# Water sorption and desorption in 2-hydroxyethylmethacrylate/ methylmethacrylate copolymers

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Cross-linked copolymers of 2-hydroxyethylmethacrylate/methylmethacrylate (HEMA/MMA) with different HEMA contents have been prepared. Water sorption and desorption kinetics have been studied at a temperature of 37°C. The results indicate that the rate controlling step of sorption and desorption is the Fickian diffusion in the swollen polymer. The diffusion coefficient is a function of the water concentration and decreases to zero below a critical value of water content, which depends on the HEMA content.

(Keywords: HEMA/MMA copolymers; water; sorption; desorption; diffusion; kinetics)

## INTRODUCTION

Cross-linked poly(2-hydroxyethylmethacrylate) (PHEMA) gels have been widely proposed as materials for biomedical applications[1], mainly because of their high biocompatibility. However, due to the poor mechanical properties of swollen PHEMA, its use has been limited to applications where good mechanical properties of the material are not required, such as for soft contact lenses or drug release carriers[1]. Only recently, by using the composite mechanics concepts, fibre or net reinforced PHEMA have been designed and proposed as materials for artificial prostheses[2]. Moreover 2-hydroxyethylmethacrylate/methylmethacrylate copolymers have been prepared where by changing the composition it is possible to obtain materials with different water contents and mechanical properties[3].

In a previous paper[3] the mechanical characterization and preliminary data on the water sorption and desorption kinetics of these copolymers were reported. In this paper a detailed analysis of the water sorption–desorption kinetics is presented.

## EXPERIMENTAL

Sparingly cross-linked copolymers of 2-hydroxyethyl-methacrylate/methylmethacrylate (HEMA/MMA) were prepared. The monomer used were: commercial HEMA produced by Rohm and Haas Inc. and MMA produced by BDH Chemicals Ltd. For each copolymer composition the proper amount of HEMA and MMA was poured in a die obtained by inserting a silicon rubber gasket between two superimposed and clamped glass plates. The mixed monomers contained also 0.5 wt% ethylenedymethacrylate (EDMA) as cross-linking agent and 0.1 wt% azoisobisbutyrronytrile (AIBN) as initiator. Copolymers with molar fraction of HEMA, $x_{HEMA}$, equal

to 0, 0.248, 0.435, 0.642, 0.755, 0.874 and 1 were obtained. The polymerization protocol was as follows: immersion of the reacting system in a thermostatic bath at $T = 90°C$ for 1 h; curing of the partially cross-linked sheet in a vacuum oven for 4 h at $T = 100°C$; swelling of the sample in distilled water at $T = 37°C$.

During the swelling step the weight was measured after different times of immersion and the results indicate that, after having attained an apparent constant value, it started to decrease toward an asymptotic value lower than the previous one. This effect can be attributed to a loss of unreacted monomer which diffused through the swollen structure of the copolymer. In fact, once the samples were desiccated, their weight was lower than that of the original material. Therefore, all the sorption and desorption experiments were carried out on samples previously washed in distilled water for a time long enough to eliminate all unreacted material.

The desorption experiments were carried out by placing the swollen samples in an oven at $T = 37°C$ in the presence of silica gel and the water loss $M_1$ was measured by weighing the samples at given time intervals until an asymptotic value $(M_{1a})$ was reached.

This $M_{1a}$ value was not equal to the initial water content, $M_i$, so that water was partly trapped in the copolymer at the end of the desorption cycle. This residual water content, $M_r$, was measured as a difference between the weight of the sample at the end of the desorption procedure and that of a sample which was placed in a vacuum oven at $T = 100°C$ for a time long enough to attain a constant weight.

The sorption kinetics on the same samples used for the desorption experiments were also recorded. The samples with an initial water content equal to $M_r$, were immersed in distilled water at $T = 37°C$, and the water gain, $M_g$, was measured util a constant value $M_{ga}$ was reached.

In *Figure 1* the quantities $M_1$, $M_{1a}$, $M_i$, $M_r$ and $M_{ga}$,

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previously defined, are shown and correlated with $m$ and $m_{d.p.}$, which are the weight of the sample at the time $t$ and the weight of the sample dried at $T = 100°C$, respectively. All the data are referred to $m_{d.p.} = 1$ g.

