

Water-gel growth: simulation & modeling exercise

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(Received April 27 2013, Revised June 28 2013, Accepted September 16 2013)

Abstract. The growth process of water-absorbing poly-acryl amide (PAA) $((-\text{CH}_2\text{CHCONH}_2-)_n)$ has been studied from the experimental point of view. We took two different sets of spherical crystal beads of varying size (one white and the other transparent), immersed them in pure water, measured their diameters and masses at regular intervals of time and plotted graphs showing the change in volume and mass of the beads with the time of immersion, to analyze their swelling properties. We have developed a model of 1st order kinetics based on some earlier works those explain the swelling of spherical hydro-gels and then interpreted our observations on its basis. We have also evaluated all the parameters involved in the process of analysis using suitable curve-fitting methods. It is shown that the results obtained from our modeling exactly match the experimental data. We may justify our approach as its successful application in the thorough explanation of the observational results through numerical and analytical ways.

Keywords: hydro-gel, virtual thickness, curve fitting

1 Introduction

Poly-acryl amide (PAA) $((-\text{CH}_2\text{CHCONH}_2-)_n)$ polymers, also known to be hydro-gel or water-gel polymers are basically odorless water-absorbing (may also absorb other liquids as well) polymer which are quite capable of growing at a fast rate to a huge size when immersed into water. The commercial PAA beads are available either in amorphous or in polycrystalline form. These synthetic dry polymer gels form tiny beads. PAA's may be of different colors. This polymer chain contains a large number of charges those attract the H_2O molecules in ionized forms. When immersed in water, the volume of each bead is found to be increased for a certain period of time and then it asymptotically saturates towards a maximum value. The solid hard beads after absorbing water become gel-like soft. The rate of increase in volume is quite large initially; it gradually slows down and finally saturates to zero (in the asymptotic region). The sensitivity of hydro-gels to a large number of chemical and physical factors like temperature, light, electrical voltage, pH, ionic strength, biological, and chemical agents make them suitable for a broad range of applications^[9] like those in agriculture, drug delivery, micro-fluid systems, contact lenses, industrial wastewater treatments, wound management and tissue engineering^[1, 3, 14]. Hydro-gels may be used in sensing applications in which the swelling or de-swelling of the material is converted via a transducer into a measurable signal^[15]. These gels are able to absorb considerable amounts of water due to their hydrophilic characteristics^[2, 23]. The water holding capacity of the hydro-gels arise mainly due to the presence of hydrophilic groups, viz. amino, carboxyl and hydroxyl groups, in the polymer chains. According to Hoffmann^[8], the amount of water present in a hydro-gel may vary from 10% to thousands of times of its weight in the dry state. In particular these hydro-gels at equilibrium comprise 60-90% fluid and only 30-10% polymer^[19, 21]. Moon et. al.^[13] studied the preparation and properties of biodegradable hydro-gel and the swelling and de-swelling behavior under different conditions. Some works^[5, 6, 14, 21] deal with the Fick's equation which analyzes the diffusion of solutes through polymer matrices and are used to

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model such systems. The diffusion coefficients of solutes through a diffusible polymer matrix are experimentally determined in double cell diffusion apparatus. The same work also shows that the diffusion coefficient has some linear relation with the time, where the structure, pore size and polymer composition of gel are taken into account. The swelling by Fickian and non Fickian mechanism in diffusion characteristics has also been studied in some other relevant works^[6, 12, 16]. In particular some studies use numerical computation to determine the diffusion coefficients of these hydro-gels for the Fickian mechanism.

The existing literatures on the swelling properties of hydro-gel discuss about various experimental techniques involving diffusion of liquid into solid objects, the parameters involved and different graphical plots regarding those data which we have already mentioned earlier. In our present approach we have adopted experimental and some new theoretical techniques to explain the growth curves of hydro-gel (both mass as well as volume growth with time) which are equipped with strong physical basis and efficient numerical computation, eliminating any need of using the standard mass diffusion method involving Fickian or any other mechanisms (and even not as complex as those due to Smolochovski^[20] and Langevin^[10]) and may be considered as a parallel treatment of normal hydro-gel swelling study using diffusion.

