Energy needs for drying of PAAm- κC composites prepared with various κC contents

Önder Pekcan[1], Gülşen Akın Evingür[2]*

[1]Kadir Has University, 34083, Cibali- İstanbul, Turkey; tel: +90 212 533 65 15; e-mail: pekcan@khas.edu.tr.
[2*]İstanbul Technical University, Department of Physics, Maslak, 34469, İstanbul, Turkey; tel: +90 212 285 63 86; e-mail: evingur@itu.edu.tr

Abstract: Various polyacrylamide (PAAm) – Kappa Carrageenan (κC) composite gels were prepared from acrylamide (AAm), N,N'- methylenebisacrylamide (BIS) and different κC contents by free radical crosslinking copolymerization in water. Pyranine (P) was introduced as a fluorescence probe, and scattered light, I_{sc}, and fluorescence intensities, I, from these gels were monitored during drying at different temperature. The fluorescence intensity of pyranine increased as drying time is increased for all samples. The behavior of I was quantified using the Stern-Volmer equation with moving boundary diffusion model. Desorption coefficient, D increased as temperature was increased for a given κC content. Supporting gravimetrical and volumetric experiments were also carried out during drying of PAAm-κC composite gels. The energy, ΔE values were measured for the drying processes for each κC content gel by using fluorescence, gravimetrical and volumetric methods, respectively. It is understood that ΔE values increase by increasing κC content, indicating that energy needs for the drying of high κC content gel is larger than low κC content gel.

Introduction

Drying mechanisms in hygroscopic materials have been studied by many investigators [1-2], but these are still not well understood. The regime of drying may change as the drying progresses. During the early part of drying, moisture evaporates from the surface of the material to the air. Once the surface water reaches the level of equilibrium content, an evaporating front forms and slowly move into the body of material dividing the material into a wet region and dry region, which have different physical properties and transfer mechanisms [3]. Special polymers and hydrogels are highly hygroscopic and the shrinking and/or drying of these materials encompass many fields of technology. The quantity of bound water associated with the polymer varies as per the internal structure of the gel i.e. monomer and cross-linking agent proportions are responsible for both the porous structure and the pore size of the gel.

Scherer investigated drying mechanisms of gels by diffusion[4], shear modulus [5] and the status of the mechanism. Practice of drying such as stresses and cracking [6] was also reviewed. A diffusive drying model for the drying of highly shrinking materials like polyacrylamide gel and cellulosic paste have been reported [7]. Recently approximate models have been used by Coumans [8] to predict the drying kinetics for slab geometry. The structural and thermodynamic properties of a water

droplet enclosed in a spherical cavity embedded in a hydrophobic material are studied by Wallqvist [9].

Fluorescence methods, such as steady state spectroscopy, fluorescence anisotropy and transient fluorescence (TRF) measurements, have been shown to be quite effective in the investigation of the microscopic environment around chromospheres. The first fluorescence study on polymer gels was carried out by Horie et al. to investigate the hydrophobicity and dynamic characteristics of crosslinked polystyrene with a dansyl probe [10]. The photon transmission technique was used to study the drying of PAAm gels with various κC contents [11] and with various water contents [12]. Steady state and TRF techniques were applied to study the drying process of selected silane gels in oxygen free atmosphere. A kinetic model of drying was suggested and drying rate constants were determined [13]. The fast transient fluorescence (FTRF) technique was used in our laboratory to study gel drying processes [14-15]. Recently the steady state fluorescence technique was employed for studying the drying of polyacrylamide [16], kappa carrageenan [17] at various temperatures, and polyacrylamide hydrogels of various crosslinker contents [18].

Carrageenans are industrially important sulphated galactans. Red algae or Rhodophyta produce carrageenan as their main cell- water material. Carrageenans are subgrouped according to their disaccharide- repeating units by assigning Greek letters. Kappa (κ-) and iota (*ı-*) are the common carrageenan groups and found in the gamet to phytic life phase of various seaweed species. Chemically, it is linear, sulphated polysaccharide composed of a repeating unit composed of the disaccharide, β-(1-3)-D-galactose-4-sulphate and α-(1-4)-3,and 6-anhydro-D-galactose [19]. Kappa carrageenan was found to enhance the properties of synthetic hydrogels by incorporation into the water soluble polymer systems such as N-isopropylacrylamide [20] and acrylamide [21]. An acrylamide derived hydrogel is a cross-linked network of polymer whose molecular weight is fairly high; it can absorb solvent (water), but is itself insoluble. During the water migration in the drying process, shrinkage corresponds simply to the compacting of solid mass. These constitute a very important class of materials in food, cosmetic, biomedical or pharmaceutical applications [22].

