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Drying process in vapor swollen heterogels

M. Erdogan · O. Pekcan

Abstract Disk-shaped heterogels were prepared by combining methyl methacrylate (MMA) and styrene (S) with ethylene glycol dimethacrylate (EGDM) as a crosslinker agent in the presence of 2,2′-azobisisobutyronitrile (AIBN). Swelling experiments were performed under chloroform vapor and the swollen gels are then allowed to dry under room temperature. Gravimetric technique was used to study drying processes. It is observed that two different regimes are present in the drying processes of these heterogels. Fickian diffusion model was used to determine desorption coefficients for each drying step in both regimes. Desorption coefficients, D_d, of heterogels were found to be strongly correlated with the mixture composition of polymeric materials in the heterogel system for both regimes. Heterogels with high S content dry much slower than the heterogels with low S content.

Keywords Drying · Desorption · Heterogels · Fickian diffusion

Introduction

Many shortcomings exist in description and prediction of drying kinetics of materials and better models for drying processes are needed. For design and optimization of drying processes, there is still a great need for stable and reliable models that can quantify and predict drying rates and drying times with reasonable accuracy. Drying is an important process for many industries such as food preservation, pharmaceutical production, and cosmetics, etc., where polymeric gels find application areas. During drying under atmospheric conditions, gels initially shrink due to loss of pore fluid

M. Erdogan (✉)
Department of Physics, Balikesir University, Cagıs Kampusu, 10145 Balikesir, Turkey
e-mail: merdogan@balikesir.edu.tr

O. Pekcan
Kadir Has University, Cibali, 34320 Istanbul, Turkey

maintaining the liquid–vapor interface at the exterior surface. At the final stage of drying, liquid–vapor menisci recede into the gel interior [1].

Polymeric gels are three-dimensional cross-linked polymeric structures that are able to swell in a solution (liquid) environment. The swelling, shrinking, and drying kinetics of polymeric gels are important in many technological applications. Due to permeability, mechanical properties, surface properties, and biocompatibility, these attractive materials have received significant attention for application in bioengineering, biotechnology, medicine, pharmacy, agriculture, food industry, and other fields [2, 3].

Especially in pharmaceutical industries for designing controlled release of drugs and for using cosmetic ingredients, understanding the kinetics of gels is highly desirable. The knowledge of the gel kinetics is an important requirement for producing storable foods in agricultural industry and developing artificial organs in medical applications. The mechanism of swelling depends on molecular-level processes that are dictated by physical and chemical properties of materials [4]. In addition to these fundamental interests, it is rather a practical but important issue to know how to control the drying processes in various industrial applications, for e.g., manufacturing polymer films [5], inkjet printing [6] and so on. In order to establish a foundation for these technologies, we must understand the underlying physics in the drying phenomena.

In general, the swelling and shrinking of polymeric gels in solvents have been extensively studied [7–9]. Several experimental techniques have been employed to study the kinetics of swelling, shrinking, and drying of chemical and physical gels; e.g., neutron scattering [10], quasielastic light-scattering [11], macroscopic experiments [12], and in situ interferometric [13] measurements. Hawlader et al. [14] used a one-dimensional diffusion model to describe the heat and mass transfer in the wet and dry regions of materials undergoing shrinkage during drying. Iglesias et al. [15] studied convective thermal drying of agar–agar gels using laboratory scale discontinuous dryer. Roques et al. [16] investigated water diffusion and drying in polyacrylamide gels. They proposed a mathematical model with independent parameters which analyze the critical physical phenomenon. The drying process of gelatin-based biofilms was analyzed in room conditions, where surprisingly a decrease in drying time was observed with increasing air temperature [17]. A study based on the receding evaporative front model and on the assumption of parabolic moisture content profile in the diffusional zone of the wet region was reported [18]. The experimental characteristic drying curve of plaster slabs were found to depend strongly on the thickness of the material. An excellent review of methods for processing the data obtained from drying kinetics was written by Kemp et al. [19] where different methods for fitting and smoothing drying curves are compared to generate curves that can be used in industrial design. Coumans [20] has provided another excellent tutorial overview of the uses of the diffusion equation to analyze drying characteristics of slabs, including lumped diffusion models, retreating front models, and the characteristic drying curve model. The method given by Coumans relates to porous and non-porous materials. Some of these models also enable the evaluation of moisture dependent diffusivities from experimental drying curves of slabs. Steady-state and time-resolved fluorescence techniques were applied to

drying processes of selected silane gels in oxygen free atmosphere. A kinetic model of drying was suggested and drying rate constants were determined [21]. The steady-state fluorescence and fast transient fluorescence (FTRF) techniques were used in our laboratory to study gel swelling [22, 23] and drying [24, 25] processes. Recently, Pekcan et al. reported a study of the drying mechanism of polyacrylamide hydrogels by using the steady-state fluorescence technique and gravimetrical technique was also introduced for measuring drying diffusion coefficients [26, 27].

