

Drying of Polyacrylamide Composite Gels Formed with Various Kappa- Carrageenan Content

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Abstract Drying of polyacrylamide (PAAm)- κ -carrageenan (κ C) composite gels were monitored by using steady-state fluorescence technique. Disc shaped gels were formed from acrylamide (AAm) and N, N'- methylenebisacrylamide(Bis) with various κ - carrageenan (κ C) contents by free radical crosslinking copolymerization in water. Pyranine (*P*) was doped as a fluorescence probe, and scattered light, I_{sc} , and fluorescence intensities, I , were monitored during drying of these gels. It is observed that fluorescence intensity of pyranine increased as drying time is increased for all samples. The increase in I was modeled using Stern-Volmer equation and diffusion with moving boundary. It is found that desorption coefficient, D decreased as κ C contents were increased. Supporting gravimetric and volumetric experiments were also carried out during drying of PAAm- κ C composite gels.

Keywords Drying · Acrylamide · Kappa-carrageenan (κ C) · Fluorescence · Composite gels

Introduction

Polysaccharides are especially important in the domain of water soluble polymers. Carrageenan is a sulfated polysac-

charide extracted from red seaweed (Rhodophyceae). Carrageenan is classified into three types as kappa (κ -), iota (ι -) or lambda (λ -) carrageenan according to the number (one, two or three) of sulfate groups per repeat unit of disaccharide, respectively. Kappa- carrageenan(κ C) is a hydrophilic polysaccharide that exists in numerous species of seaweed [1]. Chemically, it is linear, sulfated polysaccharide composed of a repeating unit of the disaccharide, β -(1-3)-D-galactose- 4- sulfate and α -(1-4)-3, and 6- anhydro- D-galactose. Recently, Kappa- carrageenan(κ C) was found to enhance the properties of synthetic hydrogels by incorporation into the water soluble polymer systems such as N-isopropylacrylamide [2] and acrylamide [3]. 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 [4].

Although the drying mechanisms in hygroscopic materials have been studied by many investigators [5, 6], these are still well not understood. The regime of drying may change as the drying progress is changed. 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 [7]. 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 macromolecule. Monomer and cross-linking agent proportions are respon-

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sible for both the porous structure and the pore size of the gel. Scherer was investigated drying mechanisms of gels by diffusion [8], shear modulus [9] and the status of the mechanism and practice of drying as stresses and cracking [10] was reviewed, with emphasis on work published [11]. A diffusive drying model for the drying of highly shrinking materials like polyacrylamide gel and cellulosic paste have been reported [12]. Approximate models have been used by Coumans [13] 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 [14].

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 chromophores. 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 [15]. The photon transmission technique was used to study the drying of PAAm gels with various kappa-carrageenan (κ C) contents [16] and with various water contents [17]. 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 [18]. More recently, the fast transient fluorescence (FTRF) technique was used in our laboratory to study gel drying processes [19, 20]. Also, the steady state fluorescence technique was employed for studying the drying of polyacrylamide [21], kappa-carrageenan (κ C) hydrogels [22] at various temperatures, and polyacrylamide hydrogels of various crosslinker contents [23].

In this work, we studied drying process of PAAm- κ C composite gels prepared at various κ -carrageenan contents by using the steady-state fluorescence technique. Pyranine was used as a fluorescence probe to monitor the drying of composite gels. It was observed that the fluorescence intensity of pyranine increased as drying time was increased during the drying process. This behavior can be modeled using the low quenching the Stern-Volmer equation [24]. Drying of composite gels at various kappa carrageenan (κ C) contents were quantified by employing moving boundary model from which desorption coefficients, D were determined.

Background

Stern- Volmer Kinetics

This model deals broadly with the variations of quantum yields of photophysical processes such as fluorescence or phosphorescence or photochemical reactions with the concen-

tration of a given reagent which may be a substrate or a quencher. The Stern- Volmer type of quenching mechanism may be proposed for the fluorescence intensity in the gel sample. According to the Stern- Volmer law, in general fluorescence intensity can be written as [24],

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

Here, τ_0 is the lifetime of the fluorescence probe [24] in the dry gel in which no quenching has taken place, k_q is quenching rate constant and $[Q]$ is the water or solvent concentration in the gel after water desorption has started, and I_0 is the fluorescence intensity for zero quencher content. This relation is called Stern- Volmer Equation.