In this work drying process of PAAm-κC composite gels prepared with different κ-carrageenan contents were studied by using the steady-state fluorescence technique at various temperatures. Pyranine was used as a fluorescence probe to monitor the gel drying. It was observed that the fluorescence intensity of pyranine increased as drying time was increased during the drying process. By combining the Stern-Volmer equation with the moving boundary model, water desorption coefficients, *D* were determined for the drying gels prepared with various kappa carrageenan content at different temperatures. Drying energies *ΔE* were measured for each composite gel.

Background

Stern- Volmer Kinetics

Stern- Volmer Kinetics applies broadly to variations of quantum yields of photophysical processes such as fluorescence or phosphoresce or photochemical reactions with the concentration of a given reagent which may be a substrate or a quencher. In the simplest case, a plot of fluorescence intensity vs. concentration of quencher, *[Q]* is linear obeying the following equation [23],

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

Here, k_q is quenching rate constant, τ_0 is the lifetime of the fluorescence probe and Q is the quencher concentration and I_0 is the fluorescence intensity for zero quencher content. This relation is called Stern- Volmer Equation.

For low quenching efficiency, ($\tau_0 k_q [Q]$<<1), Eq. 1 becomes

$$I \approx I_0 \left(1 - \tau_0 k_q [Q] \right) \tag{2}$$

If one integrates Eq. 2 over the differential volume (dv) of the sample from the initial, a_0 to final a_∞ thickness, then reorganization of the relation produces the following useful equation.

$$W = \left(1 - \frac{I}{I_0} \right) \frac{v}{k_q \tau_0} \tag{3}$$

Here, the amount of water release, W is calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W] dv \tag{4}$$

Here it is assumed that water molecules are the only quencher for the excited pyranine molecules in our system. Where v is the volume at the equilibrium drying state, which can be measured experimentally, k_q was obtained from separate measurements by using Eq. 3 where the infinity equilibrium value of water release, W was used for each sample.

Moving Boundary Diffusion Model

Diffusion in a system with a moving boundary occurs in two distinct regions separated by a moving interface. The moving interface can be marked by a discontinuous change in concentration as in the absorption by a liquid of a single component from a mixture of gases or by a discontinuity in the gradient of concentration as in the progressive freezing of a liquid. Furthermore, the movement of the boundary relative to the two regions it separates may be caused by the appearance or disappearance of matter at the boundary in one or both regions, which results in a bodily movement of the matter in one or both regions relative to the boundary. When the diffusion coefficient is discontinuous at a concentration c; i.e. the diffusion coefficient is zero below c and constant and finite above c; then the total amount, M_t of diffusing substance desorbed from unit area of a plane sheet of thickness a at time t, is given by the following relation [24]

$$\frac{M_t}{M_\infty} = 2 \left[\frac{D}{\pi a^2} \right]^{1/2} t^{1/2} \tag{5}$$

where D is a diffusion coefficient at concentration c_1. Here $M_\infty = a\, c_1$ is the equilibrium value of M_t. If one assumes that the diffusion coefficient of polymer segments in the gel is negligible compared to the desorption coefficient, D of water vapour into air, then Eq. 5 can be written as follows

$$\frac{W}{W_\infty} = 2\left[\frac{D}{\pi a^2}\right]^{1/2} t^{1/2}$$

(6)

Here it is assumed that M_t is proportional to the amount of water molecules released, W at time, t.

