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# Synthesis and Characterization of Superabsorbent Polymer Based on Carboxymethyl Cellulose-*graft*-Itaconic Acid

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**Abstract:** Superabsorbent polymers of carboxymethyl cellulose-*graft*-itaconic acid were synthesized using potassium persulfate as a free radical initiator in the presence of *N,N'*-methylene bisacrylamide as a crosslinker using solution polymerization technique. The structures of the grafted copolymers were characterized by FT-IR spectroscopy and thermogravimetric analysis. The effect of reaction variables such as concentration of carboxymethyl cellulose, itaconic acid, initiator, crosslinker, and neutralizing agent were optimized to achieve a hydrogel with high swelling capacity of 74 g/g (DI water) and 18 g/g (0.9 wt% NaCl solution). The swelling kinetics of the prepared SAP were analyzed by applying the Fickian diffusion model and the Schott's pseudo second order kinetics model. The diffusion exponents in the Fickian model, *n*, showed values of 0.73-0.93, indicating that chain relaxation behavior during absorption had a large effect on total absorbency.

**Keywords:** Superabsorbent polymer, Carboxymethyl cellulose, Itaconic acid, Swelling kinetics

## Introduction

Superabsorbent polymers (SAPs) are three-dimensionally crosslinked networks of hydrophilic polymers that can absorb and retain large amounts of water or aqueous solutions [1-3]. SAPs are widely used in a wide array of applications, including disposable diapers [4], feminine napkins [5], soil for agriculture and horticulture [6], gel actuators [7], surgical pads [8], packaging materials [9], water-blocking taps [10], chemical sensors [11], and drug delivery [12]. Natural polymers-based SAPs have gained much attention because of their biocompatibility, biodegradability, and nontoxicity [13]. Carboxymethyl cellulose (CMC) is one of the most widely used water-soluble cellulose derivative extensively used in such applications because of its low cost, biocompatibility, lack of toxicity [14-17]. To render the proper characteristics in a specific application field, CMC should be chemically modified. Among all the methods of modification, graft copolymerization of vinyl monomers, such as vinyl sulfonic acid, *N*-vinyl-2-pyrrolidone, hydroxyethyl methacrylate, acrylic acid, and acrylamide, on natural polymeric backbones is one of the best methods [18-24]. Examples of such research include CMC-*graft*-poly(acrylic acid) [25], CMC-*graft*-poly(acrylic acid-*co*-acrylamide) [26], CMC-*graft*-poly(sodium acrylate) [18,27,28], CMC-*graft*-poly(acrylic acid-*co*-2-acrylamido-2-methylpropanesulfonic acid) [29], and CMC-*graft*-poly(acrylamide-*co*-2-acrylamido-2-methylpropanesulfonic acid) [30]. Introducing such hydrophilic monomers greatly improves water absorbency and swelling rate of the prepared SAPs. Redox initiators have been widely used in the graft polymerization, due to their milder reaction conditions that renders minimum side reactions [31-37]. Many redox initiators, such as $KMnO_4$/oxalic acid, $Cu^{2+}/Na_2S_2O_5$, potassium bromate/thiomalic acid, persulfate/ascorbic acid, ammonium peroxodisulfate, and ceric ion, have been used in the graft polymerization [38-46].

Itaconic acid (IA) is an unsaturated dicarboxylic acid with one carboxyl group is conjugated to the methylene group that, upon polymerization, provide water soluble polymer chains with carboxylic side groups. It is advantageous to use IA because it can be obtained from natural resources using various processes [47-49], and there have been recent efforts of using IA in many applications [50-53]. Polymerization of IA have been generally performed in aqueous media with using persulphate as an initiator [54,55]. The polymerization of IA suffers from long reaction time and low molecular weight due to the 1,1-disubstituted bulky groups of IA and chain transfer reaction to monomers. The polymerization is also affected by reaction conditions, such as temperature and pH, due to monomer decarboxylation and decreased reaction rate [56].

In this research, the CMC-based SAPs were prepared by solution polymerization of IA onto CMC in the presence of *N,N'*-methylene bisacrylamide (MBA) as the crosslinker and potassium persulfate (KPS) is used as the initiator. Effects of various factors, such as initiator, neutralizing agent, and crosslinker, were investigated to determine the optimum conditions for high yield of the graft copolymerization and maximum water absorption. Also swelling kinetics was analyzed to investigate the absorption mechanism of the prepared CMC-based SAPs.

