Poly(vinyl alcohol)–Poly(sodium acrylate) Composite Hydrogels. I. Kinetics of Swelling and Dehydration

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SYNOPSIS

Incorporation of sodium polyacrylate (NaPAA) in poly(vinyl alcohol) (PVA) gels as small, uniformly distributed precipitates greatly accelerates their volume expansion during swelling in water to form hydrogels. In addition to the usual water absorption, the swelling process includes dissolution of the precipitates that leads to a locally high osmotic pressure that in turn causes a further increase in water penetration and volume expansion. During swelling, soluble NaPAA is released into the water phase with a high initial release rate that then decreases continuously. The release can be described by an exponential decay function with a power dependent rate coefficient. Because the diffusion of NaPAA through the PVA walls is too slow to account for this release rate, a morphology of a closed cell foamlike structure with interconnecting channels is proposed. An aqueous solution of NaPAA seems to diffuse out of the hydrogel through these channels. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recently hydrogels have attracted much attention, especially in applications in medicine, pharmaceuticals, and biotechnology, probably because of their resemblance to biological matrices. Most of the related studies have focused on the synthesis and physicochemical properties of hydrogels, but swelling and dehydration kinetics of hydrogels have not been studied as extensively as their equilibrium swelling. It is, however, widely accepted that the rate of volume expansion of a hydrogel by its solvent is controlled by a diffusion mechanism. Early work[1] on the time dependent swelling of butyl vulcanizate gums in acetone/cyclohexane solvent mixtures concluded that the diffusion coefficient was not constant during swelling. It was further shown that this diffusion coefficient increased exponentially with the volume of the network. Tanaka and Fillmore[2] argued that the swelling time could not be analyzed by the diffusion coefficient of the solvent. They postulated a theory where the swelling time of polyacrylamide gels in water depended on the bulk and shear moduli of the polymer network and the friction coefficient between the network and the fluid medium. In addition, they concluded that the swelling rate of spherical polyacrylamide hydrogels was inversely proportional to the diffusion coefficient of the network and the square of the radius of the hydrogels.

In the present work we employ a composite hydrogel based on poly(vinyl alcohol) (PVA) and sodium polyacrylate (NaPAA). Contrary to other studies where polyelectrolytes were combined with PVA[3–6] in water, which is a good solvent for both these polymers, our composite hydrogels are prepared by dispersing NaPAA particles in an aqueous dimethyl sulfoxide (DMSO) solution that contains PVA. This solution serves as a solvent for the PVA component but is a nonsolvent for the NaPAA component. Thus, after gelation of the PVA and immersing the resulting gels in water, the dispersed NaPAA is dissolved *in situ* and leads to a localized saturated solution that gives rise to extremely high volume expansion characterized for these composite hydrogels. Furthermore, in spite of the high water capacity, the mechanical strength and structural integrity of these composite hydrogels are maintained although they have no chemical crosslinking. The water swelling capacity at equilibrium as well as the kinetics of swelling of these composite hydrogels are

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different from PVA hydrogels prepared from an aqueous DMSO solution in the absence of NaPAA. It will be further shown that the swelling and dehydration kinetics of the composite hydrogels are different from conventional composite gels because of the high degree of dimensional change during the release of NaPAA. On the other hand, the release of NaPAA during swelling resembles to some extent a monolithic control drug delivery system,[7] where the rate of release is linearly proportional to the square root of time.

EXPERIMENTAL

Materials

PVA was obtained from Unitika Ltd. (Osaka, Japan). The polymer used had a degree of polymerization of 1700 with at least 99.5 mol % degree of saponification. NaPAA particles with an average size of 30 μm were obtained from Nakarai Chemicals Ltd. (Kyoto, Japan). The viscosity-average molecular weight of NaPAA was 3.0×10^5. DMSO and all other solvents were of analytical grade and used without further purification. Double distilled water was used in all experiments.

Preparation of PVA/NaPAA Hydrogels

The preparation of the hydrogels was similar to that reported earlier.[8] Briefly, solutions of 10 wt % PVA were prepared by dissolving PVA in DMSO/water (80/20, by weight) mixture at 120°C. To ensure complete dissolution, heating was continued for 2 h after apparently clear solutions were obtained. An appropriate amount of NaPAA particles was then added to the clear PVA solution and the mixtures were allowed to cool to room temperature under mild stirring. As the temperature decreased, the viscosity of the mixture increased such that no settling of NaPAA was observed. The viscous solutions were then poured into test tubes of different sizes and stored at −5°C for 24 h and then at +5°C for an additional 3 days. The composite hydrogels thus obtained consisted of fine and homogeneous dispersion of NaPAA particles within the clear PVA/DMSO/water matrix. The gels were removed from the test tubes, cut into disks and cylinders of various sizes, and kept in a large excess of methanol to extract the DMSO. The methanol solution was exchanged daily until no trace of DMSO in the hydrogels could be detected by gas chromatography.

Solution Conductance Measurement

The diameter and height of the methanol-swollen gels were measured by a micrometer to an accuracy of 0.05 mm. The concentrations of NaPAA released during swelling were calculated from the conductance of the water in which the methanol-swollen gels were suspended. A typical experiment consisted of placing the disklike gel into a beaker filled with a known volume of double distilled water and maintaining it at a controlled temperature (27°C). The beaker was covered to prevent evaporation of the water during the experiment and elevated from a magnetic stirrer placed under it so that the water temperature was unaffected by the heat generated from the magnetic stirrer motor and remained unchanged during a relatively long experimental duration. Slow speed stirring was used to maintain a constant motion of the hydrogel sample in the water. The conductance of the aqueous solution was measured by a Horiba conductivity meter (model DS-7M) connected to an XY recorder. The conductivity cell used was also made by Horiba with a cell constant of 1 at 25°C.