Results and discussion

Fig. 1 a, b and c show the emission spectra of pyranine from PAAm- κC composite gel with 2.5 wt %κC content, during drying in air at 30, 40 and 50 ^{0}C temperatures respectively.
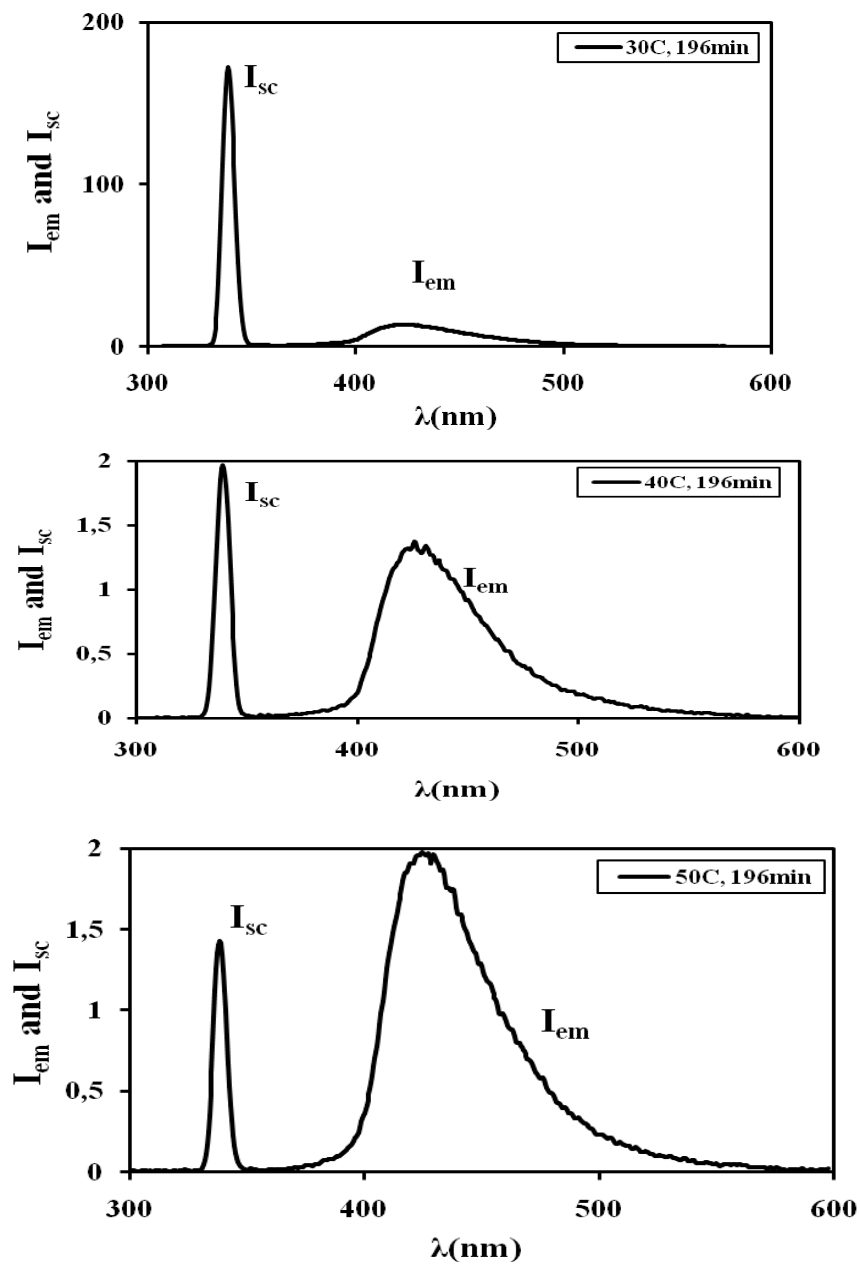

Fig. 1. Emission spectra of pyranine from the gel during drying in air at a) 30 ^{0}C, b) 40 ^{0}C and c) 50 ^{0}C for 2.5 wt %κC content gel. Each curve indicates the drying time in 196 minutes.

