

# New Smart Carrageenan-Based Superabsorbent Hydrogel Hybrid: Investigation of Swelling Rate and Environmental Responsiveness

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**ABSTRACT:** Synthesis of novel natural-based superabsorbents with improved properties is of prime importance in many applications. In this article we report an efficient synthesis of new polysaccharide-based superabsorbent hybrid composing carrageenan, acrylic acid, sodium acrylate, and 2-hydroxyethyl acrylate through homogenous solution polymerization process. Infrared spectroscopy and thermogravimetric analysis (TGA) were carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM). To deeper studies on the structure-property relation in SAP hydrogels, three hydrogels with different acrylic acid/2-hydroxyethyl acrylate (AA/HEA) weight ratios

were synthesized and swelling capacity in various media was assessed. The hydrogel hybrid was also tested to be swollen and deswollen alternatively in 0.01 and 0.1 M sodium chloride solution. Moreover, the swelling-deswelling capability of the hydrogel in alternatively changed methanol-water mixtures was studied. Additionally, the swelling kinetics of the synthesized hydrogels were examined. The absorbency under load (AUL) of hydrogel was also investigated by using an AUL tester at various applied pressures. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3228–3238, 2010

**Key words:** hydrogel; superabsorbent; carrageenan; swelling behavior; graft copolymer

## INTRODUCTION

Superabsorbents (SAPs)<sup>1,2</sup> are hydrophilic polymeric materials that swell and absorb water or aqueous solutions up to several hundred times their dried weights and have become ubiquitous and indispensable materials in many applications.<sup>1–10</sup> They are probably most well-known for their use in diapers. In 2005, an estimated \$ 8bn of disposable diapers was sold in the US.<sup>3</sup> While the hygiene market provides the chief source of demand for SAPs, there are other applications where superabsorbents can offer valuable properties such as fire fighting uses<sup>4</sup> and food packaging.<sup>5</sup> Another potential area of growth for SAPs lies in the agricultural market. These materials can help conserve water in a variety of agricultural and horticultural applications by improving the water-holding capacity of sandy soils.<sup>1</sup> Furthermore, they have many advantages for the restoration of degraded lands.<sup>10</sup> Therefore, many industries may benefit from the use of SAPs in their products.<sup>1–10</sup>

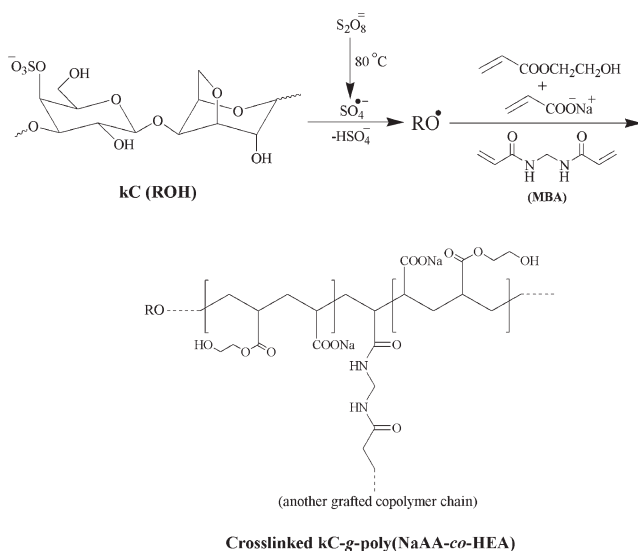
The field of SAPs has moved forward at a dramatic pace. Synthetic methods have produced numerous hydrogel materials with excellent properties. However,

their nonbiodegradability might pose long-time environmental problems and limit their use in drug delivery systems and consumer products. As a consequence, various academic and industrial research groups have put considerable amounts of effort and resources toward development of new absorbent materials from natural polymers, which would decompose in landfills.<sup>11–14</sup> Considerable interest has been focused on grafting of synthetic polymers onto natural polymers such as cellulose,<sup>15,16</sup> chitosan,<sup>17</sup> gum arabic,<sup>18,19</sup> starch,<sup>20</sup> sodium alginate,<sup>21</sup> protein,<sup>22</sup> and carrageenan.<sup>23,24</sup>

Carrageenan is a collective term for linear sulfated polysaccharides that are obtained commercially by alkaline extraction of certain red seaweeds of the “*Rhodophyceae*” class. They have been extensively used in the food industry as thickening, gelling and protein-suspending agents, and more recently by the pharmaceutical industry as excipient in pills and tablets.<sup>25</sup> Schematic diagram of the idealized structure of the repeat units for the most well-known and most important type of carrageenan family, kappa-carrageenan ( $\kappa$ C), is framed in Scheme 1. 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 superabsorbent hydrogels.

Stimuli-sensitive hydrogels or smart hydrogels which swell and contract in response to environmental

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**Scheme 1** Proposed Mechanistic Pathway for Synthesis of polysaccharide-based hydrogel hybrid.

stimuli such as temperature, pH, solvent composition and electric fields, have been explored intensively.<sup>26–31</sup> These materials are a central component in numerous applications ranging from drug delivery systems<sup>27</sup> to sensors and actuators.<sup>26</sup> Some scientists have suggested that smart gels could form the basis of a future “soft, wet” technology that might one day replace certain aspects of today’s technology, which is based on metals and other hard materials.<sup>31</sup> In the area of biomaterials research, smart hydrogels has been gaining greater momentum.<sup>27–31</sup> Response to stimuli is a basic phenomenon in living systems. Overall, responsive hydrogels have become an important area of research and development in the field of medicine, pharmacy and biotechnology.

Synthesis of SAP hydrogels with improved properties is the aim of many research groups. However, gel scientists are facing challenges in this context. Many parameters such as swelling capacity, swelling rate (SR), strength of the swollen gel (AUL), swelling capacity in salt solutions, and gel content should be considered. The majority of reported SAPs possess only high load-free absorbency. Despite many efforts to synthesize SAPs in recent years, there are few studies for improving other parameters. In the present study we attempted to synthesize a novel carrageenan-based hydrogel and investigated the effect of acrylic acid/2-hydroxyethyl acrylate (AA/HEA) weight ratio on swelling behavior and kinetics. These assessments will pave the way for new hydrogels with improved absorbency in saline solutions and SRs. The prepared hydrogel showed a reproducible on–off switching behavior when the swelling medium was alternatively changed between sodium chloride solutions with different molar concentrations. The hydrogel hybrid was also tested to be

swollen and deswollen alternatively in water-methanol mixtures with various compositions. AUL of samples was also determined by using an AUL tester at various applied pressures.<sup>32</sup> This is a very important factor that is usually given in the patent literature and technical data sheets offered by industrial hydrogel manufacturers. Therefore, this hydrogel may be considered as an excellent candidate for various applications.

