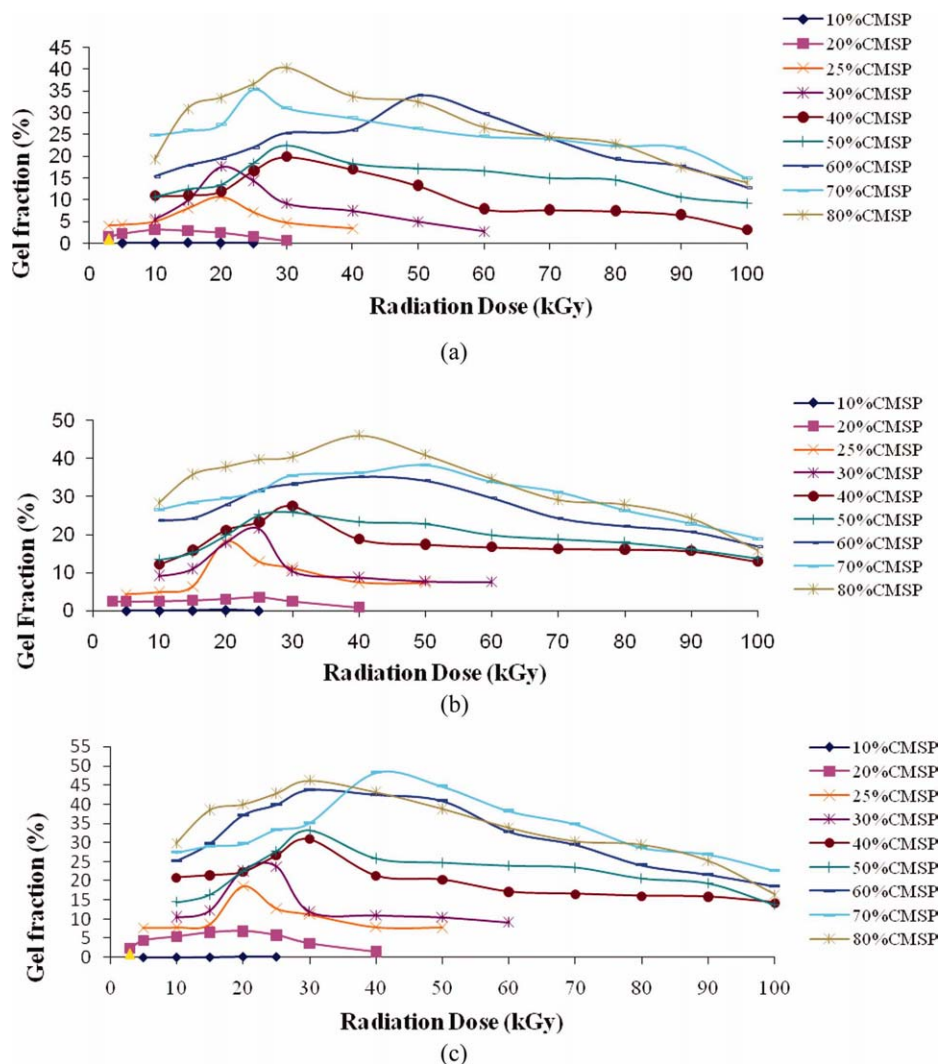
$$\%S = \frac{M_t - M_0}{M_0} \times 100 \quad (4)$$

where  $M_0$  is the mass of dry hydrogel at time zero and  $M_t$  is the mass of swollen hydrogel at time  $t$ . The equilibrium degree of swelling was calculated by changing  $M_t$  to  $M_e$  which is the equilibrium weight of the swollen gel.<sup>23,26,27</sup>

**Swelling of the CMSP Hydrogel in Various pH Media.** In order to investigate the sensitivity of the CMSP hydrogels to pH, the CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 with percentage of gel fractions of 25%, 35%, and  $\geq 40\%$  were immersed in excess buffer solutions at pH 3, 7, and 10. The hydrogels were periodically weighed after the excess surface water was removed with a filter paper. The swelling ratio was calculated using eq. 4.

## RESULTS AND DISCUSSION

In this research electron beam irradiation was used to crosslink CMSPs with degree of substitutions of 0.4, 0.6 and 0.8. The percentage of gel fraction is percentage of insoluble part (cross-linked CMSP) after immersion in distilled water. Figure 1(a) shows the percentage of gel fractions versus dose of irradiation for different concentrations of CMSP of degree of substitution of 0.4. At CMSP concentrations of 10–25% (w/v) homogeneous dilute solutions were formed and a maximum percentage of gel fractions of less than 10% (w/w) was achieved at 15 kGy. At concentrations of 30–40% (w/v) the CMSP solution was in the form of moderately viscous paste-like solution. The maximum percentage of gel fractions of 10–20% (w/w) was obtained at a radiation dose of 20 kGy. At concentration of 50–60% (w/v) CMSP, the maximum percentage of gel fractions obtained was only fractionally higher at 20–35% (w/w) and a higher dose of radiation (30 kGy) was required to achieve this result. At the



**Figure 1.** Electron beam radiation prepared CMSP hydrogel from CMSP solutions of degree of substitutions of (a) 0.4, (b) 0.6, and (c) 0.8 shows %GF (w/w %) with various radiation doses (kGy). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

highest concentrations of CMSP (70–80% w/v), the maximum percentage of gel fractions achieved was 35–40% (w/w) at 25–50 kGy.

