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Swelling Kinetics of PAAm–κ-Carrageenan Composites: A Fluorescence Technique

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The steady-state fluorescence (SSF) technique was introduced for studying swelling of disc-shaped polyacrylamide (PAAm) gels containing various amount of $\kappa-$carrageenan (κC). They were prepared by free-radical cross-linking copolymerization. N,N′-methylenebisacrylamide (BIS) and ammonium persulfate (APS) were added as a cross-linker and an initiator, respectively. Composite gels were prepared at 80°C with pyranine as a fluorescence probe. After drying of these gels, swelling kinetics were performed in water at 60°C by real-time monitoring of the pyranine fluorescence intensity, I, *which decreased as swelling proceeded. 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 gels during the swelling processes in all cases. It was observed that τ_1 decreased and D_0 increased as the κC concentrations in the composites were increased indicating that high κC gels swell faster than low κC gels.*

Keywords composite, fluorescence, hydrogels, polyacrylamide, swelling, κ-carrageenan

Introduction

A gel is a cross-linked polymer network immersed in a fluid. This network can be formed by physical and chemical cross-links.[1,2] A number of physically cross-linked gels of carrageenans are industrially important sulphated galactans. Carrageenan is a seaweed polysaccharide; the backbone of the polymer consists of alternating α-1, 3-linked D-galactopyranose and β-,1-linked 3,6-anhydro-D-galactopyranose [Fig. 1(a)]. Carrageenans are subgrouped according to their disaccharide-repeating units by assigning Greek letters. Kappa and iota are the common carrageenan groups and found in the gamet to phytic life phase of various seaweed species. Up to date, there have been many reviews articles on the science of carrageenans, such as on the biology of seaweeds and the reology and applications of marine polysaccharides.[3,4] The sulphate ester groups and galactose rings play an important role in the physicochemical properties of carrageenans, especially for their helix formation, which would affect their rheological and spectroscopic behavior.[4–6] On the other hand, polyacrylamide (PAAm) hydrogels are mainly produced by free-radical cross-linking copolymerization (FCC) of acrylamide (AAm) in the presence of N,N′-methylenebisacrylamide (BIS) as the cross-linker. Since the monomers are solid at the

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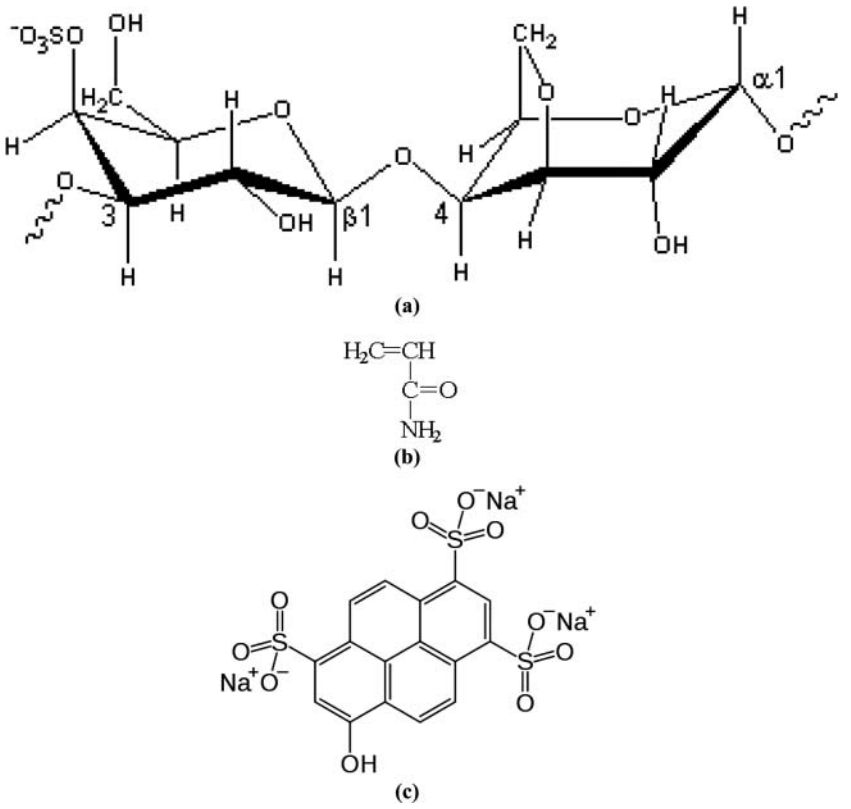