## MATERIALS AND METHODS

### Materials

$\kappa$ C (from Tordak, Tehran, Iran) was industrial grade. *N,N'*-Methylenebisacrylamide (MBA, from Merck, Darmstadt, Germany), ammonium persulfate (APS, from Fluka, Switzerland), 2-hydroxyethyl acrylate (HEA, from Fluka), and inorganic salts (all from Fluka) were of analytical grade and were used without further purification. Acrylic acid (AA, from Merck) was used after distillation. Double-distilled water was used for hydrogel preparation and swelling measurements.

### Instrumental analysis

Samples were characterized as KBr pellets on a Mattson-1000 Fourier transform infrared (FTIR) spectrophotometer. Morphology of the dried gel structures was studied by scanning electron microscopy (SEM). After dispersion in water to swell for 72 h and drying in an oven, superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Philips, XL30). Thermogravimetric analyses (TGA) of the hydrogels (after dispersion in water to swell for 72 h and drying in an oven) were performed with Polymer Laboratories systems at a heating rate of 20°C/min under nitrogen atmosphere. The sample weight taken for TGA was 10.0 mg.

### Graft copolymerization

$\kappa$ C (1 g) was dissolved in 40 mL distilled water. The solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 150 rpm) and gas inlet tube, and the reactor was immersed in a thermostated water bath preset at a desired temperature (80°C). Oxygen-free nitrogen gas (passed through a freshly prepared alkaline pyrogallol solution) was bubbling into the solution during the reaction. After 10 min, the initiator solution (0.08 g of APS in 5 mL of H<sub>2</sub>O) was added to the mixture. After the mixture was stirred for 3 min, a certain weight ratio of AA/HEA [between 0.33 (1.5 g/4.5 g) and 3 (4.5 g/1.5 g) in

5 mL of H<sub>2</sub>O] and MBA (0.08 g in 5 mL of H<sub>2</sub>O) were simultaneously added to the reaction mixture. It should be emphasized that AA was partially neutralized (70%). After completion of the reaction, the produced hydrogel was poured into excess nonsolvent ethanol (200 mL) and remained for 3 h to dewater. Then, ethanol was decanted and the product was scissored into small pieces (diameter ~5 mm). Again, 100 mL of fresh ethanol was added and the hydrogel remained for 24 h. Finally, the filtered hydrogel was dried in an oven at 50°C for 72 h. After grinding, the powdered superabsorbent was stored away from moisture, heat and light.

### Swelling measurements

The tea bag (i.e., a 100-mesh nylon screen) containing an accurately weighed powdered sample (0.1 ± 0.001 g) was immersed entirely in 200 mL of distilled water and allowed to soak for 2 h at 25°C. The sample particle sizes were 40–60 meshes (250–400 μm). The tea bag was hung up for 10 min to remove the excess solution. The equilibrium swelling (ES, g/g) was calculated according to the following equation:

$$ES = (W_2 - W_1)/W_1 \quad (1)$$

where  $W_1$  and  $W_2$  are the weights of dry and swollen gel, respectively.

### Measurement of gel content

To determine the gel content value, a weighed sample was dispersed in double distilled water to swell for 72 h. After filtration, the extracted gel was dewatered by nonsolvent ethanol, dried (45°C, 5 h), and reweighed. Gel content (Gel %) was calculated by eq. (2).

$$Gel = (m_f/m_i) \times 100 \quad (2)$$

where  $m_i$  and  $m_f$  stand for initial weight of sample and final weight of sample, respectively. According to this equation, the gel content was found to be 76% (AA/HEA = 1).

### Swelling in various salt solutions

Absorbency of sample was evaluated in different concentrations of NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub> salt solutions.

### Absorbency at various values of pH

Individual solutions with acidic and basic values of pH were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions to achieve pH ≥ 6.0 and

pH < 6.0, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ±0.1). Then, 0.1 (±0.001) g of the dried hydrogel (40–60 meshes) was used for the swelling measurements according to eq. (1).

### Responsiveness behavior of the SAP hydrogel

Salt-sensitivity of the hydrogel hybrid (AA/HEA = 3) was investigated in terms of swelling and deswelling of the final product at two solutions with different salt concentrations (0.01 and 0.1 M aq. NaCl). First, certain amount of sample (0.5 ± 0.001 g) was poured into a weighed tea bag and immersed in 200 mL of 0.01 M salt solution. Then, at consecutive time intervals, the tea bag was taken out from the water, hung up for 1 min to remove the excess solution, and then weighed. Swelling capacity of the hydrogel at each solution was measured according to eq. (1). It should be emphasized that for each cycle, a fresh solution was used.

Solvent-sensitivity was also assessed in similar manner (AA/HEA = 3). In this case, swelling-medium was alternatively changed between methanol-water mixtures 30 and 70%. Again, it should be emphasized that in this case for each cycle, a fresh solution was also used.

### Absorbency under load

AUL was measured according to a procedure similar to that reported by Ramazani-Harandi et al.,<sup>32</sup> at desired load (applied pressure 0.3 or 0.9 psi).<sup>22</sup>

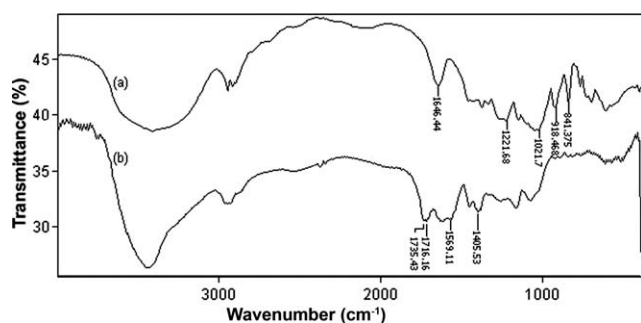
### Swelling kinetics

To study the rate of absorbency of the hydrogel, certain amount of sample (0.5 ± 0.001 g) was poured into a weighed tea bag and immersed in 200 mL of distilled water. At consecutive time intervals, the tea bag was taken out from the water, hung up for 1 min to remove the excess solution, and then weighed. The water absorbency of the hydrogel at these time intervals was calculated according to eq. (1).