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

$$\frac{I}{I_0} = (1 + k_q \tau_0 [Q])^{-1} = 1 - \tau_0 k_q [Q] + \frac{1}{2} [\tau_0 k_q [Q]]^2 - \dots \quad (2)$$

Equation 1 becomes

$$I \approx I_0 (1 - \tau_0 k_q [Q]) \quad (3)$$

If one integrates (Eq. 3) over the differential volume ($d\nu$) of the sample from the initial, a_0 to final a_∞ thickness,

$$W = \int_{a_0}^{a_\infty} [W] d\nu \quad (4)$$

then reorganization of the relation produces the following useful equation. Here, the amount of water desorption, W is calculated over differential volume by replacing Q with W as

$$W = \left(1 - \frac{I}{I_0}\right) \frac{\nu}{k_q \tau_0} \quad (5)$$

Here it is assumed that water molecules are the only quencher for the excited pyranine molecules in our system. Where ν is the volume at the equilibrium drying state, which can be measured experimentally, k_q was obtained from separate measurements by using (Eq. 1) where the infinity equilibrium value of water desorption, W was used for each sample. Since τ_0 (~300 ns.) is already known from the dry gel, and measured values of ν and I at equilibrium drying condition can be used to calculate k_q for each drying experiments separately.

Moving Boundary Model

Diffusion with a moving boundary occurs in two distinct regions separated by a moving boundary or 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 [25]. 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 desorption coefficient is discontinuous at a concentration c ; i.e. the desorption 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 [25]

$$\frac{M_t}{M_\infty} = 2 \left[\frac{D}{\pi a^2} \right]^{1/2} t^{1/2} \tag{6}$$

Where D is a desorption coefficient at concentration c_1 . Here $M_\infty = ac_1$ is the equilibrium value of M_t . If one assumes that the desorption coefficient of polymer segments in the gel is negligible compared to the desorption coefficient, D of water vapor into air, then (Eq. 6) can be written as follows

$$\frac{W}{W_\infty} = 2 \left[\frac{D}{\pi a^2} \right]^{1/2} t^{1/2} \tag{7}$$

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

Experimental

Materials

Gels were prepared by using 2M AAm (Acrylamide, Merck) with various amounts (0.5, 1, 1.5, 2, 2.5 and 3 wt%) of κC (κ-carrageenan, Sigma) concentration. AAm, the linear component; Bis (N, N'- methylenebisacrylamide, Merck), the tetra-functional crosslinking component; APS (ammonium persulfate, Merck), the initiator; and TEMED (tetramethylethylenediamine, Merck), the accelerator were dissolved in distilled water and made up to 5 ml. The initiator and pyranine concentrations were kept constant at 7×10^{-3} M and 4×10^{-4} M, respectively, for all experiments. All samples were deoxygenated by bubbling nitrogen for 10 min., just before polymerization process [3]. The drying experiments of disc shape PAAm- κC composite gels prepared with various κC contents were performed in air.

Fluorescence Measurement

Drying experiments of disc shape PAAm- κC composite gels were performed at various kappa- carrageenan (κC)

contents by using fluorescence technique. 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. A 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 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 gel and the incident light beam, I_0 for the fluorescence measurements are shown in Fig. 1 during drying of the composite gel in air where I_{em} and I_{sc} are the fluorescence emission and scattering light intensity respectively. Here one side of the quartz cell is covered by black cardboard with a circular hole which is used to clip the incoming light beam and limits its size to the dimensions of the gel disc.

Results and Discussion

Drying processes were monitored from the fluorescence spectrum of pyranine (P) in the PAAm- κC composite gels. Figure 2 shows the emission spectra of P from composite gel during the drying process at 60 °C in air. It can be seen that as water evaporates from the composite gel (by indicating decrease in quenching of P during drying), fluorescence emission intensity, I_{em} increases and the scattered light intensity, I_{sc} decreases. Since the decrease in I_{sc} corresponds to the decrease in turbidity of the drying hydrogel, the corrected fluorescence intensity, I was defined as I_{em}/I_{sc} . In other words, scattered intensity, I_{sc} is measured at the excitation wavelength 340 nm. simultaneously with the emission intensity which appears in the same spectra for each drying step. The reason behind the correction is; the