In this present study, we studied the drying process of disk-shaped heterogels composed of methylmethacrylate and styrene monomers by using conventional gravimetric technique. It was observed that two different regimes appeared during drying processes in the heterogels. Fickian diffusion model was adopted to determine diffusion coefficients for each drying step in both regimes. Desorption coefficients, D_d, were determined during the drying of heterogels prepared with various styrene, S content. Desorption coefficients were found to be strongly correlated to the polymeric compositions in the system in both regimes. Heterogels with high S content dry much slower then the heterogels with low S content.

Experiments

Ethylene glycol dimethacrylate, EGDM, has been commonly used as a crosslinker in the synthesis of polymeric networks. Here, for our use, the monomers, methyl methacrylate, MMA (Merck), styrene, S (Merck), and EGDM (Merck), all with 99% purity, were freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water, and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator 2,2′-azobisisobutyrronitrile (AIBN, Merk), was recrystallized twice from methanol.

The free radical copolymerization of MMA and S with EGDM was performed at 70 °C in the presence of 2,2′-azobisisobutyrronitrile (AIBN) (0.26 wt%) as an initiator. Here, eight different heterogels were prepared using various amounts of S and MMA monomers. The symbols and comparisons of the S-MMA heterogels are listed in Table 1. Samples were deoxygenated by bubbling nitrogen for 10 min, and then radical copolymerization of MMA and S with EGDM was performed at 70 ± 2 °C. Here, EGDM content was kept as 0.015 vol%. After gelation was completed, the heterogel samples were dried under vacuum for the swelling experiment. The swelling process was accomplished under chloroform vapor and then all the swollen heterogels samples were dried in air to study drying mechanisms. In situ drying experiments under air were carried out gravimetrically at room temperature. Microbalance TE214S Sartorios was used for gravimetric measurements.

Theoretical consideration

When Fick's second law of diffusion is applied to a plane sheet and solved by assuming a constant diffusion coefficient, the following equation is obtained for concentration changes in time [28].

Table 1 Drying parameters of heterogels

Symbols	Styrene concentration (Vol%)	a_0 (cm)	a_f (cm)	D_{ds} (cm^{2}s^{-1}) × 10^{-6}	D_d (cm^{2}s^{-1}) × 10^{-7}
S	100	0.280	0.185	1.15	3.77
S-MMA8	80	0.290	0.200	1.30	4.51
S-MMA7	70	0.275	0.210	1.50	5.33
S-MMA5	50	0.273	0.215	1.51	5.04
S-MMA4	40	0.280	0.210	1.62	5.71
S-MMA3	30	0.295	0.205	1.65	6.92
S-MMA2	20	0.270	0.205	1.82	8.04
S-MMA1	10	0.280	0.200	1.76	8.28

$$\frac{C}{C_o} = \frac{x}{a_0} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n} \sin \frac{n\pi x}{a_0} \exp\left(-\frac{Dn^2\pi^2}{a_0^2}t\right) \tag{1}$$

where a_0 is the thickness of the slab, D is the diffusion coefficient, and C_o and C are the concentration of the diffusant at time zero and t, respectively. x corresponds to the distance at which C is measured. We can replace the concentration terms directly with the amount of diffusant by using

$$M = \int_V C dV \tag{2}$$

When Eq. 2 is considered for a plane volume element and substituted in Eq. 1, the following solution is obtained [28]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D\pi^2}{a_0^2}t\right) \tag{3}$$

where M_t and M_∞ represent the amount of diffusant entering the plane sheet at time t and infinity, respectively. This equation can be reduced to a simplified form with 99% accuracy at the early times of the drying process;

$$\frac{M_t}{M_\infty} = 4\sqrt{\frac{D}{\pi a_0^2}} t^{1/2} \tag{4}$$

which is called early-time equation and this square root relation can be used to interpret the swelling data. As the term $n = 0$ is taken and the other terms are omitted from the series expansion in the Eq. 3, Crank also derived the following equation.