The dimensions of the hydrogels during swelling in water were measured with a micrometer without removing the samples out of the water. The measurements were estimated to be accurate to about ±0.5 mm in the early stage of swelling. The experimental error during this initial period was due to the sticky surface caused by the high rate of NaPAA diffusion out of the hydrogels. After several hours, the hydrogels appeared as firm rubberlike materials and the accuracy of the measurement was improved and estimated to be about ±0.05 mm. Although other methods of measuring the volume were considered, determining the dimension with a micrometer under water was found to be the most appropriate. All water evaporation experiments were conducted at 25°C and 65% relative humidity.

Calibration Curve

A solution containing 1.73 g of NaPAA was dissolved in 900 g of water and allowed to equilibrate overnight at 27°C. The conductance of successive dilutions was measured at this temperature. Measurements of the high concentrated, viscous samples were performed at least 30 min after the dilution step to insure homogeneity.

Kinetic Equations of Diffusion

It is assumed that the diffusion of NaPAA from the PVA hydrogels is similar in principle to that of a

low-molecular-weight substance from a hollow cylinder after immersion in a water sink for a sufficiently long time. Then the rate of diffusion, $dC(t)/dt$, is proportional to the amount of NaPAA, $[A]$, still remaining in the hydrogel at time t:

$$dC(t)/dt = k[A]. \quad (1)$$

As $[A]$ is given by $[C_b - C(t)]V$, where C_b is the NaPAA concentration in the water phase at $t = \infty$ and V is the volume of the water sink, eq. (1) is rewritten as

$$dC(t)/dt = Vk[C_b - C(t)]. \quad (2)$$

Integration of the above equation under the condition that $C(0) = 0$ gives eq. (3)

$$C(t) = C_b[1 - \exp(-Kt)] \quad (3)$$

where K is $-Vk$. By rearranging, one obtains

$$\ln(1 - C(t)/C_b) = -Kt. \quad (4)$$

By letting the coefficient K vary with time in a similar power dependence as suggested by Higuchi,[9] the concentration of NaPAA in the water sink can then be described by:

$$C(t) = C_b[1 - \exp(-Kt^n)] \quad (5)$$

RESULTS

Swelling

The change in the weight and volume of the methanol-swollen composite hydrogels during swelling in water and upon drying is listed in Table I. It is evident that the presence of NaPAA in these gels caused a large volume expansion from the methanol-swollen state to the final swelling in water (Fig. 1). The volume expansion ratio in all cases was about 20. No cracks were observed in the hydrogels during the large expansion and contraction cycles. In all the samples, swelling started as soon as methanol-swollen gels were immersed in water. During the swelling process, a sharp boundary layer could be observed inside the gel. The inward part of this boundary layer was a white, opaque cylinderlike region containing NaPAA precipitates, and the outward part had a ring of transparent water-swollen gel composed of the soluble NaPAA in the swollen PVA matrix. The inner white cylinder diminished and the thickness of the transparent ring expanded as the swelling process progressed until finally the whole gel appeared uniformly clear.

The rate of the volume expansion depended on the initial size of the hydrogel. A rapid increase in the hydrogel diameter was observed initially, followed by lower rates at longer swelling times. Figure 1 illustrates the volume increase of two cylindrical hydrogels during swelling. The initial diameter of these two cylindrical hydrogels was identical (1.15 cm) and only their initial height was different (0.26 and 1.60 cm). It can be seen that the smaller hydrogel expanded much faster than the larger one. Furthermore, the larger cylindrical gel did not expand uniformly as did the smaller hydrogel, but exhibited an elliptic hyperboidal shape during swelling; that is, the edges of the cylinders swelled faster than the rest of the surface, leading to distortion of the shape. A curvature appeared as soon as swelling started, but began to subside in this sample after about 1 day and almost disappeared after 2 days. Thereafter, this hydrogel returned to the original cylinder shape. The diameters recorded in Figure 1 were taken at the widest place along the hydrogel circumference.

It was difficult to determine the volume during the swelling process because of the distortion of the cylindrical shape that took place in the larger samples. The apparent diameter measured at the largest point of the circumference was plotted on a logarithmic scale in Figure 2. It is seen that the growth of the diameter with time can be described by an empirical power law equation. Soon after the diffusion of water started into the gel, the entrapped precipitates of NaPAA dissolved and increased the local osmotic pressure inside the gels. Consequently, further swelling and the release of some of the soluble NaPAA to the water sink was observed.

NaPAA Release

The NaPAA that diffused out of the swelling gels and then released into the water sink was used to follow the swelling process. Figure 3 shows the accumulated concentration, $C(t)$, of NaPAA during swelling of cylindrical gels of various sizes. The release of NaPAA into the water is characterized by an initial "burst" due to the dissolution of NaPAA from the surface of the sample. This initial release is followed by a more moderate but still relatively fast release and finally low release that slowly decreases for a long period of time. Even after allowing the gels to swell for 1 week, no apparent equilibrium was reached and the diffusion

Table I Swelling of Different Size Cylindrical Shape Hydrogel Samples

	Weight			Volume in				
Sample	Water Swollen	Dry Weight	% Solid	Methanol	Water	$C_b \times 10^{-4}$	K	n
1	9.81	0.2066	2.11	0.55	10.88	5.8	0.106	0.610 ± 0.006
2	10.14	0.2335	2.30	0.55	10.87	10.8	0.133	0.657 ± 0.008
3	4.27	0.0888	2.08	0.27	5.34	7.2	0.151	0.658 ± 0.007
4	6.15	0.1379	2.24	0.37	7.00	8.0	0.164	0.567 ± 0.003
5	32.45	0.7440	2.29	1.66	33.68	11.5	0.078	0.671 ± 0.005
6	11.34	0.2266	2.00	0.62	10.93	7.0	0.081	0.614 ± 0.003

Prepared by dissolving 10 wt % PVA in aqueous DMSO solution and adding equivalent weight of suspended NaPAA. The coefficients C_b, K, and n characterize the swelling process according to eq. (5).

of NaPAA from the water-swollen hydrogels to the water phase continued.