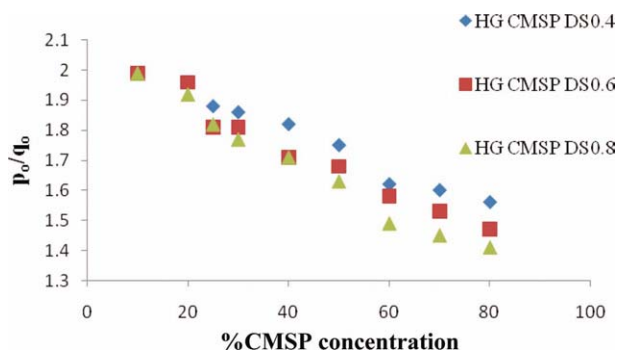
Figure 1(b,c) show the percentage of gel fractions for different concentrations of CMSP of degree of substitutions of 0.6 and 0.8 versus dose of irradiation, respectively. The same trends as for degree of substitution of 0.4 apply and the maximum percentage of gel fraction achieved with degree of substitution of 0.8 is on average higher than for the CMSP with degree of substitution of 0.6.

All CMSP mixtures of higher concentration (from 30–80% (w/v)) formed a paste like mixture. It was observed that the CMSP with degree of substitution of 0.4, at high concentration, was the hardest to knead to achieve a homogeneous mixture and was followed by degree of substitution of 0.6 and degree of substitution of 0.8. This could be attributed to the lower water solubility of the CMSP of degree of substitution of 0.4. It is important for the CMSP molecules to dissolve homogeneously in water for maximum crosslinking to occur. There are two ways that water contributes to the crosslinking of CMSP. First, it enhances the mobility of the rigid CMSP molecules allowing the diffusion of

CMSP macroradicals to decrease the distance between each radical and recombine. Second, during electron beam radiation it induces an increase in radical concentration by producing hydrogen atoms and hydroxyl radicals by water hydrolysis. These hydrogen and hydroxyl radicals abstract hydrogen from CMSP molecules and produce the CMSP macroradicals.<sup>23</sup> These macroradicals may undergo chain scission, hydrogen transfer, intermolecular, and intramolecular recombination and disproportionation of macroradicals. Recombination of CMSP macroradicals intermolecularly between two radicals on separate chains linked the chains together. Intramolecular recombination of CMSP macroradicals leads to formation of C—C bonds between the segments of a chain itself.<sup>28</sup>

At lower (5–30%) CMSP concentration, although the CMSP chain mobility is unrestricted, the distance between macroradical is too long to form crosslinking bond and therefore degradation occurs predominantly. These lower concentrations CMSP solutions also could undergo dehydrogenation, oxidative degradation, and depolymerization reactions and cause destruction of





**Figure 2.** The change of  $p_o/q_o$  ratio of chain scission to crosslinking yields for CMSP with degree of substitutions of 0.4, 0.6 and 0.8 hydrogels used in this work with initial CMSP concentrations. (HG = Hydrogel). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the CMSP chains when irradiated with high irradiation dose.<sup>29</sup> Study on electron beam radiation on different types of cellulose derivative shows that diluted solution and solid form of cellulose derivatives molecules are degraded under electron beam radiation but crosslinked under special conditions. The chemical gel can be produced by using high-energy electron beam radiation under mild conditions as paste-like solutions that do not degrade polysaccharides.<sup>23</sup> At lower CMSP concentration, there is also a possibility that the density of the macroradicals produced by the electron beam radiation is not high enough to recombine on different chains and the macroradicals then undergo a radiation degradation reaction.<sup>30</sup>

At moderate (40–50%) and high (60–80%) concentrations of CMSP, higher dose of electron beam irradiation is needed to achieve maximum percentage of gel fraction. At these concentrations of CMSP, two radicals of CMSP chains, formed upon electron beam irradiation, combined to form intermolecular crosslinking between them to result in an insoluble gel. At high concentration of CMSP, the macromolecules bearing the radicals are immobilized by restricted mobility during irradiation which favors the scission reactions. And also at high concentration of CMSP, the amount of water is insufficient to provide the indirect effect to enhance the combination of the CMSP macroradicals. At moderate and high CMSP concentrations, high electron beam dose rate may generate 10 or 100 of radicals simultaneously on each chain. Under these conditions, the probability and yield of intermolecular recombination is greatly reduced and intramolecular recombination occurs preferentially and therefore, reduces the crosslinking and reducing the percentage of gel fractions.<sup>30</sup>

