# Semi-IPN Carrageenan-Based Nanocomposite Hydrogels: Synthesis and Swelling Behavior

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**ABSTRACT:** Inclusion of nano-clays into hydrogels is an efficient approach to produce nanocomposite hydrogels. The introduction of nano-clay into hydrogels causes an increase in water absorbency. In the present work, Nanocomposite hydrogels based on kappa-carrageenan were synthesized using sodium montmorillonite as nano-clay. Acrylamide and methylenebisacrylamide were used as monomer and crosslinker, respectively. The structure of nanocomposite hydrogels was investigated by XRD and SEM techniques. Swelling behavior of nanocomposite hydrogels was studied by varying clay and carrageenan contents as well as methylenebisacrylamide concentration. An optimum swelling capacity was achieved at 12% of sodium montmorilonite. The swollen nanocomposite hydrogels were used to study water retention capacity (WRC) under heating. The results revealed an increase in WRC due to inclusion of sodium montmorilonite clay. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2989–2997, 2010

**Key words:** nanocomposite; carrageenan; hydrogel; swelling; water retention

## INTRODUCTION

Polymer hydrogels are three-dimensional hydrophilic networks that can absorb, swell, and retain aqueous fluids up to hundreds of time of their own weight.[1] Because of their excellent response to change in environment conditions such as temperature,[2] pH,[3] and solvent composition,[4] hydrogels have been attractive in many industrial applications.[5,6] The higher production cost and low gel strength of these hydrogels, however, restrict their application widely. To improve these limitations, inorganic compounds with low cost can be used. Introduction of inorganic fillers to a polymer matrix increases its strength and stiffness properties.[7] Conventional hydrogel composites have been reported by scientists.[8–10] Inclusion of conventional micro-scale clays into hydrogels produces aggregated and agglomerated points. This is attributed to the heterogeneous dispersion of clay particles.[11] It has been reported that the type of dispersion of clay in composites determines the properties of polymer composites.[12] In addition to aggregated clay-polymer composites, intercalated and exfoliated clay-polymer composites can be produced using suitable methods.[13] It is required to use nano-scale clays to achieve intercalated or exfoliated composites.[11,12]

The resulting materials are known as nanocomposites. Among these materials, nanocomposite hydrogels are a class of crosslinked polymers as they can be synthesized through insertion of water soluble polymers into layered nano-clays through polymerization of hydrophilic monomers in the presence of layered nano-clays. Because of its low cost and unique characteristic such as its good water adsorption, extensive swelling in water, and cation exchange capacity, montmorilonite as inorganic layered clay is the interest of researchers.[14,15]

Biocompatibility, non-toxicity, and biodegradability of renewable materials, hydrogels based on biopolymers such as starch, chitosan, carboxymethylcellulose, carrageenan, and sodium alginate have been widely studied.[16–21] Carrageenan is a collective term for linear sulfated polysaccharides prepared by alkaline extraction from red seaweed. The position and number of ester sulfate groups determine the type of carrageenan. In fact, carrageenan exists in three forms: lambda (non-gelling), kappa (strong gelling), and iota (weak gelling).[22] Scheme 1 shows the structure of kappa carrageenan with sulfate ester groups. During last years, not only the syntheses of nanocomposite hydrogels based on biopolymers have been widely investigated, but also their properties and applications have been the interest of scientist.[23–25]

In this work, we endeavored to synthesize kappa-carrageenan-based hydrogels using acrylamide and methylenebisacrylamide as monomer and crosslinker, respectively. Sodium montmorilonite clay was used as inorganic filler. It was our aim to study
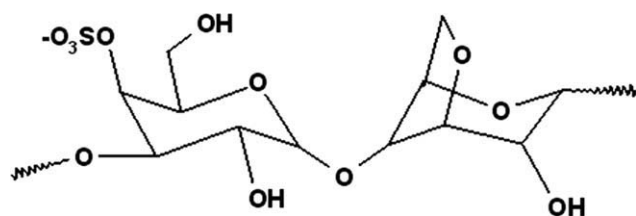
**Scheme 1** Repeating disaccharide unit of kappa carrageenan.

the effect of clay on the water absorbency of hydrogels especially in salt solutions. Also, we wanted to investigate the effect of clay on the water retention capacity (WRC) using heating as simple method. So, first the structure of the resulting nanocomposite hydrogels was investigated, and subsequently the effect of reaction variables on equilibrium swelling capacity was studied. Then, the WRC of swollen nanocomposite by heating at 80°C was investigated. Finally, by using Arrhenius method, the activation energy of reaction was calculated.

## EXPERIMENTAL

### Materials

kappa-Carrageenan (Carra) obtained from Condinson Co., Denmark. *N,N*-methylenebisacrylamide (MBA, Fluka Co. Buchs, Switzerland) and ammonium persulfate (APS, Fluka Co. Buchs, Switzerland) from Fluka (Buchs, Switzerland), and acrylamide (AAm) from Rotterdam, the Netherlands, were of analytical grade and used as received. Natural sodium-montmorillonite (sodium Cloisite, Na-MMt) (Southern Clay Co., Texas, USA) as a clay with cation exchange capacity of 92 meq/100 g of clay was provided by Southern Clay Products (Texas, United States). According to manufacturer information, 90% of clay had average size of <13 μm. All other ingredients were analytical grades and were used as received.