4

It can be seen that as the drying temperature is increased, fluorescence intensity, I_{em} increases relative to the scattered light intensity, I_{sc}. Since the decrease in I_{sc} corresponds to the decrease in turbidity of the drying gel, the corrected fluorescence intensity, I was introduced as I_{em}/I_{sc} to eliminate the turbidity effect. As far as the correction of fluorescence emission is concernd, total empirical formula was introduced to produce the meaningful results for the fluorescence quenching mechanisms [18]. Here the main idea is to eliminate the structural fluctuation due to the frozen blobs and holes [11] during drying 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. The variations of I versus drying time, t during drying of composite gel at 30, 40 and 50 ^{0}C for 0.5 wt %κC content sample are presented in Fig. 2. As the drying time, t is increased, quenching of excited pyranines decrease due to an increase in the water release from the drying PAAm- κC composite gel. It should also to be noted that quenching becomes more efficient at higher temperatures.
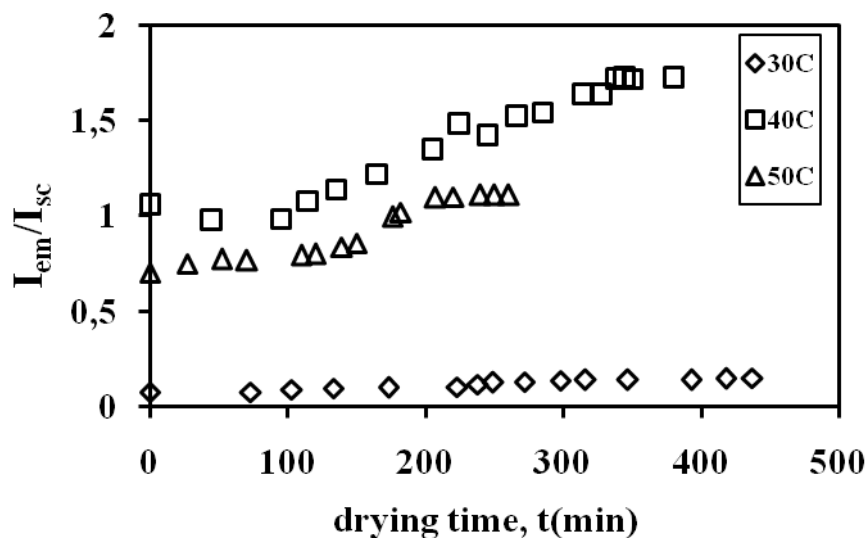

Fig. 2. Corrected fluorescence intensities of pyranine, I (=I_{em}/I_{sc}) versus drying time, t during the drying at 30 , 40 and 50 ^{0}C for 0.5 wt % κC content gel sample.

In order to quantify these results, a collisional type of quenching mechanism may be proposed for the fluorescence intensity, I emitted from the gel sample during the drying process and Eq.3 can be employed. For the dry composite gel, τ_0 (=300ns.) is already known [23], then W can be calculated from the measured I values at each drying step.

The plots of W versus t for 0.5 wt % κC content sample at various temperatures are presented in Fig. 3, where the fit of the data to Eq. 6 produced the desorption coefficients, D_l which are listed in Table 1. It is seen that D_l values increase as temperature is increased for all samples. This result is expected, since increasing temperature naturally causes increasing the Brownian motion of water molecules in the gel, which then helps some of them to escape from the gel surface resulting in faster drying. On the other hand, D_l values decrease by increasing κC content at a given temperature which can be explained by the following argument; it is well known

5

that moisture absorbing capacity of κC is much higher than PAAm which results slower drying process in high κC content composite gel. It is obvious that less κC content gel dries faster resulting in large D_l values compared to high κC content gel.

Tab. 1. Experimentally measured parameters of PAAm hydrogels for various temperatures at wt %κC content during drying process.

wt % κC	T(^{0}C)	$D_l \ast 10^{-9}$(m^2/s)	$D_w \ast 10^{-9}$(m^2/s)	$D_v \ast 10^{-9}$(m^2/s)
	30	30.16	3.54	3.11
0.5	40	41.90	4.90	4.90
	50	120.87	6.10	5.20
	60	171	6.14	6.14
	30	14.17	1.93	1.57
1	40	40.50	4.65	3.73
	50	116.40	5.61	4.70
	60	131	5.80	5.53
	30	8.21	1.27	1.19
1.5	40	13.67	3.57	2.37
	50	37.30	5.23	4.53
	60	79.80	5.27	4.65
	30	2.90	1.13	1.02
2	40	8.16	3.45	2.32
	50	22.5	4.13	3.65
	60	28.4	4.43	4.25
	30	0.82	0.91	0.91
2.5	40	0.91	3.05	2.05
	50	6.97	3.90	3.11
	60	7.40	4.06	3.29
	30	0.81	0.51	0.22
3	40	0.85	2.82	1.25
	50	6.71	3.57	2.59
	60	6.90	3.89	2.97