## RESULTS AND DISCUSSION

In *Figures 2* and *3*, data relative to the water desorption and sorption experiments are reported. The data are plotted *versus* the square root of time, $t^{1/2}$, and in both diagrams an initial rectilinear behaviour is evident. This suggests that both sorption and desorption phenomena are controlled by the Fickian diffusion. However a microscopic observation of the sample during the sorption cycle, shows a sharp boundary between the swol-
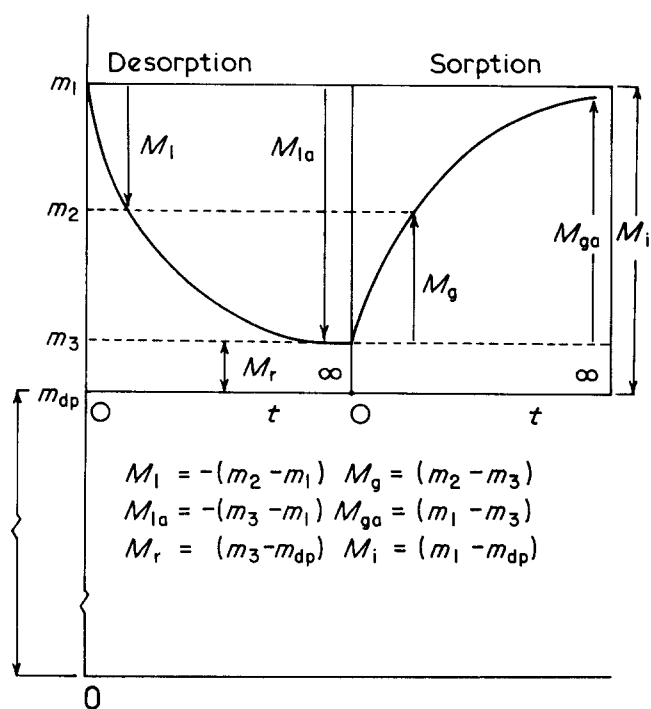
**Figure 1** Schematic diagram of the sorption and desorption kinetics showing the nomenclature used
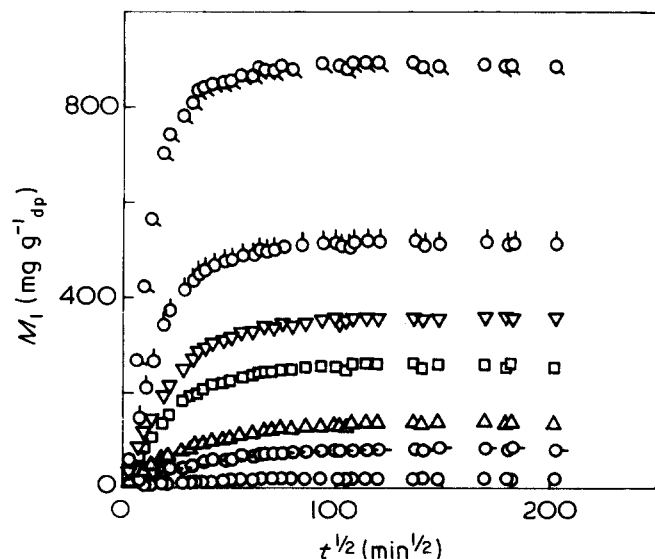
$$M_l = -(m_2 - m_1) \quad M_g = (m_2 - m_3)$$
$$M_{la} = -(m_3 - m_1) \quad M_{ga} = (m_1 - m_3)$$
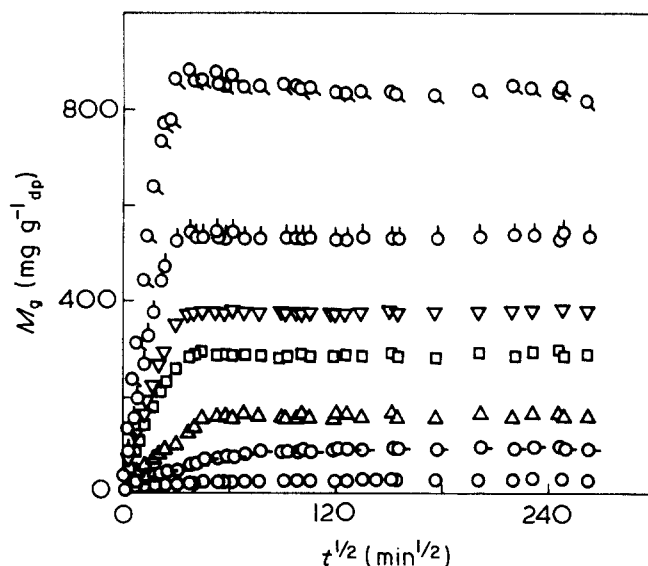$$M_r = (m_3 - m_{dp}) \quad M_i = (m_1 - m_{dp})$$