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## Experimental

### Materials and Characterization

IA (>99 %), CMC sodium salt (MW~90,000), KPS (>99 %), ceric ammonium nitrate (CAN, 99.99 %), potassium peroxymonosulfate (PMS, OXONE®), potassium bromate (KBr, ≥99.8 %), MBA (99 %), and sodium hypophosphite ($NaH_2PO_2$) were purchased from Sigma-Aldrich and used without further purification. Sodium hydroxide (NaOH) was purchased from Samchun chemicals, Korea.

FT-IR spectra were taken in the wavelength region between 3600 and 800 $cm^{-1}$ for 32 scans with a spectral resolution of 4 $cm^{-1}$ in ATR mode using Bruker VERTEX 70 FT-IR spectrometer. Thermogravimetric analysis was carried out with Mettler Toledo TGA/DSC 1 STARe System at 25-500 °C and with heating rate of 10 °C/min under nitrogen atmosphere.

### General Procedure for Graft Polymerization of IA onto CMC

Aqueous solution of NaOH, in a concentration to give a degree of neutralization of IA to 50 %, was prepared by slowly adding NaOH powder to distilled water in a 500 m*l* four-necked flask equipped with a mechanical stirrer, a reflux condenser, and thermometer. To the NaOH solution were added pre-determined amounts of IA, CMC sodium salt, and MBA under continuous stirring in ice-bath. The solution was degassed by blowing nitrogen for 1 h, and then KPS was added. The polymerization reaction was allowed to proceed at 60 °C in an oil bath under a nitrogen gas atmosphere for 5 h with stirring at 600 rpm. The resulting polymer, sodium carboxymethyl cellulose-graft-itaconic acid (CMC-*g*-IA), was precipitated with ethanol and dried at 60 °C for 24 h to a constant weight. Yield of the polymerization was determined as the weight ratio of increment after the graft polymerization to IA monomer.

$$Yield = \frac{W_{CMC\text{-}g\text{-}IA} - W_{CMC}}{W_{IA}} \tag{1}$$

where $W_{CMC\text{-}g\text{-}IA}$ is weight of the graft copolymer (CMC-*g*-IA), $W_{CMC}$ is weight of the original CMC, and $W_{IA}$ is weight of IA monomer.

### Free-absorbency Capacity

Tea bag method was used to determine the absorbency of the prepared polymers [57,58]. A tea bag (acrylic/polyester gauze with fine meshes) containing an accurately weight powdered sample (0.2±0.02 g) with average particle size between 250-400 μm was immersed entirely in 200 m*l* of aqueous saline solution (0.9 wt%) and allowed to soak for 30 min at room temperature to reach equilibrium. The tea bag was hung up for 15 min in order to remove excess fluid. The equilibrated swelling ($Q_{eq}$) was calculated using the following equation:

$$Q_{eq} = \frac{W_{TB,f} - W_{TB,i}}{W_{CMC\text{-}g\text{-}IA}} \tag{2}$$

where $W_{CMC\text{-}g\text{-}IA}$ is weight of the dried CMC-*g*-IA powder, $W_{TB,f}$ and $W_{TB,i}$ are weight of the tea bag after and before water uptake, respectively.

## Results and Discussion

Figure 1 shows the FT-IR spectra of CMC sodium salt, poly(IA), and CMC-*g*-IA. The FT-IR spectrum of CMC showed characteristic peaks of 3130, 2918, 1683, 1595, 1409, and 1159 $cm^{-1}$ for hydroxyl, aliphatic C-H, carbonyl, asymmetric and symmetric carboxylate, and C-O stretching mode, respectively [18]. However, the absorption peaks 1200-1000 $cm^{-1}$ were changed after the grafting reaction with IA, demonstrating the participation of hydroxyl groups of CMC in the copolymerization. Furthermore, the appearance of a new peak at 1731 $cm^{-1}$, characteristic peak for the