Figure 1. The chemical structures of (a) κC, (b) AAm, and (c) pyranine. [32]

polymerization temperature, the reactions are necessarily carried out in an aqueous solution of the monomers. These high-molecular-weight polymers can be modified to develop nonionic, anionic, or cationic properties for specific uses. These materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators.[6]

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 solvent molecules are kept in three-dimensional mesh and the combination of the mesh and solvent molecules creates a "world" having characteristic properties, which can be either isolated from isochore or linked to isobar.[7,8] The volume phase transition was experimentally discovered for a partially ionized AAm gel in a mixture of acetone and water by Tanaka.[9] The theory of the kinetics of the swelling of a cross-linked polymeric network has been derived by Tanaka and Fillmore.[2] Peters and Candau developed a model with nonnegligible shear modulus to characterize the kinetics of swelling of spheres, cylinders, and disks made of polymer gels.[10] Li and colleagues proposed a two-process mechanism based on the assumption that gel swelling and shrinking are not a pure diffusion process.[11–13] 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.[13] The kinetics of swelling and shrinking processes of AAm gels have been theoretically generalized and experimentally studied.[14–17]

We have used the photon transmission technique to study the swelling of PAAm gels with various cross-linker contents.[18,19] The decrease in transmitted light intensity, I_{tr}, was modeled using the Li–Tanaka equation from which time constants and collective diffusion coefficients were determined for various BIS content PAAm gels; the decrease in I_{tr} was attributed to lattice heterogeneities, which might have originated between microgels and holes in the swelling gel. We reported the PAAm hydrogel swelling for various temperatures and cross-linker contents by using steady-state fluorescence (SSF) technique.[20,21] The swelling time constants decreased and diffusion coefficients increased as the swelling temperature was increased and, also, the cooperative diffusion coefficient decreased as the cross-linker content was increased. The photon transmission technique was also used to study the swelling properties of κ-carrageenan (κC) gels prepared in various concentrations. It has been reported that gels with high carrageenan content possess more double helices and more lattice dislocations and swell slower than gels with low carrageenan content, which may contain less double helices and less lattice imperfections.[22] A SSF technique was employed to study the swelling of κC gels at various temperatures. The results presented in this reference show that the fluorescence method can be used to measure time constants and diffusion coefficients 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.[23] Universal behavior of gel formation from AAm–carrageenan composite around the gel point was investigated by our group using the SSF technique. In this article, universality of AAm–carrageenan composite gel was examined and its universality was shown to agree with percolation theory.[24] Absorbent and adhesive properties of κC graft PAAm copolymer hydrogels 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 (KPS) was used. The resultant copolymer hydrogel exhibited adhesive and superabsorbent properties.[6] Superabsorbent hydrogels of κC graft PAAm were also synthesized by a simultaneous irradiation technique using γ-rays as the energy source, initiator, and cross-linker under various conditions. The optimization of synthetic conditions to achieve maximum water absorbency was performed by the Taguchi method. The swelling behavior of the superabsorbent polymers was related to their chemical structure, chemical composition, the absorbing environment, and the nature of the solution.[25]

In this work, the objective was to study swelling process of PAAm–κC composites by using the SSF technique. The Li–Tanaka equation was used to determine the swelling time constants, τ_1, and cooperative diffusion coefficients, D_0, for the swelling processes. Supporting gravimetrical and volumetrical swelling experiments were also performed by using similar gel samples. It was observed that the swelling time constant, τ_1, decreased and cooperative diffusion coefficients, D_0, increased as the κC concentrations were increased.

