Temperature Effect on the Swelling of PAAm-κ-carrageenan Composites

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ABSTRACT: The steady-state fluorescence (SSF) technique was used for studying swelling of disc-shaped polyacrylamide (PAAm)-κ-carrageenan (κC) composites which were prepared by free-radical crosslinking copolymerization at 80°C. Pyranine was introduced as a fluorescence probe during polymerization. Swelling experiments were performed in water at various temperatures by real-time monitoring of the pyranine (Py) fluorescence intensity, I which decreased as swelling proceeded. Stern–Volmer equation is modified for low quenching efficiencies to interpret the behavior of Py intensity during the swelling of PAAm-κC composites. The Li-Tanaka equation was used to determine the swelling time constants, τ_1, and cooperative diffusion coefficients, D_0, from fluorescence intensity, weight, and volume variations of the composites at various temperatures. It was observed that τ_1 first decreased up to 40°C and then increased; naturally, D_0 increased up to 40°C and then decrease for all κC content gels. Swelling activation energies, ΔE, were measured for the swelling composites, which are found to be exothermic and endothermic in between 30–40 and 40–60°C, respectively. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1746–1754, 2012

Key words: swelling; fluorescence; polyacrylamide; κ-carrageenan; composite; hydrogels

INTRODUCTION

Carrageenans are sulfated D-galactans extracted from red algae. The κ-carrageenan (κC) is characterized by an alternating disaccharide of α-1,3-linked D-galactopyranose and β-,1-linked 3,6-anhydro-D-galactopyranose. These are commonly used in food industries for controlling physical properties and functionalities of food products such as texture, stability, and the water holding or thermal properties. Extensive research has ensured that the mechanism of gelation, swelling, and drying of carrageenan is well characterized by different techniques.[1] The gelation mechanism of κC involves a conformational transition of the carrageenan molecules as a coil-helix transition.[2–6] Carrageenan assumes a random coil conformation in sol state, and low temperature induces anhydrogalactose sequences to twist in a double helical manner. The further aggregation is also promoted among function as a helix breaker. Subsequently, the aggregation of double helices forms a crosslinking domain and leads the infinite network structure enough to complete gelation.[7]

In our previous studies, steady-state fluorescence (SSF) technique was used to investigate the swelling of κC gels at various temperatures.[8] The results presented in this reference show that the fluorescence method can be used to measure time constants and cooperative diffusion coefficients D_0 at a molecular level during swelling of a carrageenan gel in vapor. The Li-Tanaka model was used to measure these parameters. It was observed that the time constant decreased and diffusion coefficient increased as the swelling temperature was increased. We reported polyacrylamide (PAAm) hydrogel swelling for various temperatures and crosslinker contents by using the SSF technique.[9,10] It was observed that cooperative diffusion coefficients increased and/or decreased as the swelling temperature and the crosslinker content was increased, respectively. On the other hand, the photon transmission technique was used to study the swelling of PAAm gels with various crosslinker contents.[11,12] The decrease in transmitted light intensity, I_{tr}, was modeled using the Li-Tanaka equation from which the cooperative diffusion coefficients, D_0, were determined for various N,N' methylenebisacrylamide (BIS) content in PAAm (Polyacrylamide) gels; the decrease in I_{tr} was attributed to lattice heterogeneities, which might have originated between microgels and holes in the swelling gel. When PAAm gels were immersed in water the transmitted light intensity, I_{tr}, from the gel increased in the initial stages, and then decreased exponentially as the swelling time increased. The decrease in I_{tr} was modeled using the Li-Tanaka

equation,[13] and it was attributed to the lattice hetero-geneities, which might originate between "frozen blob clusters" and holes in the swelling gel.[14]

The photon transmission technique was used to study the thermal and phase transitions of κC,[15] which showed that κC gels prepared with various carrageenan concentrations in pure water were completely dried and then swollen in water. It was observed that gel with high carrageenan content possess more double helices and more lattice dislocations swell slower than gels with low carrageenan content, which may contain less double helix and less lattice imperfections.

On the other hand, chemical hydrogels loaded with biological hydrogels, e.g., κC, are of the gels with high ability of the biological gels to absorb different substances. Absorbent and adhesive properties of PAAm-κC composites were examined by using IR spectroscopy, optical microscopy, thermo gravimetrical analysis, and rheometer. A microwave-induced one-pot route for graft copolymerization of AAm onto carrageenan initiated by potassium persulfate was used. The resultant copolymer hydrogel exhibited adhesive and super absorbent properties.[16] Super absorbent PAAm-κC composites were also synthesized by a simultaneous irradiation technique using γ-rays as the energy source, initiator, and crosslinker under various conditions. The optimization of synthetic conditions to achieve maximum water absorbency was performed by the Taguchi method. The swelling behavior of the super absorbent polymers was related to their chemical structure, chemical composition, the absorbing environment, and the nature of the solution.[17] The swelling capacity of PAAm-κC composites was examined in buffer solutions, various salt solutions and temperature. The produced results were suggested for agricultural purposes.[18] Super absorbent PAAm-κC composites were used for swelling agents and devices in oral drug delivery.[19]