A study on hydropropylmethylcellulose (HPMC) irradiated with electron beam by Pekel et al. (2004) gave a similar result with the current study. The result shows that the crosslinking against chain scission is dependent on the HPMC concentration. At low and high concentrations, the prevalence of chain scission over crosslinking is observed. In moderate concentration range of HPMC, the prevalence of crosslinking over chain scission was observed and high gel values were reported.<sup>29</sup>

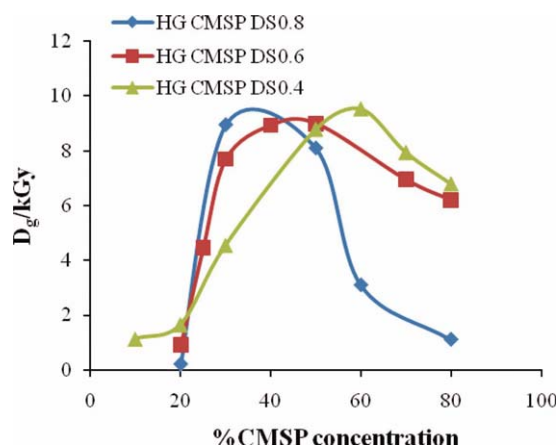
Previously a study made on various carboxymethyl cellulose (CMC) types and concentration by using electron beam radia-

tion showed that the maximum percentage of gel fraction was obtained in 60–80% (w/v) concentration – consistent with the findings herein. As crosslinking and scission occur simultaneously in the CMC mixture during irradiation, the yield of crosslinking,  $G_{(x)}$  and degradation  $G_{(s)}$  have an influence on the results of irradiation. The  $G$  value is the number of crosslink bonds or scission acts per 100 eV of absorbed energy. The yield (crosslinking and scission) values and  $D_g$  which is the minimum energy required to start the gelation process were estimated by gel-sol analysis on the basis of the Charlesby-Pinner equation.<sup>25</sup>

Figure 2 shows the  $p_o/q_o$  ratio, which measures the extent of chain scission against crosslinking, is dependent on CMSP concentration and degree of substitution. In the concentration range of 10% to 80% (w/v) CMSP with degree of substitutions of 0.4, 0.6, and 0.8, the  $p_o/q_o$  ratio decreases with increasing % CMSP showing that crosslinking processes is dominating on increasing the gel network of the CMSP hydrogel. The  $p_o/q_o$  ratio value of CMSP hydrogel decreases in the order degree of substitutions of  $0.4 > 0.6 > 0.8$  in all types of CMSP with same concentration. The trend suggests that the CMSP with degree of substitution of 0.8 has the highest crosslinking (lowest  $p_o/q_o$  ratio values) and least scission during the irradiation.

Figure 3 shows the gelation dose ( $D_g$ ) dependence on CMSP concentration and degree of substitution. The  $D_g$  is the minimum energy required to start the gelation process. In each case a pseudo parabolic shape is encountered with a unique maximum for each degree of substitution. The CMSP concentrations and maximum  $D_g$  required to start the gelation process of CMC with degree of substitutions of 0.4, 0.6, and 0.8 are 60, 50, and 30% and 9.54, 8.99, and 8.94 kGy, respectively. The results show that maximum  $D_g$  required decreases slightly as expected from degree of substitutions of 0.4 to 0.8. Crosslinking of CMSP with a high degree of substitution of (0.8) occurs at lower concentration (30%) and low degree of substitution of (0.4) needs a more concentrated solution (60%) to produce gel.<sup>23</sup>

The modified version of Charlesby equation (eq. 3) seems to be a useful and convenient tool for analyzing the results of gel-sol



**Figure 3.** The variation in  $D_g$  gelation dose yields for CMSP with degree of substitutions of 0.4, 0.6, and 0.8 hydrogels used in this work with initial CMSP concentrations. (HG = Hydrogel). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

investigations in any systems undergoing crosslinking. It may be preferable to choose a value of  $D_v$  from GelSol95 software which gives the closest approximation to a straight line (in coordinate  $s + \sqrt{s}$  versus  $(D_g + D_v)/(D + D_v)$  plot. In many cases this gives an accurate estimate of  $D_v$ , and the straight line plots also give  $D_g$  and  $p_o/q_o$ .<sup>31–33</sup>

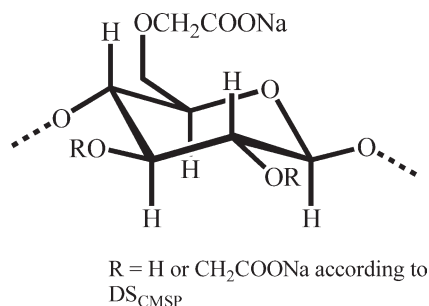
These results were consistent with a study on CMC with degree of substitutions of 0.7 to 2.2 which were irradiated with gamma radiation.<sup>23</sup> The study showed that the highest crosslinking occurred in CMC of DS 2.2 and gelation dose was lowest for the CMC with degree of substitution of 2.2 and followed by CMC with 1.29 and 0.86, respectively.