Background

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

$$\delta F_{sh} = 0, \tag{1}$$

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 over damps 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.[11] 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 Equation (1) must couple to a small shear process given by Equation (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 Equations (1) and (2) produces the following equations for the swelling of a disc gel in axial and radial directions:[11]

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

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

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:

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

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 Equation (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 relationship:

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

It should be noted from Equation (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, $M = (K + 4\mu/3)$. Once the value of B_1 is obtained, one can determine the value of $R = \mu/M$. Here, we have to note that Equation (6) can also be obtained by using theoretical results; in the case of $R \to 3/4$ ($\mu/K \to \infty$), 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. The dependence of B_1 on R for a disc is shown in Fig. 2(a).[11] τ_1 is related to the cooperative diffusion coefficient, D_0, at the surface of a gel disc by

$$D_0 = \frac{3a_f^2}{\tau_I \alpha_I^2}, \tag{8}$$

where α_1 is a function of R only and is given in Fig. 2(b)[11] 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), 0.01 g of BIS (N,N′-methylenebisacrylamide, Merck), 0.008 g of APS (ammonium persulfate, Merck), and 2 μl of TEMED (tetramethylethylenediamine, Merck) were dissolved in 5 ml distilled water (pH 6.5) by heating. The heated mixture solution was held at 80°C. Then, varying amounts of carrageenan (0.5, 1, 1.5, 2, 2.5, and 3%) were added. Py concentration was kept constant at 4×10^{-4} M, for all experiments. The chemical structures of (a) κC, (b) AAm, and (c) pyranine are shown in Fig. 1. 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]

The preparation of the composite gel begins with the three monomers: AAm, which is a small organic molecule that contains an aminocarbonyl (-$CONH_2$) group; BIS, which consists of two AAm monomers that are linked through their aminocarbonyl groups; and κC, which is a biological monomer. κC does not react chemically with the AAm and bisacrylamide but, rather, the κC becomes trapped in a very small spaces because of the compactness of the composite. The monomers were dissolved in water; then, more substances were added to initiate a chain reaction of polymerization. The initiators were APS and the organic molecule, TEMED.

The polymerization of AAm–κC composite involves a reaction between APS and TEMED in which the TEMED molecule is left with an unpaired valence electron. The activated TEMED molecule can combine with an AAm or BIS monomer; in the process, the unpaired electron is transferred to the AAm unit so that it, in turn, becomes reactive. BIS can therefore be attached and activated in the same way. The polymer can continue