This article examines the effect of temperature on the swelling process of PAAm-κC composites by using the SSF technique. The behavior of the swelling of PAAm-κC composites at different temperatures was explained by a model obtained from Stern–Volmer equation combined with Li-Tanaka equation. The swelling time constants, τ_1, and cooperative diffusion coefficients, D_0, were determined for the swelling of PAAm-κC composites prepared at various κC concentrations. Supporting gravimetric and volumetric swelling experiments were also performed by using similar gel samples. It was observed that the swelling time constant, τ_1 decreased up to 40°C and then increased from 40 to 60°C. The cooperative diffusion coefficients D_0 presented the reversed behavior. The swelling activation energies, ΔE were calculated and found to be exothermic and endothermic in between 30–40 and 40–60°C, respectively.

Li-Tanaka model

Volume phase transitions in gels may occur from dry to swollen states either continuously, or by sudden jumps between them. In a dried state, a gel is a solid material which swells until it reaches the swelling equilibrium when a solvent is added. The volume phase transition was experimentally discovered for a partially ionized acrylamide gel in a mixture of acetone and water by Tanaka.[20] The theory of the kinetics of the swelling of a crosslinked polymeric network has been derived by Tanaka and Fillmore.[21] Li and Tanaka and Zrinyi et al. proposed a two process mechanisms based on the assumption that gel swelling and shrinking are not a pure diffusion process.[21,22] The shear modulus plays an important role: it keeps the system in shape due to coupling of any change in different directions. As a result of this, the geometry of the gel plays an important role.[23]

The kinetics of the swelling of a gel is completely described by the behavior of the displacement vector as a function of space and time. Li and Tanaka showed that the equation of motion is given by

$$\frac{\partial \vec{u}}{\partial t} = D_0 \vec{\nabla}^2 \vec{u} \tag{1}$$

where $\vec{u}$ is the displacement vector measured from the final equilibrium location after the gel is fully swollen ($\vec{u} = 0$ at $t = \infty$). $D_0 = (K + 4\mu/3)/f$ is the collective diffusion coefficient. Here, t denotes the time and K is the bulk modulus. The high value of the friction coefficient, f between the network and solvent overdamps the motion of the network, resulting in a diffusion-like relaxation.

Swelling experiments of disc-shaped gels have shown that the relative changes of diameter and thickness are the same, indicating that the gel-swelling processes are not pure diffusion processes. This feature was due to the shear modulus of the network keeping the system in shape by minimizing the nonisotropic deformation. Since, during a shear relaxation process, there is no relative motion and hence no friction between gel network and solvent, the system can instantly adjust its shape to minimize the total shear energy. For a disc-shaped gel, any change in diameter is coupled to a change in thickness.

The total energy of a gel can be separated into bulk energy and shear energy. The bulk energy is related to the volume change, which is controlled by diffusion. The shear energy, on the other hand, can be minimized instantly by readjusting the shape of the gel.[22] As long as the shear modulus μ is not zero, the change of the total shear energy in response to any small change in shape that maintains constant volume element within the gel should be zero,

$$\delta F_{sh} = 0 \tag{2}$$

Each small diffusion process determined by eq. (1) must couple to a small shear process given by eq. (2) producing the following relation for a disc-shaped gel

$$\frac{u_r(r,t)}{r} = \frac{u_z(a,t)}{a} \tag{3}$$

where r is the radius and a is the half-thickness of the gel. Equation (3) indicates that the relative change in shape of the gel is isotropic, i.e., the swelling rates of a disc in the axial (z) and radial (r) directions are the same.

Simultaneous solution of eqs. (1)–(2) produces the following equations for the swelling of a disc gel in axial and radial directions.[22]

$$u_z(z,t) = u_z(z,\infty)\sum_n B_n e^{-t/\tau_n} \tag{4a}$$

$$u_r(r,t) = u_r(r,\infty)\frac{z}{a}\sum_n B_n e^{-t/\tau_n} \tag{4b}$$

where the axial and radial displacements are expressed as a series of components, each of them decaying exponentially with a time constant, τ_n. The first terms of the expressions are dominant at large t that is at the last stage of swelling. Equation (4) can also be written in terms of water uptakes W and W_f at time t and equilibrium, respectively, as follows:

$$1 - \frac{W}{W_f} = \sum_{n=1}^{\infty} B_n \exp(-t/\tau_n) \tag{5}$$

In the limit of large t, or if τ_1 is much larger than the rest of τ_n, all higher terms ($n \geq 2$) in eq. (5) can be omitted, and the swelling kinetics is given by the following relation

$$\frac{W}{W_f} = 1 - B_1 \exp(-t/\tau_1) \tag{6}$$

where B_1 is given by the following relation

$$B_1 = \frac{2(3-4R)}{\alpha_1^2 - (4R-1)(3-4R)} \tag{7}$$

where $R = \mu/M$ and α_1 is given as a function of R, i.e.,

$$R = \frac{1}{4}\left[1 + \frac{\alpha_1 J_0(\alpha_1)}{J_1(\alpha_1)}\right] \tag{8}$$

