



## Synthesis and Characterization of Partially Hydrolyzed Hydrogel Based on Kappa-Carrageenan

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The polysaccharide, kappa-carrageenan ( $\kappa$ C) was chemically modified to achieve a novel super absorbent hydrogel *via* graft copolymerization of methacrylamide (MAM) onto the substrate followed by alkaline hydrolysis. Ammonium persulfate (APS) and N,N'-methylene bisacrylamide (MBA) were used as a free-radical initiator and a crosslinker, respectively. The saponification reaction was carried out using aqueous solution of sodium hydroxide. Either  $\kappa$ C-g-PMAM or hydrolyzed  $\kappa$ C-g-PMAM was characterized by FTIR and SEM spectroscopies.

**Key Words:** Carrageenan, Hydrogel, Super absorbent, pH-Sensitive, Swelling.

### INTRODUCTION

Three-dimensional hydrophilic networks, *i.e.*, super absorbent hydrogels, are capable of absorbing large values of water, saline solution or physiological fluids<sup>1</sup>. Because of their excellent characteristics, they are widely used in many applications such as disposable diapers, feminine napkins and soil for agriculture and horticulture<sup>2-4</sup>. Since the development of the first super absorbent hydrogel, the hydrolyzed starch-g-polyacrylonitrile, by the US Department of Agriculture, Northern Regional Research Center, in the late 1960s<sup>5</sup>, monomers such as acrylic acid and acrylamide have been graft copolymerized onto polysaccharides such as starch, cellulose and their derivatives<sup>6,7</sup> to prepare super absorbent hydrogels.

Hydrogels responding to external stimuli such as heat, pH, electric field, chemical environments, *etc.*, are often referred to as "intelligent" or "smart" hydrogels. These responsive hydrogels have become an important area of research and development in the field of medicine, pharmacy and biotechnology<sup>8,9</sup>.

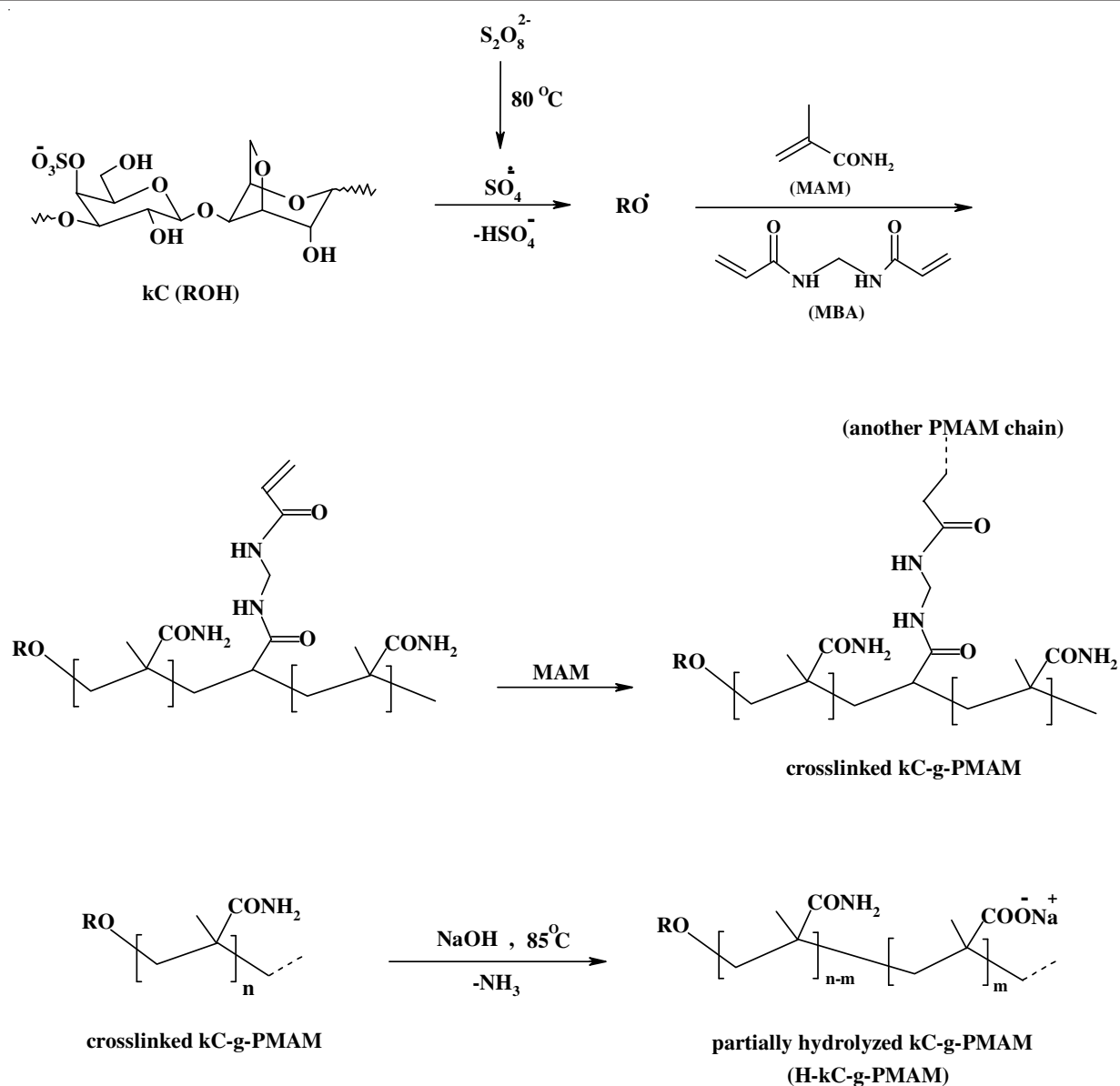
Carrageenans are relatively new polysaccharides to synthesize of natural-based super absorbent polymers. These biopolymers are linear sulfate polysaccharides that are obtained from certain species of red seaweeds<sup>10</sup>. The presence of hydrophilic sulfate groups with high ionization tendency and less sensitivity to salt solution was our main idea for synthesis of carrageenan-based super absorbent hydrogels. In addition, the presence of the natural parts guarantees biocompatibility, biodegradability and non-toxicity of the super absorbing materials. Therefore, following a continuous research on