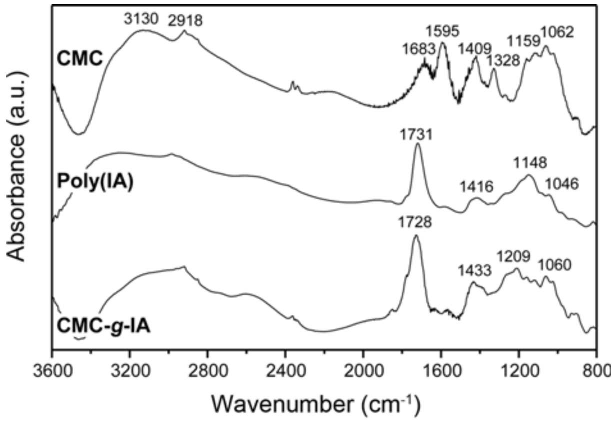

**Figure 1.** FT-IR spectra of CMC sodium salt and CMC-*g*-IA.

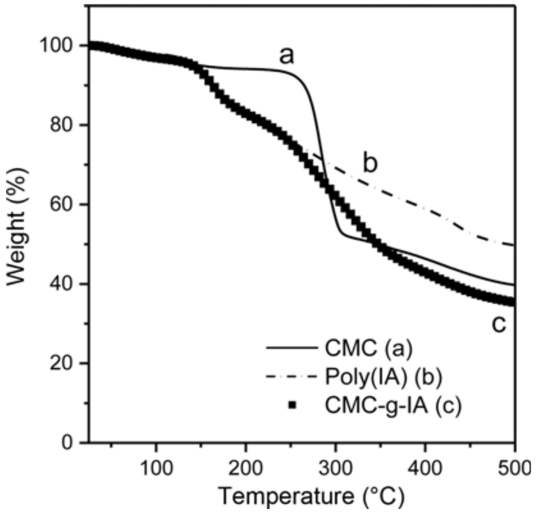

**Figure 2.** TGA thermograms of CMC sodium salt and CMC-*g*-IA.

carboxylic group of IA, was observed. The spectrum of CMC-*g*-IA was similar to the one of poly(IA), indicating the existence of poly(IA) chains in the copolymers. Overall, it could be concluded that the grafting of IA to CMC took place successfully through the active hydroxyl groups of CMC using KPS as the initiator (Figure S1) [59].

TGA curves for pure CMC sodium salt, poly(IA), and CMC-*g*-IA are shown in Figure 2. The graft copolymer has shown different thermal decomposition pattern from pure CMC sodium salt and poly(IA). The thermal decomposition pattern for the graft copolymer was composed of three stages of weight loss at 150-200 °C (10 %), 200-370 °C (40 %), and 370-500 °C (10 %). The first stage in the range of 150-200 °C was similar to the decomposition of poly(IA), and the second in the range of 200-370 °C was assigned to the dehydration of saccharide rings, the C-O-C bond breakage in CMC, and elimination of water molecules from the two neighboring carboxylic groups of the grafted polymer chains. The third weight losses in range of 370-500 °C derived from the combination of the breakage of poly(IA) chains and the destruction of crosslinked network structure [60]. One more thing to note is the residue weight at 500 °C was lower than those of the each components, probably due to the loosened structure of the grafted structure facilitate the thermal decomposition.

Various initiation systems have been conducted for the graft polymerization of vinyl monomers onto polysaccharides. We testes four different initiation systems of KPS, CAN, PMS, and KBr in the graft polymerization of IA onto CMC (Table 1). Among the initiator tested, KPS initiated systems gave the highest yield of polymerization. After 5 h of reaction, the polymerization using KPS reached 91 % of conversion while the ones using CAN, PMS, and KBr gave 80, 78, and 73 % of conversion, respectively. Also, the saline solution (0.9 wt%) absorbency of the prepared SAP was the highest value (16.6 g/g) for the KPS initiated system. Initially, persulfate ions readily dissociated thermally to sulfate anion-radicals, which abstract hydrogen from the hydroxyl groups on $C_2$ carbon in the CMC chain to form corresponding alkoxy radicals [61,62]. These radicals initiated grafting of IA onto CMC backbones, which led to crosslinked graft copolymers in the presence of MBA.

