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S0032-3861(96)00222-4

Polymer Vol. 37 No. 17, pp. 3915–3919, 1996

0032-3861/96/$15.00+0.00

Sorption/desorption properties of water vapour in poly(2-hydroxyethyl methacrylate): 1. Experimental and preliminary analysis

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(Received 16 September 1995; revised 28 November 1995)

The sorption and desorption of water vapour into and from a hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) membrane were examined with the gravimetric method in an integral manner at 37°C. The sorption isotherm of water in PHEMA at 37°C followed Henry's law at lower activities and Flory–Huggins type sorption at higher activities. The water content which leads to a glass–rubber transition within the polymer matrix at the isotherm temperature $[C_g(T)]$ was found to be 0.079, which also coincided with the transition region between the Henry's law sorption and the Flory–Huggins type sorption. When the equilibrium water content was below the $C_g(T)$, the sorption and desorption kinetics followed two-stage and pseudo-Fickian, respectively. The anomalies could be interpreted by either a slow relaxation of polymer networks or a reversible immobilization reaction coupled with the diffusion process. When the equilibrium water content was beyond the $C_g(T)$, both the sorption and desorption kinetics seemed to be sigmoidal. Such behaviour could be a result of the glass–rubber transition, and the prevailing states of water might further complicate the processes of sorption and desorption. Copyright © 1996 Elsevier Science Ltd.

(Keywords: membrane; diffusion; glassy polymer)

INTRODUCTION

Poly(2-hydroxyethyl methacrylate) (PHEMA) is characterized by its hydrophilicity and ability to imbibe water. In addition, its inertness and stability to varying conditions of pH, temperature, and tonicity make PHEMA perfect for many biomedical applications, for example: soft contact lens, prosthetic materials, implants, drug delivery systems, etc.[1–3]. The equilibrium amount of water swelling in PHEMA is probably the most important factor influencing its performance in use such as permeation properties, mechanical properties, surface properties, and biocompatibility of the polymer. Many articles have been published addressing the swelling equilibria and kinetics for the polymer in contact with aqueous solution. Up to about 40% of water can be imbibed into the polymer due to thermodynamical limitation[1,2]. The swelling kinetics are always anomalous (non-Fickian) at room temperature because the swelling involves a glassy to rubbery transition as the intrinsic glass transition temperature (T_g) of PHEMA is about 100–110°C[3–8]. Molecular relaxation of the polymer chains was proposed to explain this behaviour. In a limiting case, Case II transport can happen, that is, a sharp penetrating front of glass–rubber interface appears, the initial weight gain is directly proportional to time, rather than to $t^{1/2}$, as in the Fickian diffusion, and the swelling is completely controlled by relaxation[3–6].

However, to our knowledge, there is no report discussing the sorption of dry PHEMA under vapour water atmosphere as well as the desorption of water from swollen PHEMA under vacuum. As part of an investigation on the applications of PHEMA to controlled drug release[3–6], we studied the transport of water vapour in this polymer through classical sorption/desorption experiments as described by Crank and Park[9]. The sorption part will give us a hint of how much and how fast the water sorption is when a dehydrated dosage made of PHEMA as an excipient is in contact with a moist atmosphere. The desorption part will reveal the kinetics of drying when the dosage form is dehydrated. Furthermore, an attempt was made to understand better the transport mechanisms of water in the hydrophilic polymer.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) monomer was obtained from Kanto Chemicals Co. (Japan) and purified by vacuum distillation with 0.5% CuCl as inhibitor. Benzoyl peroxide (BPO, Kokusan Chemical Works, Ltd, Japan), the free radical polymerization initiator, was used as received. Deionized water was used in the sorption experiments.

Membrane preparation

A mixture of 70% by weight of HEMA monomer, 30% by weight of deionized water, and about 0.2% by

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weight of BPO initiator was first prepared and degassed. Then the mixture was placed between a cleaned two-plate glass mould using a silicone rubber spacer to regulate membrane thickness (about 0.5 mm). Polymerization reaction was carried out at 40°C for the first 4 h and then at 70°C for another 14 h under vacuum or nitrogen blanketing. After complete polymerization, the membrane was obtained in the form of a transparent film. The PHEMA membrane was then removed from the mould and immersed in fresh deionized water for at least 2 days to extract unreacted monomer and additive. Finally, the membrane was dried at 60°C for a week or until no weight loss due to water evaporation and then stored in desiccators under demoisturized atmosphere before further characterization.

Although no crosslinking agent was added to the monomer mixture, the polymer membrane was thought to be lightly crosslinked since diester (ethylene glycol dimethacrylate, EGDMA) is always present in the monoester (HEMA) as a by-product during the preparation of raw HEMA, and upon distillation the disproportionation of monoester[10,11] increases the amount of diester, which functions as a crosslinking agent during HEMA polymerization. In addition, some crosslinking of the polymer due to radical chain transfer mechanisms was suggested[12].

Glass transition temperature measurements

The glass transition temperatures (T_g) for PHEMA of different degree of water contents were determined using a Dupont 910 differential scanning calorimeter (DSC). For a complete dehydrated PHEMA sample, the operating cycle of the DSC started from room temperature to 140°C with 5°C min^{-1} heating rate, then quenched to room temperature to eliminate possible physical aging caused by drying and the cycle repeated. The T_g was determined from the second cycle. The water containing PHEMA samples were prepared by letting the samples be in contact with vapour from the saturated aqueous solutions of selected salts or pure water in desiccators with limited time to achieve the desired water contents. The T_g of these samples were determined by starting the DSC operating cycle from −20°C to 120°C with 5°C min^{-1} rising rate. With higher water content in the membrane, it was more difficult to determine the glass transition temperature. An extrapolating technique was used to determine the water content inside the polymer matrix at the glass transition temperature of 37°C.