### FTIR Spectral Analysis of CMSP Hydrogels

The structure of CMSP is shown in Figure 4 and the IR spectra of CMSP hydrogels of various degrees of substitutions and percentage of gel fractions are shown in Figure 5. The strong absorption bands at  $1602\text{--}1617\text{ cm}^{-1}$  confirm the presence of the  $\text{COO}^-$  groups for all CMSP hydrogels.<sup>34</sup> The absorption bands at  $1422\text{ cm}^{-1}$  and  $1326\text{ cm}^{-1}$  are assigned to  $\text{—CH}_2$  scissoring and  $\text{—OH}$  bending vibrations. Absorption bands at  $1020\text{--}1100\text{ cm}^{-1}$  are due to  $\text{C—O}$  stretching vibration of ether group of carboxymethylation of cellulose or ether linkage of the  $1,4\text{-}\beta\text{-D-glucoside}$  group ( $\text{>CH—O—CH<}$ ) of the cellulose backbone. The  $\text{C—O}$  bands arising from the two types of ethers present in CMSP hydrogels have overlapped.<sup>24,35</sup>

The absorption at  $2930\text{ cm}^{-1}$  in spectra of all CMSP hydrogels is attributable to the aliphatic  $\text{C—H}$  stretching vibration of the carboxymethyl group. The spectra of CMSP hydrogels with various DSs and GFs have similar broad  $\text{O—H}$  stretching absorption band at  $3420\text{--}3448\text{ cm}^{-1}$ . This may be due to interaction between water molecules and ionic groups with counter-ions or hydroxyl groups active as sorption sites for the water molecules and presence of hydrogen bonding.<sup>24,36</sup>

Under irradiation, macromolecular radicals are produced which lead to chain scission and side chain reactions, resulting in degradation and crosslinking of the macromolecular chains, respectively. It has been reported that cellulose and its derivatives degrade by the rupture of glycosidic bond under irradiation and the radical formed in the side chain ( $\text{R—O—}\dot{\text{C}}\text{H—COO}^-$ ) plays an important role in formation of the CMSP hydrogels which ultimately will lead to decrease in intensity of absorption bands



sodium carboxymethyl sago pulp

Figure 4. Structure of CMSP.

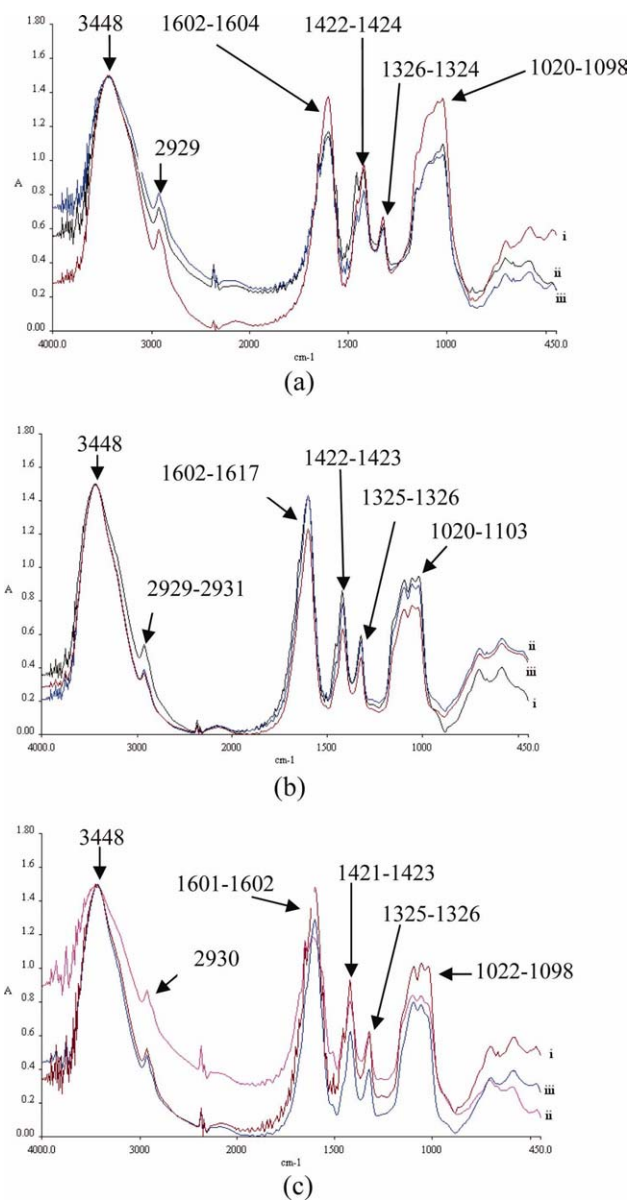


Figure 5. FTIR spectra of CMSP hydrogels as KBr pellets of degree of substitutions of (a) 0.4 with i) %GF 25, ii) %GF 35, iii) %GF 40; (b) 0.6 with i) %GF 25, (ii) %GF 35, (iii) %GF 46; (c) 0.8 with i) %GF 25, (ii) %GF 35, (iii) %GF 48. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

at  $1330$  and  $1422\text{ cm}^{-1}$  upon increase in crosslinking.<sup>19</sup> However, the radicals formed in  $\text{>CH—O—CH<}$  of main chain (glucose ring) of CMSP molecules lead to the scission of CMSP molecular chain, so the absorption decreases in intensity bands at  $1020\text{--}1100\text{ cm}^{-1}$  upon increase in chain scission (degradation). This suggests that besides crosslinking reaction, the chain scission reaction of CMSP molecules occurred simultaneously upon irradiation.<sup>20</sup>