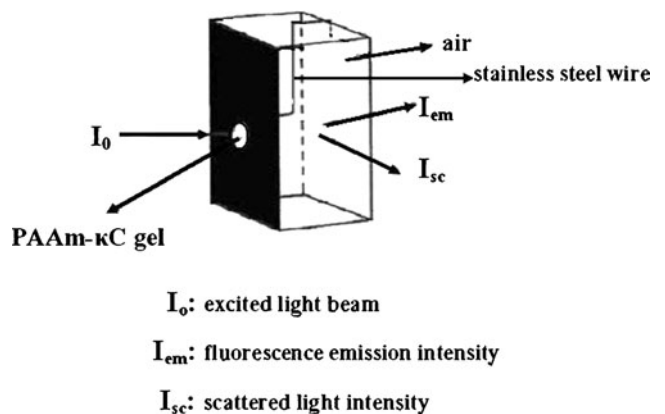


Fig. 1 The position of PAAm- κC composite gel in the fluorescence cell during drying in air. I_0 is excitation, I_{em} is emission and I_{sc} is scattered light intensities at 340 and 427 nm, respectively

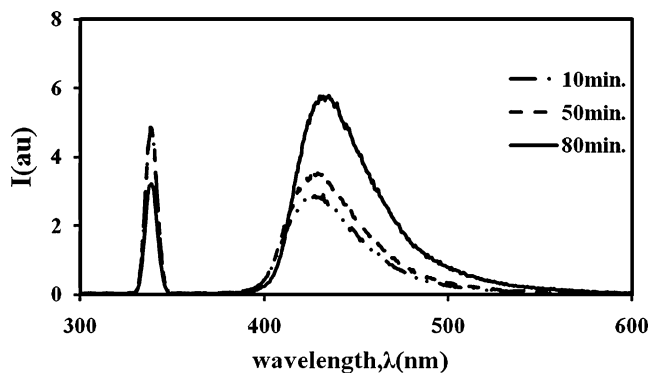


Fig. 2 Emission spectra of pyranine from the composite gel prepared with 3% κ C content during the drying process. Each curve indicates the drying times in different minutes

variation of turbidity of the gel during drying process, which was monitored by using scattered intensity. If gel goes from heterogeneous to homogeneous state, then scattering light intensity decreases by obeying Rayleigh Model. During drying any structural fluctuation can be eliminated 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 eliminate the effect of physical appearance of the gel and produce the meaningful results for the fluorescence quenching mechanisms. According to (Eq. 3), as the quencher, ($Q \sim W$) concentration decreases, I_{em}/I_{sc} values increase. In order to quantify this behavior, (Eq. 5) can be employed to calculate the amount of water desorption, W from the composite gels. Figure 3(a), and (b) present the amount of water desorption against drying time for the 1, and 3% κ C content samples, respectively.

It has also to be noted that quenching becomes less efficient at higher κ C content. In order to quantify these results the collisional type of quenching mechanism may be proposed for the excited pyranine in the composite gel during the drying process. For pyranine in the composite gel, τ_0 (~ 300 ns.) is already known [24], then W can be calculated by using (Eq. 5) and the measured I values, at each drying step.

The plots of W versus $t^{1/2}$ at various κ C content are presented in Fig. 4 where the fit of the data to (Eq. 7) produced the desorption coefficient, D_f which are listed in Table 1. It is seen that D_f values decreased as the κ C content is increased. It is well known that moisture absorbing capacity of κ C is much higher than PAAm which results slower drying process in high κ C content composite gel. It is obvious that less κ C content gel dries faster resulting large D_f values compare to high κ C content gel.

On the other hand, by using the gravimetrical method water desorption was also measured from the drying PAAm- κ C gels prepared at various kappa- carrageenan (κ C) contents. The plots of the data versus t are presented in Fig. 5 for 0.5, 1.5 and 2.5% κ C content gels. The fits of