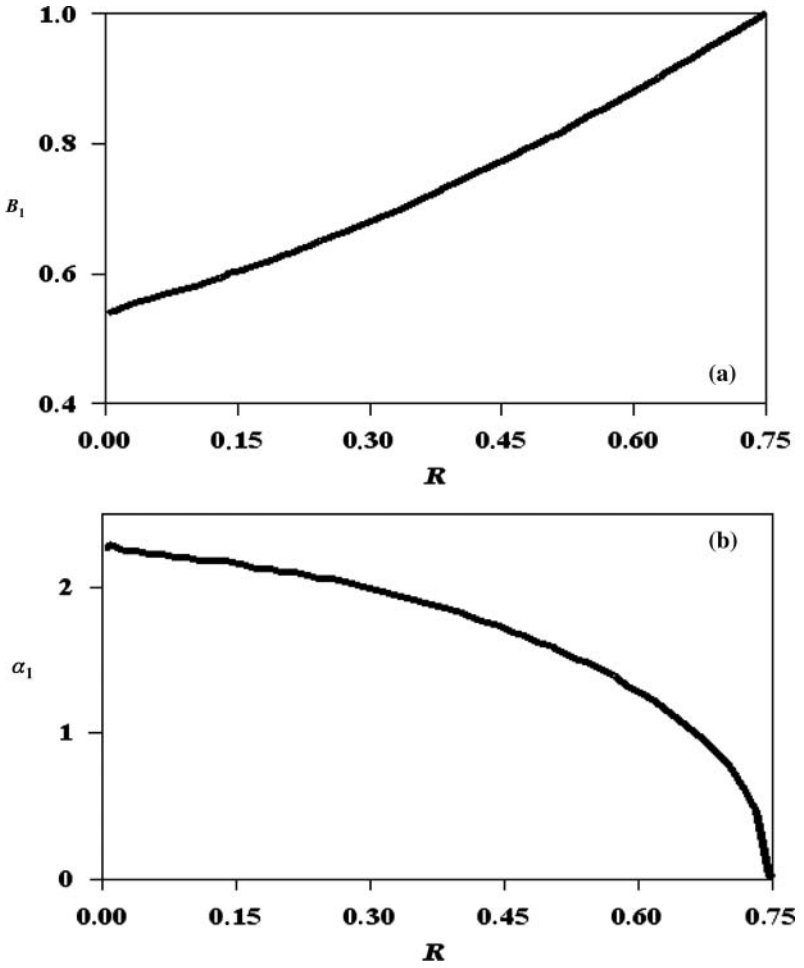

Figure 2. The relationships between (a) $B_1 - R$ and (b) $\alpha_1 - R$.

growing indefinitely (or until the supply of monomers is exhausted) with the active center being continually shifted to the free end of the chain.[1,26,27]

After drying these gels, swelling experiments of disc-shaped PAAm–κC composites were performed at 60°C in water. The fluorescence intensity measurements were carried out using a Model LS-50 spectrometer from Perkin-Elmer, equipped with a temperature controller. All measurements were made at 90° position and spectral bandwidths were kept at 5 nm. Disc-shaped gel samples were placed on the wall of a 1 cm path length, square quartz cell filled with water for the swelling experiments. 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 [Fig. 1(c)]. The Py can be attached to the gel by Coulombic attractions.[28]

Composite gels were excited at 340 nm during in-situ experiments and emission intensities of the pyranine 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 scattered light intensity, I_{sc}, increased due to the increase in turbidity of the swelling gel. The position of the PAAm–κC composite gel that was behind the hole in the cell and fixed by stainless

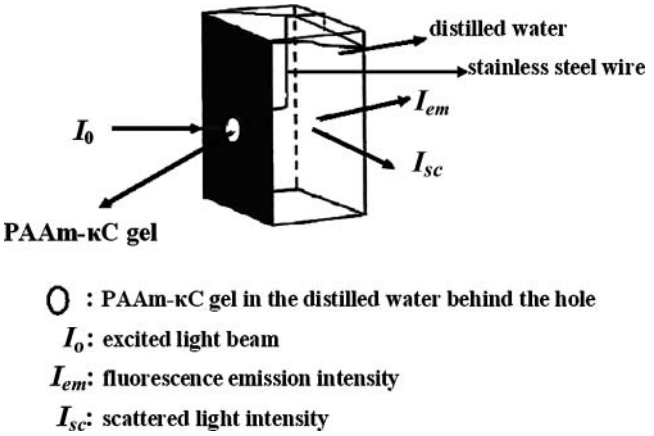

Figure 3. The position of PAAm–κC composite gel in the fluorescence cell during swelling in water. I_0 is excitation, I_{sc} is scattered, and I_{em} is emission maximum light intensities at 340 and 427 nm, respectively. The PAAm–κC composite gel is behind the circular hole in the black cardboard and fixed by stainless steel wire in the cell.

steel wire and the incoming light beam for the fluorescence measurements is shown in Fig. 3 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.