Water desorption from the drying PAAm- κC composite gel, prepared at various κC content was also studied by using the gravimetrical methods at different temperatures. The plots of the data are presented in Fig. 4 at 30, 40 and 60 ^{0}C for 0.5 wt %κC content gel respectively. The fits of water release, W to Eq.6 for the gels dried at 30, 40, 50 and 60 ^{0}C for various κC contents produced the desorption

coefficients D_W which are listed in Table 1. A similar increase in D_W as that for D_l was observed as the temperature was increased, which can be explained with the same arguments given above.
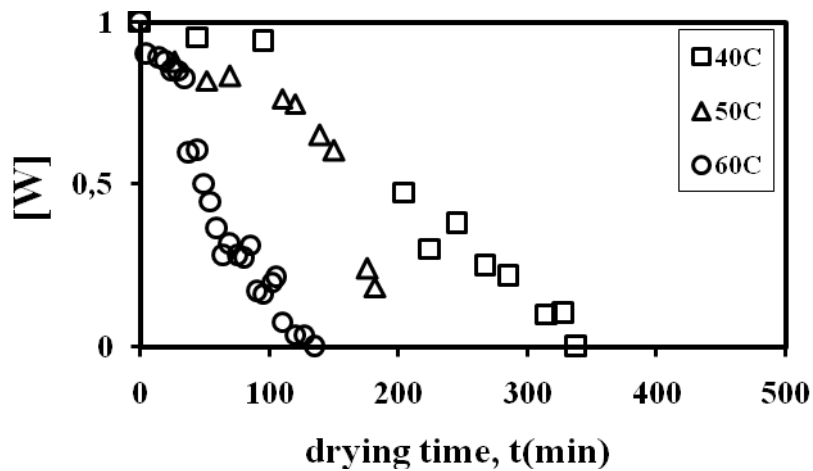

Fig. 3. The plots of water release versus drying time, *t*, for PAAm- κC composite gel dried in air measured by fluorescence technique for 0.5 wt %κC content samples at 40, 50 and 60 ^{0}C temperatures, respectively.
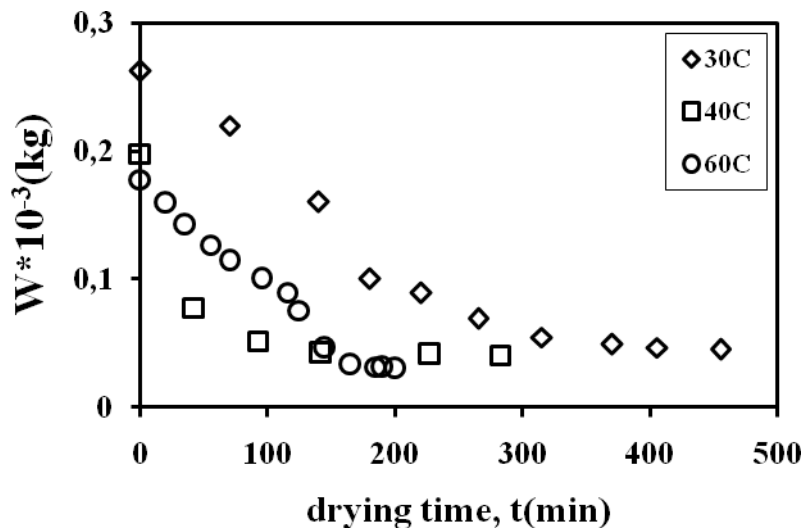

Fig. 4. The plots of the water release, *W* versus drying time, *t*, for PAAm- κC composite gel dried in air and measured by gravimetrically technique for 0.5 wt % κC content samples at 30 , 40 and 60 ^{0}C temperatures, respectively.

The variations in volume, *V* of PAAm- κC composite gels during the drying process are also monitored. The plots of the volume *V*, versus drying time for PAAm- κC composite gels, dried in air are presented in Fig. 6. The data in Fig. 6 are fitted to the following relation produced from Eq. 6

$$\frac{V}{V_\infty} = 2\left(\frac{D}{\pi a^2}\right)^{1/2} t_d^{1/2} \tag{7}$$

Here it is assumed, that the relation between *W* and *V* are linear. Then using Eq. 7 volumetric desorption coefficients D_V, were determined and listed in Table 1. Again, it