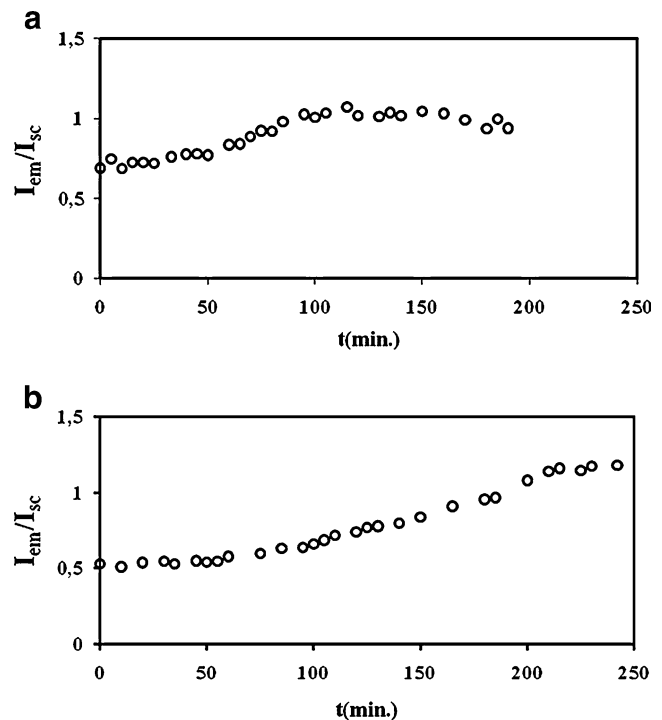


Fig. 3 Corrected fluorescence intensities of pyranine, $I(= I_{em}/I_{sc})$ versus drying time, t during the drying process for a) 1 and b) 3% κ C content samples

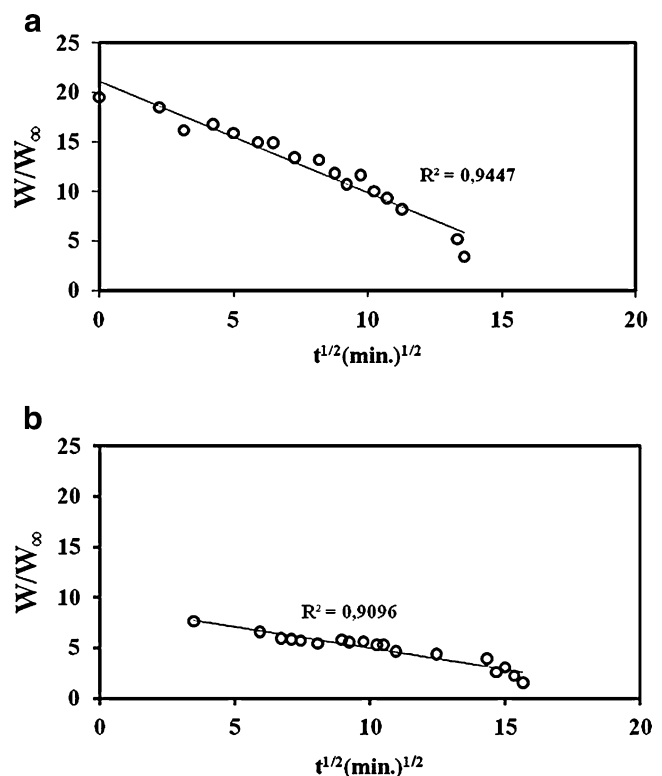


Fig. 4 Fit of the data by using (Eq. 7) for PAAm- κ C gels dried in air for a) 1.5 and b) 2.5% κ C content samples

Table 1 Experimentally measured parameters of PAAm composites for various%κC content during drying process

%κC	$d_i \times 10^{-2}$ (m)	$d_f \times 10^{-2}$ (m)	$r_i \times 10^{-2}$ (m)	$r_f \times 10^{-2}$ (m)	$D_f \times 10^{-9}$ (m ² /s)	$D_W \times 10^{-9}$ (m ² /s)	$D_V \times 10^{-9}$ (m ² /s)
0	0.29	0.15	0.42	0.23	172	4.40	6.14
0.5	0.30	0.15	0.45	0.24	171	6.14	6.14
1	0.36	0.20	0.42	0.25	131	5.80	5.53
1.5	0.36	0.22	0.38	0.25	79.8	5.27	4.65
2	0.34	0.16	0.45	0.25	28.4	4.43	4.25
2.5	0.34	0.18	0.46	0.24	7.4	4.06	3.29
3	0.33	0.22	0.42	0.26	6.9	3.89	2.97

d_i : the disc thickness in the initial infinite equilibrium

d_f : the disc thickness in the final infinite equilibrium

r_i : radius of the disc in the initial infinite equilibrium

r_f : radius of the disc in the final infinite equilibrium

D_f : fluorescence desorption coefficient

D_W : gravimetric desorption coefficient

D_V : volumetric desorption coefficient

water desorption, W_W using (Eq. 7) are given in Fig. 6 for the composites prepared with 0.5, 1.5 and 2.5%κC content. The desorption coefficients, D_W were obtained from the slopes of the linear relations and are listed in Table 1, where it is seen that desorption coefficient decreases as the kappa-carrageenan (κC) content is increased, similar to the fluorescence results.