where J_0 and J_1 represent Bessel functions. It should be noted from eq. (5) that $\sum B_n = 1$, therefore, B_1 should be less than 1. B_1 is related to the ratio, R, of

the shear modulus, μ and longitudinal osmotic modulus, $M = (K + 4\mu/3)$.[22] Once the value of B_1 is obtained, one can determine the value of $R = \mu/M$. Here, we have to note that eq. (6) can also be obtained by using theoretical results; in the case of $R \rightarrow 3/4$ ($\mu/K \rightarrow \infty$), the time constant $\tau_1 \approx (3/4 - R)^{-1}$ goes to infinity and all B_n go to zero except B_1, which goes to unity. τ_1 is related to the cooperative diffusion coefficient, D_0, at the surface of a gel disc by

$$D_0 = \frac{3a_f^2}{\tau_I \alpha_I^2} \tag{9}$$

where α_1 is a function of R only,[22] and a_f stands for the half-thickness of the gel in the final equilibrium state. Hence, D_0 can be calculated.

MATERIALS AND METHODS

Gels were formed by free radical copolymerization as follows: 0.71 g of AAm (Acrylamide, Merck), varying amounts of κC (0.5, 1, 1.5, 2, 2.5, and 3 wt %), 0.01 g of BIS (N,N′-methylenebisacrylamide, Merck), 0.008 g of ammonium persulfate (Merck) and 2 μL of tetramethylethylenediamine (Merck) were dissolved in 5 mL distilled water (pH 6.5) 80°C, respectively. κC concentrations kept constant. We used Py in the PAAm-κC composites as a fluorescence probe. The Py is a derivative of pyrene including three SO_3^- groups, which can form bonds with positive charges on the gel. The Py can be attached to the gel by Coulombic attractions. Py concentration was kept constant at 4×10^{-4} M, for all experiments. The solution was stirred (200 rpm) for 15 min to achieve a homogenous solution. All samples were deoxygenated by bubbling nitrogen for 10 min just before polymerization process.[24] Gelation[24] and swelling process were performed by a Model LS-50 spectrometer from PerkinElmer, equipped with a temperature controller. Before drying was started, Composites were cut into discs with 10 mm in diameter and 4 mm in thickness from the injector. Disc-shaped gel samples were placed on the wall of a 1 cm pathlength, square quartz cell filled with air and water for drying and swelling experiments, respectively. As soon as drying completed, swelling experiment was started. In this article, swelling experiments of disc-shape PAAm-κC composites were performed at various temperatures in water. All measurements were made at 90° position and spectral bandwidths were kept at 5 nm. PAAm-κC composites were excited at 340 nm during *in situ* experiments and emission intensities of the pyranine (Py) were monitored at 427 nm as a function of swelling time. As the water diffusion was increased, the fluorescence intensity, I_{em}, decreased and the
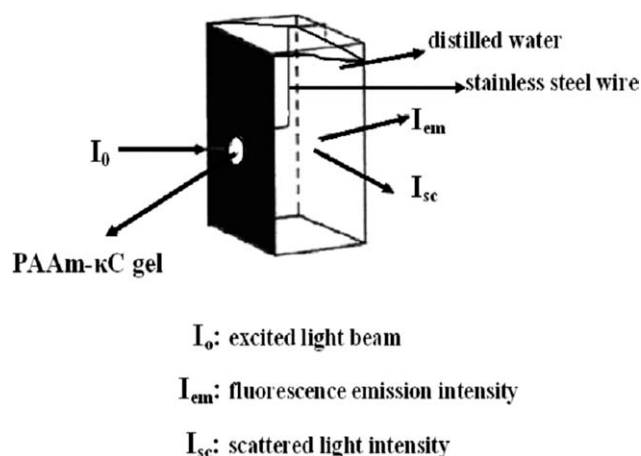
I_o: excited light beam

I_{em}: fluorescence emission intensity

I_{sc}: scattered light intensity

Figure 1 The position of PAAm-κC composite gel in the fluorescence cell during swelling in water. I_0 is excitation, I_{sc} is scattered, and I_{em} is emission maximum light intensities at 340 and 427 nm. The PAAm-κC composite gel is behind the circular hole in the black cardboard and fixed by stainless steel wire in the cell.

scattered light intensity, I_{sc}, increased due to the increase in turbidity of the swelling gel. The position of the PAAm-κC composites which was behind the hole in the cell and fixed by stainless steel wire and the incoming light beam for the fluorescence measurements are shown in Figure 1 during swelling in distilled water. Here, one side of the quartz cell is covered by black cardboard with a circular hole, which was used to define the incoming light beam and limit its size to the initial dimensions of the gel disc. At the same time, gravimetric measurement was performed by measuring weight. The distance and thickness of PAAm-κC composites were also measured to calculate volume of PAAm-κC composites from cylinder's volume formula.