**Table 1.** Effect of various initiators on solution polymerization of CMC-*g*-IA[a]

| Initiator | Yield (%) | Absorbency (g/g) |
|---|---|---|
| Potassium persulfate (KPS) | 91 | 16.6 |
| Ceric ammonium nitrate (CAN) | 80 | 14.1 |
| Potassium peroxymonosulfate (PMS) | 78 | 11.5 |
| Potassium bromate (KBr) | 73 | 11.0 |

[a] Conditions; [CMC]/[IA]=1/2 (in weight), [Initiator]=1.0 wt% (to IA), [MBA]=0.8 wt% (to IA), [IA]/[water]=1/5 (in weight), [NaOH]= 50 mol% (to IA), Temperature 60 °C, Time 2 h.

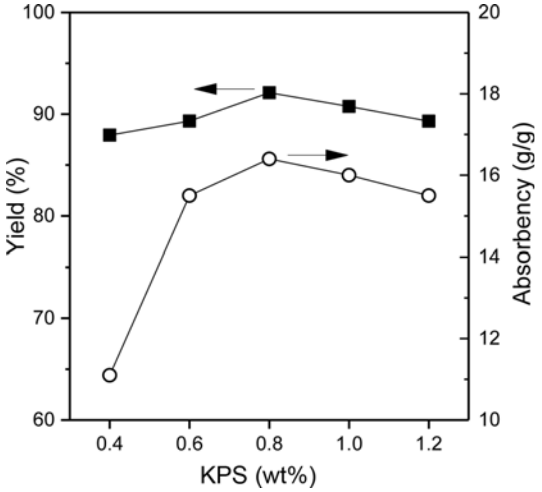

**Figure 3.** Effect of KPS concentration on (a) yield of graft polymerization and (b) absorbency of the resulting CMC-*g*-IA. Reaction conditions; [CMC]/[IA]=1/2 (in weight), [MBA]=0.6 wt% (to IA), [IA]/[water]=1/5 (in weight), [NaOH]=50 mol% (to IA), Temperature 60 °C, Time 2 h.

The initiator concentration has a remarkable effect on water absorbency. The relationship between the initiator concentration and water absorbency values was studied by varying the KPS concentration from 0.4 to 1.2 wt% (to IA) (Figure 3). In the range of initiator concentration tested, the yield of polymerization was 87-92 %, indicating that the graft polymerization was proceeded effectively. The yield increased initially with the initiator concentration, but decreased with the initiator concentration of higher than 0.8 wt%. The water absorbency also increased substantially with KPS concentration and then decreased again with the KPS concentration of higher than 0.8 wt%. The initial increment in water absorbency may be attributed to increased number of active free radicals on the CMC backbone. Subsequent decrease in swelling is originated from increasing in un-grafted linear homopolymer formation and additional terminating step reaction via bimolecular collision, which, in turn, causes to enhance crosslinking density. This possible phenomenon is referred to as self-crosslinking, which has been reported in other graft polymerizations of vinyl monomer onto polysaccharides [44,63,64].

The effect of neutralizing agent on graft copolymerization was investigated. Two different neutralizers, NaOH and $NaH_2PO_2$, in concentrations ranging from 12.5 to 100 mol% (to IA) were tested. As the concentration of the neutralizing agent increased, the grafting yield increased remarkably and reached the highest value at 50 % NaOH concentration. On the other hand, the effect of $NaH_2PO_2$ was not so eminent as that of NaOH. The graft yield increased initially with low concentration of $NaH_2PO_2$, but decreased with further addition of $NaH_2PO_2$. Not only acts as a neutralizing agent,