**Figure 3** Water gain, $M_g$, *versus* the square root of time. For symbols see *Table 1*

len and the unswolled regions, which should generally result in a non-rectilinear dependence of $M_g$ on $t^{1/2}$. As reported in the literature (see for example ref. 4), the penetration of a solvent in a glassy polymer can be divided in two principal steps: (1) diffusion of the solvent in the swollen matrix; and (2) advancement of the swollen–unswollen boundary[5-8]. Here the rectilinear dependency on $t^{1/2}$ suggests that the rate controlling step is the Fickian diffusion in the swollen region, i.e., the penetration of the water in HEMA/MMA copolymers should be a case of pseudo-Fickian diffusion. As previously indicated, the desorption experiment leaves in the polymer a residual water content $M_r$. For the moment assume that the polymers with the $M_r$ initial water content have in sorption a pseudo-Fickian behaviour with constant diffusivity coefficient $D$. In this hypothesis, the sorption data should obey equation (9):

$$\frac{M_g}{M_{ga}} = 1 - \frac{8}{\pi^2} \sum_0^\infty \frac{1}{(2m+1)^2} \exp\left\{ -\frac{D(2m+1)^2\pi^2 t}{l^2} \right\} \quad (1)$$

where $l$ is the thickness of the specimen and $D$ is the diffusion coefficient.

Equation (1) has been derived for a non-swelling solvent but, following Crank[9], it can still be used here provided an appropriate set of references is chosen. With this procedure the thickness of the sheet is constant and equal to the original thickness of the unswollen sample and the diffusion coefficient is that relative to the diffusion of penetrant into the stationary sheet (i.e. $D = D_B^A$, where A is the penetrant and B is the polymer in the sheet[9]).

Therefore, from the sorption data, $M_g/M_{ga}$ for each $x_{HEMA}$ can be calculated and compared with equation (1). Equation (1) gives an unique curve when plotted as $M_g/M_{ga}$ *versus* $\tau^{1/2}$, where $\tau = Dt/l^2$ is a dimensionless time. The initial part of the curve is rectilinear and can be correlated with the equation[9]:

$$M_g/M_{ga} = \frac{4}{\pi^{1/2}} \tau^{1/2} \quad (2)$$

**Figure 2** Water loss, $M_l$, *versus* the square root of time. For symbols see *Table 1*

Using equation (2) with a linear regression on the data

of *Figure 3*, in the rectilinear region, the diffusion coefficients have been calculated for each $x_{HEMA}$ and have been reported in *Table 1* as $D_s$.

In *Figure 4* the experimental data reported *versus* $\tau^{1/2}$ show a very good agreement with the theoretical curve given by equation (1).

The desorption data, reported in *Figure 2*, are apparently similar to those of *Figure 3*, showing an initial rectlinear region and an asymptotic region. But, as previously mentioned, the $M_{la}$ values calculated as the arithmetic mean of the data in the asymptotic region, do not coincide with the $M_i$ values, i.e. the initial water content at $t = 0$. Therefore, there is in the polymer a residual water content. The presence of a residual water content can suggest that the diffusion coefficient of the water becomes zero when the concentration of water decreases below a value $c^*$ corresponding to the residual water content. In this case, in fact, it is theoretically expected[9] that the asymptotic value reached in desorption is $M_{la} = M_i - M_r$, where $M_r$ is the residual water content at the concentration $c^*$. Therefore, assuming a dependency of $D$ on water concentration of the type reported in the insert of *Figure 5*, the desorption kinetics should satisfy equation (1), replacing $M_g/M_{ga}$ with $M_l/M_{la}$ and $D$ with $D_d$.