## RESULTS AND DISCUSSION

### Synthesis and mechanism aspects

The hydrogel was prepared by simultaneous graft copolymerization of AA and HEA onto κC as a natural polymeric backbone in the presence of a cross-linking agent (Scheme 1). As shown in the scheme, the persulfate initiator is decomposed under heating to generate sulfate anion radical. Then the anion radical abstracts hydrogen from the existing OH groups



**Figure 1** FTIR spectra of (a) kappa-carrageenan and (b) superabsorbing hydrogel hybrid.

in the carrageenan backbone to form corresponding macroinitiator. So, this system results in active centers on the substrate to radically initiate polymerization of monomers, leading to a graft copolymer. However, this is a complex system. Since a cross-linking agent (MBA) is present in the system, the copolymer comprises a three-dimensional cross-linked structure. Separation of the homopolymeric (nongrafted) network from the copolymeric (grafted) one is not possible through solubility differences. Therefore, the product may be a mixture of homopolymeric (nongrafted) and copolymeric (grafted) networks. Formation of a semi-IPN network is also possible in some extent. The exact chemical structure of the hybrid remains a subject of debate at this stage of our study.

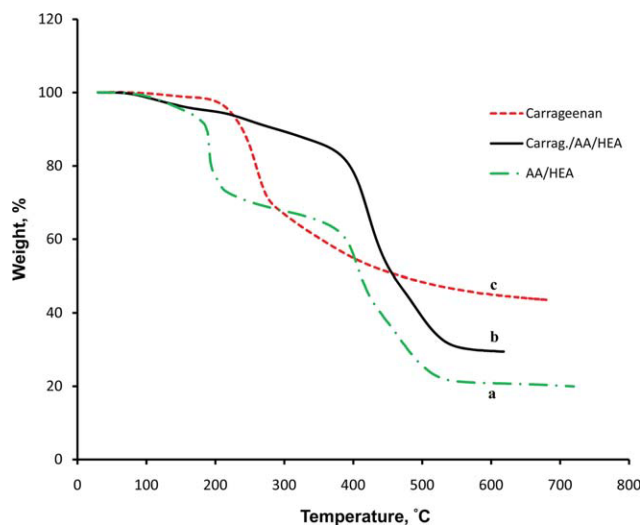
It should be pointed out that the mechanism given here (Scheme 1) is based on the known reactions ascertained basically by other researchers.<sup>33</sup> Providing meticulous mechanistic proofs is far from the scope of this applied research.

### Spectral analysis

The chemical structure of the product was studied by the FTIR technique. Figure 1 shows the FTIR spectra of polysaccharide,  $\kappa$ C, and superabsorbing hydrogel hybrid. The bands observed at 841, 919, 1022, and 1222  $\text{cm}^{-1}$  can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of  $\kappa$ C backbone, respectively [Fig. 1(a)]. The broad band at 3340  $\text{cm}^{-1}$  is due to stretching of  $-\text{OH}$  groups of  $\kappa$ C. The IR spectrum of the hydrogel hybrid [Fig. 1(b)] shows four new characteristic absorption bands at 1735, 1716, 1569, and 1405  $\text{cm}^{-1}$ . These peaks attributed to carbonyl stretching of the ester and carboxylic acid groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively.

### Thermal analysis

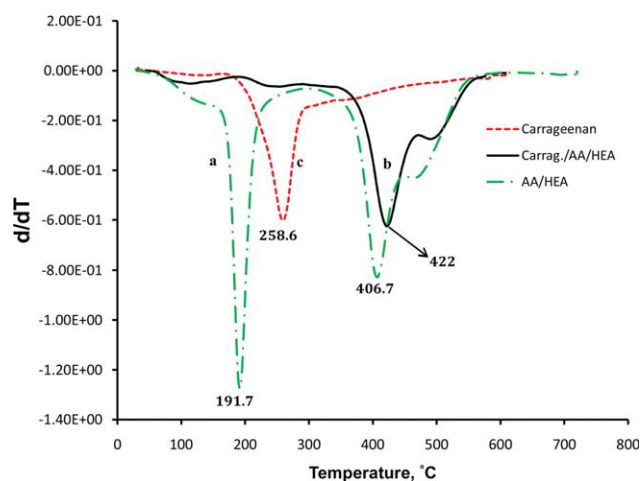
To investigate thermal properties of the product, a weighed sample was dispersed in double distilled water to swell for 72 h. After filtration, the extracted



**Figure 2** TGA traces of (a) poly(AA-co-NaAA-co-HEA) hydrogel (AA/HEA = 1), (b) hydrogel hybrid (AA/HEA = 1), and (c) kappa-carrageenan. Heating rate was 20°C/min under  $\text{N}_2$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

gel was dried and then studied by use of a Polymer Laboratories system at a heating rate of 20°C/min under nitrogen atmosphere. Since the sample was dispersed in water before study, residual monomers and low molecular weight polymer chains (extractables), which are not incorporated in to the polymer network, can be readily extracted in excess liquid.

TGA and differential thermogravimetric (DTG) traces of  $\kappa$ C, poly(AA-co-NaAA-co-HEA) hydrogel (where NaAA is sodium acrylate), and  $\kappa$ C-g-poly(AA-co-NaAA-co-HEA) are presented in Figures 2 and 3. It is obvious that TGA and DTG traces of



**Figure 3** DTG traces of (a) poly(AA-co-NaAA-co-HEA) hydrogel (AA/HEA = 1), (b) hydrogel hybrid (AA/HEA = 1), and (c) kappa-carrageenan. Heating rate was 20°C/min under  $\text{N}_2$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