### Synthesis of nanocomposite hydrogels

Table I shows the reaction variables contents used to synthesize the nanocomposite hydrogels. The suffix *m*, *n*, and *z* in Clay*m*, Carra*n*, and MBA*z* are wt % of Clay and Carra, and mmol of MBA, respectively. In general, clay was dispersed in 30 mL of distilled water and stirred under magnetic stirrer for 24 h. Dispersed clay solution was transferred to a one-liter reactor equipped with mechanical stirrer. To control the reaction temperature, the reactor was placed in a water bath preset at 60°C. Then, 0.5 g of Carra was added to the solution containing clay and stirred for 2 h until completion of dissolution. AAm and MBA (MBA dissolved in 3 mL of water) were simultaneously added into solution and allowed to stir for

**TABLE I**
Reaction Conditions for Preparation of Nanocomposite Hydrogels (AAm 3 g, APS 0.05 g, $H_2O$ 30 mL, $T = 60°C$)

| No. | Carra0 | Carra7 | Carra14 | Carra20 | Carra24 | Clay0 | Clay1.5 | Clay3 | Clay5 | Clay12 | Clay17 | Clay22 | MBA4 | MBA8 | MBA12 | MBA16 | MBA20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carra (g) | 0 | 0.25 | 0.5 | 0.75 | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Clay (g) | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.05 | 0.1 | 0.2 | 0.5 | 0.7 | 1.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| MBA (mmol) | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.26 | 0.13 | 0.26 | 0.39 | 0.52 | 0.65 |

1 h. It may be noted that according to Pourjavadi et al. report,[26] synthesis of nanocomposite hydrogels was carried out under air condition. Finally, APS (0.05 g in 2 mL of water) was added as initiator into solution and stirred for 3 min. After this time, the solution was transferred into a test tube (interior size: 12 mm in diameter and 160 mm long) and was kept in an oven at 60°C for 4 h. The resulted nanocomposite hydrogels were cooled to ambient temperature and cut into discs with 0.5 cm long. To remove the unreacted substrates, the hydrogels were immersed in excess amount of deionized water for 6 days with daily refreshment of water. After this time, the purified hydrogels discs were dried at ambient temperature for 1 week.

As mentioned above, the reactions were carried out without removing $O_2$ gas. To study the effect of degassing or nondegassing on the gel content, we examined polymerization of Clay12 sample under both inert $N_2$ and air condition. The results showed that the gel content for samples synthesized through inert medium and air condition is 89.2% and 87%, respectively. The low difference in gel content may be attributed to low solubility of $O_2$ in water at 60°C.

### Swelling study

Dried nanocomposite discs were used to determine the degree of swelling. The equilibrium swelling (ES) was determined by immersing the nanocomposite hydrogels (~0.2 g, two discs of dried hydrogels) in distilled water (100 mL) or saline solutions (0.15 $M$ of $CaCl_2$ or NaCl) and was allowed to soak for 72 h at room temperature, removed from the water, blotted with filter paper to remove surface water, weighed, and the ES was calculated using eq. (1):

$$ES = (W_s - W_d)/W_d \qquad (1)$$

where $W_s$ and $W_d$ are the weights of the samples swollen in water and in dry state, respectively.

### Water retention capacity

To measure the water retention at constant temperature, the swollen nanocomposite discs were put into an oven which passed a current of hot dry air at constant temperature (e.g., 80°C). The weights of the discs were measured in every half an hour to investigate the relationship between their weights and the heating time.

### Instrumental analysis

For XRD and SEM studies, hydrogel nanocomposite containing 5 wt % of clay was synthesized in a glassy petri dish. Then, it was cut into thin discs
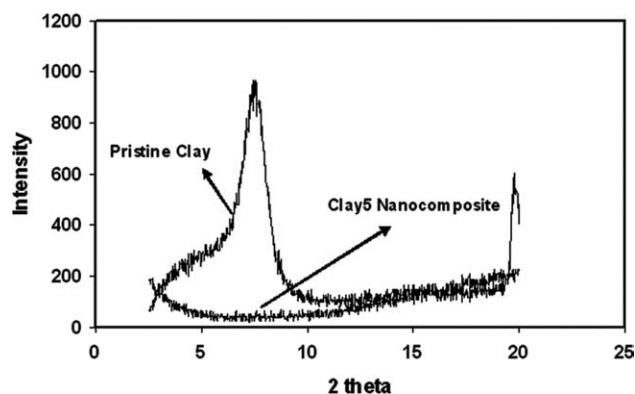


**Figure 1** XRD patterns of pristine clay and nanocomposite hydrogel containing 5 wt % of clay (Clay5).

with diameter of ~10 mm. After purifying the samples like other samples, the discs were dried at ambient temperature. Dried nanocomposite was coated with a thin layer of gold and imaged in a SEM (Vega, Tescan). One-dimensional, wide angle X-ray diffraction patterns were obtained by using a Siemens D-500 X-ray diffractometer with wavelength, λ = 1.54 Å (Cu-Kα), at a tube voltage of 35 KV, and tube current of 30 mA.

A thermal analyzer (Perkin Elmer Pyris Diamond) was used for thermogravimetric analysis (TGA) under nitrogen. The heating rate was 20°C/min.