2 Experimental method

We have performed two different experiments; one with five transparent hydro-gel beads sampled from a large group of varying sizes and the other with five white hydro-gel beads again sampled from a large group also having different sizes (obtained from standard sources widely available in Kolkata, India) and have explained the experimental plots so obtained on the basis of analytical modeling and numerical analysis, using the data collected and normalized during our experiments. Considering the water absorption as a dynamical process we have predicted some empirical relations and equations. In our first experiment we have only measured the diameters at multiple points of the beads and make a volumetric analysis. In the other study we have shown that with the measurement of both the diameter (at multiple points) as well as mass of the beads at fixed time intervals the study may be considerably improved. These spherical beads of hydro-gel were kept immersed in distilled water and the mass (in experiment 2) and the diameter (in both experiments) of each bead were measured at regular time intervals and hence tabulated. Each time, after taking the beads out of water, it was put in contact with blotting paper to remove the excess water from its surface. The diameter of a bead was measured by a screw gauge having an accuracy of 0.001 cm and the mass was measured by a digital weighing machine having an accuracy of 0.001 gm. Stop watches, having an accuracy of one second, were used for time measurement. The swelling behaviors of beads were studied. The collected data sets (normalized) are presented below in tabular form.

3 Modeling

Most of the natural growth processes may follow either the kinetic model where the growth rate always increases with time: no upper limit of the growing variable, e.g. population of a living community, alternatively it may follow a sigmoidal type of growth kinetics where the growth rate first increases and then decreases after a certain point of time, consequently having some finite saturation value e.g. length of any living organism^[22]. Considering the hydro-gels we may notice that their growth does not fall on either of the two categories mentioned above. Experimental observations reveal that hydro-gel growth-rates decrease from the very initiation of the process and after a finite span of time the radius and hence the volume of PAA's reach some saturation level depending upon its composition and color. Suppose the initial radius of a spherical hydro-gel bead is R_0 . The radius $R(t)$ increases with time t and finally reaches the maximum value R_{\max} . At a certain instant t the thickness of the additional layer on the bead

$$T(t) = R(t) - R_0. \quad (1)$$

So that $T(0) = 0$ and $T_{\max} = R_{\max} - R_0$. We introduce a new term virtual thickness defined as [11]

$$\tau(t) = R_{\max} - Rt, \quad (2)$$

at a certain instant it is the deficit of the present thickness from the maximum thickness. Since the initial absorption of water molecules occur only in the additional layer, we may assume that the growth process follows such a kinetics in which the mechanism itself knows how large it has to grow, namely R_{\max} here. Also each absorbing centre in the additional layer is capable of absorbing only a single water molecule and the probability that a single absorbing centre will absorb a water molecule is independent of the total number of such centers present in an elemental cylindrical pore of length equal to the depth of that layer. Keeping in mind these facts we may set up the equation of the kinetics corresponding to the system: the rate of decrease of the virtual thickness will be proportional to the virtual thickness itself (we have mentioned that there is no cross dependence hence these virtual system must follow the 1st order kinetics)

$$d\tau(t)/d(t) = -p\tau(t), \quad (3)$$

p is a decay constant similar to the one in radio-active process. It may be defined as the fractional decrease in virtual thickness per unit time. The solution to this equation.

$$R(t) = R_0 + (R_{\max} - R_0)[1 - \exp(-pt)], \quad (4)$$

resembles with Eq. (3) of the work of Gunasekaran^[7]. We may also arrive at the same result from a functional analysis^[17]. As we know that at $t = 0 \Rightarrow R(t) = R_0$ and at $t \rightarrow \infty \Rightarrow R(t) = R_{\max}$, hence we may express the time dependent radius

$$R(t) = R_0 + (R_{\max} - R_0)f(t), \quad (5)$$

$f(t)$ is some time dependent function satisfying $f(0) = 0, f(\infty) = 1$ Let us now define a new function $\phi(t) = 1 - f(t)$. Hence $\phi(0) = 1, \phi(\infty) = 0$ The simplest function that may satisfy the above relation will be $\phi(t) = k^{-t}$, k is some positive constant.

$$f(t) = 1 - \phi(t) = 1 - k^{-t} = 1 - \exp[(-\ln k)t] = 1 - \exp(-pt), \quad (6)$$

$p = \ln k$, is a new constant which finally leads to Eq. (4).

4 Matching the model with experimental data

One may now fit Eq. (4) to the set of data presented in Tab. 1 and Tab. 2 (obviously after converting the diameter to radius). The fitting is done using MATLAB in Intel platform (we have already performed some other works on polymers on fitting a curve to a set of experimental data^[4, 11, 17, 18]). The fitted parameters to the graph are R_{\max} and p , which are presented in Tab. 4 and Tab. 5 below. Fig. 1 and Fig. 2 show the original data using symbols, while the fitted model with the solid lines.