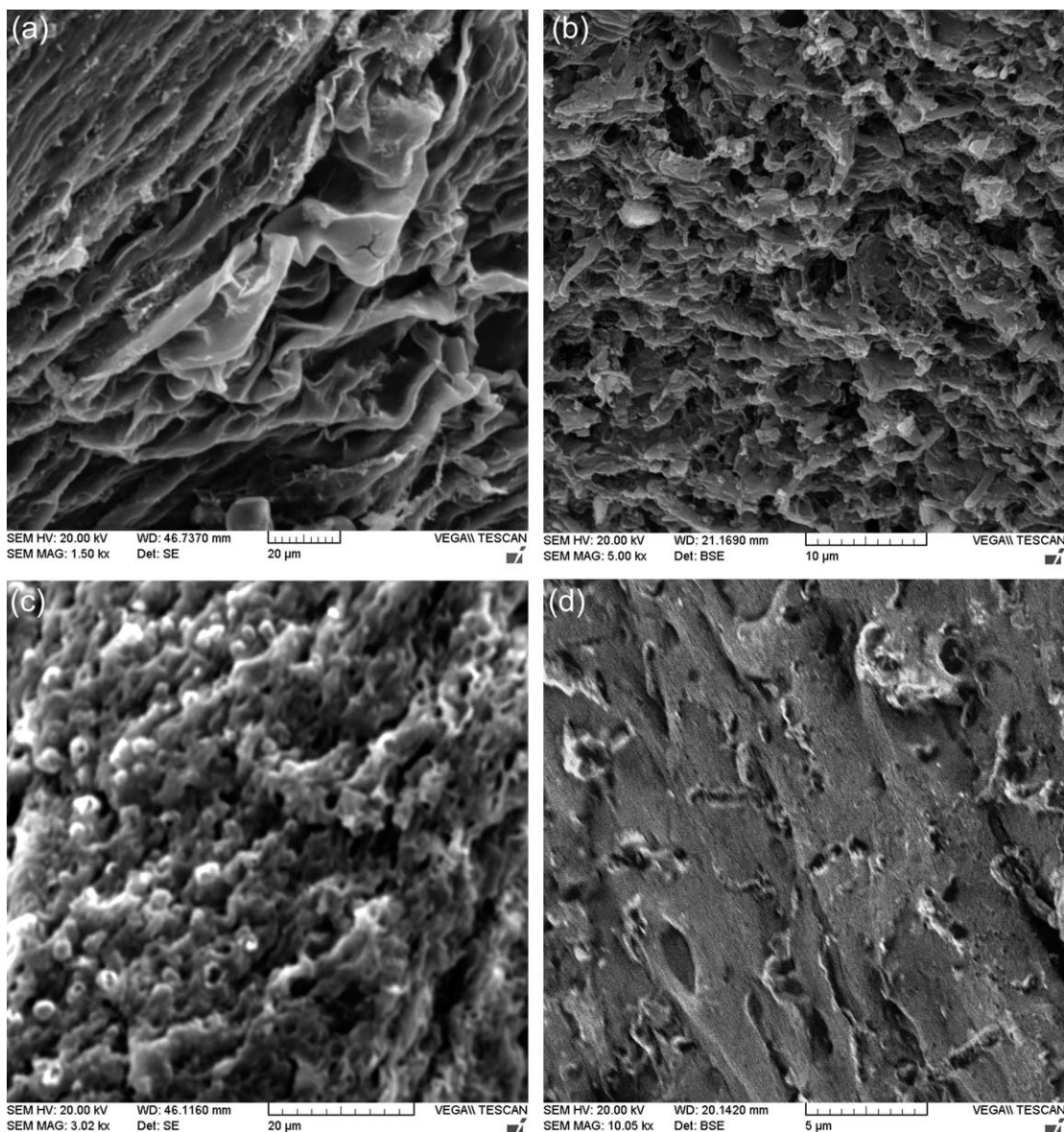
**TABLE I**  
**Thermal Properties of Kappa-Carrageenan, Poly(AA-co-NaAA-co-HEA) Hydrogel (AA/HEA = 1), and Synthesized SAP Hybrid (AA/HEA = 1). Heating Rate 20°C/min, Under N<sub>2</sub>**

Polymer	Temperature (°C) at weight loss			DTG maxima	Y <sup>a</sup> (wt %)
	5%	10%	30%		
Carrageenan	220.4	239.2	280.3	258.6	44.9
Poly(AA-co-NaAA-co-HEA) hydrogel	155.1	186.88	252.91	191.7 406.7	20.8
Carrageenan-g-poly(AA-co-NaAA-co-HEA) hydrogel	192.5	288.3	416.8	422	29.6

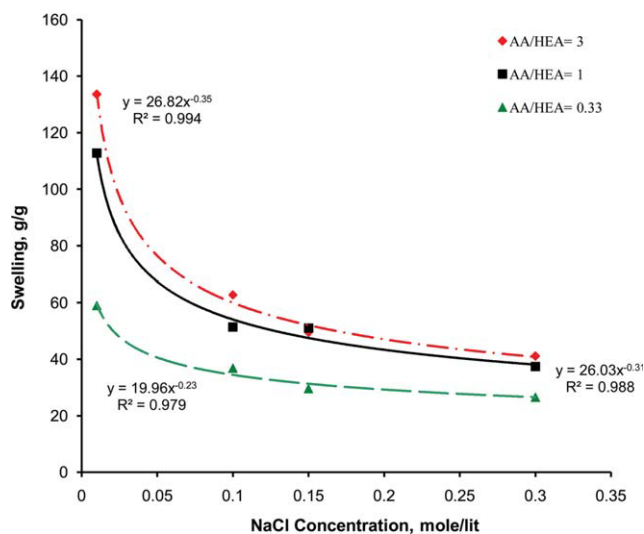
<sup>a</sup> Char yield at 600°C in nitrogen.

poly(AA-co-NaAA-co-HEA) hydrogel and the resultant hydrogel hybrid are quite different. Improved thermal stability of the superabsorbent hydrogel

may be concluded from Figure 2 and data summarized in Table I. According to this table, values related to the superabsorbent hybrid such as  $T_{10}$



**Figure 4** SEM photographs of resultant hydrogel hybrid (AA/HEA = 1). Images were taken at different magnifications from various parts of the sample.



**Figure 5** Swelling capacity variations of the synthesized superabsorbent hybrids in saline solutions with various concentrations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

(288.3°C) and char yield at 600°C (29.6%) are higher than those of the polysaccharide-free hydrogel ( $T_{10} = 186.88^\circ\text{C}$ ,  $Y = 20.8\%$ ).

#### Scanning electron microscopy

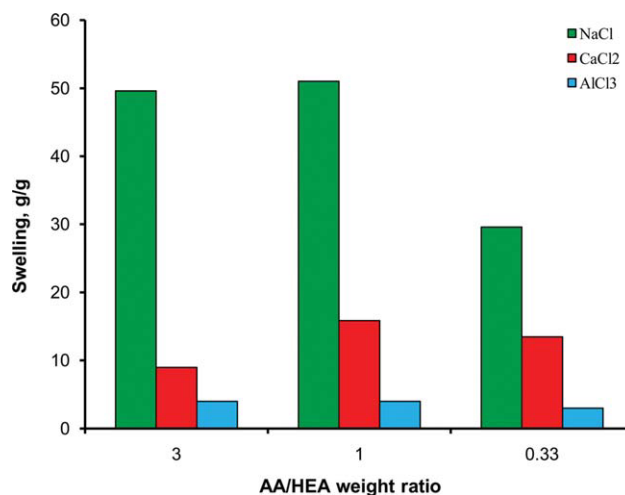
Surface morphology of the resultant hydrogel hybrid was examined under SEM. Figure 4 shows the outer surfaces of various parts of the sample at different magnifications. As shown, the hybrid has a porous structure. However, the pore sizes are quite different in various parts of the surface. Moreover, pores are not distributed on the surface uniformly. This can be attributed to bubble nitrogen gas into the solution during the reaction. It is thought that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the product.