modification of kappa-carrageenan ( $\kappa$ C), the most well-known type of carrageenan family that its structure is framed in **Scheme-I**<sup>11-14</sup>, in this paper, we report the synthesis and characterization of a novel super absorbing hydrogel from  $\kappa$ C-g-poly(methacrylamide).

### EXPERIMENTAL

The polysaccharide, kappa-carrageenan (Condinson Co., Denmark); N,N'-methylene bisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from Fluka), methacrylamide (MAM, from Merck), were of analytical grade and were used as received.

**Graft copolymerization:** The graft copolymerization reactions were carried out using ammonium persulfate as an initiator and N,N'-methylene bisacrylamide as a crosslinker in an aqueous solution. A general procedure was conducted as follows.  $\kappa$ C (1.00 g) was dissolved in 50 mL degassed distilled water in a three-neck reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 600 rpm). The reactor was placed in a water bath preset at 80 °C. After complete dissolution of the polysaccharide to form a homogeneous solution, a definite amount of ammonium persulfate solution (0.10-0.66 g in 5 mL H<sub>2</sub>O) was added into the mixture and was allowed to stir for 15 min. Then certain amounts of methacrylamide (0.50-5.50 g in 5 mL H<sub>2</sub>O) and N,N'-methylene bisacrylamide (0.04-0.20 g in 5 mL H<sub>2</sub>O) were simultaneously added to the reaction mixture. After 1 h, the reaction product was allowed to cool to ambient temperature. The obtained hydrogel was then poured into methanol (500 mL). After complete dewatering for 24 h, the hardened gel



Scheme-I: Proposed mechanistic pathway for synthesis of  $\kappa\text{C}$ -based hydrogels

particles product were filtered, washed with fresh methanol (2 mL  $\times$  50 mL) and dried at 50 °C. After grinding, the powdered super absorbent hydrogel was stored away from moisture, heat and light.

**Swelling measurements using tea bag method:** The tea bag (*i.e.*, a 100 mesh nylon screen) containing an accurately weighed powdered sample ( $0.5 \pm 0.001$  g) with average particle sizes between 40-60 mesh (250-350  $\mu\text{m}$ ) was immersed entirely in distilled water (200 mL), desired salt solution (100 mL) or buffer solution (100 mL) and allowed to soak for 3 h at room temperature. The buffer solutions were composed hydrochloric acid and potassium chloride (for acidic pHs), potassium dihydrogen phosphate and di-sodium hydrogen phosphate (for pH 7.0) and borate, boric acid, hydrochloric acid and sodium hydroxide (for basic pHs). The tea bag was hung up for 15 min in order to remove the excess solution. The equilibrated swelling (ES) was measured twice using the following equation:

$$\text{ES}(\text{g/g}) = \frac{W_2 - W_1}{W_1} \quad (1)$$

where  $W_1$  and  $W_2$  are the weights of dry and swollen gel, respectively. The accuracy of the measurements was  $\pm 3\%$ .