## RESULTS AND DISCUSSIONS

### Synthesis and characterization

Semi-interpenetrating polymer network (Semi-IPN) nanocomposite hydrogels based on Carra were synthesized using solution polymerization. Na-MMt was used as clay. Polymerization of AAm in the presence of MBA produces network that Carra will exist as linear biopolymer in this network. The XRD patterns of clay and nanocomposite were studied and shown in Figure 1. As shown in this figure, the XRD profile of pristine Na-MMt shows a diffractive peak at 2θ = 7.6 corresponding to the distance of clay sheets with $d$ spacing 11.61 Å. Stirring of clay for 24 h subsequently *in situ* polymerization of AAm in the presence of MBA crosslinker leads to a nanocomposite hydrogel that the XRD profile of this hydrogel shown in Figure 1. No diffraction peak was observed in nanocomposite containing 5 wt % of clay (Clay5), and it can be concluded that the clay layers are completely exfoliated.

One of the most important properties of nanocomposites which can be considered is hydrogel microstructure morphology. Figure 2 depicts surface morphology of hydrogel without clay [Fig. 2(a)] and nanocomposite hydrogel [Fig. 2(b)]. While the hydrogels without clay shows a relatively smooth
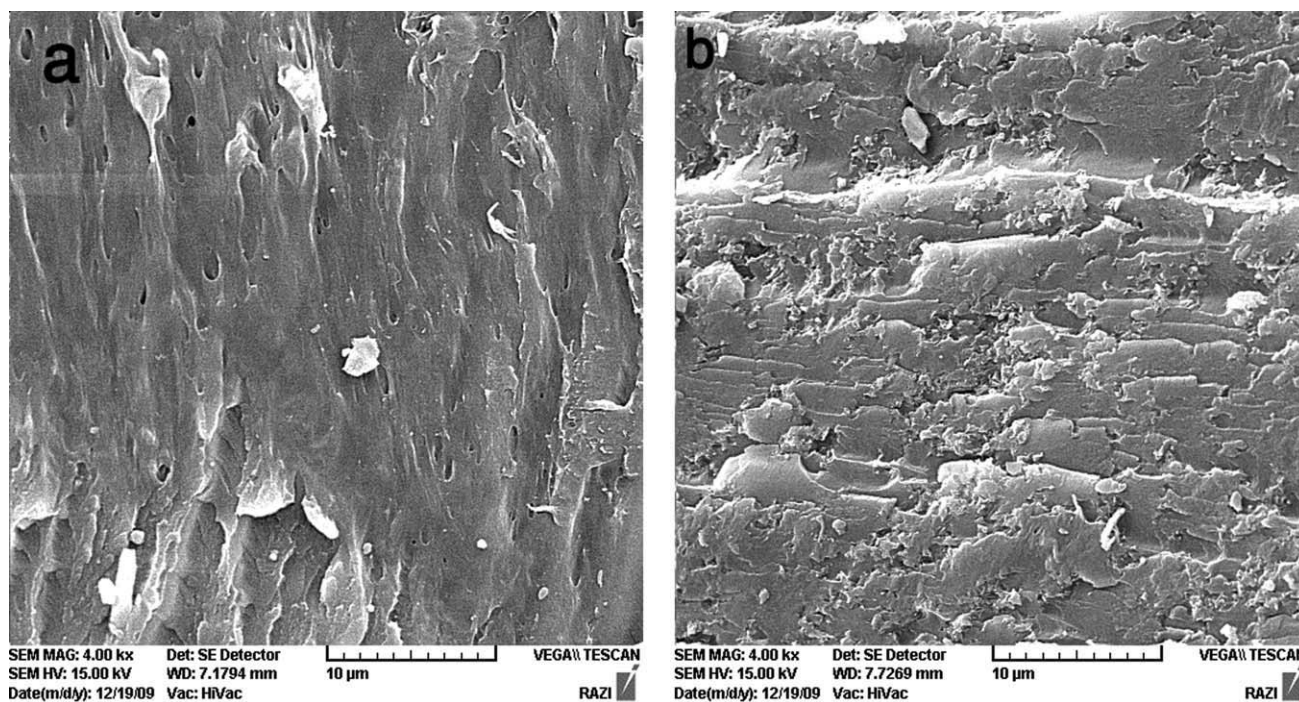
**Figure 2** SEM micrographs of clay-free hydrogel (a: Clay0) and nanocomposite (b: Clay5).

surface, the nanocomposite contains coarse and undulant surface. This observation can be attributed to insertion of clay into hydrogel.