#### Environmental sensitivity

##### Salinity

SAPs have become the subject of considerable and increasing interest in many practical applications, especially agricultural and horticultural ones. In this context, one of the key issues associated with swelling behavior in salt solutions. Therefore, in the present study effect of monomer ratio on swelling in salt solutions has been investigated. For this purpose, three hydrogels with different AA/HEA weight ratios were prepared, and the effect of salt concentration (Fig. 5) and cation charge (Fig. 6) on swelling capacity was examined. Moreover, on-off switching behavior was assessed (Fig. 7).

As indicated in Figure 5, with increasing NaCl concentration, the swelling capacity considerably

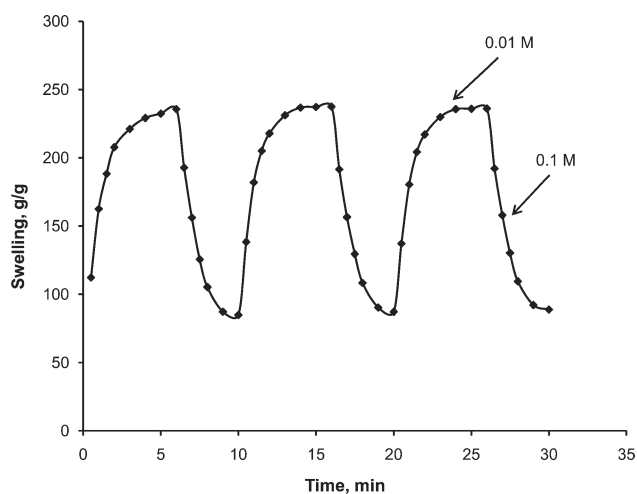


**Figure 6** Swelling capacity values of synthesized hydrogels in different chloride salt solutions (0.15 M). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

decreased, which may be attributed to the reduced osmotic pressure difference between the superabsorbent hydrogel hybrid and the external salt solution with increasing ionic strength. Furthermore, Figure 5 illustrates that increasing the salt concentration above  $\sim 0.15$  M has no appreciable influence on superabsorbency of the hydrogel.

A reverse and power-law relationship is obvious between concentration of NaCl solution and swelling capacities of the hydrogels. It is a well-known relationship that is stated earlier in the literature<sup>34</sup>:

$$\text{Swelling} = k[\text{salt}]^{-n} \quad (3)$$



**Figure 7** Responsiveness behavior of the carrageenan-based SAP hydrogel hybrid (AA/HEA = 3) when the ionic aqueous swelling media is alternatively changed between 0.01 and 0.1 M NaCl solutions.

**TABLE II**  
Values of  $k$  and  $n^a$  for Hydrogel Hybrids with Different AA/HEA Weight Ratios

AA/HEA weight ratios	$k$	$n$
3	26.82	0.35
1	26.03	0.31
0.33	19.96	0.23

<sup>a</sup> As obtained from the curve fitting in Figure 5.

where  $k$  and  $n$  are constant values for an individual superabsorbent. The  $k$  value is swelling at a high concentration of salt, and the  $n$  value is a measure of salt sensitivity. The results are summarized in Table II. According to these data,  $n$  values decreased with decreasing AA/HEA weight ratios.

To achieve a more comparative measure of salt sensitivity of the hydrogels, a dimensionless salt sensitivity factor ( $f$ ) is defined as follows<sup>35</sup>:

$$f = 1 - (S_s/S_w) \quad (4)$$

where  $S_s$  and  $S_w$  are the swelling in saline solution and in deionized water, respectively. The  $f$  values are given in Table III. The obvious low salt sensitivity of the hydrogels with high HEA content is certainly due to increasing nonionizable OH groups.

As shown, cation charge has a great influence on swelling capacity (Fig. 6). This phenomenon can be attributed to increasing degree of crosslinking with increasing charge of the cation, which in turn give rise to appreciable reduction of swelling capacity. Therefore, absorbency for the hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. Similar results have been reported in previous studies.<sup>22</sup>

According to Figure 6, hydrogels with AA/HEA = 0.33 or 1 have rather higher absorbencies in 0.15 M Ca<sup>2+</sup> solution in comparison with hydrogel hybrid with AA/HEA weight ratio equal to 3. As a matter of fact, with decreasing ionic groups existing in copolymer chains, Ca<sup>2+</sup> ions cannot act as crosslinker more easily. Therefore, swelling capacity is increased.

As mentioned previously, Stimuli-sensitive or smart hydrogels which swell and contract in response to environmental stimuli,<sup>26-31</sup> are a central component in numerous applications. This hydrogel also showed reproducible swelling-deswelling cycles as demonstrated in Figure 7. At 0.01 M sodium chloride solution the anionic hydrogel swell up, while in a 0.1 M solution, it shrinks within a few minutes. This sudden and sharp swelling-deswelling behavior at different salt concentrations makes the system highly salt-responsive and potentially suitable for various applications.

## pH

pH-sensitive polymers which respond to changes in pH, contain acidic or alkaline functional groups.<sup>26,29</sup> These materials have found many applications in recent years.<sup>26,29</sup> In the present study, swelling capacity of the hydrogels with different AA/HEA weight ratios was examined in various pH solutions ranged from 2.0 to 12.0. Since the water absorbency of all "ionic" hydrogels is appreciably decreased by addition of counterions to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pH values, respectively.

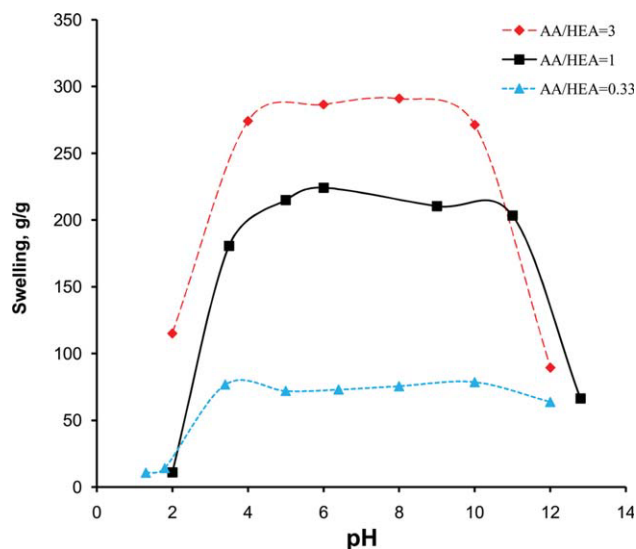
According to Figure 8, in highly acidic solutions, water absorbency values of these gels are considerably decreased. At these pHs, most of the -COO<sup>-</sup> groups are protonated; thus the main anion-anion repulsive forces are eliminated, and as a result swelling capacity values are significantly decreased. In highly basic solutions, however, a slightly different behavior was observed. When AA/HEA weight ratios are equal to 3 or 1, swelling values appreciably decreased. The swelling loss in these cases can be attributed to the "charge screening effect" of excess Na in the swelling medium, which in turn shields the carboxylate anions and prevents effective anion-anion repulsion. However, when this ratio is 0.33, absorbency values are not reduce meaningfully, that probably is due to increasing nonionic OH groups in polymer chains.