As evidence to our theory we may compute p from our experimental data on radius vs. time using the relation below. We may do it for all the beads.

$$p \approx \frac{R(t + \Delta t) - R(t)}{\Delta t(R_{\max} - R_t)}. \quad (7)$$

Table 1. Experiment 1: Variation of the diameters of five transparent hydro-gel beads arranged in ascending order of their sizes with time when immersed in water

Time (min.)	Bead 1 (cm.)	Bead 2 (cm.)	Bead 3 (cm.)	Bead 4 (cm.)	Bead 5 (cm.)
0	0.15	0.20	0.23	0.28	0.40
30	0.53	0.60	0.65	0.70	0.95
60	0.64	0.69	0.75	0.78	1.10
90	0.65	0.74	0.83	0.94	1.23
120		0.74	0.87	1.00	1.25
150			0.87	1.03	1.33
180				1.04	1.36
210				1.05	1.37
240					1.39
270					1.43
300					1.45
330					1.45
360					1.47

Table 2. Experiment 2: Variation of the diameters of five white hydro-gel beads arranged in descending order of their sizes, with time when immersed in water

Time (min)	Bead 1 (cm)	Bead 2 (cm)	Bead 3 (cm)	Bead 4 (cm)	Bead 5 (cm)
0	0.488	0.439	0.380	0.240	0.238
15	0.880	0.656	0.627	0.554	0.544
30	1.048	0.793	0.792	0.720	0.655
45	1.139	0.979	0.956	0.730	0.845
60	1.335	1.047	1.075	0.928	0.980
75	1.414	1.179	1.184	1.058	1.020
90	1.530	1.223	1.276	1.120	1.140
105	1.623	1.276	1.421	1.170	1.196
120	1.630	1.398	1.455	1.187	1.230
135	1.718	1.416	1.516	1.225	1.260
150	1.758	1.440	1.553	1.255	1.303
165	1.790	1.494	1.583	1.270	1.370
180	1.798	1.565	1.624	1.280	1.380
195	1.824	1.586	1.641	1.315	1.396

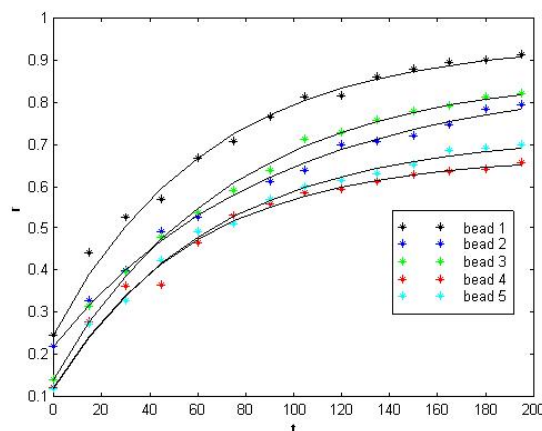
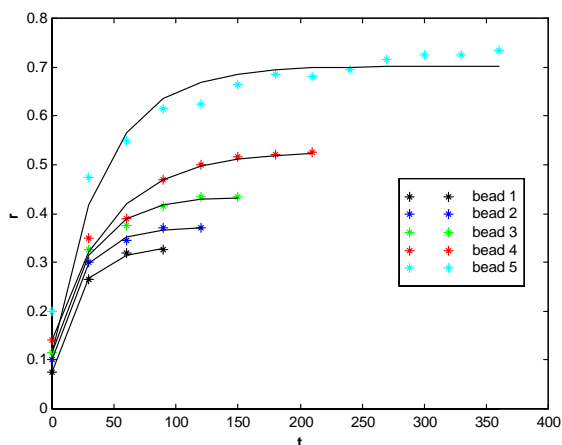


Fig. 1. Radius vs. time data plotted for five transparent hydro-gel beads during experiment 1 as mentioned in the article. The continuous lines are the best fits to those data. The corresponding fitted parameters are mentioned in Tab. 4

Fig. 2. Radius vs. time data plotted for five white hydro-gel beads during experiment 2. The continuous lines are the best fits to those data. The corresponding fitted parameters are mentioned in Tab. 5

Table 3. Experiment 2: Variation of the masses of above five hydro-gel beads with time when immersed in water