In this work, the CMSP hydrogels spectra show differences in the intensity of the absorption bands at  $1020\text{--}1100$ ,  $1326$ , and  $1422\text{ cm}^{-1}$  with different DS and percentage of gel fractions [Figure 5 (a–c)]. The intensity of absorption bands at  $1326$  and

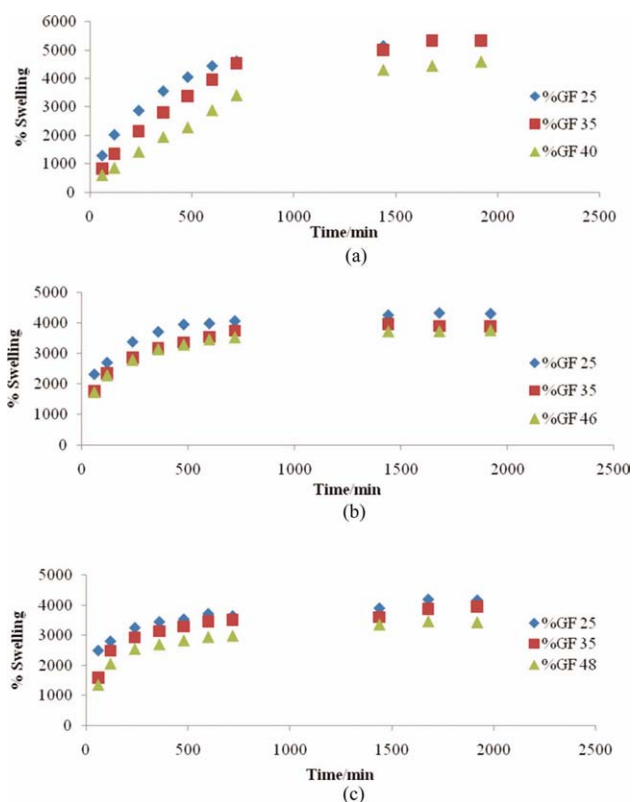
1422  $\text{cm}^{-1}$  decrease with the increase in degree of substitution and percentage of gel fraction. The decrease in the intensity absorption bands at 1326 and 1422  $\text{cm}^{-1}$  means that more  $-\text{OH}$  and  $-\text{CH}_2$  groups are taking part in crosslinking reaction of CMSP molecules due to the formation of radical  $-\text{OH}$  and  $-\text{CH}_2$  groups of the side chain of CMSP molecules.<sup>20</sup> The FTIR spectra of CMSP hydrogel of DS 0.4, 0.6, and 0.8 also shows that the intensity of absorption bands at 1020–1100  $\text{cm}^{-1}$  decrease with the increase in degree of substitution and percentage of gel fraction. The decrease in the intensity absorption bands at 1020–1100  $\text{cm}^{-1}$  means the radicals are formed in  $>\text{CH}-\text{O}-\text{CH}<$  of main chain of CMSP molecules, leading to chain scission of CMSP molecules. The spectra also show that the intensity at 1602–1617  $\text{cm}^{-1}$  was significantly weakened with the increase in degree of substitution and percentage of gel fractions. This may be due to the participation of the  $\text{COO}^-$  at the side chain to form radicals that leads to crosslinking.<sup>20</sup>

Similar results were observed in the research work by Qiu et al. (2007) on comparison studies of CMC hydrogels and activated carbon added CMC hydrogel irradiated with  $\gamma$ -radiation. The FTIR spectra of the hydrogel show a decrease in the intensity at absorption 1020–1100, 1326, 1422, and 1602  $\text{cm}^{-1}$  with increasing crosslinking caused by the radical of the side chain of CMC molecules.<sup>20</sup>