RESULTS AND DISCUSSION

Figure 2(a,b) presents the fluorescence spectra of Py from PAAm-κC composites during the swelling process in pure water at 40 and 50°C for 2.5 wt % κC. In both cases, as the water uptake is increased, the fluorescence intensity, I_{em}, decreased and the scattered light intensity, I_{sc}, increased. To elaborate the above findings, first of all, we have to be mentioned that two different phenomena causes the decrease in the fluorescence emission intensity, I_{em}; first one is the quenching of excited Pys, and the other one is the scattering of light from the gel due to turbidity. As far as the turbidity is concern, it has been known that the swelling and elastic properties of acrylamide gels are strongly influenced by large-scale heterogeneities in the network structure.[25,26] In the swollen state, these imperfections manifest themselves in a nonuniformity of polymer concentration. These

large-scale concentration heterogeneities do not appear in the dry state but only in the gel at the swollen, equilibrium state.[27] Light scattering experiments by Bastide et al. seem to confirm this picture.[28] A gel can be described as a random distribution of crosslinks on a lattice formed by the interchain contact points. When two junctions are located on neighboring lattice sites, a "frozen blob" is formed in that region.[27] In the swollen state of a gel, these crosslinks cannot move apart from each other, as they are chemically connected by a chain segment, which is in an optimal excluded volume conformation. Frozen blobs are often connected and form clusters of first topological neighbors. As a result, the random crosslinking of chains can be described as a site percolation on a blob lattice. When the gel is in a good solvent it swells and frozen blob clusters expand less than the interstitial medium. Here, the swelling of gel leads to an excess scattering of light which comes from the contrast between frozen blob clusters and holes created by the dilution. During the dilution process in gel swelling, the partial separation of frozen blob clusters leads to a strong increase of the scattering intensity, I_{sc} or decrease in the transmitted light intensity, I_{tr}.

As far as the correction of fluorescence emission is concern, total empirical formula was introduced[9,10] to produce the meaningful results for the fluorescence
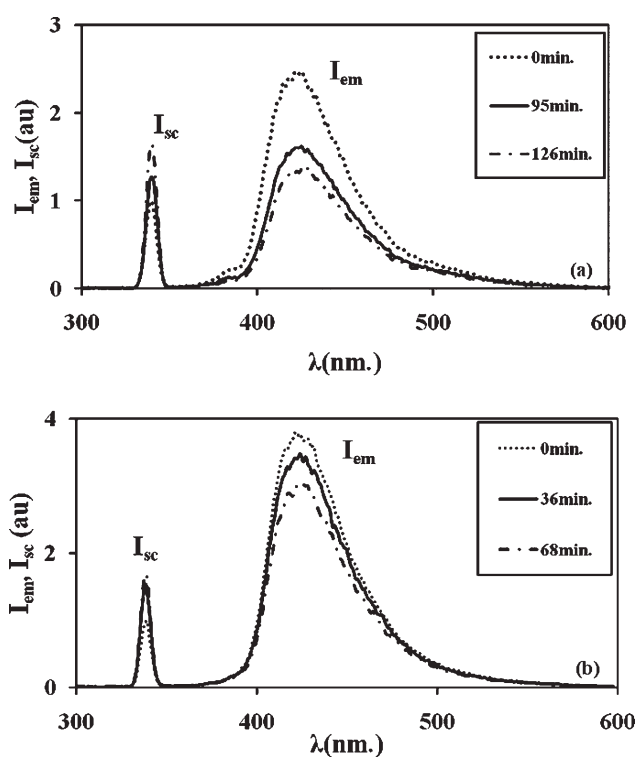

Figure 2 Fluorescence spectra of pyranine from the composite during swelling in water at (a) 40°C and (b) 50°C for 2.5 wt % κC. Each curve indicates the drying times in different minutes.
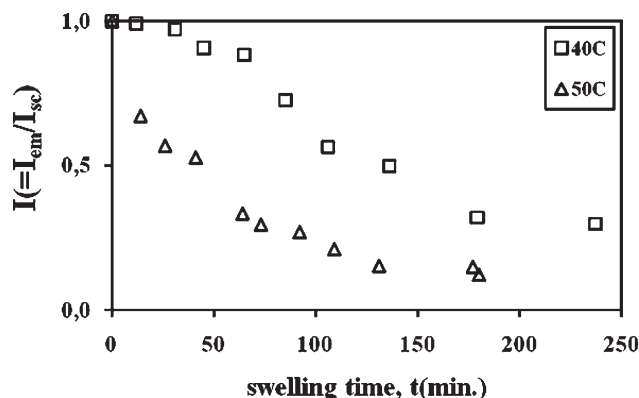
Figure 3 Corrected fluorescence intensities of pyranine, I ($= I_{em}/I_{sc}$) versus swelling time, t during the swelling process at 40 and 50°C for 2.5 wt % κC concentration samples, respectively.

quenching mechanisms. *In situ* photon transmission technique for studying the aging of acrylamide gels due to multiple swelling was reported from our laboratory, where it was observed that the transmitted light intensity, I_{tr}, decreases continuously when PAAm gel swells. The same technique was used to study swelling of PAAm gels with various crosslinker concentrations, where decrease in I_{tr} was explained using the frozen blob model.[12] Here, the main idea is to eliminate the structural fluctuation due to the frozen blobs and holes during swelling by using I_{sc}, i.e., one has to produce the corrected fluorescence intensity, I by dividing emission intensity, I_{em} to scattering intensity, I_{sc} to exclude the effect of turbidity of the gel on the fluorescence emission intensity and elaborate the Stern–Volmer model by using solely fluorescence intensity, I.