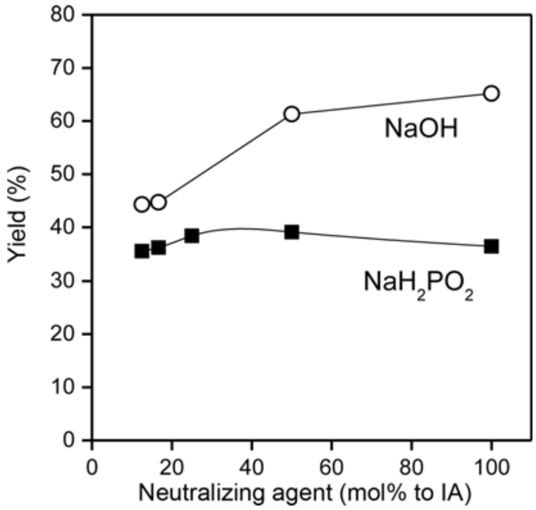

**Figure 4.** Effect of neutralizing agent on yield of graft polymerization.

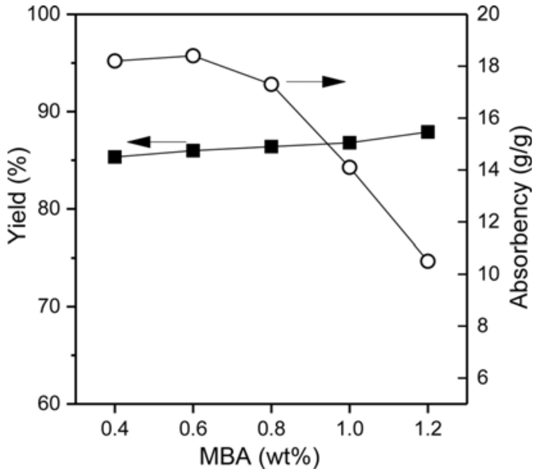

**Figure 5.** Effect of MBA concentration on (a) yield of graft polymerization and (b) absorbency of the resulting CMC-*g*-IA. Reaction conditions; [CMC]/[IA]=1/2 (in weight), [KPS]=1.0 wt% (to IA), [IA]/[water]=1/5 (in weight), [NaOH]=50 mol% (to IA), Temperature 60 °C, Time 2 h.

but $NaH_2PO_2$ also acts as a KPS decomposition promoter to be an effective additive for polymerization of IA [65]. As can be seen from the effect of KPS concentration, the higher the concentration of radicals by $NaH_2PO_2$, the more homopolymer formation and self-termination processes are induced. Also, $NaH_2PO_2$ has less neutralizing effect than NaOH due to its lower basicity and therefore had no positive effect on the graft copolymerization, different from the polymerization of IA.

Effects of the crosslinker concentration were also studied (Figure 5). Regardless of the crosslinker concentration, the yield of the graft polymerization was higher than 85 %. Higher absorbency was obtained using lower cross-linker concentration, however, the prepared hydrogels did not possess good dimensional stability, as reported previously [66]. Higher crosslinker concentration reduces space between polymer chains and, consequently, the highly crosslinked rigid structure cannot be expanded to hold a large quantity of water [67].

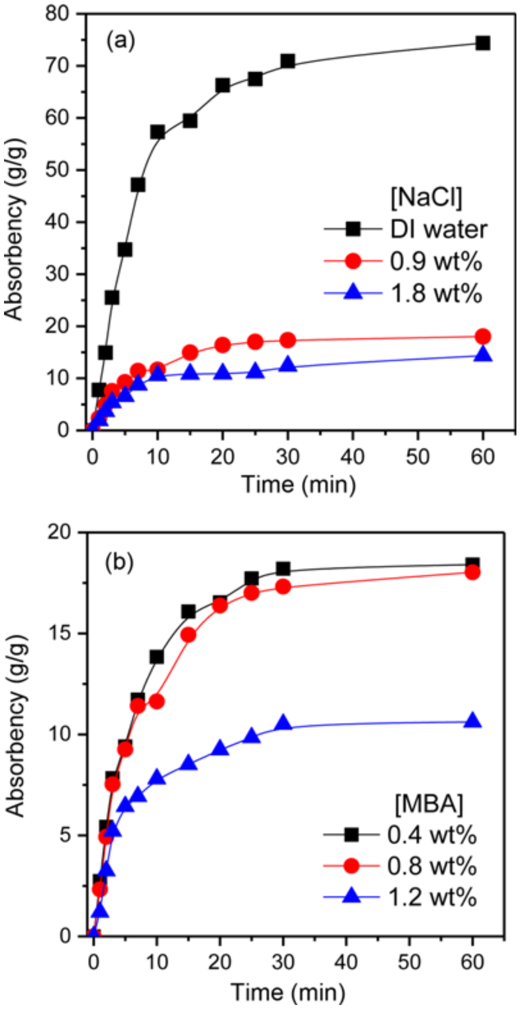

**Figure 6.** Swelling kinetic curves of the CMC-*g*-IA graft copolymer in DI water; (a) effect of ionic strength of the aqueous solution and (b) effect of crosslinker concentration.