Results and Discussion

Figure 4 shows the emission spectra of pyranine from PAAm–κC composites during the swelling process in pure water for 0.5% κC. As the water uptake was increased, the fluorescence intensity, I_{em}, decreased and the scattered light intensity, I_{sc}, increased. In

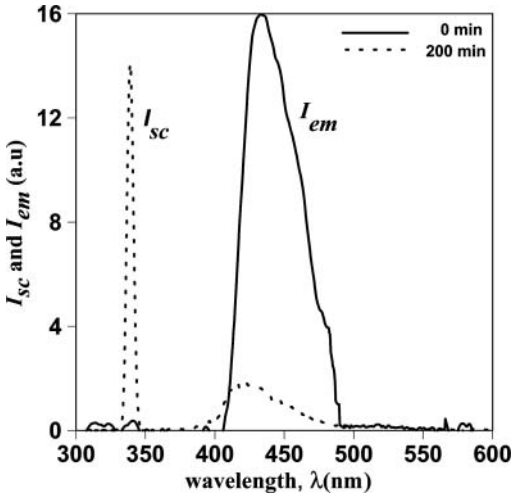

Figure 4. Fluorescence spectra of pyranine during the swelling process for 0.5% κC concentration. The numbers indicate the swelling times.

order to elaborate the above findings, first of all we have to mentioned that two different phenomenon cause the decrease in the fluorescence emission intensity, I_{em}; the first one is the quenching of excited pyranines and the other one is the scattering of light from the gel due to turbidity. As far as the turbidity is concerned, it has been known that the swelling and elastic properties of AAm gels are strongly influenced by large-scale heterogeneities in the network structure.[29,30] 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.[31] Light scattering experiments by Bastide et al. seem to confirm this picture.[32] When two junctions are located on neighboring lattice sites, a "frozen blob" is formed.[31] In the swollen state of the gel, these cross-links cannot move apart from each other, since 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 cross-linking 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}.

In-situ photon transmission technique for study the aging of AAm gels due to multiple swelling was reported from our laboratory,[33] where it was observed that the transmitted light intensity, I_{tr}, decreased continuously at the PAAm gel swelled. The same technique was employed to study swelling of AAm gels with various cross-linker concentrations, where decrease in I_{tr} was explained using the frozen blob model.[19]

As far as the correction of fluorescence emission is concerned that a totally empirical formula has been introduced[20,21] to produce the meaningful results for the fluorescence quenching mechanisms. 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 the emission intensity, I_{em}, by the 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 the fluorescence intensity, I.

Figure 5 shows the variations of the corrected pyranine intensities, I ($=I_{em}/I_{sc}$) of PAAm–κC composites vs. swelling time during swelling for 1%, 2.5%, and 3% κC content

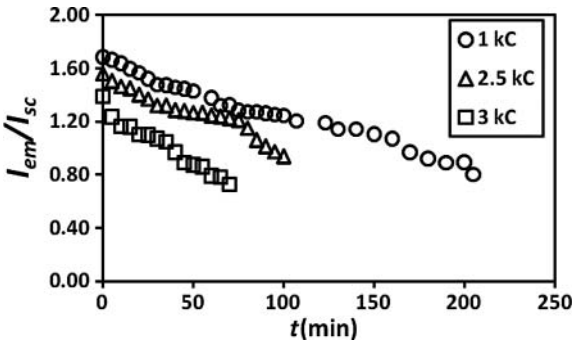

Figure 5. Corrected fluorescence intensities of pyranine, I ($=I_{em}/I_{sc}$) during the swelling process for 1%, 2.5%, and 3% κC concentrations, respectively.

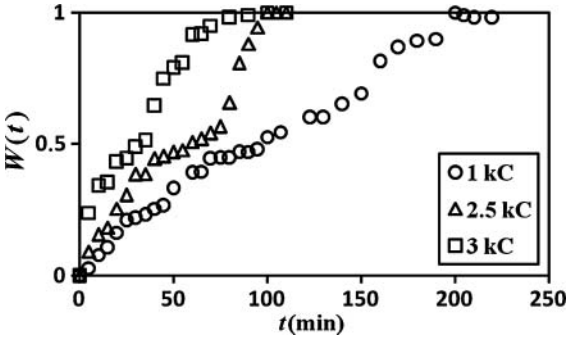

Figure 6. The plots of water uptake, *W (t)* vs. swelling time, *t* for PAAm–κC composite gels swollen in water at 1%, 2.5%, and 3% κC concentrations, respectively.

