Evaluation of Superabsorbent Hydrogel Composites Based on Carrageenans-Graft-Poly(sodium acrylate)/Kaolin

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Graft copolymerization of acrylic acid in presence of kaolin powder using methylenebisacrylamide as a crosslinking agent and ammonium persulfate as an initiator was carried out under argon atmosphere in a homogeneous aqueous medium onto kappa-carrageenan. A plausible reaction mechanism of grafting has been suggested. The morphology of the samples was examined by scanning electron microscopy. The composite structure was confirmed using FTIR spectroscopy. A new absorption band at 1707 cm^{-1} in the composite spectrum confirmed kaolin-organic polymer linkage. According to the empirical rates of the polymerization and the graft copolymerization of acrylic acid onto carrageenan backbone, the overall activation energy of the graft copolymerization reaction was estimated to be 17.33 kJ/mol.

Key Words: Kappa-carrageenan, Acrylic acid, Hydrogel composite, Graft, Kaolin powder.

INTRODUCTION

Vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels and hydrogel composites. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method. These biopolymer materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline or physiological solutions. They are widely used in many fields such as hygienic, cosmetics, and agriculture[1-5].

Carrageenan is the generic term for linear polysaccharides that are obtained commercially by alkaline extraction of certain species of red seaweeds. Carrageenans are composed of a linear galactose backbone linked with alternating $\alpha(1\rightarrow3)$ and $\beta(1\rightarrow4)$ linkages. In addition, the galactose units linked $\alpha(1\rightarrow3)$ in this general structure often occur as 3,6-anhydro-D-galactose and sulfate ester groups may be present on some or all galactose units.

Modification of these biopolymers has been our main goal to achieve natural polymer-based materials with ultra high water absorption capacity. These hydrophilic networks (hydrogels) are being increasingly used in various applications, from disposable hygiene products to agricultural water reservoir systems[3,4]. The presence of the natural parts guarantees biodegradability of the superabsorbing materials. On the other hand, hydrogels itself occupy a unique position in the field of medicine and pharmacy[6-8] because of the ways in which the imbibed water strongly influences the transport, surface and mechanical properties of the polymers.

The present work deals with chemical modification of the most convenient member of the carrageenan family (*i.e.* kappa-carrageenan, kC) through graft copolymerization as a method for adding new properties to the biopolymer with a minimum loss of native properties. Thus, acrylic acid was graft polymerized onto kC in the presence of a crosslinking agent and clay particles to form superabsorbent hydrogel composite. Finally, the calculation of the rates of polymerization (Rp) and graft copolymerization (Rg) values for hydrogel composite was preliminary investigated as well.

EXPERIMENTAL

Kappa-carrageenan (kC, from Condinson Co., Denmark), was used as received. Acrylic acid (Merck), was used after vacuum distillation. Ammonium persulfate (APS, Merck) was used without purification. Methylenebisacrylamide (MBA, Fluka) and Kaolin powder (Fluka, particle size < 5 μm) were used as received. All other chemicals were of analytical grade.

Superabsorbent composite synthesis: In a 500 mL reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type), variable amounts of kappa-carrageenan (0.5-1.5 g) were added to 50 mL degassed distilled water. The reactor was placed in a thermostated water bath to control the reaction temperature at 65 ℃. After complete dissolution of kappa-carrageenan, various amounts of Kaolin

powder (0.25-1.25 g) were added to the kappa-carrageenan solution and allowed to stir (300 rpm) for 15 min. After complete dissolution of the polysaccharide to form a homogeneous solution, a definite amount of ammonium persulfate solution (0.10-0.50 g in 5 mL H_2O) was added into the mixture and was allowed to stir for 15 min. Then certain amounts of acrylic acid (0.50-3.50 mL) and methylenebisacrylamide (0.04-0.20 g in 5 mL H_2O) were simultaneously added to the reaction mixture. All the reactions were carried out at 65 ºC under an argon gas atmosphere and the reaction mixture was continuously stirred (300 rpm) for 1 h. At the end of the propagation reaction, the gelly product was poured in ethanol (300 mL) and allowed to dewater for 24 h. Then, the product was filtered and washed with 100 mL ethanol. The filtered product was dried in an oven at 50 ºC for 10 h. After grinding, the powdered superabsorbent composite was stored away from moisture, heat and light[9-11].