Time (min)	Bead 1 (gm)	Bead 2 (gm)	Bead 3 (gm)	Bead 4 (gm)	Bead 5 (gm)
0	0.036	0.022	0.023	0.011	0.010
15	0.282	0.175	0.19	0.127	0.138
30	0.603	0.424	0.487	0.296	0.327
45	0.955	0.618	0.815	0.456	0.506
60	1.272	0.847	1.12	0.581	0.645
75	1.508	1.062	1.322	0.669	0.748
90	1.773	1.28	1.588	0.767	0.806
105	2.023	1.472	1.882	0.881	0.94
120	2.206	1.622	2.117	0.964	1.04
135	2.384	1.766	2.252	1.033	1.113
150	2.614	1.949	2.496	1.1	1.189
165	2.804	2.055	2.6	1.145	1.235
180	2.88	2.165	2.707	1.171	1.265
195	3.072	2.3	2.868	1.201	1.302

Table 4. Data obtained by curve fitting in Fig. 1

$R_{max}(cm)$	0.3322	0.3715	0.4352	0.5278	0.7016
$p(min^{-1})$	0.0456	0.0433	0.0325	0.0212	0.0243

Table 5. Data obtained by curve fitting in Fig. 2

Bead no.	1	2	3	4	5
$R_{max}(cm)$	0.9406	0.8549	0.8696	0.6712	0.7230
$p(min^{-1})$	0.0156	0.0111	0.0137	0.0169	0.0151

Table 6. Computation of p following Eq. (7) during experiment 1

Bead No.	1	2	3	4	5
t	30	60	90	150	240
Δt	30	30	60	30	90
P	0.0273	0.0314	0.0206	0.0130	0.0505

Table 7. Computation of p following Eq. (7) during experiment 2

Bead No.	1	2	3	4	5
t	30	90	75	150	60
Δt	15	30	45	15	30
p	0.0073	0.0120	0.0108	0.0114	0.0114

The value of p using the above relation has been computed in Tab. 6 and Tab. 7 below and may easily be checked with the corresponding value of p obtained from curve fitting method. The value of R_{max} required to compute p (in Tab. 6 and Tab. 7) from Eq. (7), may be obtained from Tab. 4 and Tab. 5 respectively.

Comparison of the values of p obtained using two different methods show that there are not much of differences between them. The agreement could have been made better if during our experiment we have chosen very small Δt values. But that would not be possible in practice, understandably because of time limitations.

Using Eq. (4) we may now obtain the volume of a hydro-gel bead at time t and its growth rate

$$V(t) = \frac{4}{3}\pi \left[R_0 + (R_{max} - R_0)[1 - \exp(-pt)] \right]^3, \tag{8}$$

$$\frac{dV(t)}{dt} = 4\pi \left[R_0 + (R_{max} - R_0)[1 - \exp(-pt)] \right]^2 (R_{max} - R_0) \exp(-pt). \tag{9}$$

Introducing the parameter ω (following our idea^[11]), the mean increase in the volume of a hydro-gel bead due to absorption of a single water molecule, we obtain (we are applying this lattice model for a normalized data set on a large number of beads as mentioned in [11])

$$V(t) = v + n(t)w, \tag{10}$$

$v = \frac{4}{3}\pi R$ is the initial volume of a bead and $n(t)$ is the number of water molecules absorbed at the corresponding time instant.

$$\frac{dn(t)}{dt} = \frac{4\pi}{\omega} \left[R_0 + (R_{\max} - R_0)[1 - \exp(-pt)] \right]^2 (R_{\max} - R_0) \exp(-pt). \tag{11}$$

Assuming the mass of a single water molecule as m we may write the mass growth rate for the hydro-gels

$$\frac{dM(t)}{dt} = \frac{4\pi m}{\omega} \left[R_0 + (R_{\max} - R_0)[1 - \exp(-pt)] \right]^2 (R_{\max} - R_0) \exp(-pt). \tag{12}$$

The solution to the above equation with the boundary condition that yields

$$M(t) = \frac{4\pi m}{3w} \left[R_0 + (R_{\max} - R_0)[1 - \exp(-pt)] \right]^3 + M_0 - \frac{vm}{\omega}. \tag{13}$$

We may fit the above equation to the mass time data as shown in Fig. 3 below.