### Swelling Behavior

In Figure 6, all the nine types of CMSP hydrogels were swelled in distilled water for 55 h and the degree of swelling was determined by gravimetric methods. For the hydrogels of CMSP with degree of substitution of 0.4 with percentage of gel fractions of 25, 35, and 40, the percentage of swelling increases with time of immersion and reaches the equilibrium mass swelling value at around 25 h. The equilibrium swellings of CMSP hydrogels of degree of substitution of 0.4 of percentage of gel fractions of 25, 35, and 40 achieved were 5300%, 5300%, and 4600%, respectively. For CMSP hydrogels with degree of substitution of 0.6 with %GF of 25, 35, and 46, the equilibrium swellings achieved were 4300%, 3900%, and 3800%, respectively. For CMSP hydrogels with degree of substitution of 0.8 with percentage of gel fractions of 25, 35, and 48, the equilibrium swellings achieved were 4200%, 3900%, and 3500%, respectively. All the CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 at percentage of gel fraction of 25 had the highest maximum equilibrium swelling and followed by the CMSP hydrogel with percentage of gel fractions of 35 and 40, respectively. Research work by Wang et al. (2007) showed that 20% CMC with degree of substitution of 1.89, which was irradiated with  $\gamma$ -rays from  $^{60}\text{Co}$  source, produced CMC hydrogel with maximum percentage of gel fractions of 40–50 and the maximum degree of swelling was  $\sim 3000\%$ . In another study, the degree of swelling in distilled water was 6000% for a CMC hydrogel which was prepared by adding CMC of degree of substitution of 0.9 solution to a crosslink agent, 1,3-diaminopropane to obtain 50% crosslinking.<sup>37</sup>

At a percentage of gel fraction of 25 the CMSP hydrogels are relatively weak and consist of a low number of intermolecular bonds and, as a result, are able to expand by absorbing water



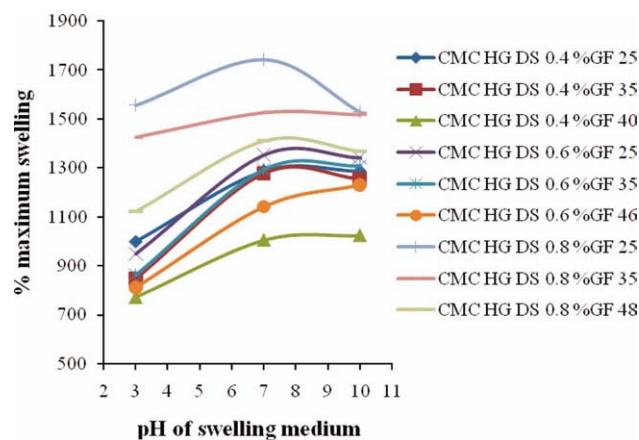
**Figure 6.** A plot of swelling over time for CMSP hydrogels of degree of substitutions of (a) 0.4, (b) 0.6, and (c) 0.8 in distilled water with percentage of gel fractions of (blue diamond) 25, (Red square) 35, and (green triangle)  $>40$  at 25°C, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and holding it in their voids. When the percentage of gel fraction is increased to 35 and above 40, the number of intermolecular bonds has increased and the crosslink density has increased. As a result, the hydrogels become tightly packed and firmer, lessening the ability of the hydrogel to absorb water. The increase in the crosslink density reduces the average chain length between crosslinks and restricting the chain motion and extension. Volumetric expansion of the network reduces as a function of increasing crosslink density.<sup>29</sup> In short, the best solvent for swelling all the CMSP hydrogels prepared by the EB irradiation in this study is water and it could be used as water retainer in the agricultural and water absorber in medical utility sectors.

### Swelling in Various pH Medium

The swelling ability of pH-sensitive hydrogels depends on the functional pendant groups which could be either acidic or basic groups (in our case conjugate base of acetic acid) that are attached to the backbone of the hydrogel. The dissociation of these groups will cause an influx of counterions to balance the charge, which makes the concentration of ions in the hydrogel higher than in the surrounding. As a result there will be difference in osmotic pressure and a solution flux into the hydrogel happens, resulting in swelling. The elastic restoring force of the hydrogel network balances the osmotic forces that result in an equilibrium ionic hydrogel. In essence, swelling of the hydrogel

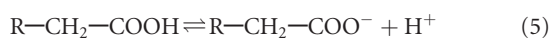




**Figure 7.** Equilibrium swelling of all the CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 and with percentage of gel fractions of 25, 35, and above 40 in various pH media. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

happens when the hydroxide ions are transported into the acidic hydrogel and shrinking of hydrogel results when the proton diffuse into the hydrogel and neutralize the negative charge of acidic carboxylate groups.<sup>36</sup>

Carboxymethyl groups in the CMSP hydrogel are an acidic pendant group that remains in equilibrium between neutral and ionized form. Any addition of electrolyte disturbs that equilibrium and will lead to the establishment of another one. The dissociation degree is shifted to the right or left side of the Equation 5 depending on the pH value of the solution.<sup>19</sup>



From Figure 7, it can be seen that the percentage of maximum swelling ratio increases from pH 3 to pH 7 and attain maximum swelling at pH 7 and the swelling ratio slightly decreases at pH 10. The maximum swelling ratio at pH 7 for hydrogel of CMSP of degree of substitution of 0.4 with percentage of gel fraction of 25, 35, and 40 are  $1250 \pm 50\%$ . The maximum swelling ratio at pH 7 for hydrogels of CMSP of degree of substitution of 0.6 with percentage of gel fraction of 25, 35, and 46 are 1355%, 1295%, and 1142%, respectively. The maximum swelling ratio at pH 7 for hydrogel of CMSP of degree of substitution of 0.8 with percentage of gel fraction of 25, 35, and 48 are 1744%, 1528%, and 1411%, respectively. It is observed that higher the degree of substitution of CMSP forming the CMSP hydrogel has higher maximum swelling ratio and the higher the percentage of gel fraction resulted in the lower maximum swelling ratio. It can be concluded that the optimum pH for swelling CMSP hydrogel is at pH 7.