RESULTS AND DISCUSSION

Mechanism, characterization and reaction rate: The superabsorbent composite was prepared by graft copolymerization of acrylic acid onto kappa-carrageenan in the presence of a crosslinking agent and powdery kaolin (**Scheme-I**). Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that abstract hydrogen from one of the functional groups in side chains of carrageenan backbones. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of acrylic acid led to a graft copolymer. Since a crosslinking agent, *e.g.* methylenebisacrylamide, is presented in the system, the copolymer comprises a crosslinked structure[9].
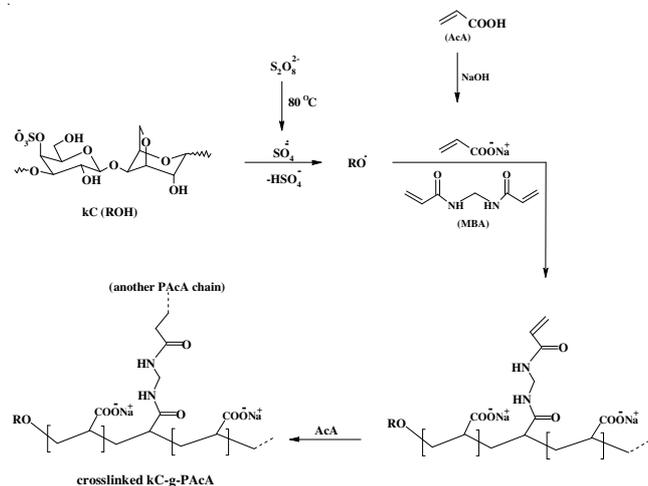
Scheme-I: Proposed mechanism for synthesis of carrageenan-g-poly(acrylic acid) hydrogel

For identification of the hydrogel, infrared spectroscopy was used. Fig. 1 shows the IR spectroscopy of kC and kC-g-PAcA/kaolin hydrogel composite. The bands observed at 841, 918, 1021 and 1222 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of kappa-carrageenan, respectively (Fig. 1a). The broad band at 3600-3100 cm^{-1} is due to stretching of

-OH groups of kappa-carrageenan. The IR spectrum of the hydrogel composite, kC-g-PAcA/kaolin (Fig. 1b) shows three new characteristic absorption bands at 1707, 1542 and 1402 cm^{-1} verifying the formation of graft copolymer product. These peaks attributed to carbonyl stretching of the carboxylic acid groups and symmetric and asymmetric stretching modes of carboxylate anions, respectively[12,13]. Combination of absorption of the carboxylate and alcoholic O-H stretching bands is appeared in the wide range of 3600-2550 cm^{-1}.
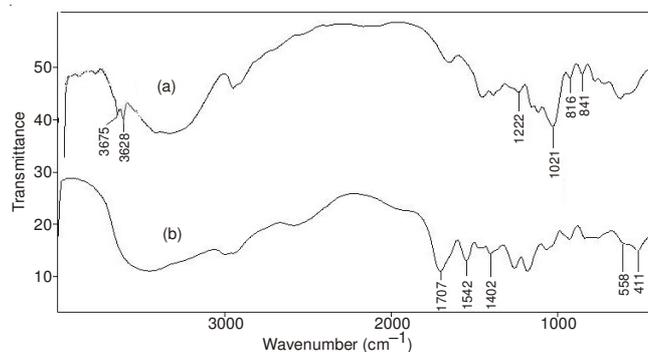
Fig. 1. FTIR spectra of (a) pure carrageenan and (b) carrageenan-g-poly(acrylic acid)/kaolin composite

The absorption band at 1707 cm^{-1} can be corresponding to the ester groups that can be formed during the graft polymerization reaction. The carboxylate groups of the grafted poly(acrylic acid) onto carrageenan can be react with the -OH groups on the kaolin surface. The replacement of -OH groups in the surface of kaolin by carboxylate anions results in the ester formation. The reaction can be shown as follows[14]:
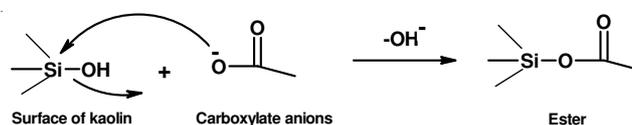
As shown in this figure, the absorption bands of -OH of kaolin at 3674-3628 cm^{-1} are disappeared.