## Solvent-induced phase transition

Swelling capacity of SAP hydrogels in solution is a strong function of the kind of the solvent. Common polyelectrolyte gels that swell and absorb water up

**TABLE III**  
Swelling Data in Water and Saline Solutions (0.15 M) and Salt Sensitivity Factor ( $f$ ) for Synthesized Hydrogel Hybrids

AA/HEA weight ratio	Swelling medium	ES (g/g)	$f$
0.33	H <sub>2</sub> O	81	-
	NaCl	30	0.63
	CaCl <sub>2</sub>	13.5	0.83
	AlCl <sub>3</sub>	3	0.96
1	H <sub>2</sub> O	237	-
	NaCl	51	0.78
	CaCl <sub>2</sub>	16	0.93
	AlCl <sub>3</sub>	4	0.98
3	H <sub>2</sub> O	295	-
	NaCl	50	0.83
	CaCl <sub>2</sub>	9	0.97
	AlCl <sub>3</sub>	4	0.99



**Figure 8** Effect of solution pH on swelling capacities of hydrogel hybrids with various AA/HEA weight ratios. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

to several hundred times their dried weights collapse in organic solvents. Despite intense scrutiny by scientists worldwide for more than four decades, however, this feature has not been often investigated in the case of new synthesized hydrogels in the literature, and only a few studies reported in this context.<sup>36,37</sup> On the other hand, many researchers have focused on volume phase transition of polyelectrolyte gel in mixture of solvents mainly because of its smartness aspects. As an example, chemo-mechanical valves were designed on this basis.<sup>38,39</sup> Moreover, chemicals such as alcohols can be molecularly recognized by volume phase transition of gels.<sup>40</sup>

To deeper studies on the structure-property relation in SAP hydrogels, in the present work, the swelling changes of hydrogels with AA/HEA weight ratios of 3, 1, and 0.33 were examined in various water-methanol mixtures. With increasing ratio, the ES capacities of SAPs in distilled water also increase from 81 to 237 and then 295 g/g, respectively. This behavior can be attributed to the increase of ionic groups existing in copolymer chains due to increasing AA content in the gel, which allows polymer coils to expand more easily. Moreover, the behavior of hydrogels in water-methanol mixtures is also different. As shown in Figure 9, both two and three solvent-induced phase transitions were observed. The results are summarized in Table IV. Two major transitions were occurred in the case of AA/HEA = 3 at a range of 0–50 and 50–80 v/v % methanol/water mixture; however, the other two hydrogels show three transitions (for AA/HEA = 1: 0–50, 50–70, and 70–90 v/v %; for AA/HEA = 0.33: 0–50, 50–60, and 60–100 v/v %).

The swelling loss of the SAP hydrogels under these circumstances can be easily explained by the dissolving rules of linear polymers or Hildebrand equation.<sup>41</sup> This is a good assumption, because a solvent that can dissolve a linear polymer can also swell a crosslinked network of the same polymer. Thus, the swelling of the network would conform of the dissolving rules of linear polymer:

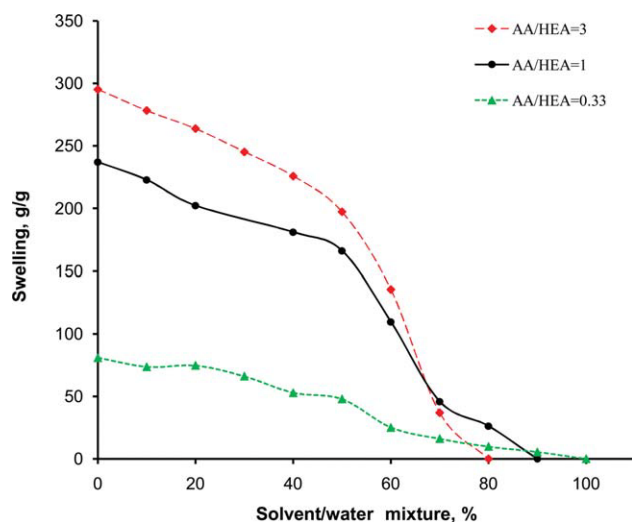
$$\Delta H_m / (V\Phi_1\Phi_2) = (\delta_1 - \delta_2)^2 \quad (5)$$

where  $\Delta H_m$  is the enthalpy change on mixing of a polymer and a solvent,  $\Phi_1$  and  $\Phi_2$  are the volume fractions for the solvent and the polymer,  $V$  is the whole volume of the solution, and  $\delta_1$  and  $\delta_2$  are the solubility parameters for the solvent and polymer, respectively.

According to this equation, if the  $\delta$  values of a solvent and a polymer are close to each other, the solvent can dissolve the polymer. Therefore, to explain the swelling loss in water-methanol mixtures,  $\delta$  values should be calculated. As swelling capacity of the synthesized hydrogel in water is maximum, the  $\delta$  value of water [ $23.4 \text{ (cal/cm}^3)^{1/2}$ ] can be regarded as its solubility parameter. The solubility parameter for water-methanol mixtures ( $\delta_{\text{mix}}$ ) can be calculated from the following equation<sup>42</sup>:

$$\delta_{\text{mix}} = \delta_1\Phi_1 + \delta_2\Phi_2 \quad (6)$$

where  $\Phi_1$  and  $\Phi_2$  are the volume fractions and  $\delta_1$  and  $\delta_2$  are the solubility parameters of the two solvents.