Equation (1) is plotted in *Figure 5* as $M_l/M_{la}$ *versus* $\tau^{1/2} = (D_d t/l^2)^{1/2}$ where $D_d$ has been determined for each set of data by means of equation (2), replacing $M_g/M_{ga}$ with $M_l/M_{la}$. The values of $D_d$ are reported in *Table 1*.

In *Figure 5* the experimental values of $M_l/M_{la}$ are also reported and compare well with the theoretical curve.

Table 1 Values of the water diffusion coefficients of copolymers of HEMA/MMA at different HEMA content

| $x_{HEMA}$ | $D_s \times 10^7$ (cm$^2$ s$^{-1}$) | $D_d \times 10^7$ (cm$^2$ s$^{-1}$) | Symbol used |
|---|---|---|---|
| 0 (PMMA) | 0.217 | 0.345 | |
| 0.248 | 0.210 | 0.403 | |
| 0.435 | 0.491 | 0.656 | |
| 0.642 | 1.154 | 1.080 | |
| 0.755 | 1.433 | 1.490 | |
| 0.874 | 1.581 | 1.360 | |
| 1 (PHEMA) | 1.850 | 2.110 | |



Figure 5 Water loss, $M_l$, referred to its asymptotic value, $M_{la}$, *versus* the square root of the dimensionless time. The full line is the plot of the equation (2). For symbols see *Table 1*

In the sorption cycle the initial water concentration is $c^*$ and the diffusion coefficient never becomes zero. Therefore, the calculated diffusion coefficient in sorption $D_s$ is expected to be equal to $D_d$. *Table 1*, however shows some difference especially at the higher MMA content. This could be explained assuming that the diffusion coefficient at concentration $>c^*$ is a more complex function of concentration than that reported in the insert of *Figure 5*. In this case $D_s$ and $D_d$ are mean values of the diffusivity on the concentration range between $c^*$ and $c_0$, where $c_0$ is the equilibrium concentration with water at 37°C. Therefore, $D_s$ and $D_d$ can be different if the concentration profiles in desorption and sorption are different.

In fact, previous results[10] on water sorption and desorption in amorphous PMMA show that diffusion coefficients depend on water content and that in the desorption cycle are larger than in sorption. Unfortunately, a quantitative comparison between the results reported here and those of refs. 10 and 11 is not possible for the different structure of the polymers and for the different test temperatures. However, from Figure 3 of ref. 12, for uncross-linked PMMA at 37°C, a value of $0.221 \times 10^{-7}$ cm$^2$ s$^{-1}$ of the water diffusion coefficient in desorption can be obtained. This value compares well with $D_d$ in *Table 1*. The difference can perhaps be attributed to the fact that the PMMA here is sparingly cross-linked.

In the case of PHEMA swollen in water at 37°C, a value of the tracer diffusion coefficient, $D_1 = 2.1 \times 10^{-5}$ cm$^2$ s$^{-1}$ is reported[13].