To obtain additional evidence of grafting, a similar polymerization was conducted in the absence of the crosslinker and clay. After extracting the homopolymer, poly(acrylic acid) and unreacted monomers using a cellophane membrane dialysis bag (D9402, Sigma-Aldrich), an appreciable amount of grafted carrageenan (86.3 %) was observed. The graft copolymer spectrum was very similar to Fig. 1b. Also according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.9 %. This fact practically proves that all acrylic acid monomers is involved in the polymer network. So, the monomer per cent in the network will be similar to that of the initial feed of reaction.

The percentage of grafting efficiency (Ge %) was evaluated with the following weight-basis equation[15]:

$$Ge(\%) = \frac{\text{Monomer grafted}}{\text{Monomer charged}} \times 100 \tag{1}$$

The Ge % stands for the grafted monomer formed from initial monomer charged.

One of the most important properties that must be considered is hydrogel microstructure morphologies. Fig. 2 shows

the scanning electron microscope (SEM) photographs of the surface (Fig. 2A) and the cross-sectional area (Fig. 2B) of the hydrogel composite with interconnected pores. The composite has 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. The cross-sectional view of hydrogels composite (Fig. 2B) also exhibited large, open, channel-like structure.
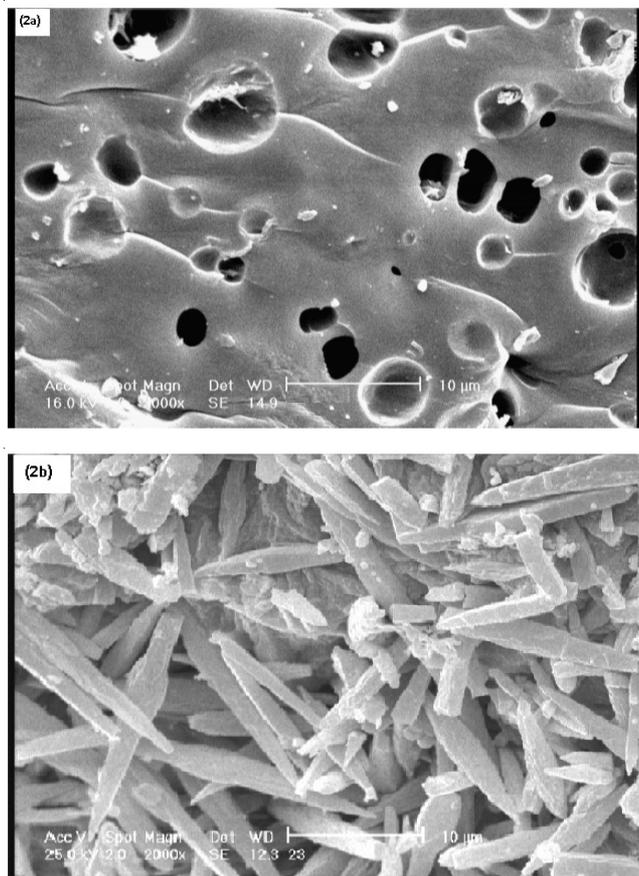

Fig. 2.   SEM photograph of the hydrogel. (A) Surface of porous hydrogel composite; (B) Cross-sectional area of porous hydrogen compositel. The average pore diameter of the synthesized hydrogel was 8.2 nm

The results of BET analysis showed that the average pore diameter of the synthesized hydrogel composite was 8.2 nm. In general, the size of the pores can be controlled by adjusting the various factors such as the type and amount of surfactant, porosigens and gas forming agent during crosslinking polymerization, and the amount of diluent in the monomer (*i.e.*, monomer-diluent ratio). For example, as the amount of diluent (usually water) in the monomer mixture increases, the pore size also increases up to the micrometer (μm) range[16].