**Thermogravimetric analysis**

TGAs of clay-free hydrogel, Clay3, and Clay22 were studied up to 300°C. As shown in Figure 3, two stages of decomposition can be seen for the samples. The first is in the range from 70 to 190°C. This weight loss can be attributed to the moisture in the samples. The values of weight loss for hydrogel clay-free, Clay3, and Clay22 are 4.3, 4.1, and 3 wt %. These data show that while water content in clay-free hydrogel and Clay3 is close, but the moisture for Clay22 nanocomposite is lower than clay-free
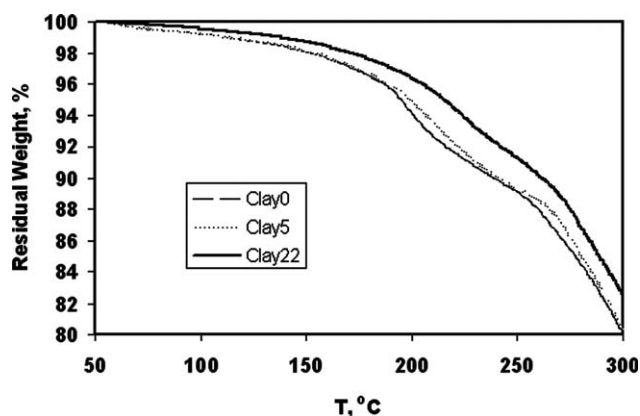


**Figure 3** TGA curves of clay-free hydrogel and nanocomposites.

hydrogel. The other stage range from 190 to 266°C that attribute to decomposition of amide groups of PAAm chains. $T_{10}$ (temperature of the 10% weight loss) and $T_{20}$ (temperature of the 20% weight loss) of samples were summarized in Table II. According to these data, while the thermal stability of Clay3 nanocomposite is similar to clay-free hydrogel, but Clay22 shows high thermal stability than hydrogel without clay.

**Effect of reaction variables on the swelling**

The relationship between the swelling ratio and network structure parameters given by Flory is usually used as the following equation[27]:

$$q_m^{5/3} \cong \frac{(i/2\nu_u S^{\bullet^{1/2}}) + (1/2 - \chi_1)\nu_1}{\nu_e/V_0} \quad (2)$$

Here, $i/2\nu_u$ is the concentration of the fixed charges of the unswollen networks, and $S^{\bullet}$ is ionic strength in the external solution; $\nu_e/V_0$ is the cross-link density which refers to the number of effectively crosslinked points between chains in unit

**TABLE II**
**Weight Loss of Hydrogel and Nanocomposites at Temperatures $T_{10}$ and $T_{20}$**

|          | Free-clay hydrogel | Clay3 | Clay22 |
|----------|--------------------|-------|--------|
| $T_{10}$ | 227                | 230   | 252    |
| $T_{20}$ | 296                | 297   | 308    |
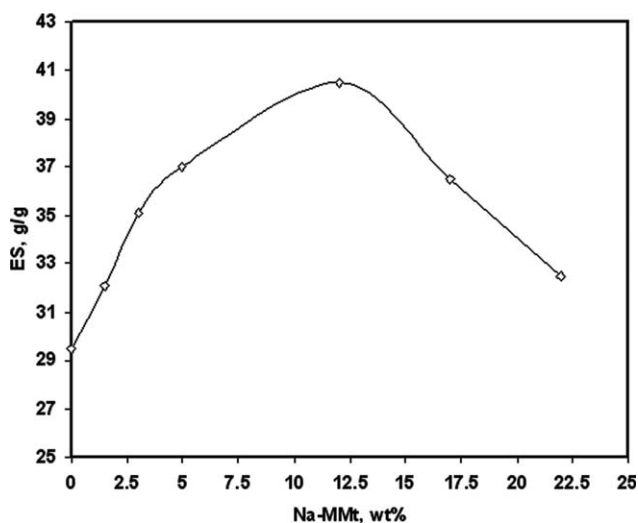
**Figure 4** Swelling dependency of nanocomposite hydrogels on clay content.

volume. The term $(1/2 - \chi_1)v_1$ represents the interaction parameter, i.e., affinity of the hydrogel to water. The $q_m$ term is swelling ratio of the hydrogel.[28]

The swelling capacity of nanocomposite in water as a function of nano-clay content was studied by varying the nanoclay amount from 1.5 to 22 wt % (Fig. 4). Maximum swelling (40.5 g/g) was obtained at 12 wt % of nano-clay. It is observed that the absorbency is substantially increased by increasing in the Na-MMt content and then decreases. When the Na-MMt content in hydrogel composition is low, the ionization of sodium MMt takes place easily, and subsequently the osmotic pressure of inside of nanocomposite is increased. Enhancement of osmotic pressure in hydrogel causes an increase in water absorbency of hydrogel.[29] In fact, the ionization of Na-MMt not only causes an increase in osmotic pressure, but also, according to Flory equation [eq. (2)], the fixed charges $(i/2v_u)$ in hydrogel will be higher. However, the swelling-loss after the maximum may originate from decrease in ionization of Na-MMt leading to a decrease in osmotic pressure. Also, it has been reported that MMt can act as crosslinker in hydrogel systems. It is clear that by increasing Na-MMt content, crosslinking points increase resulting in low swelling capacity.[30,31]