Figure 4 shows the diffusion rate of NaPAA. As is clearly seen, it drastically decreases after the initial burst and, thereafter, more moderate and continuously decreasing release rates are observed at longer times. The release rate may be considered constant only in the first hour after swelling starts (Fig. 4 insert). Many solid precipitates of NaPAA were seen inside the swelling hydrogel even after the diffusion rate began to subside.

Figure 5 is a plot of the left-hand side term of eq. (4) against time. It can be seen that after long swelling a good agreement is observed between this mechanistic equation and the experimental data (a correlation coefficient of 0.996 was obtained for the linear regression of the data between 55 and 122 h). However, relatively large deviation of the regression line from the experimental points is observed initially. Obviously the reason for the deviation is that during this period the rate of diffusion is not constant because of the continuous expansion of the hydrogel volume. Using similar arguments as forwarded by Higuchi,[9] a reasonably good fit could be obtained in this initial period by plotting the concentration of NaPAA as a function of the square

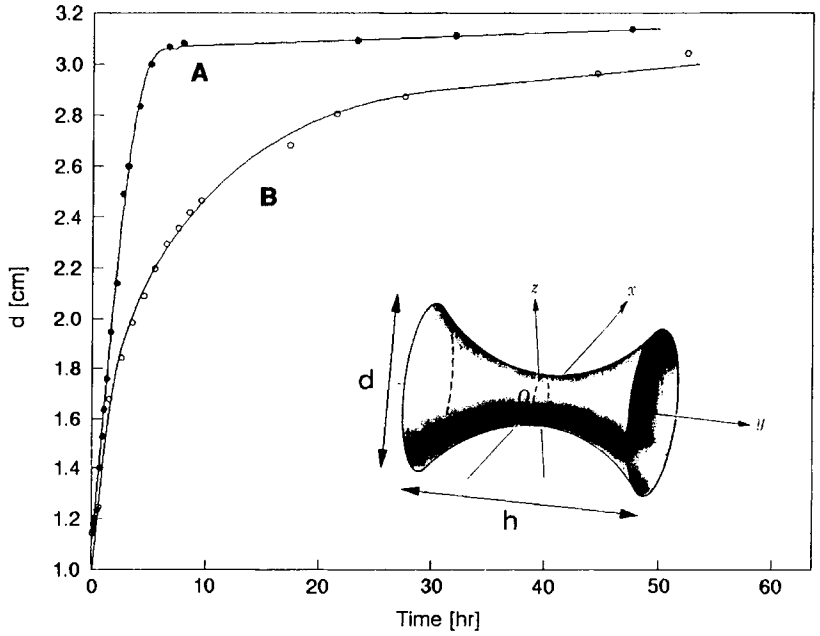

Figure 1 Observed hydrogel diameter, d, during swelling in water. (A) small cylinder, $d_{(t0)}$ = 1.15 cm and $h_{(t0)}$ = 0.26 cm (sample 3); (B) large cylinder, $d_{(t0)}$ = 1.15 cm and $h_{(t0)}$ = 1.60 cm (sample 5). An elliptic hyperboid shape (insert) was observed when large cylinders such as sample 5 were swollen.

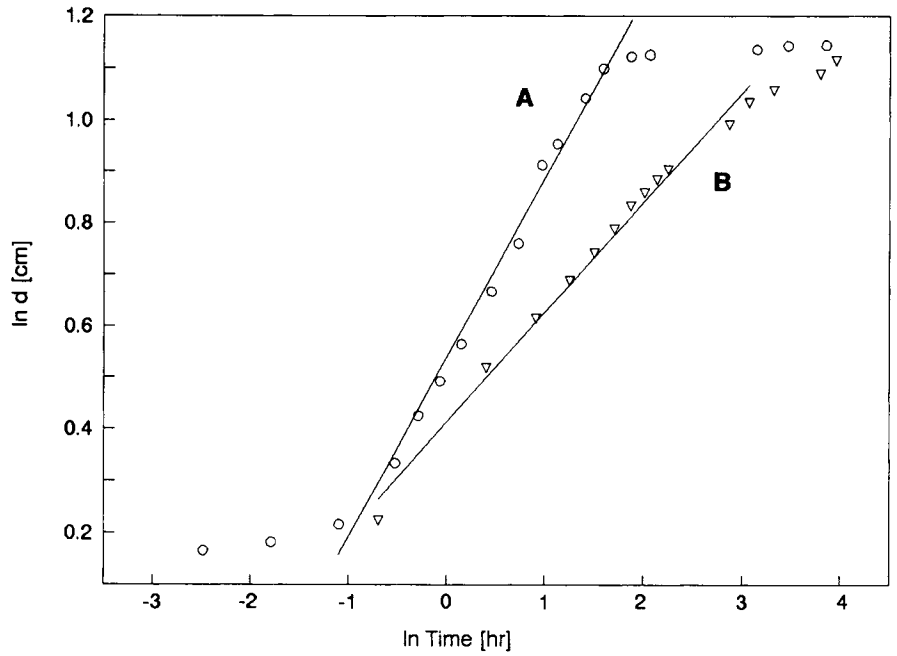

Figure 2 A logarithmic plot of the hydrogel diameter during swelling of small (A; sample 3) and large (B, sample 5) cylindrical samples. See Figure 1 for the dimensions of A and B.