Reaction rate: The rate of polymerization (Rp) and graft copolymerization (Rg) hydrogel composite may be evaluated as measures of the rate of monomer disappearance by using the following equations[17]:

$$Rp(mol\ s^{-1}.m^{-3}) = \frac{Weight\ of\ total\ hydrogel\ composite\ formed}{Molecular\ weight\ of\ monomer \times [rection\ time\ (s)] \times volume\ (m^3)} \quad (2)$$

$$Rg(mol\ s^{-1}.m^{-3}) = \frac{Weight\ of\ grafted\ copolymer}{Molecular\ weight\ of\ monomer \times [rection\ time\ (s)] \times volume\ (m^3)} \quad (3)$$

The calculation of Rp values may be of significant importance in confirming a proposed reaction mechanism and kinetics. Therefore, we investigated the relation between rate of graft copolymerization and concentration of ammonium persulfate, acrylic acid, Kaolin and Kapa-carrageenan. Figs. 2-6 show that the plots of Rp *versus* the monomer concentration, [acrylic acid], half-order of the initiator concentration, [ammonium persulfate]$^{1/2}$ and the polysaccharide concentration, [kC]$^{1/2}$, are linear[13,18]. This is in agreement with a modified kinetic scheme recently explored for APS-initiated methacrylate grafting onto sago starch. The statement of rate of polymerization according to the scheme is as follows:

$$R_p = k_p\ (K\ k_d/k_t)^{1/2}[kC]^{1/2}[APS]^{1/2}\ [AA]\ [Kaolin] \quad (4)$$

The coefficient K is the equilibrium constant, k_p, k_d and k_t are the rate constants for propagation, kC-APS complex dissociation, and termination reactions, respectively. Therefore, we preliminarily conclude that the ammonium persulfate-initiated grafting Acrylic acid in the presence of kaolin powder onto kapa-carrageenan is also fitted with this kind of rate statement[19,20].
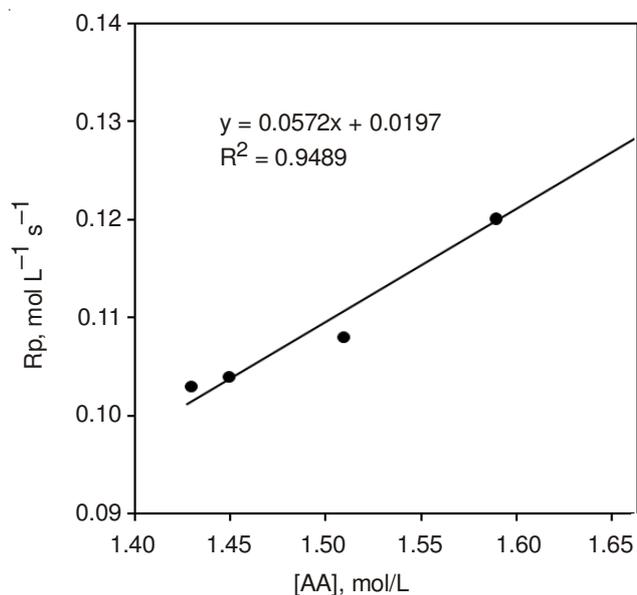