To study the effect of Carra content on the swelling capacity of nanocomposite, its content was varied from 7 to 24 wt %. As shown in Figure 5, increase in Carra causes an increase in water absorbency. Carrageenan is a sulfonated polysaccharide and known as ionic biopolymer. The high swelling by increasing carrageenan content is attributed to the enhancement of the ionic sulfate anions.[32] The higher the anionic groups in hydrogel, the higher the water absorbency. It is in agreement to Flory equation and confirms the
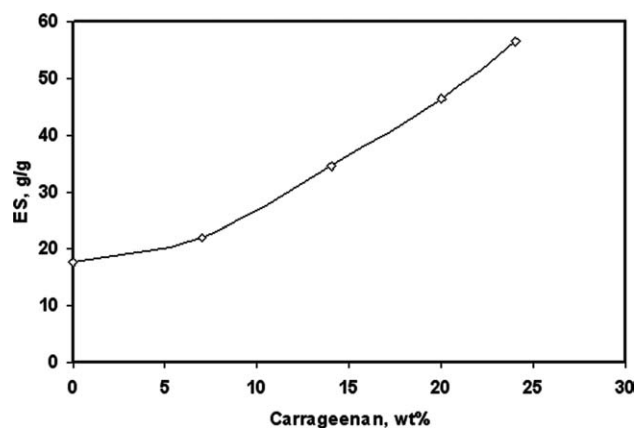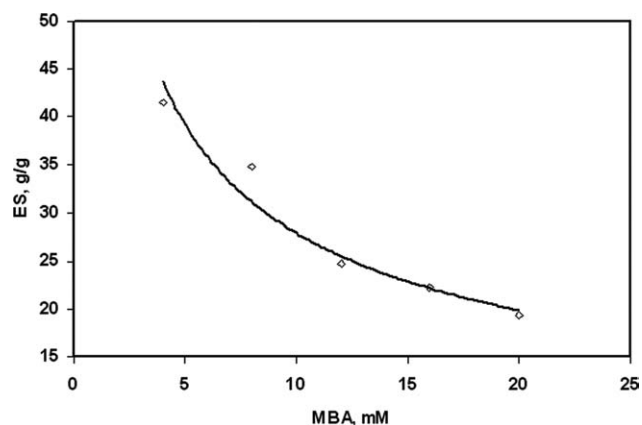


**Figure 5** Swelling dependency of nanocomposite hydrogels on carrageenan content.

high fixed charges on the hydrogel $(i/2v_u)$. Water absorbency of hydrogels containing no-carrageenan and high content of carrageenan was found to be 17.7 and 56.6 g/g, respectively.

The effect of the extent of crosslinking on water absorbency of nanocomposite hydrogel is shown in Figure 6. In this series of reactions, the MBA concentration was varied from 4 to 20 mmol/L. According to this figure, by increasing in crosslinker concentration, the water absorbency is decreased. High crosslinker concentration produces more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, resulting in less swelling when it is brought in the contact with water. Wang et al. have been reported similar observation for superabsorbent composite.[33] Also, according to the eq. (2), at high values of crosslinker, the $v_e/V_0$ parameter was increased. So, the water absorbency $(q_m)$ is decreased.

## Swelling in salt solutions

In this series of experiments, the swelling capacity was measured in 0.15 $M$ of NaCl and CaCl$_2$ salt
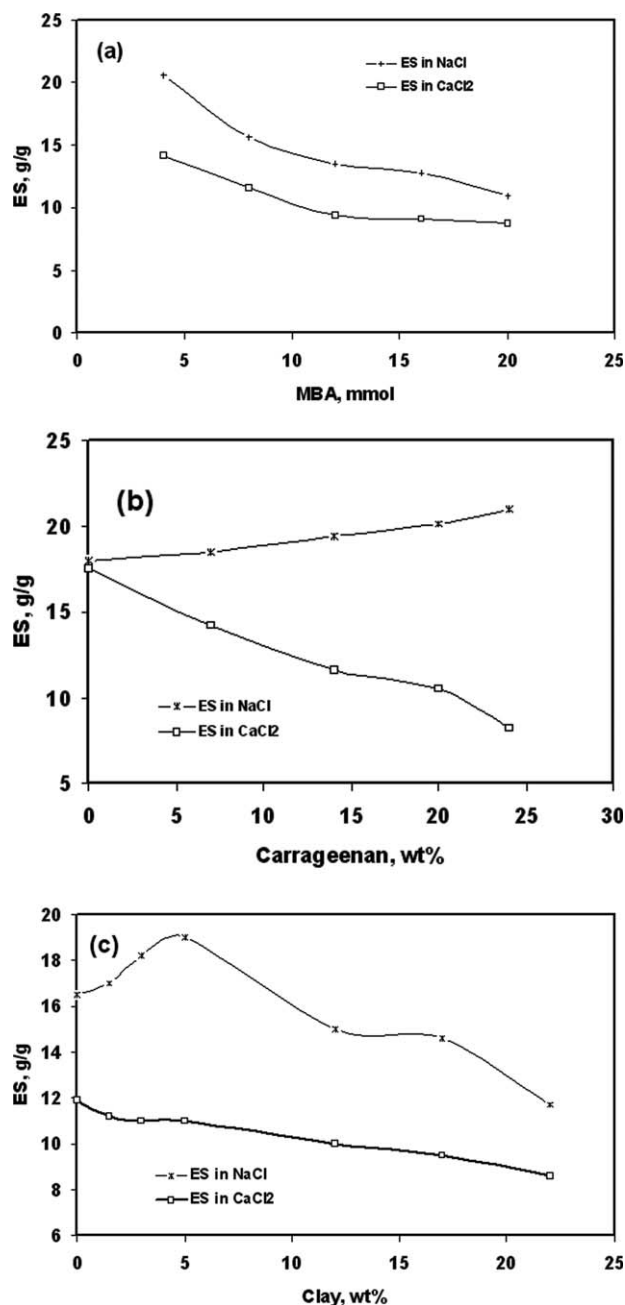