In practical applications, a higher swelling rate is required as well as a higher swelling capacity. Various factors, such as size distribution of powder particles, specific surface area, and composition of polymer, influenced the swelling kinetics. Figure 6 shows the swelling kinetics of the prepared CMC-*g*-IA crosslinked material. The pure water absorbency of the CMC-*g*-IA increased rapidly to give 57 g/g in 10 min and reached a steady value of ~70 g/g in 30 min (Figure 6(a)). With increasing ionic strength of the absorbing water using 0.9 and 1.8 % (w/v) NaCl (0.15 and 0.3 M), the equilibrium absorbency value reduced to 18 and 14 g/g, respectively, while showing similar swelling kinetics of initial rapid increase in 10 min and reaching equilibrium state in 30 min. For all the MBA concentration variation, the swelling kinetics of the CMC-*g*-IA was similar to reach equilibrium absorbency in 30 min (Figure 6(b)).

To analyze the swelling kinetics in more detail, two different kinetic models were applied. Generally, the swelling process can be composed of two different events; initial diffusion of water molecules into the voids in the molecules and the subsequent chain relaxation. The initial diffusion can be analyzed by conventional Fickian diffusion model (equation (3)) [68] and the whole process was evaluated generally the Schott's pseudo second order kinetics model

**Table 2.** Swelling kinetic parameters of CMC-*g*-IA in aqueous solution with different ionic strength[a]

| NaCl (wt%) | Fickian diffusion model | | | Schott's pseudo second order kinetics model | | | | |
|---|---|---|---|---|---|---|---|---|
| | Intercept (*ln K*) | Slope (*n*) | $R^2$ | Intercept ($1/k_{is}$) | Slope ($1/Q_{eq}$) | $R^2$ | $k_{is}$ | $Q_{eq}$ |
| 0 | 2.084 | 0.930 | 0.985 | 0.083 | 0.012 | 0.990 | 12.027 | 85.3 |
| 0.9 | 0.962 | 0.806 | 0.950 | 0.288 | 0.050 | 0.996 | 3.469 | 20.2 |
| 1.8 | 0.731 | 0.755 | 0.974 | 0.429 | 0.065 | 0.991 | 2.331 | 15.5 |

[a]Conditions; [CMC]/[IA]=1/2 (in weight), [KPS]=1.0 wt% (to IA), [MBA]=0.8 wt% (to IA), [IA]/[water]=1/5 (in weight), [NaOH]=50 mol% (to IA), Temperature 60 °C, Time 2 h.