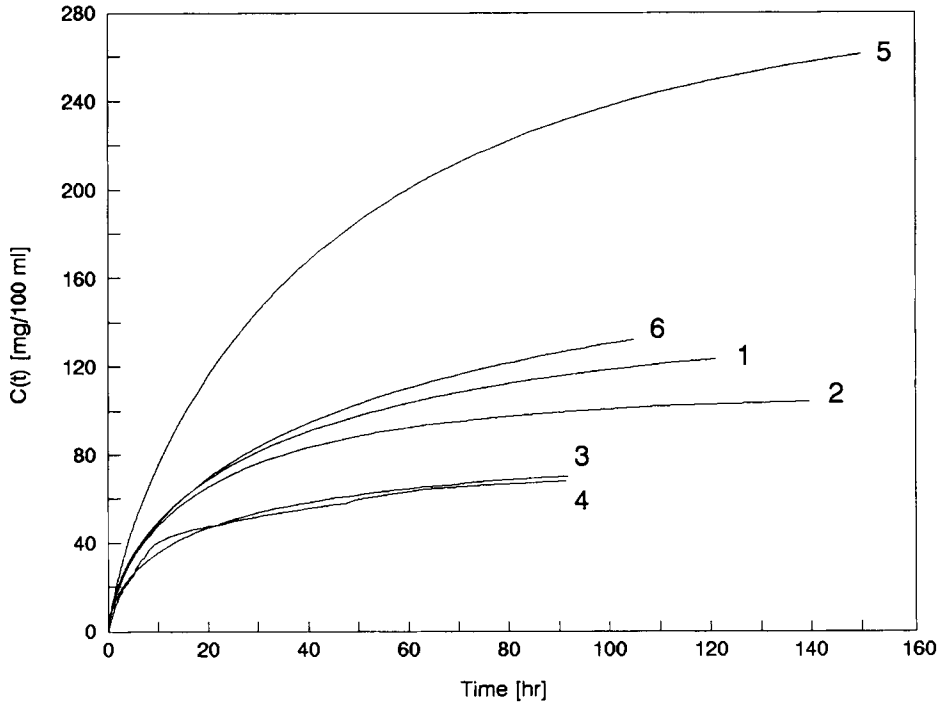

Figure 3 Accumulated concentration, $C(t)$, of Na PAA released from cylindrical PVA hydrogels into the water sink. The numbers identify the samples listed in Table I.

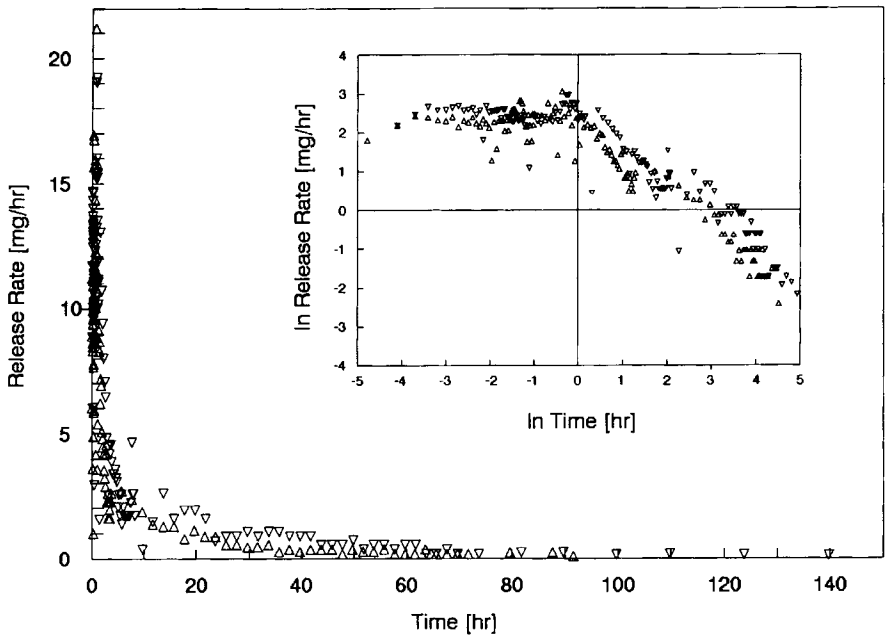

Figure 4 Release rate of NaPAA during swelling of composite hydrogel (sample 2) in 100 mL water.

root of time. The result is shown in Figure 6. Low solubility and diffusion of the solute through the polymer wall were assumed originally in developing this relationship. Thus, in the usual case of highly water-soluble, low-molecular-weight substances, it does not provide a good approximation because the component of the driving force related to osmotic pressure is much larger than the concentration gradient across a membrane wall (diffusion mechanism).

The plot of the data according to eq. (5) is shown in Figure 7. The observed NaPAA concentration was

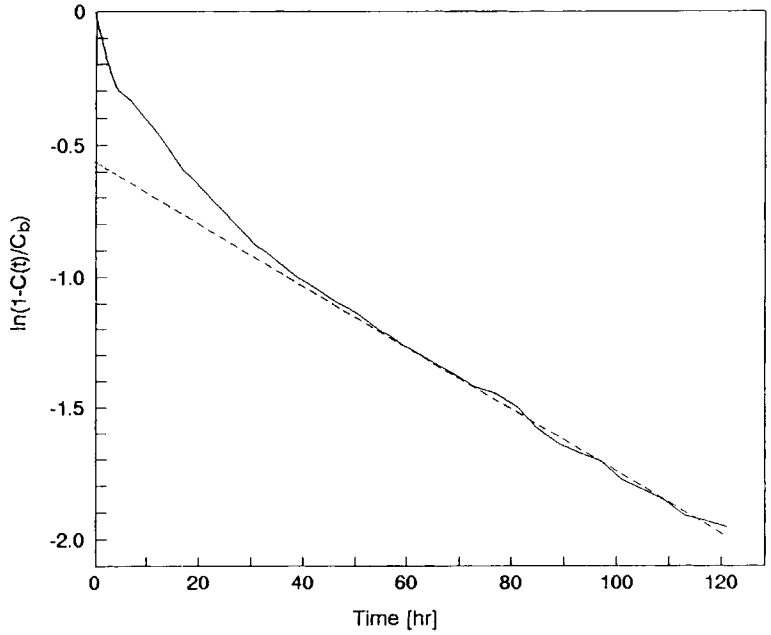

Figure 5 An example of the fit of the accumulated NaPAA concentration (—) during swelling of sample 1 in water to (---) eq. (4).