CMC hydrogel prepared by Wach et al. (2003) by  $\gamma$ -irradiation by using 30% CMC concentration of degree of substitution of 2.2 at 30 kGy resulted in 80–90% percentage of gel fraction whereby using electron beam irradiation on the sample of same concentration resulted in 75–95%. The CMC hydrogel produced using  $\gamma$ -irradiation was used to study the swelling behavior in pH 7 buffer solution which resulted percentage of swelling of

750%.<sup>3</sup> Another CMC hydrogel was prepared using 25% CMC concentration of degree of substitution of 0.64 at 15 kGy of  $\gamma$ -irradiation resulted in percentage of gel fraction of 45 and the swelling behavior in pH 7 buffer solution had percentage of swelling of  $\sim 3400\%$ .<sup>10</sup> Similar results by Liu et al. have been obtained by swelling the CMC hydrogels formed by  $\gamma$ -irradiation in different pH buffer solutions. The CMC hydrogels swelled to a maximum at pH 7.<sup>10,14</sup> They proposed the network of hydrogel absorbs a large amount of solution resulting in an increase in the osmotic pressure inside in accordance with Donnan equilibrium theory and that the density of crosslinks confines the magnification of the mutual repulsion of the polysaccharide chains.<sup>19</sup>

## CONCLUSION

In summary, nine types of CMSP hydrogels were successfully prepared by electron beam irradiation. In the investigated concentration range of CMSP with degree of substitutions of 0.4, 0.6, and 0.8, the  $p_o/q_o$  ratio decreases with increasing percentage of CMSP showing that crosslinking process is dominating and increasing the gel network of the CMSP hydrogel. The gelation dose ( $D_g$ ) and  $p_o/q_o$  ratios are dependent on CMSP concentration and degree of substitution. The  $p_o/q_o$  ratio value of CMSP hydrogel decreases in the order degree of substitutions of  $0.4 > 0.6 > 0.8$  in all types of CMSP with same concentration. The FTIR spectra of CMSP hydrogels of degree of substitutions of 0.4, 0.6, and 0.8 with percentage of gel fractions of 25, 35, and  $\geq 40$  show differences in the intensity of the absorption bands at 1020–1100, 1326, and 1422  $\text{cm}^{-1}$  with different degree of substitutions and percentage of gel fractions which correspond to different extents of chain scission and crosslinking. The swelling behavior in water shows that CMSP hydrogels could absorb 3500–5300% of water by 1 g of CMSP hydrogel. The ability to absorb water increases with the decrease of degree of substitution and percentage of gel fractions of all the CMSP hydrogels. The capability of holding large amount of water in the CMSP hydrogel could lead to using these CMSP hydrogels as a multifunctional water managing material which may find application in agriculture, pharmaceuticals, and in the renewal of arid and desert environments. It can be concluded that the optimum pH for swelling CMSP hydrogel is at pH 7. At the optimum pH 7, the higher the degree of substitution of CMSP forming the CMSP hydrogel has higher maximum swelling ratio and the higher the percentage of gel fraction resulted in the lower maximum swelling ratio. The crosslinked CMSP hydrogels are endowed with pH responsive characteristic which could be used in drug delivery systems to improve methods of delivering molecules for therapeutic applications and we anticipate that in future this natural modified biomaterial hydrogels will play a greater role in biomedical applications.

## ACKNOWLEDGMENTS

Financial support from the center for Green Chemistry and School of Chemistry at Monash University, Clayton, Australia is gratefully acknowledged. The authors would like to acknowledge Malaysian Nuclear Agency for their help in the EB irradiation.