## RESULTS AND DISCUSSION

**Synthesis and spectral characterization:** Scheme-I shows a simple mechanism for crosslinking graft copolymerization of methylacrylamide onto  $\kappa\text{C}$  backbones and alkaline hydrolysis of the resulted graft copolymer. At the first step, the thermally dissociating initiator, *i.e.*, ammonium persulfate, is decomposed under heating (80 °C) to produce sulfate anion-radical. Then the anion-radical abstracts hydrogen from the hydroxyl group of the  $\kappa\text{C}$  substrate to form corresponding alkoxy radicals. So, these macroradicals initiate methacrylamide grafting onto  $\kappa\text{C}$  backbones led to a graft copolymer so called  $\kappa\text{C}$ -g-PMAM. In addition, crosslinking reaction was occurred in the presence of a crosslinker, *i.e.*, N,N'-methylene bisacrylamide. The  $\kappa\text{C}$ -g-PMAM was then hydrolyzed with NaOH solution to produce a super swelling hydrogel, H- $\kappa\text{C}$ -g-PMAM. During the partially saponification,  $\text{NH}_3$  gas was

evolved and some of the 'non-ionic' carboxamide groups are converted to 'ionic' carboxylate salt (**Scheme-II**).

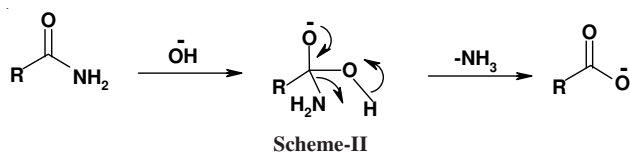


Fig. 1 shows the FTIR spectra of  $\kappa$ C,  $\kappa$ C-g-PMAM and H- $\kappa$ Cg-PMAM. The bands observed at 842, 913, 1016, 1222 and 3400-3200  $\text{cm}^{-1}$  can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage, ester sulfate stretching and stretching of -OH groups of non-modified  $\kappa$ C, respectively (Fig. 1a). The graft copolymer,  $\kappa$ C-g-PMAM, comprise a  $\kappa$ C backbone with side chains that carry carboxamide functional groups that are evidenced by a new peak at 1660  $\text{cm}^{-1}$  (Fig. 1b). This peak attributed to C=O stretching in carboxamide functional groups of poly(methacrylamide). The stretching band of -NH overlapped with the -OH stretching band of the  $\kappa$ C portion of the copolymer. After alkaline hydrolysis, the new absorption modes at 1459 and 1557  $\text{cm}^{-1}$  can be attributed to symmetric and asymmetric stretching modes of carboxylate groups, respectively (Fig. 1c)<sup>15</sup>. As shown in Fig. 2a and **Scheme- I**, after partially alkaline hydrolysis of the  $\kappa$ C-g-PMAM, some of the amide groups are converted to carboxylate anions.

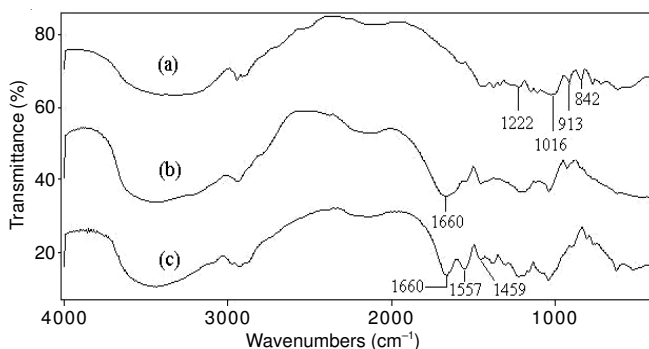


Fig. 1. FTIR spectra of  $\kappa$ C (a),  $\kappa$ C-g-PMAM (b), and H- $\kappa$ C-g-PMAM (c)

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. After extracting the homopolymer (PMAM), appreciable amount of synthetic polymer percentage of the graft copolymer (85 %) were concluded. The graft copolymer spectrum was similar to Fig. 2b. Also according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.0 %. This fact practically proves that all methacrylamide are involved in the polymer network. So, the monomer percent in the network will be very similar to that of the initial feed of reaction.