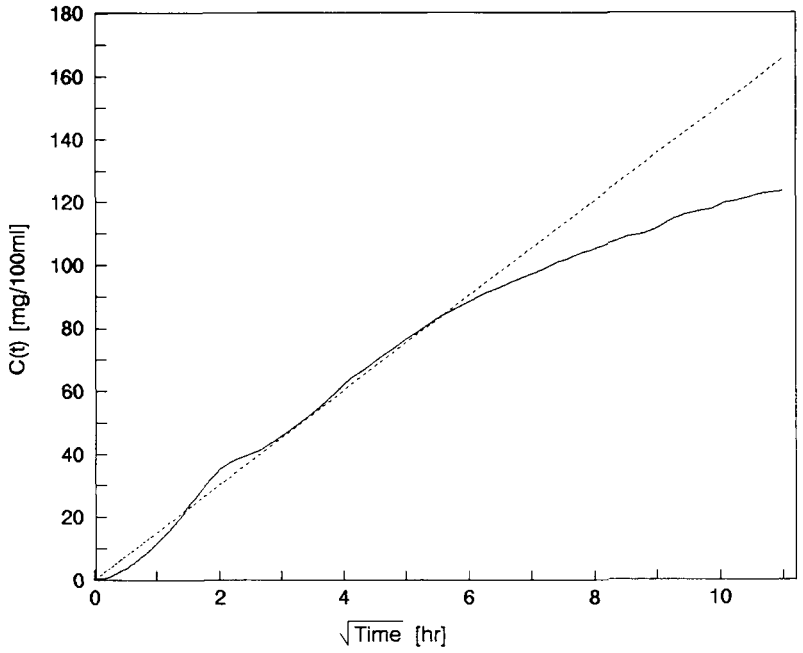

Figure 6 An example of the fit of the accumulated NaPAA concentration (—) during swelling of sample 1 in water to (· · ·) the square root time dependence.

also plotted together with the concentrations calculated according to the square root time dependence and eq. (3). As mentioned above, eq. (3) provides a good fit at long times, while the square root time dependence is a good approximation at short swelling times. The combined feature of these short and long time processes into eq. (5) may have provided a good fit throughout the swelling.

The most fittable coefficients in eq. (5) are given in Table I. It appears that *Cb* decreased proportion-

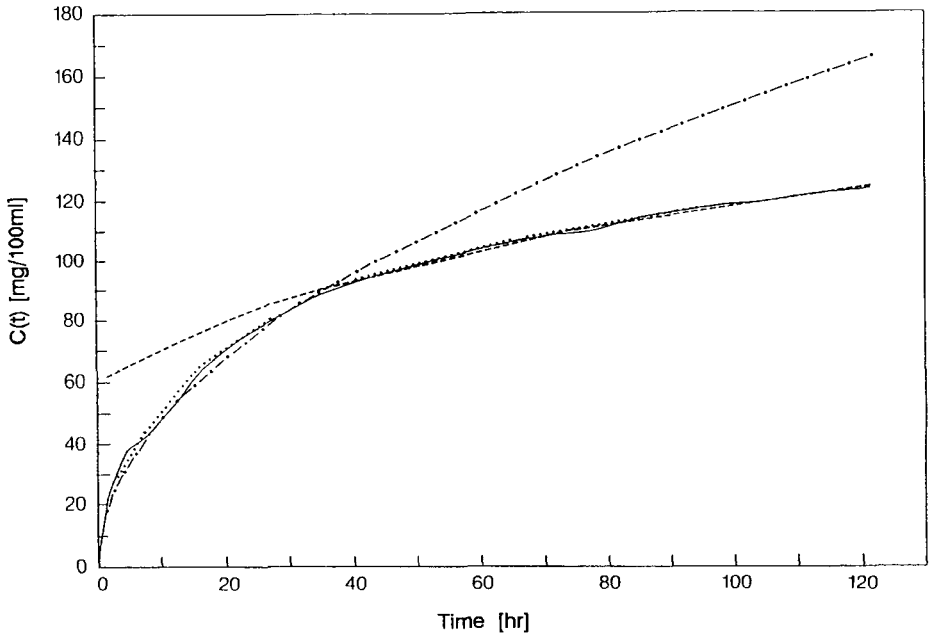

Figure 7 Examples of the fit of the accumulated NaPAA concentration (—) during swelling of sample 1 in water to (· · ·) eq. (5), (---) eq. (3), and (– · – ·) power law time dependence.

ally to the volume of the water sink. This is expected from the experimental conditions, as NaPAA was not removed from the system but remained in the water phase. The final concentration will be its weight divided by the water volume, provided all NaPAA is free to diffuse out of the hydrogel. However, adjusting *Cb* to the proper water volume alone is not sufficient to describe the release rate as a function of the size of the water sink. Samples 1 and 4 are identical and were studied in water sinks of different sizes. The relationship between the amount of NaPAA diffused from these samples at various times and the swelling ratio depends on the shape and the volume of the sample.

The derivative of eq. (5) with respect to time gives the release rate of NaPAA from the hydrogel and is plotted after the first 2 h (Fig. 8). A significant decrease in the release rate is observed during the swelling period for several days thereafter. Apparently, these composite PVA hydrogels are not suitable as a zero-order drug release system when a high-molecular-weight water-soluble solute is used.