gels. As the swelling time, *t*, increased, quenching of excited pyranines increased due to water uptake. It has also to be noted that quenching became more efficient at higher κC concentrations. In order 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 the following relationships (Stern–Volmer Model) have been proposed as derived:[34]

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q]. \tag{9}$$

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, ($\tau_0 k_q [Q] << 1$), Equation (9) becomes

$$I \approx I_0(1 - k_q \tau_0 [Q]). \tag{10}$$

If one integrates Equation (10) over the differential volume (dv) of the gel from the initial, a_0, to final, a_∞, thickness, reorganization of the relationship produces the following

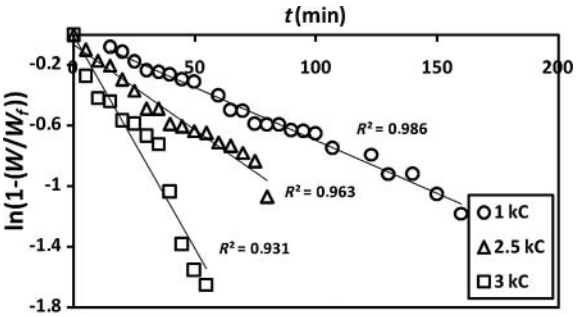

Figure 7. Fit of the data in Fig. 6 to Equation (13) for PAAm–κC composite gels swollen in water at 1%, 2.5%, and 3% κC concentrations, respectively.

Table 1
Calculated parameters of PAAm hydrogel for various κC concentrations

κC%	τ_{1I} (min)	$D_{0I}{}^{*}10^{-9}$ (m^2/s)	τ_{1w} (min)	$D_{0w}{}^{*}10^{-9}$ (m^2/s)	τ_{1v} (min)	$D_{0v}{}^{*}10^{-9}$ (m^2/s)
0.5	166.66	4.54	63.29	1.32	83.33	1.24
1	142.85	4.69	62.50	2.11	62.50	1.94
1.5	125	6.75	47.61	2.34	55.55	2.00
2	111.11	8.41	47.16	2.82	41.66	4.06
2.5	100	9.35	42.30	3.53	40.90	4.49
3	37.03	13.95	28.54	5.24	40	4.60

τ_{1I}: fluorescence time constant.
τ_{1w}: gravimetric time constant.
τ_{1v}: volumetric time constant.
D_{0I}: fluorescence cooperative diffusion coefficient.
D_{0w}: gravimetric cooperative diffusion coefficient.
D_{0v}: volumetric cooperative diffusion coefficient.

useful equation:

$$W = \left(1 - \frac{I}{I_0}\right) \frac{\upsilon}{k_q \tau_0}. \tag{11}$$

Here, water uptake, W, was calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W]\, d\upsilon, \tag{12}$$

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 Equation (11) where the infinity equilibrium value of water uptake, W_f, was used for each κC concentrations. Since τ_0 ($\approx$5 ns) was already known for pyranine, measured values of υ can be used to calculate k_q for each sample separately. The average value of k_q was found to be 0.47×10^7 $M^{-1}s^{-1}$. 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.

Plots of water uptake, W, vs. swelling time are presented in Fig. 6. The logarithmic form of the data in Fig. 6 was fitted to the following relation produced from Equation (6):

$$\ln\left(1 - \frac{W}{W_f}\right) = \ln B_1 - \frac{t}{\tau_{11}}. \tag{13}$$

Here, τ_{1I} is the 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 Equation (7). Using Equation (13), linear regression of the curves in Fig. 7 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 $\alpha_1 - R$ dependence, the α_1 value was produced from Fig. 2. The experimental determination of these values was based on the method described by Li and Tanaka.[11]

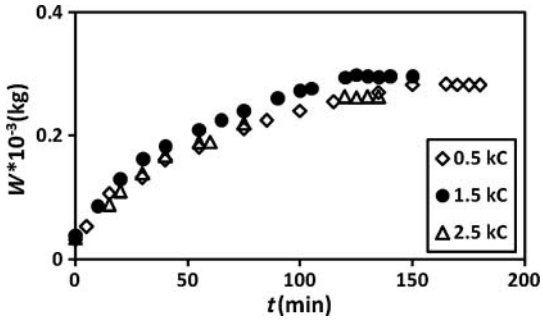

Figure 8. The plots of the water uptake, *W,* measured gravimetrically vs. swelling time, *t*, for PAAm–κC composite gels swollen in water at 0.5%, 1.5%, and 2.5% κC concentrations, respectively.