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left[\frac{\pi^2 D}{a_0^2}t\right] \tag{5}$$

This equation is termed late-time equation and mainly used to obtain desorption coefficients, D_d, during the release of the diffusant from swollen materials such as polymeric films, gels, etc.

Results and discussion

Drying processes were monitored from the change of mass in the swollen heterogels at room temperature. Figure 1a–c presents change of mass in heterogels versus drying time, t_d, for the S-MMA1, S-MMA5, and S gel samples, respectively. In order to obtain the amount of chloroform vapor desorbed from swollen gels, one needs to subtract initial mass of swollen gels from the data given in Fig. 1. Figure 2a–c shows desorption of chloroform vapor from swollen gels versus drying time, t_d, for the S-MMA1, S-MMA5, and S gel samples, respectively. It is seen that the amount of chloroform vapor from swollen gels increased as the drying time, t_d, increased, as expected. In order to quantify this behavior, Eq. 5 can be used to calculate the desorption coefficients of drying processes. The following equation can be obtained from the logarithmic form of Eq. 5, as:

$$\ln\left[1 - \frac{M_t}{M_\infty}\right] = \ln\left[\frac{8}{\pi^2}\right] - \frac{D\pi^2}{a_0^2}t \tag{6}$$

The results and fits are presented in Fig. 3a–c for the gel samples S-MMA1, S-MMA5, and S, respectively. It is seen that two different regimes appeared during drying processes in heterogels. It can also be seen that excellent linear fitting can be obtained in Fig. 3, which states that desorption model employed here is reliable for the drying processes. The desorption coefficients, D_d and D_{ds} for long and short drying regimes were obtained from the slopes of the linear relations in Fig. 3 at both regimes, and the produced results are listed in Table 1. The behavior of desorption coefficients for both regimes are shown in Fig. 4a, b versus various styrene contents in the heterogels. In the short drying regime, desorption coefficients D_{ds} decrease almost linearly as the amount of styrene increased in heterogels while desorption coefficients D_d in the long drying regime decreased roughly exponentially as the amount of styrene increased in heterogels. This behavior of heterogels may be explained as follows: Swollen gels are considered as a polymer solution and if these gels are exposed to dry air, initially chloroform molecules which are located near the surface of gels during swelling, start immediately to evaporate from the gel surface. In fact, at this stage elastic property of the gel does not affect the drying process so that this stage can be considered a simple evaporation stage. This explanation is supported by the experimental findings in Table 1 where D_{ds} values are at least two orders of magnitude larger than D_d values. In other words, chloroform molecules located near the surface of gels need less energy to escape from swollen gels under consideration. At the second stage of drying; since elastic forces are activated in favor of the evaporation, gels start spending more energy to accomplish the late-time drying process. As a result,. D_d values decrease due to the slower drying process compared to the early-time evaporation where D_{ds} values are found to be much larger.

Fig. 1 Change of weight
against drying time t_d in
heterogels during drying for the
S-MMA1 (**a**), S-MMA5 (**b**) and
S (**c**) gel samples, respectively
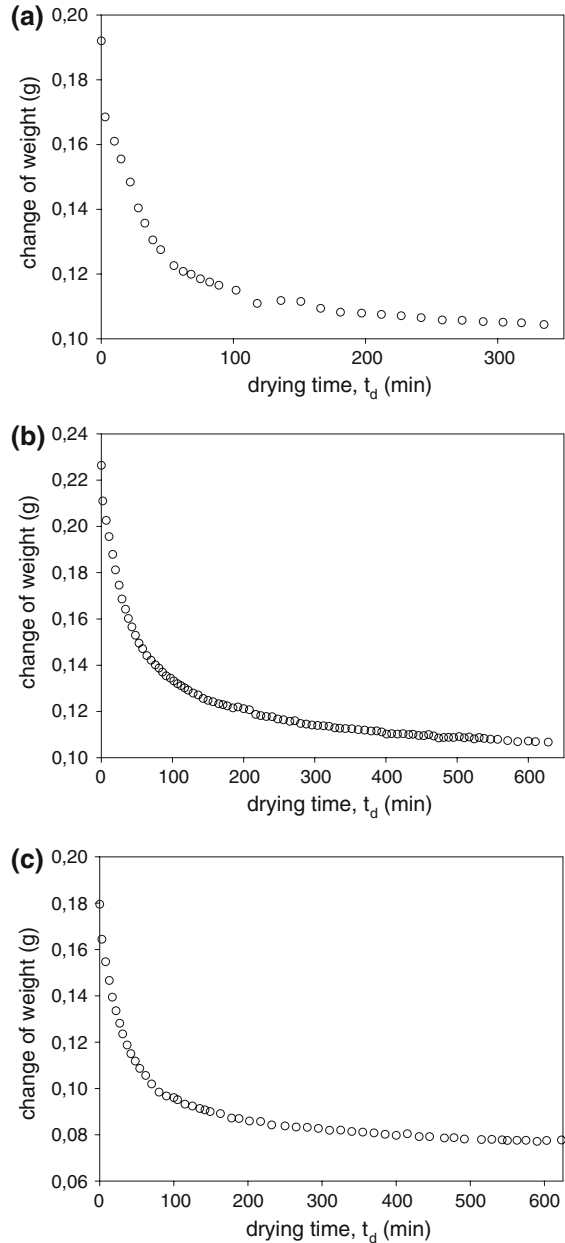
Decrease of desorption coefficients at both regimes with respect to styrene contents implies that MMA-rich heterogels release the chloroform vapor much faster than S-rich heterogels. Even though the expulsion of molecules and/or drying of heterogels are complicated phenomena, the behavior of D values for both regimes versus styrene content still can be explained with the solubility parameters of the