Drying of Swollen Hydrogels

Nonuniform shrinkage was observed during slow water evaporation from these hydrogels at 25°C and 65% relative humidity. The water weight remaining for a hydrogel during drying is shown in Figure 9. The diameter (d) and height (h) of the original methanol-swollen sample are 1.15 and 1.60 cm, respectively; the corresponding dimensions of this sample after swelling in water are d = 3.12 cm and h = 4.35 cm. At the bottom is a scaled drawing approximating the size and shape of the gel during drying at the times when the dimensions were recorded. It can be seen that the dependence of the water weight on time is not constant in contrast to the case of an unrestricted, constant surface area evaporation process. Relatively fast weight loss was observed initially, followed by slower loss at longer times. The initially cylindrical swollen sample contracted faster near the top edge than along the bottom, where no evaporation or much less evaporation could take place. During this drying process the initially smooth surface turned rough with a blisterlike appearance and remained rough throughout the drying period. After 1 week, the approximately cylindrical shape recovered again and the dimension of the sample appeared very close to the original size before swelling in water. At this time only about 3% water remained that subsequently could be removed by placing the sample in a vacuum.

The rate of dehydration decreased exponentially with time. An example is shown in Figure 10. The decrease in the rate must be due primarily to the reduction in the surface area as the hydrogel volume decreased during drying. The surface area was calculated and the dehydration rate per unit area of the hydrogel during drying was plotted in Figure 11.

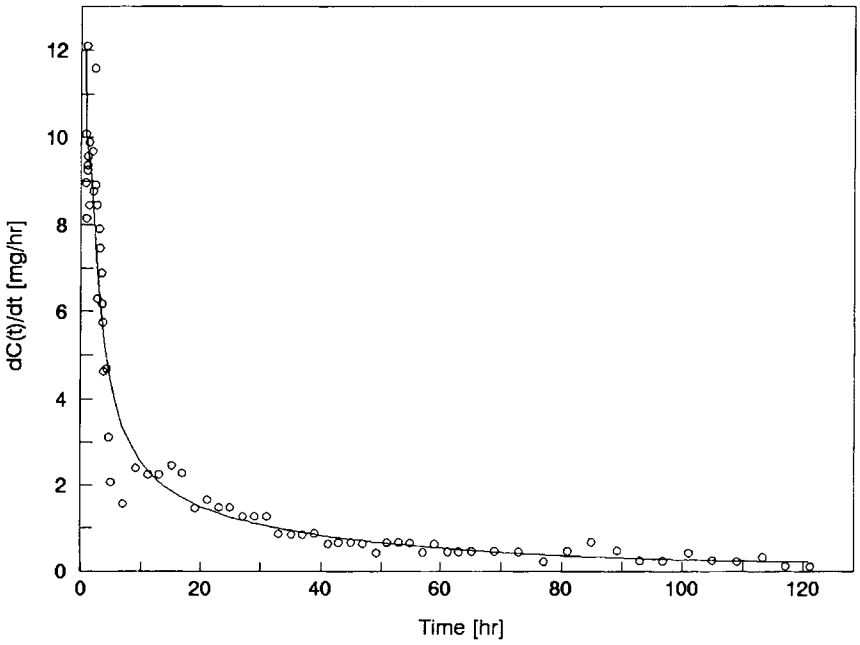

Figure 8 The observed release rate of NaPAA from sample 1 (data points) and (—) the calculated rate obtained by differentiating eq. (5).

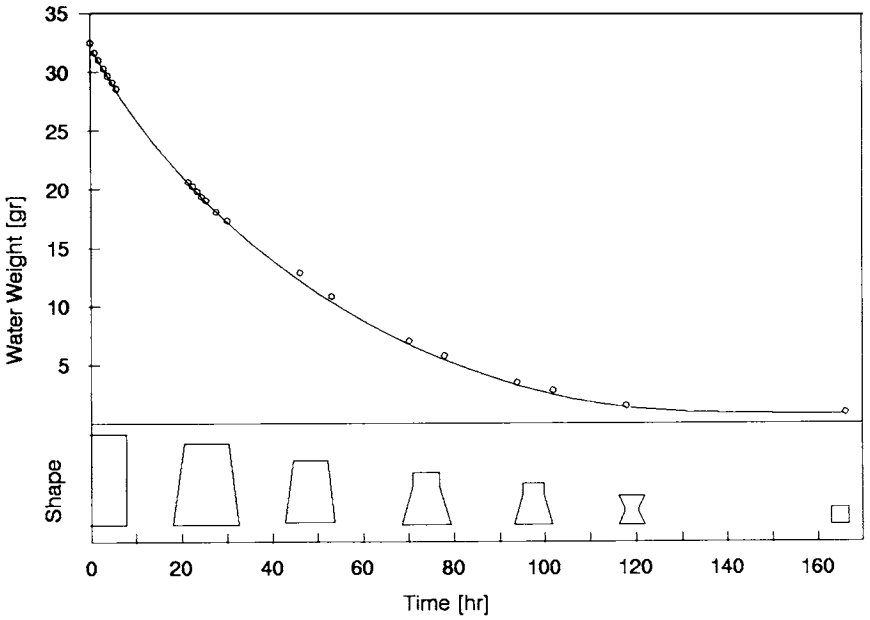

Figure 9 Loss of water during dehydration of a cylindrical hydrogel at 25°C and 65% relative humidity. The hydrogel size and shape during this time are represented at the bottom of the figure.