**Figure 6** Swelling dependency of nanocomposite hydrogels on MBA concentration.

solutions. It is obvious that swelling is strongly dependent on the presence of salt added to the swelling medium. The swelling of the nanocomposites in saline solutions was appreciably decreased compared to the values measured in deionized water. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels, is often attributed to a screening effect of the additional cations causing a nonperfect anion–anion electrostatic repulsion, leading to a decreased osmotic pressure (increase the $S^{\bullet}$ in Flory equation causes the decrease in swelling) difference between the hydrogel network and the external solution.[34] Also, the swelling capacity decreases with an increase in charge of the metal cation ($Ca^{2+} < Na^{+}$). This can be explained by the exchange capacities of the different valency cations. The higher the cation valency, the higher the exchange capacity of the cation. It may be explained by complexing ability arising from the coordination of the divalent cations with nanocomposite anionic groups.[35]

The water absorbency of MBA, Clay, and Carra series in 0.15 $M$ of NaCl and CaCl$_2$ solutions were depicted in Figure 7. As it is clear from data, the swelling capacity of all samples in NaCl solution is higher than that of CaCl$_2$ solution and it can be explained as mentioned above. In the case of MBA series [Fig. 7(a)], it was observed that for both media the swelling of hydrogel nanocomposite is decreased as MBA concentration is increased. The higher content in crosslinker causes a decrease in swelling capacity. For Carra series [Fig. 7(b)], while increasing of Carra content results in hydrogel with high swelling in NaCl solution, but a decrease was observed for CaCl$_2$ solution. In spite of the fact that the introducing ionic component in hydrogel composition should cause an increase of swelling, it was not observed for these series of hydrogels when they immersed into CaCl$_2$ solution. In fact, increase in carrageenan content causes an increase in complexing ability arising from the coordination of the divalent $Ca^{2+}$ cations with ionic carrageenan polar groups. So, the swelling capacity is decreased as Carra content is increased.

Swelling of nanocomposite in salt solution as a function of clay content was shown in Figure 7(c). By varying clay content, an optimum was obtained in NaCl solution and this can be explained similar to swelling in water. Only that while a maximum absorbency was achieved at 12 wt % of clay in distilled water, but in NaCl solution, it was observed at 5 wt % of Na-MMt. Similar to Carra series, the results showed a decrease of absorbency in CaCl$_2$ solution as the clay content was increased. It may be attributed to presence of ionic —O$^-$ groups on clay surface that can cause an aggregation in the presence of Ca$^{2+}$ cation and act as crosslinker.

**Figure 7** Swelling dependency of hydrogels on (a) MBA, (b) Carra, and (c) nano-clay series in 0.15 $M$ concentration of NaCl and CaCl$_2$ solutions.

To achieve a comparative measure of sensitivity of the nanocomposites to the kind of aqueous fluid, we defined a dimensionless swelling factor, $f$, as follows:

$$f = 1 - (\text{Absorption in a given fluid} / \text{Absorption in deionized water}) \quad (3)$$

The $f$ values are given in Table III. The effect of increasing cation charge on ultimate absorption for the different nanocomposite can be found from the

| Sample | $f_{NaCl}$ | $f_{CaCl_2}$ |
|--------|------------|--------------|
| Carra0 | ~0 | 0.1 |
| Carra7 | 0.31 | 0.35 |
| Carra14 | 0.54 | 0.66 |
| Carra20 | 0.64 | 0.77 |
| Carra24 | 0.7 | 0.85 |
| Clay0 | 0.44 | 0.6 |
| Clay1.5 | 0.53 | 0.61 |
| Clay3 | 0.57 | 0.68 |
| Clay5 | 0.56 | 0.7 |
| Clay12 | 0.63 | 0.75 |
| Clay17 | 0.6 | 0.73 |
| Clay22 | 0.64 | 0.73 |
| MBA4 | 0.5 | 0.65 |
| MBA8 | 0.55 | 0.66 |
| MBA12 | 0.45 | 0.45 |
| MBA16 | 0.42 | 0.59 |
| MBA20 | 0.43 | 0.55 |

values, so that the lower the cations charge, the lower the salt sensitivity.