**Morphology of hydrogel:** Fig. 2 shows the scanning electron microscope images of kappa-carrageenan (3a),  $\kappa$ C-g-PMAM (2b) and H- $\kappa$ C-g-PMAM hydrogel (2c). These pictures verify that the synthesized polymer have a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

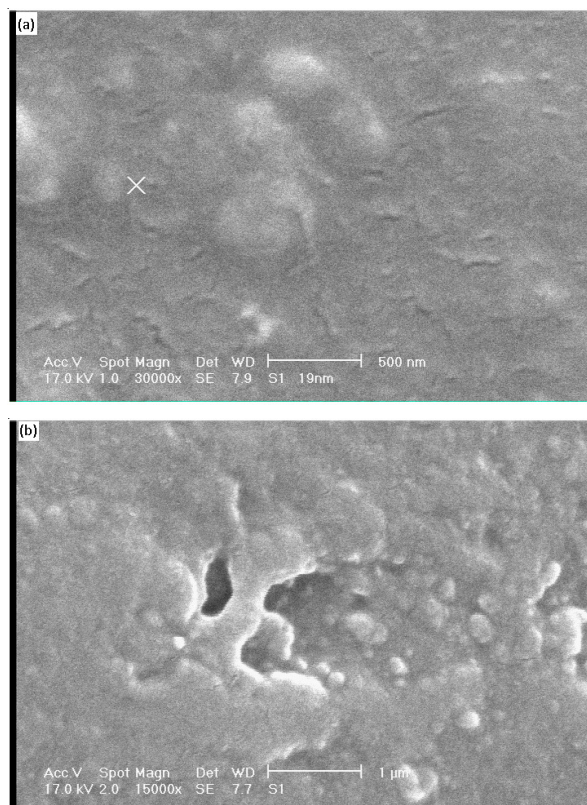


Fig. 2. SEM photograph of the graft copolymer. (a) Surface of porous hydrogel (b)

**Thermal analysis:** Thermogravimetric analysis (TGA) was employed to thermally characterize the H- $\kappa$ C-g-PMAM hydrogel in comparison with the graft copolymer  $\kappa$ C-g-PMAM (Fig. 3). The thermal stability of the resulted biosuper absorbent hydrogel is improved as is clear from the TGA curve. TGA curves of copolymer and biosuper absorbent hydrogel (Fig. 3a-3b) show a weight loss in two distinct stages. The first stage ranges between 10 and 135  $^{\circ}\text{C}$  and shows about 17 % loss in weight. This may correspond to the loss of adsorbed and bound water<sup>16,17</sup>. No such inflexion was observed in the TGA curve of synthesized hydrogel (Fig. 3b). This indicated that the crosslinked polymers were resistant to moisture absorption. The second stage of weight loss starts at almost 210  $^{\circ}\text{C}$  and continues up to 310  $^{\circ}\text{C}$  during which there was 53 % weight loss due to the degradation of carrageenan. In general, degradation of  $\kappa$ C-g-PMAM is faster than that of H- $\kappa$ C-g-PMAM hydrogel. Ca. 53 % weight loss takes place in the temperature range of 210-310  $^{\circ}\text{C}$  for  $\kappa$ C-g-PMAM. In the hydrogel sample, a residual weight of 77 % was observed at 310  $^{\circ}\text{C}$ . The appearance of these stages indicates the structure of carrageenan backbones has been changed, which might be due to the crosslinking of carrageenan chains.

## Conclusion

In this work, we prepared a novel super absorbent hydrogel, H- $\kappa$ C-g-PMAM, by graft copolymerization of methacrylamide onto  $\kappa$ C backbones followed by alkaline hydrolysis of the  $\kappa$ C-g-PMAM graft copolymer. So, swelling capacity of the hydrogels was recognized to affect by the grafting and alkaline hydrolysis variables. The maximum water absorbency (435 g/g) was achieved.

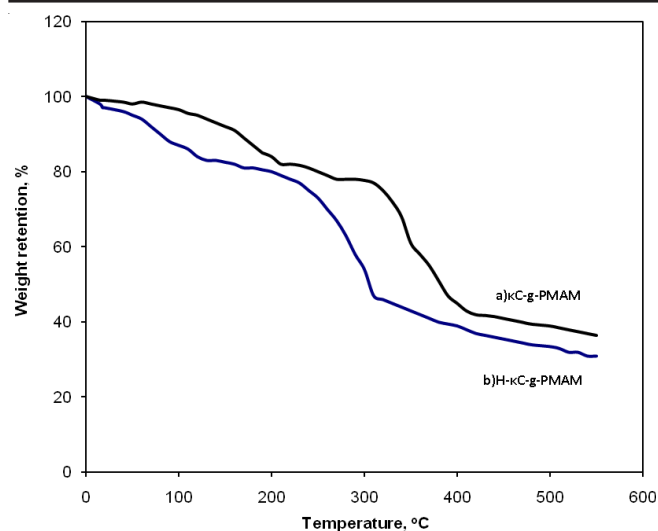


Fig. 3. TGA of kappa-carrageenan (a),  $\kappa$ C-g-PMAM (b) and H- $\kappa$ C-g-PMAM hydrogel (c)

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