Figure 3 shows the variations of the corrected Py intensities, I ($= I_{em}/I_{sc}$) of PAAm-κC composites versus swelling time during swelling process for 2.5 wt % κC concentration gels at 40 and 50°C. As the swelling time, t increased, quenching of excited Pys increased due to water uptake. To quantify these results, the collision type of quenching mechanism may be proposed for the fluorescence intensity, I, in the gel sample during the swelling process, where Stern–Volmer model have been proposed,[29]

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \qquad (10)$$

Here, k_q is quenching rate constant, τ_0 is the lifetime of the fluorescence probe, and Q is the quencher concentration.

For low quenching efficiency, ($\tau_0 k_q [Q] \ll 1$), eq. (10) becomes

$$I \approx I_0 (1 - k_q \tau_0 [Q]) \qquad (11)$$

If one integrates eq. (11) over the differential volume ($d\upsilon$) of the gel from the initial, a_0, to final, a_∞, thick-

ness; here, water uptake, W, was calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W] d\upsilon \qquad (12)$$

reorganization of the relationship produces the following useful equation.

$$W = \left(1 - \frac{I}{I_0}\right) \frac{\upsilon}{k_q \tau_0} \qquad (13)$$

where υ is the swollen volume of the gel at the equilibrium swelling, which can be measured experimentally. k_q was obtained from separate measurements by using eq. (13) where the infinity equilibrium value of water uptake, W_f, was used for each κC concentrations. As τ_0 (≈ 5 ns) was already known for pyranine. Once k_q values are measured, the water uptakes, W, can be calculated from the measured τ_0 values at each swelling step. Here, it is assumed that the k_q values do not vary during the swelling processes, i.e., the quenching process solely originates from the water molecules.
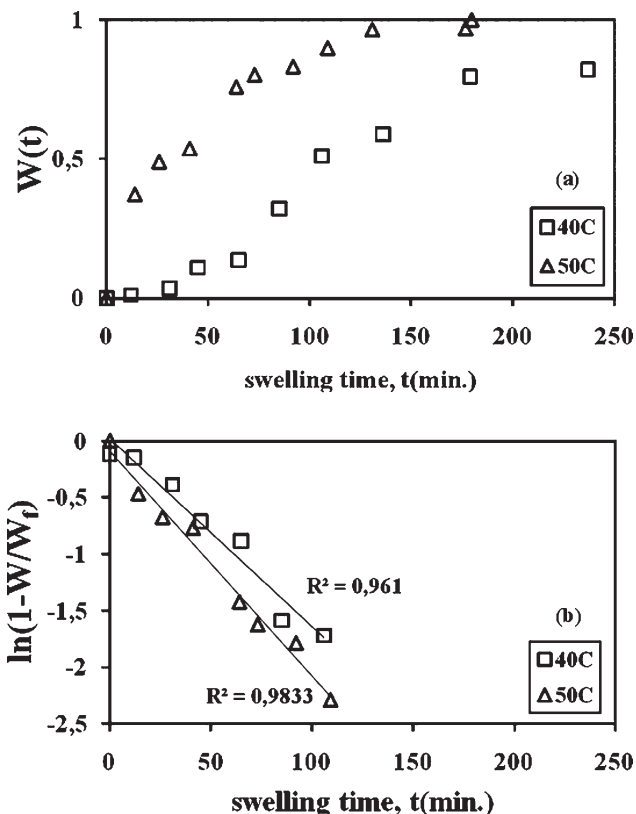

Figure 4 (a) The plots of fluorescence data by using eq. 13. (b) Linear regression of Figure 4(a) by using eq. (14), versus swelling time, t, for PAAm-κC composites swelling in water measured by fluorescence technique at 40, and 50°C for 2.5 wt % κC concentration samples, respectively.
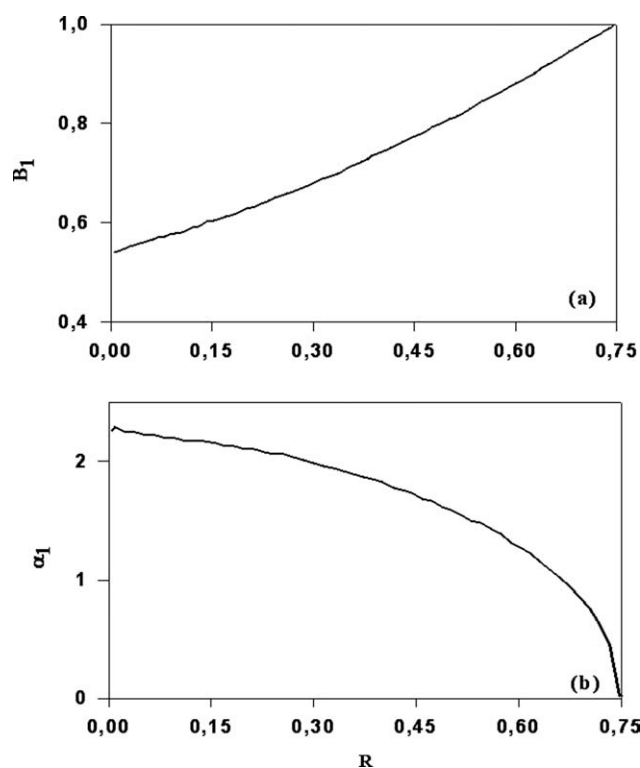
Figure 5 Relationship between (a) B_1 and R, and (b) α_1 and R. The plots are taken from ref. 16.