is seen that D_V values increased as temperature is increased, similar to D_l and D_W behavior. Here D_W and D_V coefficients are also found to be much smaller at high κC content gels for 30, 40, 50 and 60 ^{0}C temperatures, which can be explained with the similar reasoning as given for the D_l values.
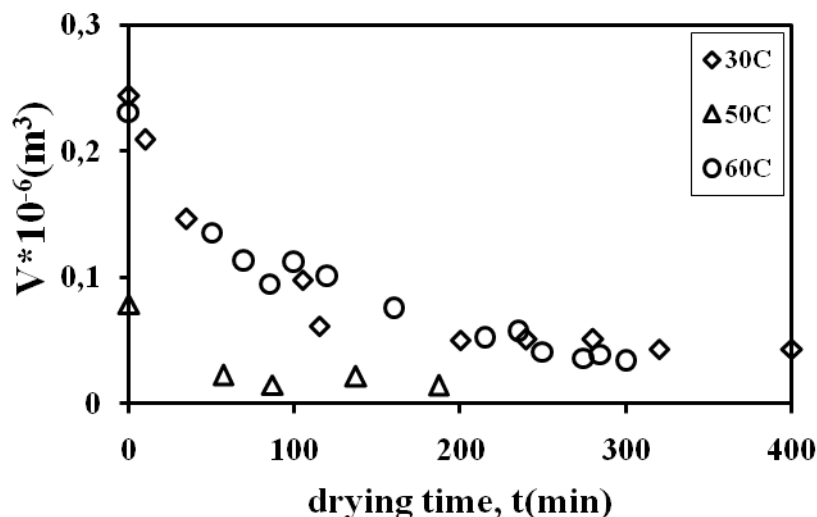

Fig. 5. The plots of the gel volume, V versus drying time, t, for PAAm- κC composite gel dried in air and measured by volumetric technique for 2.5 wt % κC content samples at 30, 50 and 60 ^{0}C temperatures, respectively.

As seen in Table 1 that D values measured by using fluorescence technique are 10 to 30 times larger than the values measured by volumetric and gravimetric techniques, which may predict the observation of different mechanisms of the drying composite 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 fluorescence technique which then monitors the drying network 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 10 to 30 times faster than the bulk polymeric material itself during the drying process.

On the other hand the behavior of the desorption coefficients (D_l, D_W, and D_V) versus T predicts that $D - T$ relation may obey the following Arrhenius law:

$$D=D_0 \, exp \, (-\Delta E/kT) \tag{8}$$

where ΔE is the energy of drying, k is Boltzmann's constant, and D_0 is the desorption coefficients at $T=\infty$ for each techniques. The logarithmic form of Eq. 8 is presented in Fig. 6 a, b and c for the data obtained by fluorescence, gravimetrical and volumetric techniques respectively, from which ΔE values are produced and listed in Table 2. It is seen that the drying energies increase by increasing κC content i.e. when the high κC content gels are dried they need more energy. In fact D values for high κC content gels are smaller and needs more energy for drying, however the gels with low water absorbing capacity possess large D values and needs smaller energy for drying.