**Figure 9** Swelling capacity variations of synthesized hydrogels in methanol-water mixtures with varied composition ( $[V_{\text{MeOH}} / (V_{\text{MeOH}} + V_{\text{H}_2\text{O}})] \times 100$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**TABLE IV**  
Methanol-water concentrations in which the hydrogel exhibits volume-phase transition<sup>a</sup>

AA/HEA weight ratio	Transition I			Transition II			Transition III		
	Solvent % range	$\delta_{\text{mix}}^b$	Swelling-loss <sup>c</sup> (%)	Solvent % range	$\delta_{\text{mix}}^b$	Swelling-loss <sup>c</sup> (%)	Solvent % range	$\delta_{\text{mix}}^b$	Swelling-loss <sup>c</sup> (%)
3	0–50	23.4–18.95	33.2	50–80	18.95–16.28	66.8	NOT	–	–
1	0–50	23.4–18.95	30	50–70	18.95–17.17	50.7	70–90	17.17–15.39	19.3
0.33	0–50	23.4–18.95	40.8	50–60	18.95–18.06	28.2	60–100	18.06–14.5	31

<sup>a</sup>  $\delta_{\text{MeOH}} = 14.5 \text{ (cal/cm}^3)^{1/2}$ ;  $\delta_{\text{water}} = 23.4 \text{ (cal/cm}^3)^{1/2}$ .<sup>41</sup>

<sup>b</sup> Symbol  $\delta_{\text{mix}}$  [(cal/cm<sup>3</sup>)<sup>1/2</sup>] is the solubility parameter for the methanol–water mixture.

<sup>c</sup> Swelling loss (%) was calculated from following equation:  $(S_m - S_n / S_w) \times 100$ , where  $S_m$ ,  $S_n$ , and  $S_w$  are swelling capacities in water-methanol mixtures with  $m$  and  $n\%$  methanol, and in distilled water, respectively.

The data summarized in Table IV clearly indicates that the swelling capacity of the hydrogel in the methanol-water mixture will be close to that in pure water if  $\delta_{\text{mix}}$  is close to  $\delta_{\text{water}}$ .

It can be seen from Figure 9, while hydrogel with AA/HEA weight ratio 3 shows no absorbency at all in 80 v/v % methanol/water mixture, 26 and 10 g/g absorbency is observed with AA/HEA weight ratios 1 and 0.33 in this mixture, respectively. Sodium carboxylate (NaAA) groups are easily solvated by water molecules. However, solvation is widely restricted in 80% methanol/water mixture because the alcohol (MeOH) molecules cannot solvate the ionic carboxylic groups. With increasing HEA content this effect is considerably decreased, so that measurable swelling is observed in solvent mixtures with higher methanol content.

The hydrogel hybrid also showed a reproducible swelling-deswelling behavior when the environmental medium was changed alternatively between the methanol-water mixtures 30 and 70 v/v % (Fig. 10). As described earlier, such on-off behavior paves the way for further applications in the future.

### Swelling kinetics

Another key characteristic of SAP hydrogels is SR. In many practical applications such as personal care products, a higher SR is extremely needed. Buchholz<sup>6</sup> has suggested that the swelling kinetics for the SAPs is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area, and composition of polymer. In the present study, effect of SAP particle size and composition of polymer on SR was investigated.

Figure 11 represents the dynamic swelling behavior of the superabsorbent samples with various particle sizes in water. A power law behavior is obvious from this figure. The data may be well fitted with a Voigt-based equation [eq. (7)]<sup>43</sup>:

$$S_t = S_e(1 - e^{-t/\tau}) \quad (7)$$

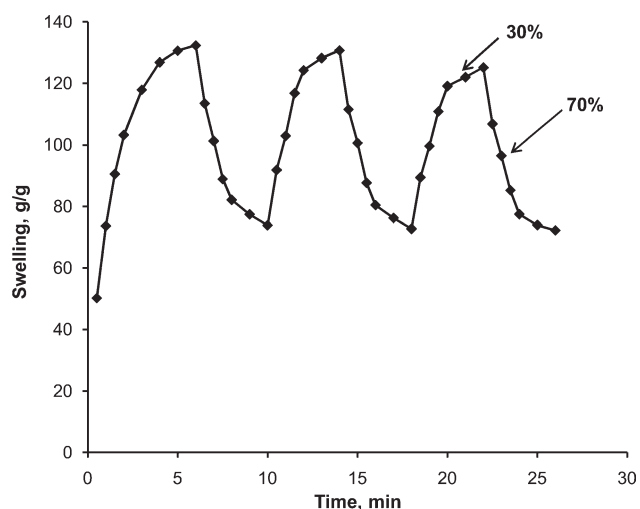
where  $S_t$  (g/g) is swelling at time  $t$ ;  $S_e$ , ES (power parameter, g/g), is swelling at infinite time or maximum water-holding capacity;  $t$  is time (sec) for swelling  $S_t$ , and  $\tau$  (sec) stands for the rate parameter.

To find the rate ( $\tau$ ) and power ( $S_e$ ) parameters for SAP hydrogels, the data obtained from swelling of the hydrogels at consecutive time intervals were fitted into eq. (7), using Origin 6.1 software. The results are summarized in Table V. The values of swelling rate (SR, g/g sec) for the individual samples were determined from the following equation<sup>19,22,44,45</sup>:

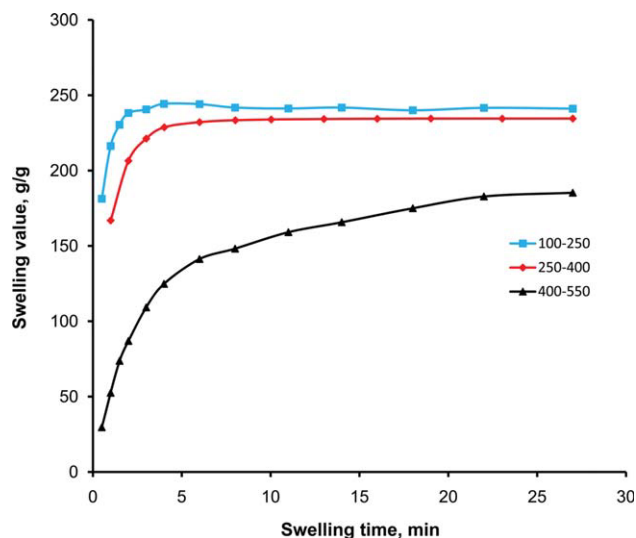
$$SR = S_{m\tau} / \tau_{\text{min}} \quad (8)$$

where  $S_{m\tau}$  stands for swelling at the time related to the minimum rate parameter  $\tau_{\text{min}}$  (sec) (22.8 sec in this case) obtained from superabsorbents from a set of similar experiments (Table V).

The SR are found to be 6.7, 3.7, and 0.9 g/g.s for SAP hybrids with particle sizes of 100–250, 250–400,



**Figure 10** The water-methanol composition-responsiveness of the SAP hydrogel hybrid (AA/HEA = 3) when the swelling medium is alternatively changed between 30 and 70% methanol.