Plots of water uptake (swelling), W versus swelling time is presented in Figure 4(a). The logarithmic form of the data as shown in Figure 4(b) was fitted to the following relation produced from eq. (6)

$$\ln\left(1 - \frac{W}{W_f}\right) = \ln B_1 - \frac{t}{\tau_1} \qquad (14)$$

Here, τ_1 is the swelling time constant, measured by fluorescence technique and B_1 is related to the ratio of the shear modulus, μ and longitudinal osmotic modulus, M by eq. (7). Using eq. (14), linear regression of the curves in Figure 4(b) provided us with B_1 and τ_{1I} values. Taking into account, the dependence of B_1 on R, one obtains R values and from the α_1-R dependence α_1 value as shown in Figure 5 was based on the method described by Li and Tanaka.[22] Then, using eq. (9), cooperative diffusion coefficients D_0 were determined for these disc-shaped hydrogels and found to be around 10^{-9} m^2/s. Experimentally obtained τ_{1I} and D_{0I} values are summarized in Table I. It should be noticed that D_{0I} values increased as the temperature was increased to 40°C and then decreased to 60°C.

The plots of the solvent uptake (swelling), W, versus swelling time measured gravimetric for 1.5 and 2.5 wt % κC content composites swollen in water are shown in Figure 6(a,b), respectively. These are typical solvent uptake (swelling) curves, obeying the Li-Tanaka equation, eq. (6). The logarithmic forms of the data in Figure 6(a,b) were fitted by using eq. (14), from which B_1 and time constant, τ_{1w} measured by gravimetric technique were determined. Then, using eq. (9), gravimetric cooperative diffusion coefficient D_{0w} was determined and is listed in Table I with the τ_{1w} values. A similar increase in D_{0w} as

TABLE I
Experimentally Measured Parameters of PAAm-κC Composites for Various Temperature and wt % κC Content During Swelling Process

| wt % κC	T (°C)	τ_{1I} (min)	$D_{0I} \times 10^{-9}$ (m^2/s)	τ_{1w} (min)	$D_{0w} \times 10^{-9}$ (m^2/s)	τ_{1v} (min)	$D_{0v} \times 10^{-9}$ (m^2/s)
0.5	30	333.33	0.53	111.11	0.97	166.66	0.72
	40	71.42	5.81	58.82	3.06	58.82	6.22
	50	91.74	4.73	62.50	1.47	62.50	6.17
	60	166.66	4.54	63.29	1.32	83.33	1.24
1	30	1000	0.12	142.85	0.86	200	0.47
	40	32.57	6.29	43.47	3.44	55.00	6.23
	50	62.89	4.93	54.05	2.82	58.82	6.21
	60	142.85	4.69	62.50	2.11	62.50	1.94
1.5	30	500	0.25	142.5	0.90	166.66	0.99
	40	26.73	9.22	38.46	3.51	52.63	7.20
	50	57.14	8.76	41.66	3.35	54.05	6.67
	60	125	6.75	47.61	2.34	55.55	2.00
2	30	333.33	0.26	111.11	3.84	142.85	1.85
	40	25.00	10.05	34.38	5.60	37.03	7.38
	50	56.81	9.18	37.04	3.41	40.00	6.83
	60	111.11	8.41	47.16	2.82	41.66	4.06
2.5	30	200	0.33	90.90	4.16	125	3.69
	40	23.52	14.05	33.00	8.15	33.00	8.07
	50	48.30	12.72	35.71	4.387	37.00	7.52
	60	100	9.35	42.3	3.53	40.90	4.49
3	30	166.67	0.76	55.55	8.95	58.82	6.22
	40	22.72	22.03	20.00	39.98	27.77	22.14
	50	34.01	18.10	27.77	24.39	35.71	7.79
	60	37.03	13.95	28.54	5.24	40.00	4.60
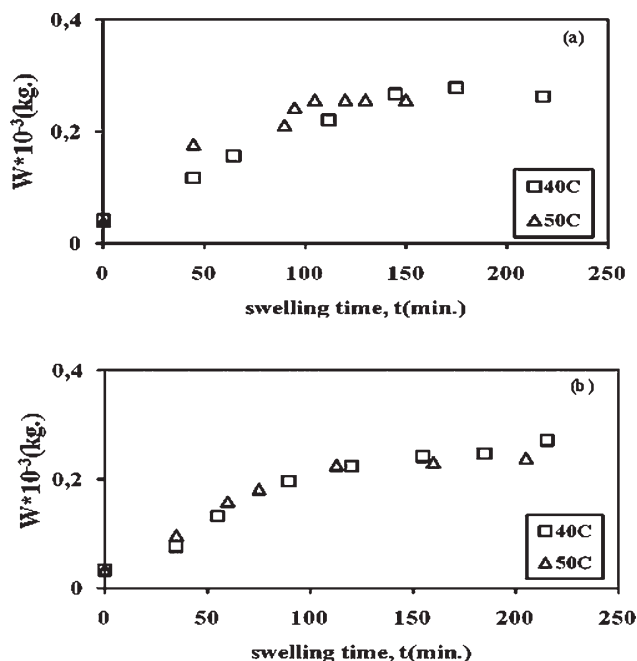
Figure 6 The plots of the water uptake (swelling), W, variation versus swelling time, t, for PAAm-κC composites swollen in water measured by gravimetric technique at 40 and 50°C for (a) 1.5 and (b) 2.5 wt % κC concentration samples, respectively.