8

It is also interesting to note that ΔE values measured with the fluorescence method is 2 to 3 times larger than they were measured with the others techniques, indicating that the segmental motion in the gel network needs more energy than the bulk motion to perform drying. Here, one may also notice that the drying energy for the gel network do not vary much for the gel samples prepared with different κC contents i.e. κC contents is not very critical for the segmental motion of the gel network during drying.
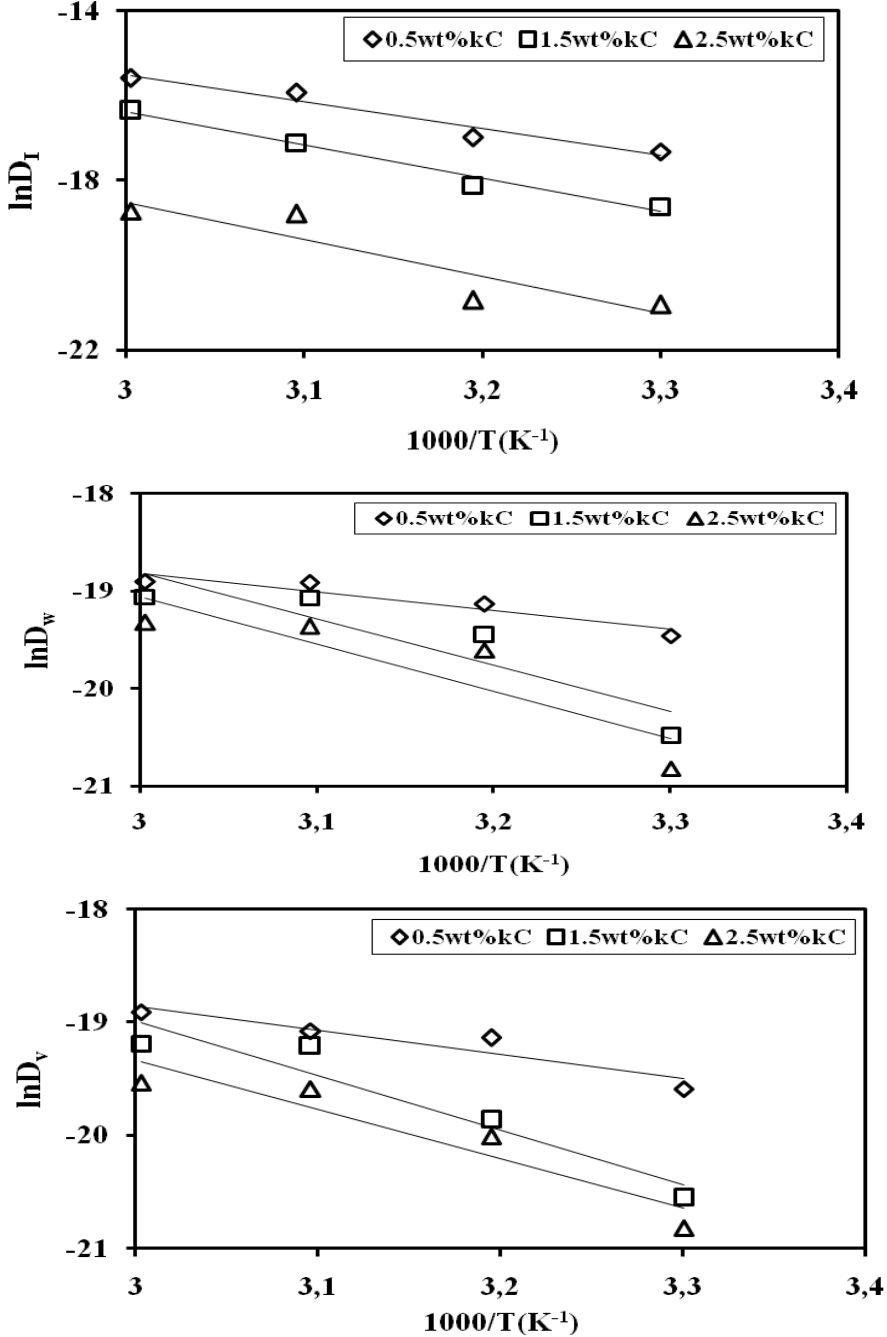

Fig. 6. Linear regressions of desorption diffusion coefficients versus temperature measured by a) fluorescence b) gravimetrically, and c) volumetric techniques for 0.5, 1.5, and 2.5 wt % κC content gel samples.

9

Tab. 2. Drying energies for various wt %κC contents during drying process by fluorescence, gravimetrical and volumetric techniques.

wt % κC	ΔE_I(kJ/mol)	ΔE_w(kJ/mol)	ΔE_v(kJ/mol)
0.5	50.62	15.28	17.12
1	62.94	28.63	32.76
1.5	63.13	38.12	38.62
2	63.93	35.12	38.61
2.5	69.81	38.85	34.92
3	68.65	52.01	69.83

In conclusion, this work has presented a novel method for the study of drying kinetics of PAAm- κC composite gel in various κC contents. A moving boundary model combined with Stern-Volmer kinetics was used to measure the desorption coefficients for drying process. It is well understood that energy needs for microscopic drying is larger than it is in macroscopic drying.

Experimental

Materials

Gels were formed by free radical copolymerization as follows: 0.71 gr of AAm (acrylamide, Merck), 0.01 g of bis(N,N'-methylenebisacrylamide, Merck), 0.008 g of APS (ammonium persulfate, Merck) and 2μl of TEMED (tetramethylethylenediamine, Merck) were dissolved in 5 ml. distilled water (pH 6.5) by heating. The heated mixture solution was held at 80 ^{0}C. Then varying amounts of kappa carrageenan (0.5, 1, 1.5, 2, 2.5 and 3 wt %) (κC) were added. *P* 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 [21]. The drying experiments of disc shape PAAm- κC composite gels prepared with various κC contents were performed in air at temperatures of 30, 40, 50 and 60 ^{0}C.