However by introducing Carra in nanocomposite, the $f$ values tend to increase but in comparison to other hydrogels containing carboxylate groups, these values are low and can be attributed to the present sulfate groups on Carra backbones. The reason for this low salt sensitivity behavior seems to be due to the carrageenan in the hydrogels which contains sulfate groups that dissociate in aqueous media more readily than the carboxylate groups of the hydrogels containing carboxylate groups (pKa of methane sulfonic acid is approximately −1.86, while that of acetic acid is 4.8). Since the sulfate ions do not have counter cations in their vicinity, the "charge screening effect" is not a factor. Thus, the resulting swelling loss is less. A similar behavior has been reported by Doo-Won Lim et al.; while hydrolyzed starch-g-poly(AN) hydrogel has 61.5 g/g absorbency in saline, but by introducing sulfate groups in starch backbones, hydrolyzed starch sulfate-g-poly(AN) hydrogel show 126.5 g/g absorbency in saline.[36] Hydrogels from hydrolysis of chitosan-g-poly(Acrylonitrile) with 84.8 add-on value (named H-chito-PAN) contain carboxylate groups, and the $f$ values have been reported as 0.911 (in NaCl solution) and 0.944 (in CaCl$_2$ solution).[35]
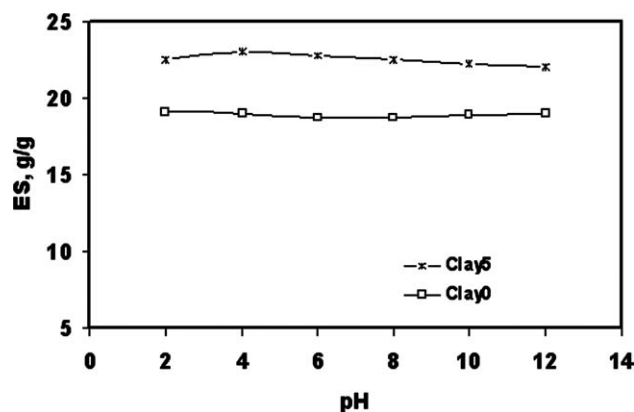
## Effect of pH on the swelling

The equilibrium swelling clay-free hydrogel and hydrogel containing 5 wt % of clay was studied using buffer solutions by various pHs ranged from 2.0 to 12.0 (Fig. 8). It was observed that swelling behavior of hydrogels containing clay or no-clay is pH independent. Non-ionic amide and ionic sulfonate groups exist in both hydrogels. It has been

reported that hydrogels containing sulfonate groups exhibit pH independent swelling behavior.[37] In fact, all sulfonate groups dissociate completely in the overall pH range (the pK$_a$ of methanesulfonic acid is −1.86[38]). According to results, the presence of montmorillonite in the nanocomposite does not affect the swelling of nanocomposite at various pHs.

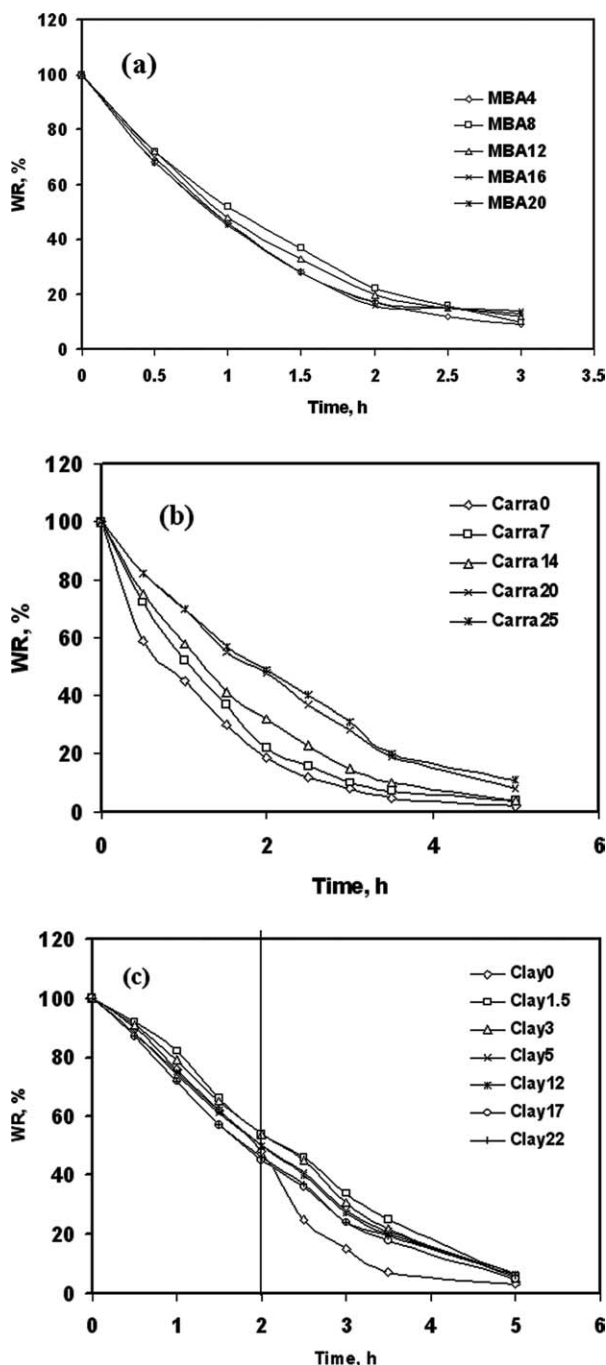## Water retention under heating

It is important to investigate the water retention ability of a hydrogels in view of practical application. Figure 9 shows the water retention ability of MBA, Carra, and Clay series of swollen nanocomposite hydrogel at 80°C. While the difference in water retention for MBA series is low [Fig. 9(a)], but by changing Carra and clay contents in Carra and Clay series the retention capacity is varied. Figure 9(b) depicts WR of nanocomposite hydrogel containing various content of carrageenan. Increase in carrageenan content in nanocomposite composition, the WRC increased. This behavior can be attributed to increase of hydrophilicity of hydrogels by increasing ionic Carra.