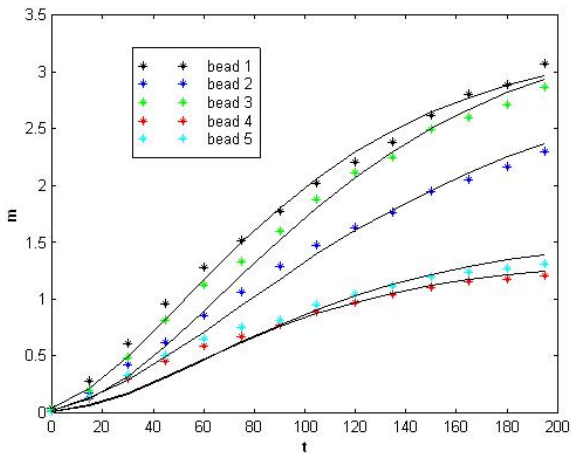


Fig. 3. Mass vs. time data plotted for five white hydro-gel beads during experiment 2. The continuous lines are the best fits to those data

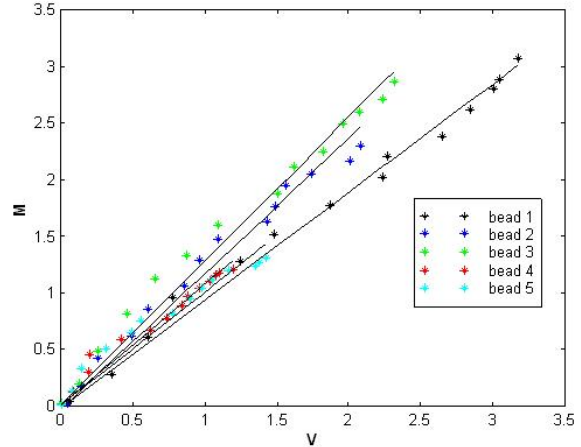


Fig. 4. Mass vs. volume plot for five white beads during experiment 2

w values for different beads may be obtained from the above fit and is tabulated below.

Following our idea in [11]

$$w = \lambda u, \tag{14}$$

where the net increase in volume of each bead (ω) is due to the absorption of water molecules (each having a volume $u = 3 \times 10^{-23} c.c.$) only and hence it must be proportional to the entire volume of the water molecules absorbed in the process. Let the corresponding constant of proportionality be λ which [11] may be defined as

Table 8. Data obtained by curve fitting in Fig. 3

Bead No.	1	2	3	4	5
ω ($X 10^{-23} c.c.$)	3.1396	2.4996	2.3562	2.7906	2.9975
$M_{\max}(gm.)$	3.2727	3.0880	3.4925	1.3539	1.5773

Table 9. Determination of λ following Tab. 8

Bead No.	1	2	3	4	5
λ	1.0465	0.8332	0.7854	0.9302	0.9992

$$\lambda = \frac{\text{maximum increase in volume of a crystal bead due to swelling}}{\text{volume of water absorbed by the bead}}. \quad (15)$$

Following the above definition and the data tabulated in Tab. 8 one obtains

The above tabulation clearly establishes the accuracy of our theory.

$$M(t) = \left(\frac{m}{w}\right) V(t) + \left(M_0 - \frac{mV_0}{w}\right) = AV(t) + B, \quad (16)$$

where A and B are two parameters of the model. Eq. (16) has been fitted to the mass-volume data and the fitting parameters so obtained as well as their theoretical expectation values (following Eq. (16)) is presented in Tab. 10.

Table 10. Theoretical and experimental values of A and B

Bead No.	1	2	3	4	5
A_{fitted}	0.9199	0.7010	0.8898	0.3665	0.3927
B_{fitted}	0.0594	-0.0151	-0.0245	0.0719	0.0855
A_{theo}	0.9555	1.2002	1.2732	1.0750	1.008
B_{theo}	-0.0221	-0.0312	0.0084	0.0022	0.0039

5 Concluding remarks

In our analysis we have estimated all the constants of our process hence propose a new model that governs the growth mechanism of spherical hydro-gel bead (PAA). Also we have analyzed various swelling properties. The variations of radius and mass with time have also been analyzed by suitable curve-fitting methods. Our theoretical models are in very good agreement with experimental findings. We have introduced two new parameters w and λ . By computing the parameter λ we have shown that the increase in volume of the hydro-gel is less than the volume of water absorbed, supporting the porous nature of the material as predicted by us. To verify the predictions of the present model experimentally, one must measure both the mass and the volume of swelling hydro-gel with as much precision as possible. In the present study mass measurement has greater accuracy than that of volume measurement, owing mainly due to the deviations from spherical shape. The unique feature of this study is that, on the basis of a completely new concept based on the virtual kinetics, the mechanisms of mass rise and volume expansion for hydro-gels have been rigorously explained.

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