Then, using Equation (8), 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 1. It should be noticed that D_{0I} values increased as the κC concentration was increased.

The plots of the solvent uptake, W, vs. swelling time measured gravimetrically for three of the PAAm–κC composites swollen in water are shown in Fig. 8. These are typical solvent uptake curves, obeying the Li–Tanaka equation, Equation (6). The logarithmic forms of the data in Fig. 8 were fitted to the following relation produced from Equation (6):

$$\ln\left(1 - \frac{W}{W_f}\right) = \ln B_1 - \frac{t}{\tau_{1w}}. \tag{14}$$

The fits are presented in Fig. 9, from which B_1 and gravimetric time constant, τ_{1w}, were determined. Then, using Equation (8), gravimetric cooperative diffusion coefficients, D_{0w}, were determined and are listed in Table 1 with the τ_{1w} values. A similar increase in D_{0w} as that for D_{0I} was observed as the κC concentrations were increased.

The variations in the volume, v, of the PAAm–κC composites during the swelling process were also measured. The plots of the volume, v, vs. swelling time for PAAm–κC composites, swollen in water are presented in Fig. 10, which are again typical solvent

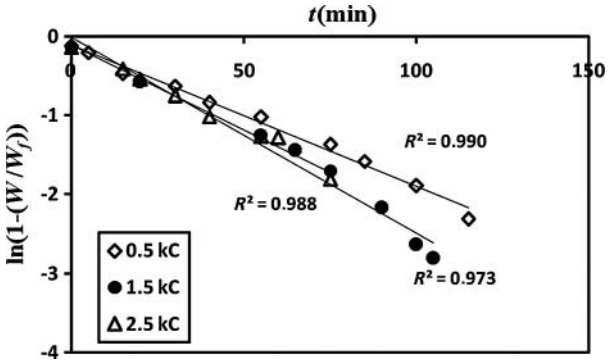

Figure 9. Linear regression of the data in Fig. 8 according to Equation (14) for PAAm–κC composite gels swollen in water at 0.5%, 1.5%, and 2.5% κC concentrations, respectively.

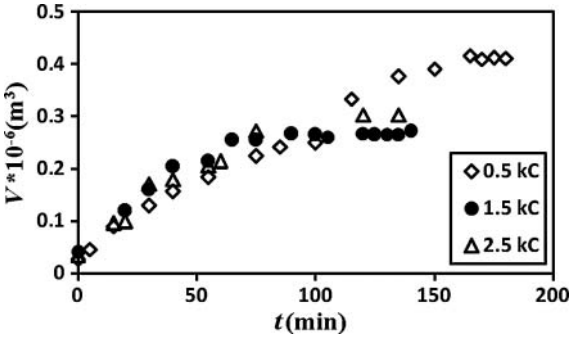

Figure 10. The plots of the change in volume, V, vs. swelling time, t, for PAAm–κC composite gels swollen in water 0.5%, 1.5%, and 2.5% κC concentrations, respectively.

uptake curves, obeying the Li–Tanaka equation [see Equation (6)]. The logarithmic forms of the data in Figure 10 were fitted to the following relation produced from Equation (6):

$$\ln\left(1 - \frac{v}{v_f}\right) = \ln B - \frac{t}{\tau_{1v}}. \tag{15}$$

Here, it is assumed that the relation between W and v was linear. The fits are presented in Fig. 11, from which B_1 and τ_{1v}, volumetric time constants, were determined. Then, using Equation (8), the volumetric cooperative diffusion coefficients, D_{0v}, were determined and are listed in Table 1 with the τ_{1v} values.