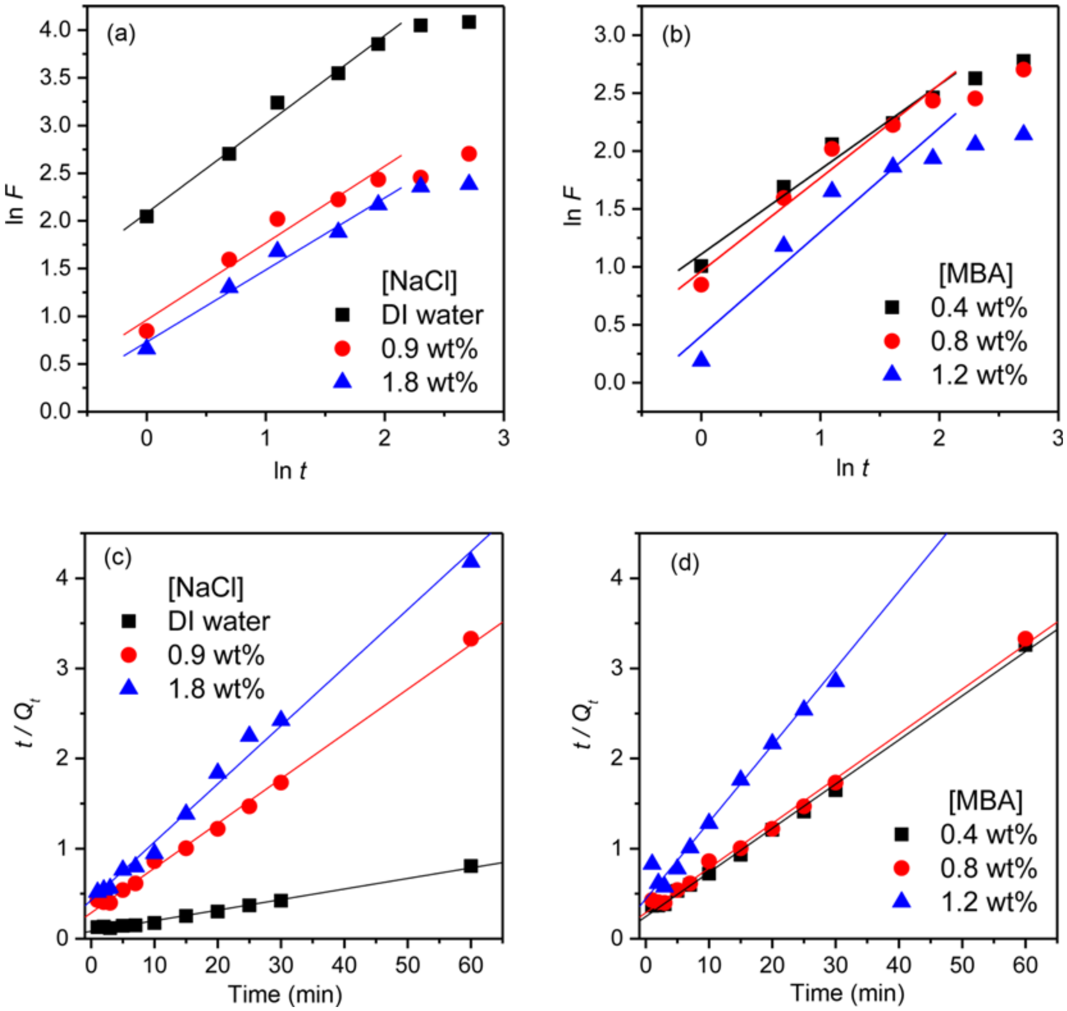

**Figure 7.** Swelling kinetic fitting curves of the CMC-*g*-IA. The plots of ln *F* against ln *t* (Fickian diffusion model) (a and b) and the plots of $t/Q_t$ against *t* (Schott's pseudo second order kinetics model) (c and d) for the CMC-*g*-IA in aqueous solution with varying ionic strength (a and c), and for the CMC-*g*-IA prepared with different crosslinker concentration (b and d).

(equation (4)) [69].

$$F = \frac{W_t}{W_{eq}} = Kt^n \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{k_{is}} + \frac{t}{Q_{eq}} \tag{4}$$

where $F$ is the fractional uptake at a given time $t$ (min); $W_t$ (g) and $W_{eq}$ (g) are the weight (g) of water absorbed at time $t$ and equilibrium, respectively; $K$ is a characteristic constant of the crosslinked materials; $n$ is the diffusional exponent, corresponding to the transport mode of the penetration; $Q_t$ and $Q_{eq}$ is the swelling ratio (g/g) of the crosslinked materials at time $t$ and equilibrium; and $k_{is}$ (g/gmin) is the initial swelling rate constant. The determined kinetic parameters were listed in Table 2 and 3. As seen in Figure 7(a) and Figure 7(b), the Fickian diffusion model could be successfully applied to the initial swelling process (<10 min) to give straight fitted linear lines with good correlation coefficient ($R^2$>0.95). Notably, the determined $n$ values were in the range of 0.5-1.0, indicating and the water uptake was controlled collaboratively by water diffusion and relaxation of polymer chains (non-Fickian diffusion) [70]. The $n$ value was the highest for the pure DI water (0.930) and decreased with ionic strength (0.806 and 0.755 for 0.9 and 1.8 wt% NaCl solution, respectively), which implied that the chains relaxed faster in water with low ionic strength [71]. The chain relaxation behavior became more dominant in the materials with increasing crosslinking density to give the $n$ values of 0.731, 0.806, and 0.898 for the systems with [MBA] of 0.4, 0.8, and 1.2 wt%, respectively. Since the chain relaxation got more difficult with increasing [MBA], the swelling ratio decreased eventually.