that for D_{0I} was observed as the temperature was increased.

The variations in the volume, v, of the PAAm-κC composites during the swelling process were also
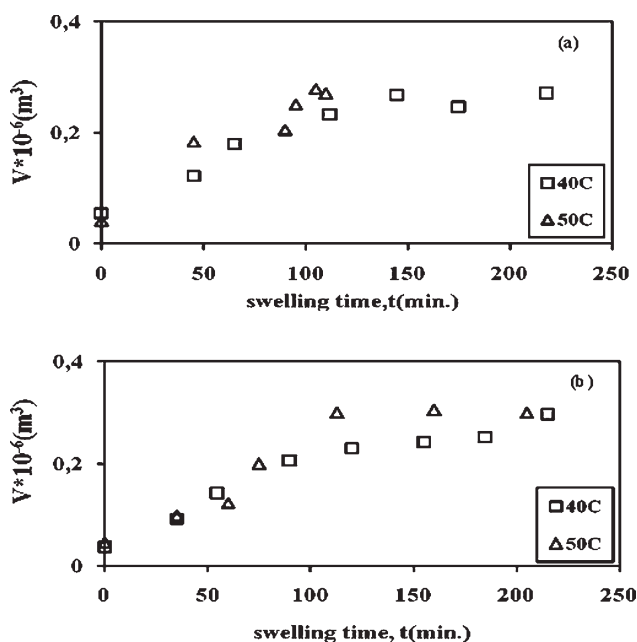

Figure 7 The plots of the volume, V, variation versus swelling time, t, for PAAm-κC composites swollen in water measured by volumetric technique at 40, and 50°C for (a) 1.5 and (b) 2.5 wt % κC concentration samples, respectively.

measured. The plots of the volume, v, versus swelling time for 1.5 and 2.5 wt % κC content composites, swollen in water are presented in Figure 7(a,b), respectively, which are again typical solvent uptake (swelling) curves, obeying the Li-Tanaka equation, eq. (6). The logarithmic forms of the data in Figure 7(a,b) were fitted by using eq. (14) from which B_1 and τ_{1v}, time constants measured by volumetric technique, were determined. Here, it is assumed that the relation between W and v was linear, then using eq. (9), the cooperative diffusion coefficients, D_{0v} measured by volumetric technique were produced and are listed in Table I with the τ_{1v} values. All the swelling time constants, τ_1 with respect to temperature measured by fluorescence, gravimetric, and volumetric techniques presented similar behaviors, i.e., gel swells slower below 40°C during swelling process. Minimum swelling time constant has been observed at 40°C. The swelling time constants increased again with increasing temperature from 40 to 60°C for all samples under consideration.
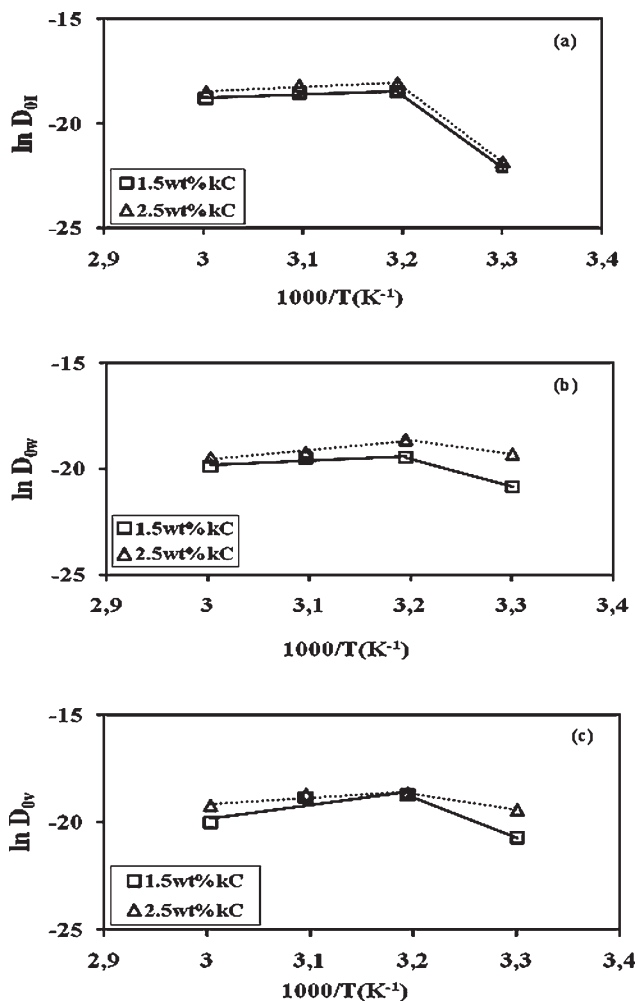

Figure 8 Linear regressions of diffusion coefficients versus reversed temperature measured by (a) fluorescence (b) gravimetric, and (c) volumetric techniques for 1.5 and 2.5 wt % κC concentration samples, respectively.