It is apparent that these normalized rates are higher by only about 60–70% than a simple surface dehydration rate under the identical temperature and relative humidity conditions. These values appear to indicate that the surface area should be larger but not as large as what would be expected from a open cell or a fibrillar structure. The surface blistering observed during drying will lead to higher surface area, but it would not be the only factor accounting for the higher rate. Furthermore, almost throughout

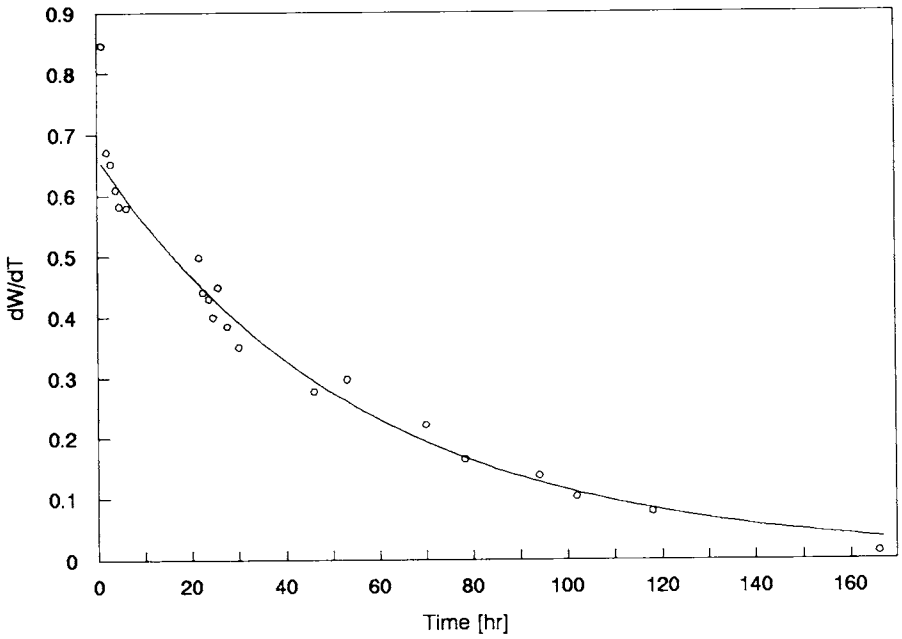

Figure 10 Dehydration rate of sample 5 at 25°C and 65% relative humidity. The continuous line was computed from the exponential dependence of the dehydration rate on the time.

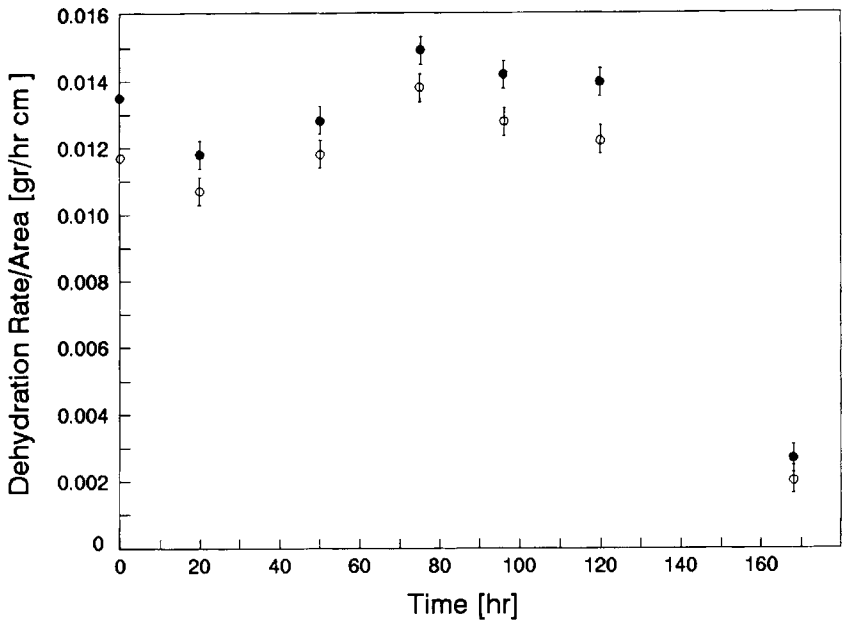

Figure 11 Normalized dehydration rate per unit area at 25°C and 65% relative humidity for sample 5. (Solid circles include the area of lower surface; open circles do not include the area of the lower surface.)

the drying process the dehydration rate per unit area remained constant, although the volume and surface area decreased significantly; and only during the last stage of drying, the water evaporation rate dropped. This dehydration process apparently indicates that no fundamental changes in the morphology occurred during the first 5 days of drying when the water content decreased from about 3600% to about 100% of the polymer dry weight.

DISCUSSION

The swelling of the PVA hydrogels containing NaPAA precipitates is more complex than the swelling of typical noncomposite gels. It may include the following processes:

1. Water molecules diffuse into the hydrogel while methanol diffuses out into the water sink.
2. Precipitates of NaPAA are dissolved as water molecules that penetrate the interior of the gel creating localized high osmotic pressure regions, which further lead to an increase in the rate of water infusion and swelling.
3. The NaPAA chains dissolved in aqueous medium are released out of the hydrogel into the water sink through the hydrogel matrix.

The first process is a typical volume expansion of a network by diffusion of solvent molecules into the gel that leads to a deformation of the constituent polymer chains. In the present case the swelling process is somewhat more complicated as the PVA hydrogels have been swollen in methanol prior to immersing them in water. Thus, during the swelling in water, methanol molecules diffuse out of the gel while water molecules diffuse into the gel. A volume increase corresponding to this process was only about 300% for PVA hydrogels having no NaPAA, whereas addition of equal weight of NaPAA to PVA enhanced the volume expansion to 2000%.

Major volume expansion will occur by the second mechanism. The dissolution of NaPAA leads to a saturated solution of a high osmotic pressure in the gel. This excess pressure can be released by a further increase in the concentration of water in the gel and by the diffusion of the saturated NaPAA solution out of the gel. Apparently, the water infusion rate into the gel is higher than the NaPAA diffusion rate from the gel. This difference will lead to swelling and large volume expansion of the hydrogels. The general phenomenon resembles to some extent an osmotic pump,[10] where the delivery rate is initially constant and proportional to the rate of the water permeation through the membrane wall and the osmotic pressure of the membrane. However, in the PVA gels the pressure leads to the volume expansion, while in the osmotic pump the volume remains

constant and the pressure is released by diffusion of a solution through a delivery orifice. Although a constant rate was observed for the release of NaPAA during the first hour (Fig. 4), this is most likely due to the initial constant dissolution rate of the high-molecular-weight NaPAA and not due to the permeation rate through the PVA hydrogel wall as is the case of the osmotic pump. It should also be noted that the diffusion rate of the osmotic pump starts to decrease after all of the core solute have been dissolved.