Fig. 2 The plots of vapor
desorption, $M(t)$ versus drying
time, t_d for the S-MMA1 (**a**),
S-MMA5 (**b**) and S (**c**) gel
samples, respectively
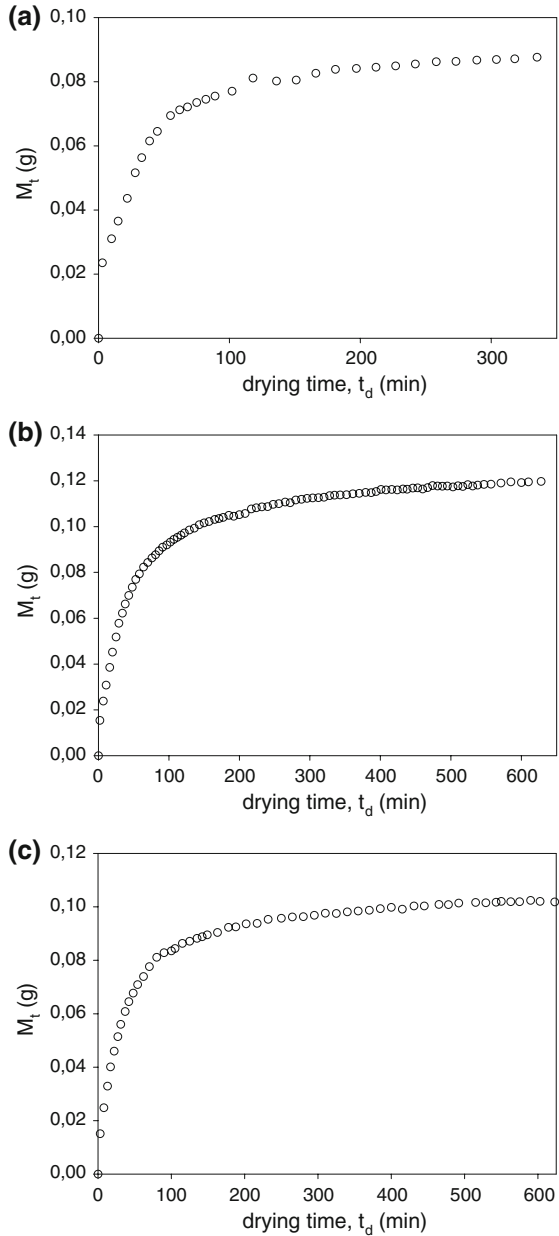
solvent (chloroform) and the the polymeric materials in the heterogel system. Since
the polymer solvent interaction between polystyrene, PS, and chloroform is much
weaker than poly(methyl methacrylate) (PMMA)–chloroform interaction, desorp-
tion from S-rich heterogel takes much longer than with MMA-rich heterogel. In
other words, vapor desorption is much quicker from MMA-rich heterogel than
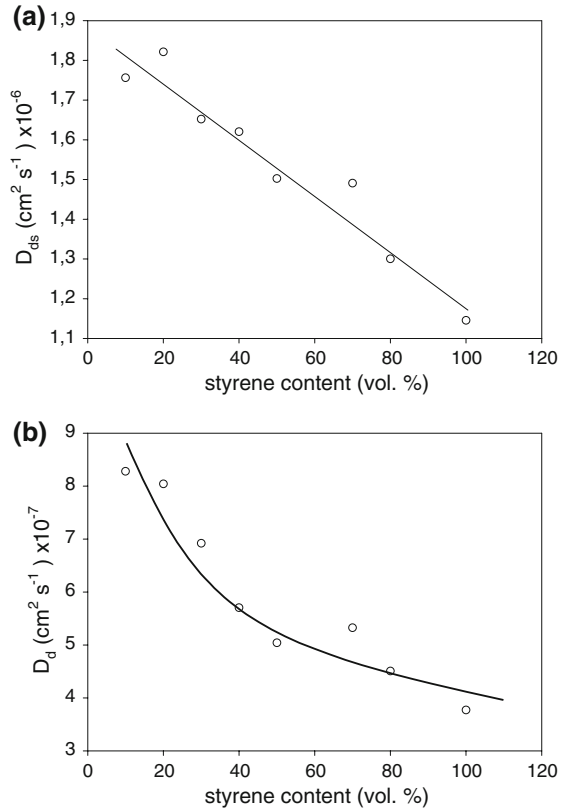S-rich heterogels due to strong interaction of chloroform with PMMA.