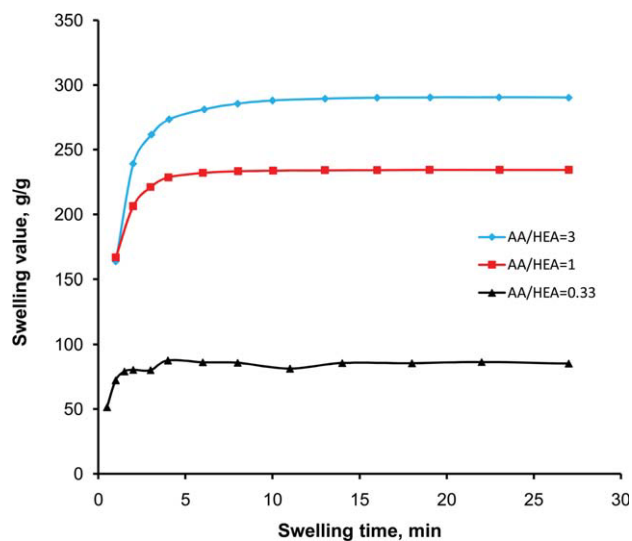
**Figure 11** Representative swelling kinetics of SAP hydrogel hybrids (AA/HEA = 1) with various particle sizes. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and 400–550  $\mu\text{m}$ , respectively. As it is obvious, with decrease of particle size, water uptake is significantly increased. It is a well-known behavior<sup>46</sup> that can be attributed to the increase in surface area with decreasing particle size of the hydrogel hybrid.

Effect of polymer composition on SR of SAP hybrid was also investigated (Fig. 12). According to data summarized in Table V, sample with AA/HEA = 0.33 has the lowest SR in comparison with the other two samples (AA/HEA = 1 or 3). Again, this behavior can be attributed to the decrease in ionic groups existing in copolymer chains along with increasing HEA in the gel, which does not allow polymer coils to expand more easily.

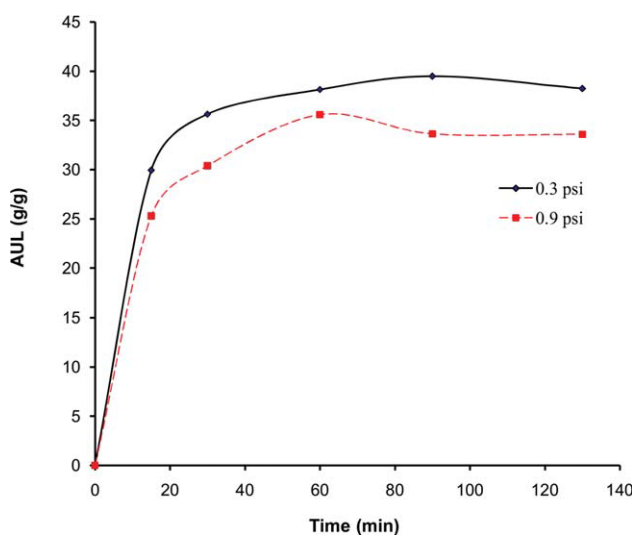
### Absorbency under load

AUL<sup>32,47–50</sup> is undoubtedly another gel characteristic that is of prime significance in many practical applications ranging from baby diapers and female personal care absorbent products to water protection systems in communication cables. AUL are often reported in the technical data sheets and patent articles. In the present study, we determined it by using a simple AUL tester at various applied pressures (0.3 and 0.9 psi) in 0.9% saline solution ( $\approx 0.15\text{ M}$ ).<sup>32</sup> This method is suitable for hydrogels with sugar-like particles. As Figure 13 clearly shown, the minimum time needed for the highest AUL in the case of each load was determined to be  $\sim 60$  min. After this time, the AUL values were unchanged. Moreover, AUL slightly decreases with



**Figure 12** Representative swelling kinetics of synthesized hydrogels with various AA/HEA weight ratios and certain particle sizes (250–400  $\mu\text{m}$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

tems in communication cables. AUL are often reported in the technical data sheets and patent articles. In the present study, we determined it by using a simple AUL tester at various applied pressures (0.3 and 0.9 psi) in 0.9% saline solution ( $\approx 0.15\text{ M}$ ).<sup>32</sup> This method is suitable for hydrogels with sugar-like particles. As Figure 13 clearly shown, the minimum time needed for the highest AUL in the case of each load was determined to be  $\sim 60$  min. After this time, the AUL values were unchanged. Moreover, AUL slightly decreases with



**Figure 13** Time dependence of the AUL values for carrageenan-based SAP hydrogel hybrid (AA/HEA = 1) swollen in 0.9% NaCl solution ( $\approx 0.15\text{ M}$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE V**  
Values of  $\tau$ (sec),  $S_e$  (g/g),  $S_{m\tau}$  (g/g), and SR (g/g s) for Synthesized SAP Hybrids ( $\tau_{\text{min}} = 22.8$  sec)

AA/HEA weight ratio	Sample particle size ( $\mu\text{m}$ )	$\tau$ (sec)	$S_e$ (g/g)	$S_{m\tau}$ (g/g)	SR (g/g s)
0.33	250–400	32.5	84.7	42.7	1.9
1	250–400	50.3	232.9	84.8	3.7
3	250–400	71.4	287.9	78.7	3.5
1	100–250	<b>22.8</b>	240.8	152.1	6.7
1	400–550	184.8	173	20.1	0.9

Bold indicates minimum rate parameter.

increasing amount of loading, which confirms low sensitivity of the hydrogel to different loads.

## CONCLUSIONS

The increase in prices of petroleum products in recent years forced the chemical manufacturers to switch over to other kinds of feedstocks. Chemical feedstock from biomass is undoubtedly an alternative to the high-cost and fluctuating prices of petroleum products. Thus, synthesis of natural-based SAPs is quite reasonable.

In the present study, new SAP hydrogel hybrid composing carrageenan, acrylic acid, sodium acrylate, and HEA was synthesized through homogeneous solution polymerization process. The superabsorbent hybrid exhibited improved thermal stability in comparison with polysaccharide-free hydrogel. Investigation of swelling behavior of hydrogel hybrids with different AA/HEA weight ratios in various salt solutions results in proving this fact that with increase of HEA content salt sensitivity is improved in some extent (Table III). This is attributed to the existence of nonionizable OH groups. The hydrogel also exhibited rather high water AUL in comparison with existing hydrogels.<sup>2,6</sup> Moreover, this hybrid material showed smartness property when the swelling medium was alternatively changed between solutions with different salt concentrations and also between various water-methanol mixtures with altered compositions. Such smartness behavior paves the way for further applications in the future.

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