TABLE II
The Measured Energy of Endothermic (1) and Exothermic (2) Process During Swelling for Various wt% κC Content Gels by Fluorescence, Gravimetrically, and Volumetric Techniques

wt % κC	ΔE_1 (kJ/mol) 1	ΔE_1 (kJ/mol) 2	ΔE_w (kJ/mol) 1	ΔE_w (kJ/mol) 2	ΔE_v (kJ/mol) 1	ΔE_v (kJ/mol) 2
0.5	10.3	−181.9	35.3	−87.30	66.6	−163.9
1	12.3	−300.9	20.3	−105.3	48.2	−196.5
1.5	12.9	−274.2	16.7	−103.4	53.0	−150.8
2	7.4	−277.8	28.7	−28.6	24.7	−105.1
2.5	16.9	−285.1	35.1	−51.1	24.2	−59.4
3	19.0	−255.9	84.4	−113.7	65.8	−96.5

On the other hand, all the cooperative diffusion coefficients are increased up to 40°C, and then decreased to 60°C for a given κC concentration. This is because these gels were recognized to be affected by the alkaline hydrolysis, which can be explained by the low osmotic pressure that increases up to 40°C, then decreases again from 40 to 60°C. Practically, most of acrylamide-based polymers are actually partially hydrolyzed to introduce some carboxylic groups into the chain. The presence of these charged units improve water solubility and increase hydrodynamic volume of the chain due to the mutual repulsion of the negative charges. In other words, the presence of κC in the PAAm gel at 40°C creates larger water absorbing volumes, which then result in faster swelling for all κC content composites.[17,30] Here, it has also to be noted that high κC content gels swell much faster than low κC content, indicating that high water absorbing capacity of κC helps κC content gels swell much faster than the others.

Temperature-dependent behavior of swelling of PAAm-κC composites predicts that $D - 1000/T$ relation may obey the following Arrhenius law:

$$D = D_0 \, \exp \, (-\Delta E/kT) \qquad (15)$$

where ΔE is the swelling activation energy, k is Boltzmann's constant, and D_0 is the cooperative diffusion coefficients at $T = \infty$. The logarithmic form of eq. (15) is presented in Figure 8 (a–c) for the data obtained by fluorescence, gravimetrical, and volumetric techniques from which ΔE values are produced and listed in Table II. ΔE_1 and ΔE_2 defined by endothermic and exothermic swelling activation energies, respectively. The composites behave exothermic and endothermic in between 30–40 and 40–60°C during swelling, respectively. Here, 40°C is the critical temperature between these processes, below which gel swells slowly and releases some heat; however, above the critical temperature, gel absorb some heat during swelling process. Here, it is

seen in Table II that, exothermic and endothermic swelling activation energy, values measured by using fluorescence technique are at least two times larger and/or smaller than the values measured by volumetric and gravimetric techniques, which may present the different behaviors of the gel swelling. It is obvious that the fluorescence technique measure the behavior of the microstructure of the gel, i.e., segmental motion of the gel network can be monitored by using fluorescence intensity, because Py molecules are bounded to the polymer chains and monitors the swelling at a molecular level. However, volumetric and gravimetric measurements may provide us with the information of the macroscopic (bulk) behavior. As a result, the measured activation energies totally represent the energy needs for segmental and/or bulk motions of the composite gel system.

CONCLUSIONS

This study has presented the swelling kinetics of PAAm-κC composites in water at various temperatures by using fluorescence, gravimetric, and volumetric measurements. The Li-Tanaka model combined with Stern–Volmer kinetics was used to measure the swelling time constants, τ_1, and cooperative diffusion coefficients, D_0 for the swelling processes. It is observed that the fast water absorbency was achieved at 40°C. The swelling capacity of the composites was recognized to be affected by the alkaline hydrolysis and osmotic pressure, in turn, results in carboxylate anion increment and consequently, absorbency enhancement. Decreasing the swelling capacity may be attributed to alkaline degradation of the κC part of the hydrogel over 40°C.[18] Therefore, the composites act exothermic between 30 and 40°C and endothermic between 40 and 60°C during swelling processes. The most important conclusion of this article is presented that energy needs for segmental and/or bulk motions of the composite gel system which present the different behaviors of the gel swelling. It is understood that the fluorescence technique measure the segmental motion of the gel network, because Py molecules are bounded to the polymer chains and monitors the swelling at a molecular level. However, volumetric and gravimetric measurements provide us with the information of the bulk behavior.

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