Interesting data was obtained for samples with various content of clay. While up to 2 h the difference in water retention for samples with or without clay is low [Fig. 9(c)], but after this time a high rate of water loss was observed for sample without clay. According to Figure 10, it is observed that the sample without clay was easily burst. The bursting of hydrogels causes an increase in surface area subsequently the rate of water loosing is increased. In fact, nanocomposite containing clay resists against bursting and it can be attributed to high mechanical strength of nanocomposite hydrogel. Homogeneous dispersion of clay in hydrogel causes a high interaction between clay and polar groups of hydrogel component and results a hydrogel with high strength.[39,40]



**Figure 8** Effect of pH on the swelling of hydrogel and hydrogel nanocomposite.

(a) MBA series plot



(b) carra series plot



(c) clay series plot

**Figure 9** Effect of heating on the water retention capacities of nanocomposite hydrogels (a) MBA series, (b) carra series, and (c) clay series.

## Activation energy

In this section of study, apparent activation energy ($E_a$) determined according to Arrhenius equation[41]:

$$\ln t_{gel} = A + \frac{E_a}{RT} \qquad (4)$$

where $t_{gel}$ is the gelation time (s), $T$ (K) denotes the reaction temperature, and $R$ is the universal gas con-
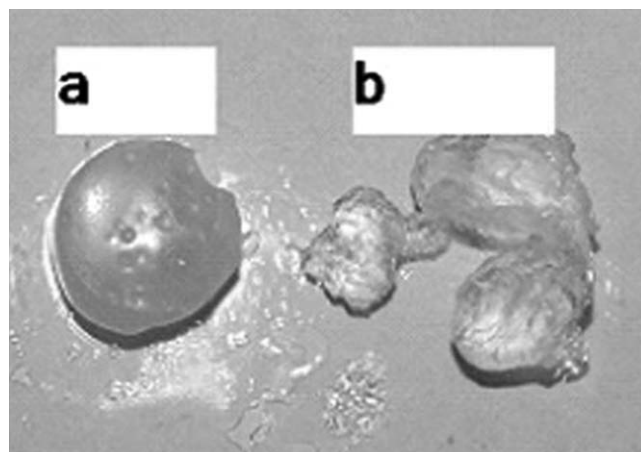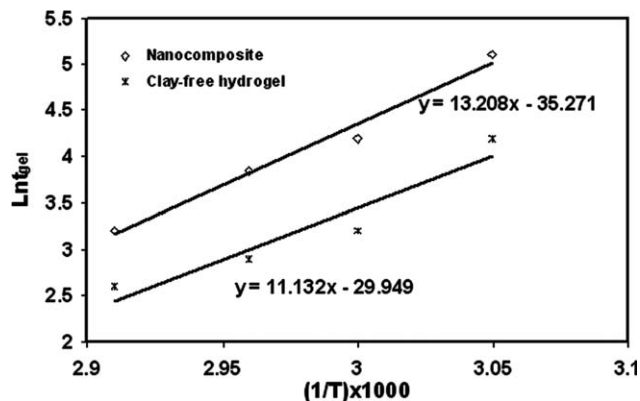
**Figure 10** (a) nanocomposite hydrogel and (b) clay-free hydrogel after 2 h under heating: bursting of clay-free hydrogel under heating.

stant (8.314 J mol$^{-1}$ K$^{-1}$). The polymerization of Clay5 and clay-free samples was carried out at four temperatures (55, 60, 65, 70°C). According to Figure 11, the slops of plots ln $t_{gel}$ versus $1/T$ are linear and show that temperature can affect gelation time, then the activation energies can be determined using eq. (4) and they were found to be 110.4 kJ/mol and 92.5 kJ/mol for Clay5 and clay-free hydrogels, respectively. High activation energy in the case of nanocomposite can be attributed to the presence of clay. In fact, the viscosity of polymerization media is higher using clay, and subsequently the movement of monomer will be lower.

## CONCLUSIONS

Nanocomposite hydrogels based on Carrageenan were synthesized using *in situ* polymerization of AAm and MBA in the presence of Na-MMt clay. XRD pattern of nanocomposite showed that clay



**Figure 11** Plot of ln $t_{gel}$ versus ($1/T$). (Clay5: Carr 0.5 g, AAm 3 g, MBA 0.26 mmol, clay 0.2 g).

layers are completely exfoliated. The SEM graph depicted no agglomeration or flocculation.

Swelling of nanocomposite hydrogels as a function of clay, carrageenan, and MBA content was investigated. It was revealed that an optimum of swelling is observed at 12 wt % of clay. While an increase in swelling was obtained by increasing the carrageenan content, but a decrease in water absorbency was observed as the MBA concentration is increased.

WRC under heating was examined for nanocomposite hydrogels. The results showed that water loosing for MBA series is similar. Also, for Carra series, water retention was increased by increasing Carra content in nanocomposite composition. Under heating, while the hydrogel without clay burst, but hydrogels containing clay resisted against bursting and this fact confirms high mechanical strength of nanocomposite hydrogels.

Finally, the apparent activation energy ($E_a$) according to Arrhenius equation was calculated by carrying out the polymerization at four different temperatures and it was found to be 110.4 and 92.5 kJ/mol for Clay5 and clay-free hydrogel, respectively.

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