The mutual diffusion coefficient $D^v$ can be calculated by means of the following equations[14]:
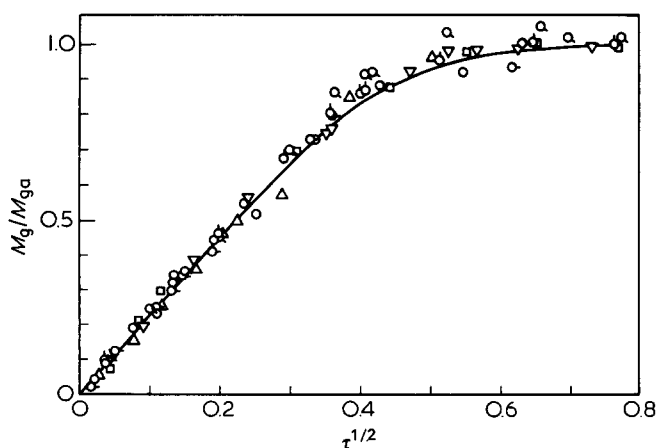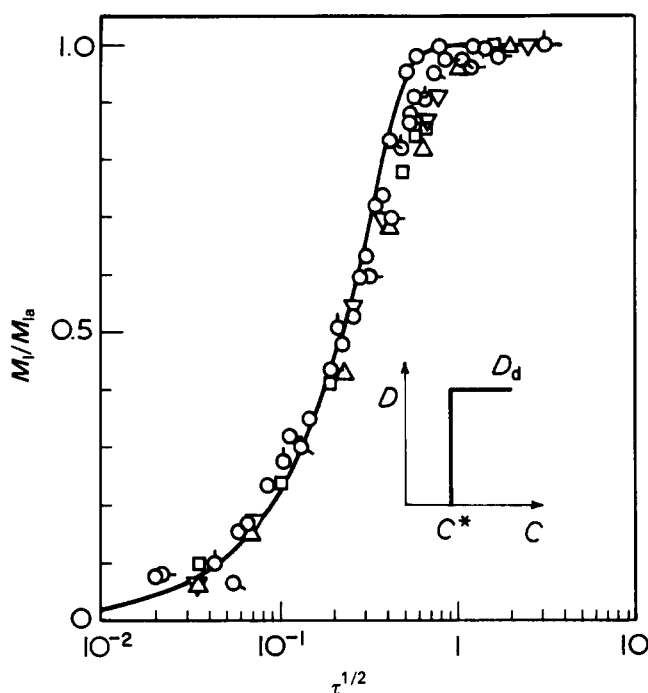


Figure 4 Water gain, $M_g$, referred to its asymptotic value, $M_{ga}$, *versus* the square root of the dimensionless time. The full line is the plot of equation (1). For symbols see *Table 1*

$$D^v = D_1 \frac{d(\ln a_1)}{d(\ln v_1)} \qquad (3)$$

$$\frac{d(\ln a_1)}{d(\ln v_1)} = 2 - v_{ro} + \frac{2(1-v_{ro})\ln(1-v_{ro})}{v_{ro}} + v_1\frac{v_e}{v_o}(1-v_{ro})\left(\frac{1}{v_{ro}^{2/3}} - \frac{1}{2}\right)$$

(4)

where: $a_1$, solvent activity; $v_1$, solvent volume fraction; $v_{ro}$, equilibrium polymer volume fraction; $V_1$, partial molar volume of solvent; $v_e$, number of effective chains in the network; and $V_0$, total volume of undeformed unswollen network.

By using the data reported in the present and a previous paper[13] $d(\ln a_1)/d(\ln v_1) = 0.103$ and $D^v = 2.16 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ have been calculated. Moreover, using the diffusion coefficient $D_A^B$, a $D^v$ value can be computed with the equation[9]:

$$D^v = \frac{D_A^B}{v_{ro}^2}$$

(5)

and it has been established that $D^v = 0.803 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ or $D^v = 0.916 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ if the diffusion coefficient $D_s$ or $D_d$, respectively, is used for $D_A^B$ of PHEMA (see *Table 1*).

These values of $D^v$ are reasonably close taking into account that they are relative to different water concentration conditions.

In conclusion, the kinetics of water sorption and desorption of MMA/HEMA copolymers can be interpretated by a simple diffusional mechanism characterized by a zero diffusion coefficient at water concentration smaller than $c^*$ measured as the residual water content in the desorption cycle.

A final remark concerns this residual water content $M_r$. It has been reported (see e.g. ref. 15) that in PHEMA a part of the absorbed water molecules is strongly bound to specific sites within the polymer networks. It is important to establish whether the residual water is this bound water.

In ref. 15 the bound water in cross-linked PHEMA amounts to 0.28 $\mathrm{g/g_{d.p.}}$, while in ref. 3 a value of 0.0355 $\mathrm{g/g_{d.p.}}$ for $M_r$ is reported. It seems, therefore, that the residual water is not bound water. The residual water seems to be water trapped in a matrix which is not swollen in presence of such small water content and, therefore, has a very low diffusion coefficient.

## ACKNOWLEDGEMENT

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