The behavior of the cooperative diffusion coefficients, measured from fluorescence, gravimetric, and volumetric techniques, is plotted vs. κC concentrations in Fig. 12, respectively. Cooperative diffusion constants were found to be in the range of (1.32–13.95) $\times$ 10^{-9} m^2s^{-1} for the gels prepared with increasing κC concentrations (0.5%–3%). D_0 values were found to be larger in high κC content gels. This is because these gels swell much faster than low κC content gels, which can be explained by the high moisture absorption capacity of carrageenan compared to PAAm. In other words, the presence of κC in the PAAm gel creates larger water absorbing volumes, which then result in faster swelling of high κC content composites.

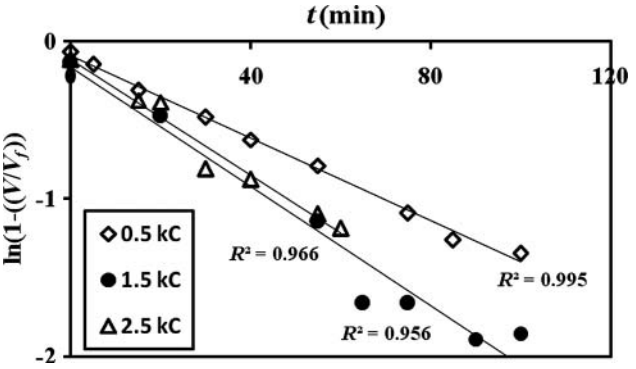

Figure 11. Linear regression of the data in Fig. 10 according to Equation (15) for PAAm–κC composite gels swollen in water at 0.5%, 1.5%, and 2.5% κC concentrations, respectively.

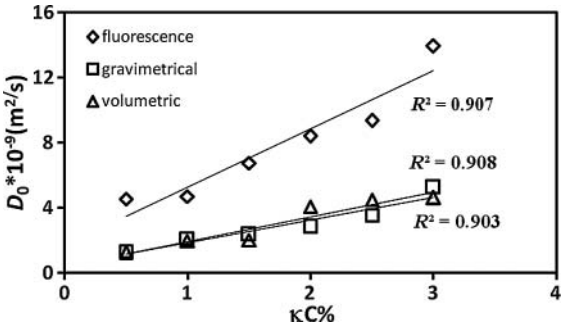

Figure 12. Cooperative diffusion constants vs. κC concentration measured by fluorescence, gravimetrical, and volumetrical techniques, respectively.

Conclusion

The results in this work have shown that the fluorescence method can be used to monitor swelling kinetics of PAAm–κC composites in water. This technique was employed to measure the swelling time constants, τ_1, and cooperative diffusion coefficients, D_0, for composite samples prepared with various κC content. The Li–Tanaka model was applied to measure these parameters. It was previously shown that the swelling process of PAAm–κC composite gels is affected by the presence of κC. The results, here, were interpreted in terms of the swelling time constants; τ_1 decreased and D_0 increased while the κC concentrations were increased. It was observed that high κC content composites swell much faster due to having larger D_0 coefficients for all measurements compared to low κC content composites. On the other hand, it is seen in Table 1 that D_0 values measured by using fluorescence technique are two to three times larger than the values measured by volumetric and gravimetric techniques, which may suggest the observation of different mechanisms of the swelling of the gel. It is obvious that the fluorescence technique measures the behavior of the microstructure of the gel, i.e., since pyranine molecules are bound to the polymer chains, segmental motion of the gel network can be monitored by using the fluorescence technique, which, thus, monitors the swelling of the gel at a molecular level. However, volumetric and gravimetric measurements provide us with the information of the macroscopic (i.e., bulk) behavior of the gel. According to the above presented argument, one may suggest that chain segments move two to three times faster than the bulk polymeric material itself during the swelling process.

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