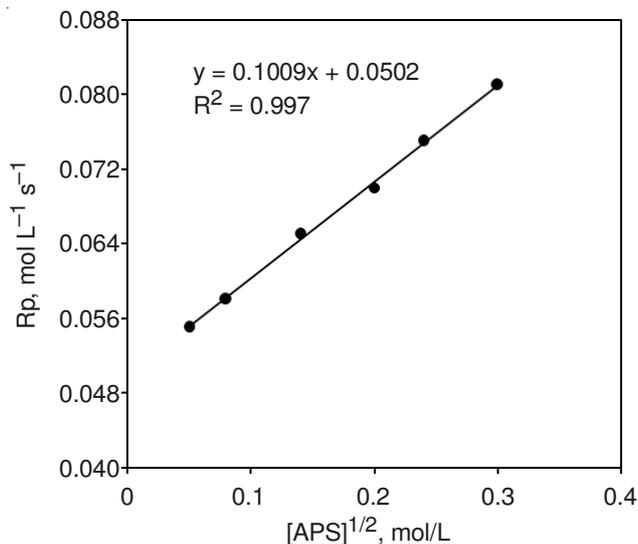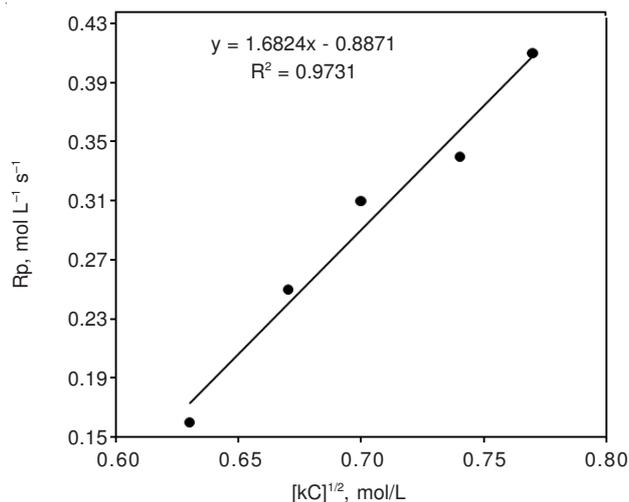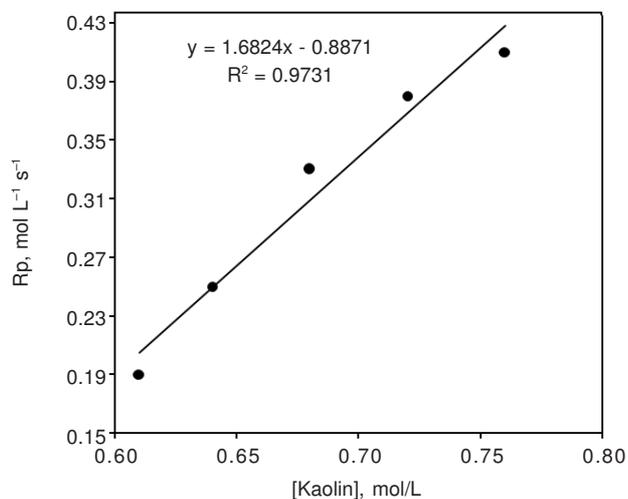Fig. 3. Plot of Rp *versus* acrylic acid (AA) concentration

Fig. 4. Plot of Rp *versus* initiator [APS]$^{1/2}$

Fig. 5. Plot of Rp *versus* carrageenan [kC]$^{1/2}$

Fig. 6. Plot of Rp *versus* [Kaolin]$^{1/2}$

The overall activation energy (Ea) of the graft polymerization reaction was calculated by using of the eqn. (3) and the slope of the plot ln Rg *versus* 1/T (Fig. 7) based on Arrhenius relationship [$k_p = A_{exp}(-Ea/RT)$]. Therefore, Ea for the graft copolymerization was found to be 17.33 kJ/mol.
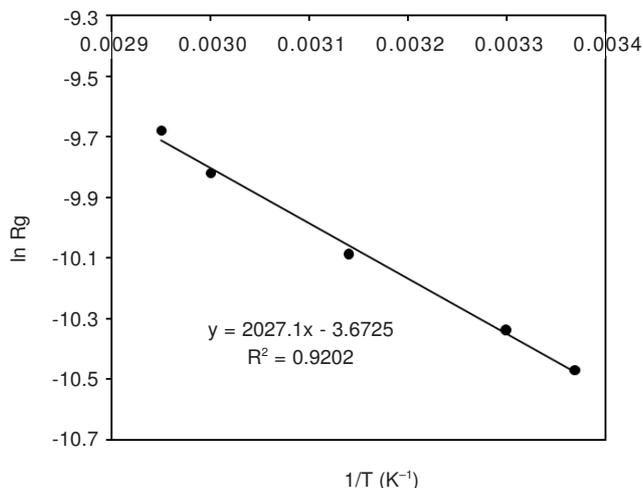
Fig. 7. Plot of ln Rg *versus* 1/T for estimating the activation energy of the graft polymerization reaction

Conclusion

A novel superabsorbent composite was prepared by graft copolymerization of acrylic acid onto kapa-carrageenan in the presence of a crosslinking agent methylene bisacrylamide. The resultant superabsorbent composite had a large degree of water absorbency. The study of FTIR spectra shows that in the composite spectrum a new absorption band at 1707 cm^{-1} was appeared that attributed to the ester formation from replacement of hydroxyl groups of Kaolin with grafted carboxylate anions onto polysaccharide backbones. Empirical polymerization rate showed a first-order dependence on the monomers concentration and a half-order dependence on the initiator concentration. According to the slope of ln Rg *versus* 1/T, the overall activation energy for graft copolymerization reaction was estimated to be 17.33 kJ/mol.

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