Fluorescence Measurements

The fluorescence intensity measurements were carried out using a Model LS-50 spectrometer of Perkin-Elmer, equipped with 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 1 cm path length square quartz cell filled with air for the drying experiments. Pyranines in the PAAm- κC 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 drying time. The position of the PAAm- κC composite gel 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 Fig. 7. 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 dimensions of the gel disc.
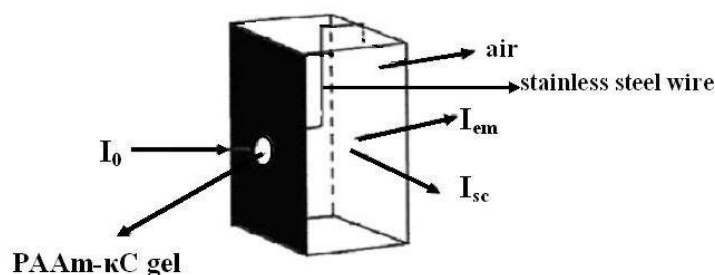
Fig. 7. The position of PAAm- κC composite gel in the fluorescence cell during drying in air. I_0 is excitation, I_{em} is emission and I_{sc} is scattered light intensities at 340 and 427 nm, respectively.

References

[1] Harmanty, T. Z. *Ind. Eng. Chem. Fund.* **1969**, *8*, 92.
[2] Mikhailov, M. D. *Int. J. Heat Mass Trans.* **1975**, *18*, 797.
[3] Hawlader, M.N. A.; Ho J. C.; Qing Z. *Dry Tech.* **1999**, *17*, 27.
[4] Scherer, W. G. *J. Non-Crys. Solids* **1989**, *107*, 135.
[5] Scherer, W. G. *J. Non-Crys. Solids* **1989**, *109*, 183.
[6] Scherer, W. G. *J. Non-Crys. Solids* **1992**, *147-148*, 363.
[7] Jomma, W.; Aregba, W.; Puiggali, J. R.; Quintard, M. *Drying*, **1991**, *91*.
[8] Coumans, W. J. *Chem. Eng. Pro.* **2000**, *39*, 53.
[9] Wallqvist, A.; Gallicchio, E.; Levy, R. M. *J. Phys. Chem. B* **2001**, *105*, 6745.
[10] Horie, K.; Mita, I.; Kawabata, J.; Nakahama, S.; Hirao, A.; Yamazaki, N. *Polym J.*, **1980**, *12*, 319.
[11] Kara, S.; Pekcan, Ö. *J. App. Polym. Sci.* **2001**, *80*, 1898.
[12] Kara, S.; Pekcan, Ö. *J. App. Polym. Sci.* **2001**, *82*, 1944.
[13] Miller, E. *J. Photochem. Photobio. A Chem.* **2002**, *152*, 249.
[14] Erdogan, M.; Pekcan, Ö. *Comp. Inter.*; **2003**, *10*, 547..
[15] Erdogan, M.; Pekcan, Ö. *Polymer*; **2004**, *45*, 2551.
[16] Aktaş, D. K.; Evingür, G. A.; Pekcan, Ö. *J. Macro. Sci. B Phys.* **2007**, *46*, 581.
[17] Tari, Ö.; Pekcan, Ö. *Dry. Tech.* **2008**, *26*, 101.
[18] Evingur, G. A.; Aktaş, D. K.; Pekcan, Ö. *Chem. Eng. Pro: Pro. Inten.* **2009**, *48*, 600.
[19] de Ruitter, G. A.; Rudolph, B. *Trend Food Sci. Tech.* **1997**, *8*, 389.
[20] Zhai, M.; Zhangi, Y.; Ren, J.; Yi, M.; Ha, H.; Kennedy, J. F. *Carb. Polym.* **2004**, *58*, 35.
[21] Aktaş, D. K.; Evingür, G. A.; Pekcan, Ö. *J. Bio. Struc. Dyn.* **2006**, *24(1)*, 83.
[22] Waje, S. S.; Meshram, M. W.; Chaudhary, V.; Pandey, R.; Mahanawar, P. A.; Thorat, B. N. *Bra. J. Chem. Eng.* **2005**, *22*, 209.
[23] Birks, J. B. *Photopyhsics of aromatic molecules*, New York: Wiley, Interscience, **1971**.
[24] Crank, J. *The Mathematics of Diffusion*, Oxford: Clarendon Press, **1975**.