Mechanism 3, where embedded solid in a polymer matrix is excluded by diffusion, was extensively studied in various papers dealing with drug delivery systems.[11] It was shown that if the solute is homogeneously dispersed in small precipitates throughout the polymer matrix; the solute concentration increases toward the interior upon immersing the test sample in water.[12] Subsequently, the solute concentration remains constant from a point where a saturated solution is present by the still precipitated solute. Under these conditions the amount of diffused solute is proportional to the square root of the diffusion time. It is interesting to note that during the diffusion of a solute (e.g. water-soluble drug) from a swollen hydrogel, the polymer matrix usually shrinks. For instance, during the release process the size and weight of a water-swollen poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogels was found to decrease.[13] Excessive shrinkage during the release process is significant enough above a certain solute concentration and degree of crosslinking to rupture the hydrogel. No such rupture was observed during the swelling of our PVA hydrogels, even when the concentration of the solute (NaPAA) was higher than that of the PVA matrix. Further, the volume either increased or remained constant, but was not observed to decrease in contrast to the PHEMA hydrogel.

The diffusion of low-molecular-weight solute through water-swollen PVA hydrogels was extensively studied elsewhere[14-21] and was found to be primarily dependent on the crosslink density of the hydrogel, morphology, degree of swelling, and the size and nature of the diffusing species. Simple diffusion of the high-molecular-weight NaPAA through the PVA matrix is most likely too slow to account for its high rate of release into the water phase observed here. Unlike a simple diffusion mechanism of nonionic, low-molecular-weight substances through polymer walls, it is conceivable that in the present case small channels connecting the highly concentrated NaPAA domains are formed upon immersing the sample in water. Through these channels the NaPAA solution will diffuse to the surface of the hydrogel and out into the water sink. After long equilibration the volume of the hydrogels may not change and the NaPAA concentration in the cylindrical sample may decrease so slowly that the diffusive flow will actually adjust to the instantaneous concentration. Under these conditions the rate of diffusion should be proportional to the concentration of NaPAA still remaining in the hydrogel.[22]

Using the data of sample 1 as an example, the mechanism of NaPAA release can be proposed as follows. The swelling of the composite PVA hydrogels does not follow a pure osmotic driven release mechanism. In addition, the polymeric solute is released out from the matrix and the morphology of the composite is altered during the dissolution and swelling process. Thus, the following arguments may justify the use of the power law equation. Namely,

1. the solute particles are small compared to the size of the PVA matrix;
2. they are uniformly dispersed;
3. a sharp front is formed as water molecules penetrate the gel, resulting in the solute concentration gradient that increases linearly toward the center of the sample;
4. the concentration of the solute is constant beyond the water front from a point where precipitates still exist; and
5. the solute is released at a quasisteady rate.

As is demonstrated in Figure 7, the experimental results fit well with this equation [eq. (5)]. The evaluated parameters K and n in eq. (5) further indicate that high initial release rates and further deviation from a time squared dependence are observed for small-sized samples of the composite hydrogels. This is expected because in such samples with a high surface to volume ratio, both the inflow of water and the release (outflow) of NaPAA molecules occur through short pathways before reaching equilibrium. Although the equilibrium volume expansion ratio was independent of the initial sample volume, the rate of the volume expansion during swelling depended on the initial size and shape of the hydrogels. Thus, smaller cylindrical samples expanded faster than larger samples, although all had initially the same diameter but different heights. Generally it appears that a large ratio of surface to volume leads to a high expansion rate.

The inflow of water that triggers the release of NaPAA during swelling is not only affected by the shape and size of the sample, but also by the con-

centration of NaPAA in the PVA gels, the particle size of the suspended NaPAA, and the experimental conditions such as temperature and other solutes in the water. Further complications, which are of great concern primarily when these hydrogels are considered for drug delivery applications, are the relatively large initial burst of release accompanied by a severe distortion of the original shape during swelling, which is particularly noticeable with large samples.

Interesting information can be obtained on the structure of the PVA assembly in the swollen state from the dehydration process. Low water evaporation rates per unit area are expected in cases that water evaporates by diffusing through the polymer matrix, in contrast to direct evaporation from the surface. Furthermore, even if the dehydration is from a surface, even lower rates will result if a significant concentration of solute is present in the water. On the other hand, if the structure of the hydrogel consists of an open cell foamlike interior or fiberlike structure, the real surface area is much larger and will lead to significantly higher dehydration rates. Another possibility is a nonpreferred conformation of the polymer chains in the swollen state. This higher free energy would be an additional driving force for contraction and lead to higher than expected dehydration rates. Usually, swelling of a network lowers the free energy of the system, but it is also possible that the presence of NaPAA and hence the local high osmotic pressure would initially cause a high rate of water infusion and large swelling. Then, after releasing most of the NaPAA, an unfavorable structure will remain.

The morphology consistent with the observed results is a closed cell, foamlike structure with interconnected channels. A similar type of structure was proposed for an ethylene-vinyl acetate copolymer containing water-soluble proteins upon their dissolution in water.[23] This two-phase morphology is plausible from the initial structure where precipitates of NaPAA were embedded in the PVA matrix. Upon dissolution of NaPAA, phase separation takes place where aqueous NaPAA solutions are excluded into domains because PVA and NaPAA are only partially miscible. The high osmotic pressure may lead to the formation of thin interconnecting channels. During drying, water evaporation must proceed primarily by diffusion through the thin water-swollen PVA hydrogel walls and to a lesser extent from the openings of the small channels. The surface blisters mentioned earlier probably are formed at the openings of these channels.

A more detailed study of the morphology is reserved for the subsequent publication of this series.

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