The variations in volume, V of PAAm- κC gels during the drying process are calculated from the thickness and diameter of drying gels. The plots of the volume V , versus drying time for PAAm- κC gels, dried in air are presented in Fig. 7. The data in Fig. 7 are fitted to the following relation produced from (Eq. 7)

$$\frac{V}{V_\infty} = 2 \left(\frac{D_V}{\pi a^2} \right)^{1/2} t_d^{1/2} \tag{8}$$

Here it is assumed, that the relation between W and V are linear. The fits are presented in Fig. 8, where using (Eq. 8)

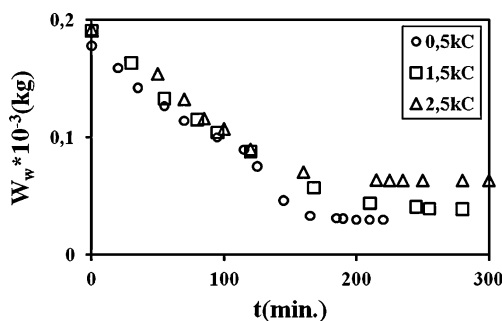


Fig. 5 The plots of the water desorption, W_W measured by gravimetrically, versus drying time, t , for PAAm- κC gels dried in air for 0.5, 1.5, and 2.5%κC content samples

volumetric desorption coefficients D_V , were determined and listed in Table 1. Again, it is seen that D_V values decreased as the κC content is increased, similar to D_W behavior i.e. D_W and D_V coefficients are found to be much smaller at high κC content gels. From here similar conclusion can be reached as was done in fluorescence measurements, in other words high κC content gels dry much slower than less κC content gels. Figure 9 compares desorption coefficients (D_f , D_W , and D_V) for the drying processes which were obtained by using (Eqs. 7 and 8). All measured D values are listed in Table 1, where it is observed that the desorption coefficient decreased as the κC content is increased as was stated before.

Here it is seen in Table 1 that, D_f values measured by using fluorescence technique are at least two orders of magnitude much larger than the values measured by volumetric and gravimetric techniques, which may predict the different physical behaviors of the gels during drying. It is obvious that the fluorescence technique measures the behavior of the microstructure of the gel. Since fluores-

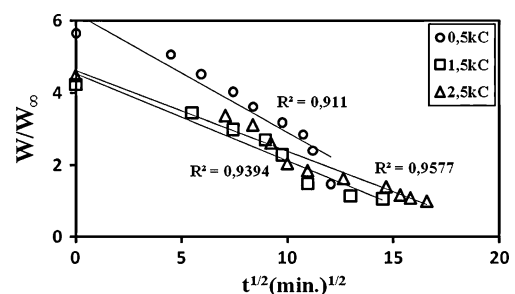


Fig. 6 Linear regressions of the data in Fig. 5 according to (Eq. 7) for PAAm- κC gels dried in air for 0.5, 1.5, and 2.5%κC content samples

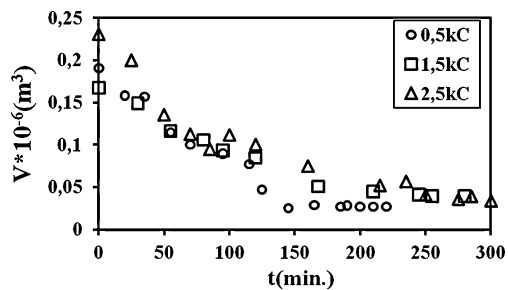


Fig. 7 The plots of the volume, V , variation versus drying time, t , for PAAm- κ C gels dried in air for 0.5, 1.5, and 2.5% κ C content samples