The whole swelling process of the prepared CMC-*g*-IA could be successfully described by the Schott's pseudo second order kinetics model, as seen from Figure 7(c) and Figure 7(d). For all the cased, the plots of $t/Q_t$ versus $t$ showed perfect straight lines with high linear correlation coefficient, $R^2$>0.99. Initial swelling rate ($k_{is}$) and equilibrium swelling ratio ($Q_{eq}$) could be calculated from the intercept and slope of the straight line, with giving trends of decreasing those values with ionic strength (Figure 7(c)). Interestingly, the calculated values of equilibrium swelling ratio were higher than the experimental values after 60 min of swelling (85.3 *vs.* 74.4, 20.2 *vs.* 18.0, and 15.5 *vs.* 14.4 for DI water, 0.9 wt%, and 1.8 wt% of NaCl, respectively), indicating the samples were not in fully swollen state.

Figure 7(d) shows that when [MBA] was 0.4 and 0.8 wt%, it had little effect on the water absorbency of the materials. The $k_{is}$ value was slightly higher when [MBA]=0.4 wt% (4.065 g/g·min) than that of [MBA]=0.8 wt% (3.469 g/g·min), but the theoretical value of $Q_{eq}$ were almost same (~20 g/g) for both samples. The higher $n$ values in the Fickian diffusion model and lower $k_{is}$ value in the Schott's model on [MBA]=0.8 wt% indicated that the chain relaxation in the initial swelling process was kinetically hindered with increased crosslinking density, but the thermodynamically equilibrium capacity of retaining water in the CMC-*g*-IA would not be affected compared to the one on [MBA]= 0.4 wt%. On the other hand, when [MBA] increased as high as 1.2 wt%, the waster absorbency decreased a lot to give $k_{is}$=2.259 g/g·min and $Q_{eq}$=11.7 g/g, indicating both kinetic and thermodynamic deterioration of water absorbency due to the increased crosslinking density.

## Conclusion

In summary, crosslinked graft copolymers of CMC-*g*-IA was successfully synthesized through grafting of IA onto CMC by solution polymerization in water at 60 °C in presence of KPS and MBA as a free radical initiators and crosslinkers, respectively. Various reaction conditions, such as IA concentration, IA/CMC ratio, initiation system, initiator/crosslinker concentration, and the degree of neutralization were optimized to achieve maximum grafting yield of IA (>90 %), ultimately high water absorption levels (74 and 18 g/g for DI water and 0.9 wt% NaCl solution, respectively). On applying the Fickian diffusion model and the Schott's pseudo second order kinetics model to study the swelling kinetics of the prepared SAP, it is revealed that chain relaxation during absorption has a large effect on the total absorbency. Furthermore, maintaining the concentration of the crosslinking agent appropriately provides favorable conditions for absorption in terms of kinetic and thermodynamic

**Table 3.** Swelling kinetic parameters for the CMC-*g*-IA prepared with different crosslinker concentration in 0.9 % nacl solution[a]

| MBA (wt%) | Fickian diffusion model | | | Schott's pseudo second order kinetics model | | | | |
|---|---|---|---|---|---|---|---|---|
| | Intercept (*ln K*) | Slope (*n*) | $R^2$ | Intercept ($1/k_{is}$) | slope ($1/Q_{eq}$) | $R^2$ | $k_{is}$ | $Q_{eq}$ |
| 0.4 | 1.111 | 0.731 | 0.955 | 0.246 | 0.049 | 0.996 | 4.065 | 20.4 |
| 0.8 | 0.962 | 0.806 | 0.950 | 0.288 | 0.050 | 0.996 | 3.469 | 20.2 |
| 1.2 | 0.404 | 0.898 | 0.882 | 0.443 | 0.085 | 0.993 | 2.259 | 11.7 |

[a]Conditions; [CMC]/[IA]=1/2 (in weight), [KPS]=1.0 wt% (to IA), [MBA]=0.8 wt% (to IA), [IA]/[water]=1/5 (in weight), [NaOH]=50 mol% (to IA), Temperature 60 °C, Time 2 h.

aspects. This study provided the possibility of using CMC-*g*-IA as SAP materials with proper optimization of polymerization parameters. Because IA is known to be biodegradable, the prepared CMC-*g*-IA would be one of candidates for biodegradable SAP.

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