Fig. 3 Linear regression of the
data given in Fig. 2 according to
Eq. 6 for the S-MMA1 (**a**),
S-MMA5 (**b**) and S (**c**) gel
samples, respectively
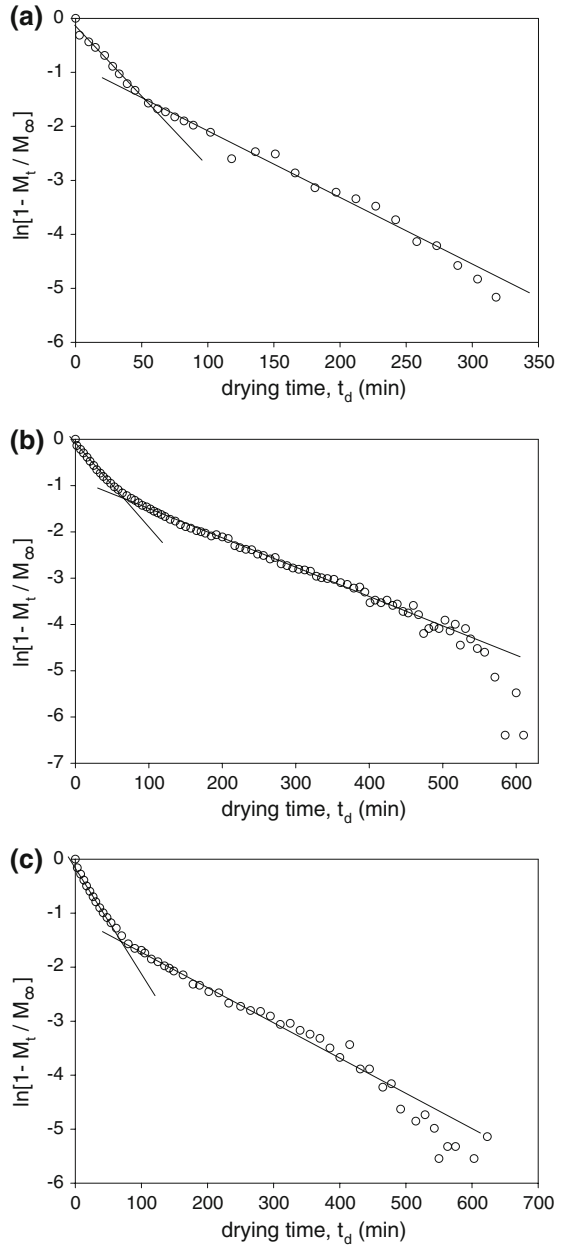
Conclusion

In this study, it is believed that gravimetric technique can be used for real-time
monitoring of the drying processes for heterogels. It is easy to perform and provide
quite sensitive results allowing investigation of early and late times in drying

Fig. 4 Desorption coefficients versus styrene content (%) in the heterogels for short drying regime (**a**) and long drying regime (**b**), respectively

processes. It is observed that polymer–solvent interaction plays a dominant role during the drying process, i.e., MMA-rich heterogels dry much faster than S-rich heterogels. In other words, with chloroform molecules, motion of gel segments is more effective in MMA-rich heterogels than S-rich heterogels at both observed regimes.

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