cence is quite sensitive to local environment, one can be encouraged to use this technique to study at a molecular level. Here we have to reemphasize that monitoring the drying process by fluorescence method is quite novel compared to the other conventional techniques such as (a) periodic sampling or weighing, (b) continuous weighing, (c) intermittent weighing, and (d) indirect methods [26]. It can be argued that all these classical techniques somehow disturb the drying sample. Besides, measuring the sample weight does not provide any information about the texture reorganization during the drying process. However, fluorescence is a nondestructive method and exceptionally powerful for supplying us with the structural organization of the drying sample. As mentioned above, segmental motion can be monitored by the turbidity and fluorescence studies. In other words the segmental motion of the gel network is monitored by using fluorescence probe, because pyranine molecules are bounded to the polymer chains and monitors the drying process at a molecular level. However, volumetric and gravimetric measurements may provide us with the information of the macroscopic and/or bulk behavior of the gel. Here, it is understood that segmental organization in composite gels are much faster than the bulk behavior during drying process. These findings were supported by [21, 23].

Some studies related to drying and shrinkage of polymer hydrogels such as pure acrylamide (PAAm) [21, 23] and κ C [22] have been reported. The drying

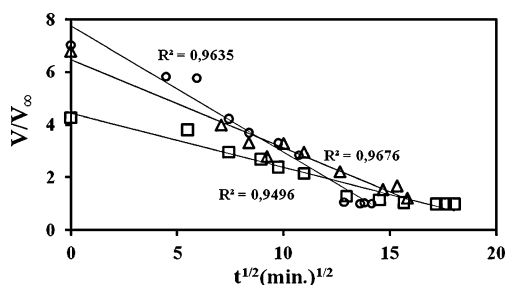


Fig. 8 Linear regressions of the data in Fig. 7 according to (Eq. 8) for PAAm- κ C gels dried in air for 0.5, 1.5, and 2.5% κ C content samples

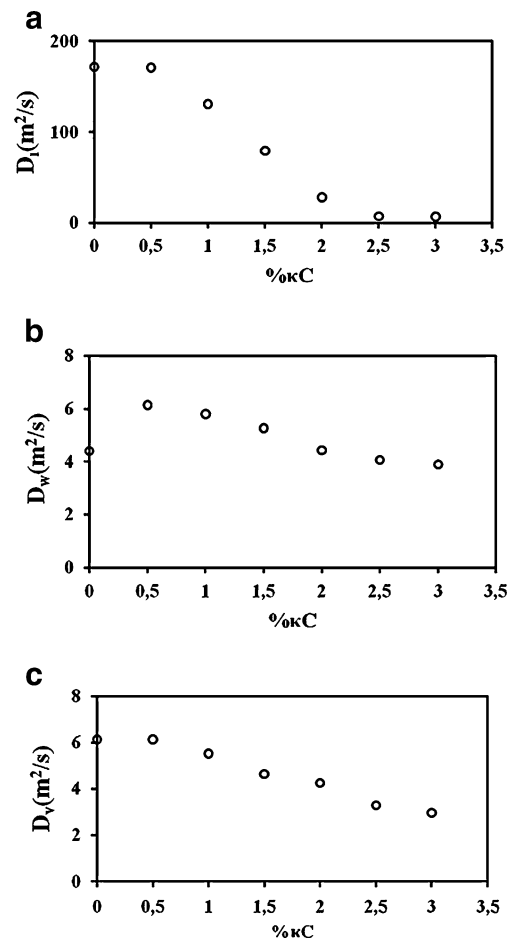


Fig. 9 Desorption coefficients versus κ C content measured by a) fluorescence b) gravimetrically, and c) volumetric techniques

mechanism of pure acrylamide with respect to different crosslinker and different temperatures was studied [21, 23]. The desorption coefficient of pure acrylamide was found to be around 10^{-9} m^2/s . When the desorption coefficient of pure acrylamide on drying was compared with the desorption coefficient of PAAm- κ C contents, the drying desorption coefficient of PAAm- κ C contents was found to be smaller than the drying desorption coefficient of pure acrylamide. Since both values were produced at the same temperature range by using fluorescence technique, the differences between the desorption coefficients can be explained with the moisture absorbing capacity of κ C in composite.

In conclusion, this work has presented a novel method for the study of drying kinetics of PAAm- κ C composite gels at various κ C contents. A moving boundary model combined with Stern-Volmer kinetics was used to measure the desorption coefficients for drying process. It is understood that high κ C content gels dried slower than low κ C content gels, predicting the moisture absorbing capacity of κ C plays an important role during the drying process of these composite gels.

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