REFERENCES

- Rana, V.; Rai, P.; Tiwary, A. K.; Singh, R. S.; Kennedy, J. F.; Knill, C. J. *Carbohydr. Polym.* **2011**, *83*, 1031.
- Nagasawa, N.; Yagi, T.; Kume, T. *Carbohydr. Polym.* **2004**, *58*, 109.
- Wach, R. A.; Mitomo, H.; Yoshii, F.; Kume, T. *J. Appl. Polym. Sci.* **2001**, *81*, 3030.
- Kume, T.; Nagasawa, N.; Yoshii, F. *Radiat. Phys. Chem.* **2002**, *63*, 625.
- Huang, L.; Zhai, M.; Peng, J.; Li, J.; Wei, G. *Carbohydr. Polym.* **2007**, *67*, 305.
- Zhao, L.; Mitomo, H.; Nagasawa, N.; Yoshii, F.; Kume, T. *Carbohydr. Polym.* **2003**, *51*, 169.
- Abdul El-Rehim, H. *J. Appl. Polym. Sci.* **2006**, *101*, 3572.
- Zhai, M.; Kudoh, H.; Wu, G.; Wach, R. A.; Muroya, Y.; Katsumura, Y.; Nagasawa, N.; Zhao, L.; Yoshii, F. *Biomacromolecules* **2004**, *5*, 453.
- Rosiak, J. M.; Ulanski, P.; Pajewski, L. A.; Yoshii, F.; Makuuchi, K. *Radiat. Phys. Chem.* **1995**, *46*, 161.
- Liu, P.; Peng, J.; Li, J.; Wu, J. *Radiat. Phys. Chem.* **2005**, *72*, 635.
- Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R. *Adv. Mater.* **2006**, *18*, 1345.
- Bhat, R.; Karim, A. A. **2009**, *8*, 44.
- Karadağ, E.; Saraydin, D.; Caldiran, Y.; Güven, O. *Polym. Adv. Technol.* **2000**, *11*, 59.
- Liu, P.; Zhai, M.; Li, J.; Peng, J.; Wu, J. *Radiat. Phys. Chem.* **2002**, *63*, 525.
- Bardajee, G. R.; Pourjavadi, A.; Soleyman, R.; Sheikh, N. *Nucl. Instr. Meth. Phys. Res. B* **2008**, *266*, 3932.
- Suk Kim, M.; Ho Kim, J.; Hyun Min, B.; Jae Chun, H.; Keun Han, D.; Bang Lee, H. *Polym. Rev.* **2011**, *51*, 23.
- Weibin, W.; Peizhi, S.; Xingguo, W.; Jinghui, L. *Radiat. Phys. Chem.* **1993**, *42*, 947.
- Wach, R. A.; Mitomo, H.; Yoshii, F.; Kume, T. *Macromol. Mater. Eng.* **2002**, *287*, 285.
- Wach, R. A.; Mitomo, H.; Nagasawa, N.; Yoshii, F. *Radiat. Phys. Chem.* **2003**, *68*, 771.
- Qiu, J.; Xu, L.; Peng, J.; Zhai, M.; Zhao, L.; Li, J.; Wei, G. *Carbohydr. Polym.* **2007**, *70*, 236.
- Pushpamalar, V. Preparation and Characterisation of Carboxymethyl Cellulose and Carboxymethyl Cellulose Hydrogels from Sago Waste. Ph.D. Thesis; Monash University, Clayton: Australia, **2010**.
- Pushpamalar, V.; Langford, S. J.; Ahmad, M.; Lim, Y. Y. *Carbohydr. Polym.* **2006**, *64*, 312.
- Fei, B.; Wach, R. A.; Mitomo, H.; Yoshii, F.; Kume, T. *J. Appl. Polym. Sci.* **2000**, *78*, 278.
- Said, H. M.; Alla, S. G. A.; El-Naggar, A. W. M. *React. Funct. Polym.* **2004**, *61*, 397.
- Charlesby, A. In Atomic Radiation and Polymers; Pergamon Press: New York, **1960**; pp. 25–35.
- Karadağ, E.; Saraydin, D.; Caldiran, Y.; Güven, O. *Macromol. Mater. Eng.* **2001**, *286*, 34.
- Francis, S.; Kumar, M.; Varshney, L. *Radiat. Phys. Chem.* **2004**, *69*, 481.
- Ulański, P.; Janik, I.; Rosiak, J. M. *Radiat. Phys. Chem.* **1998**, *52*, 289.
- Pekel, N.; Yoshii, F.; Kume, T.; Güven, O. *Carbohydr. Polym.* **2004**, *55*, 139.
- Xu, L.; Nagasawa, N.; Yoshii, F.; Kume, T. *J. Appl. Polym. Sci.* **2003**, *89*, 2123.
- Rosiak, J. M. *Radiat. Phys. Chem.* **1998**, *51*, 13.
- Olejniczak, J.; Rosiak, J.; Charlesby, A. *Radiat. Phys. Chem.* **1991**, *37*, 499.
- Gottlieb, R.; Schmidt, T.; Arndt, K. F. *Nucl. Instr. Meth. Phys. Res. B* **2005**, *236*, 371.
- Biswal, D. R.; Singh, R. P. *Carbohydr. Polym.* **2004**, *57*, 379.
- Heydarzadeh, H. D.; Najafpour, G. D.; Nazari-Moghaddam, A. A. *World Appl. Sci. J.* **2009**, *6*, 564.
- Gerlach, G.; Guenther, M.; Sorber, J.; Suchanek, G.; Arndt, K. -F.; Richter, A. *Sens. Actuators B* **2005**, *111–112*, 555.
- Wang, H.; Wang, Z.; Zhu, B. *React. Funct. Polym.* **2007**, *67*, 225.