Sorption/desorption measurements

The integral sorption/desorption kinetics of water vapours in a PHEMA membrane was determined gravimetrically following the method of Crank and Park[9]. A continuous microbalance (Cahn, C-1000) was used to monitor the water vapour gain or loss in the sample during the sorption or desorption experiment. Detailed descriptions of the apparatus and experimental procedures were given elsewhere[13]. The thickness of the membrane was measured by a digital thickness gauge (Mitutoyo, IDF-112), and was given as 0.046 ± 0.002 cm for an average of 10 measures at different points of the membrane. In the sorption experiments, the membrane was fully desorbed before next run. In the desorption experiments, a pre-equilibrated water-containing PHEMA membrane was used. The water-containing membrane was prepared by equilibrating the sample with a saturated aqueous solution of the selected salt at room temperature.

RESULTS AND DISCUSSION

Sorption isotherm

The sorption isotherm of equilibrium water content in the PHEMA membrane at 37°C is shown in *Figure 1*. The thermodynamic activity of water was determined by the ratio of actual water vapour pressure to the saturated water vapour pressure. The water content was defined as the fraction of sorbed water in the swollen membrane. Because it was difficult to operate the vapour sorption experiment close to the saturated water vapour pressure due to the problem of vapour condensation, the equilibrium sorption amount at unit activity was determined by dipping the PHEMA film into liquid water.

The isotherm behaved differently at lower and higher water activities. The amount of sorbed water at equilibrium increased almost linearly at low water vapour activities, obeying Henry's law isotherm of ideal solution behaviour[14,15]. At higher water vapour activities ($a_1 > 0.6$), the equilibrium amount rose sharply away from the activity axis, and the isotherm of this part could be best decried by the Flory–Huggins type sorption where interaction between water molecules becomes more important than that between water–polymer pairs[15].

It is well known that the hydroxyl groups in PHEMA account for most of the hydrophilicity of the polymer and bring about the hydrogel characteristics due to the formation of hydrogen bonding between them and water molecules. It has been confirmed by both experimental results and molecular dynamic simulation that hydroxyl and many other oxygenated groups are capable of binding water but not so strong to hinder the water from the diffusion process[16,17]. The sorption isotherm of water in PHEMA may be explained from the stoichiometric point of view of the hydrogen bonding formation reaction. One gram of polymer contains about 7.69×10^{-3} moles of hydroxyl group (the same as the number of repeating units of 1 g of polymer). If two hydroxyl groups are needed to interact with one water molecule as shown in *Figure 2*, then 0.069 g of water is needed to saturate all the hydroxyl groups in 1 g of polymer. The

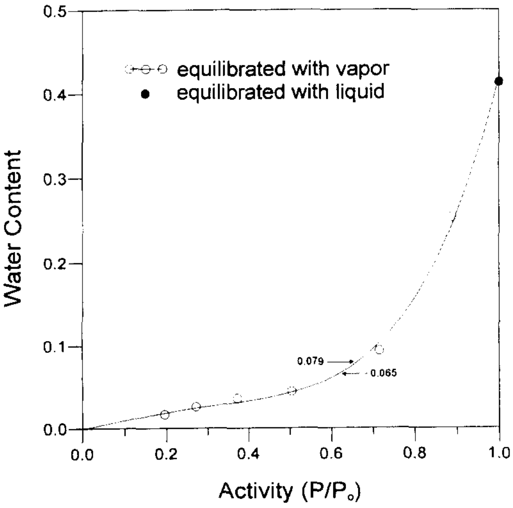

Figure 1 Sorption isotherm of water in PHEMA at 37°C

corresponding water content in the polymer is 0.065 which is also close to the upper limit in the Henry's law region and the incipient of the Flory–Huggins type sorption in the isotherm.

The proposed explanation, in principle, coincides with the concepts of three different states of water, i.e. bounded water, interfacial water and free bulk water[18]. The hydroxyl groups provide sites for hydrogen bonding formation between the polymer segments and water molecules (bounded water). The interaction is significant but is still not strong enough to change the intrinsic properties of a glassy polymer. *Figure 3* indicates that the glass transition temperature (T_g) of PHEMA is linearly decreased by increasing the water content sorbed but still higher than the temperature of the sorption experiments with water content not exceeding 0.079, being recognized as $C_g(T)$, i.e. the penetrant content which leads to a glass–rubber transition within the polymer matrix at the isotherm temperature T ($T = 37°C$ in this case)[19]. The water content with which the polymer has a T_g at 37°C is not far beyond that of the transition point between Henry's law sorption and the Flory–Huggins sorption. It was conceived that the glassy structure of the polymer was preserved and water was sorbed throughout the polymer matrix in the Henry's law sorption region, while a rubbery state of the polymer prevailed as a result of preference for penetrant–penetrant pairs in the Flory–Huggins sorption region[15]. The incorporation of water molecules within the gel will come either as interfacial water or free bulk water, leading to significant swelling and plasticization.

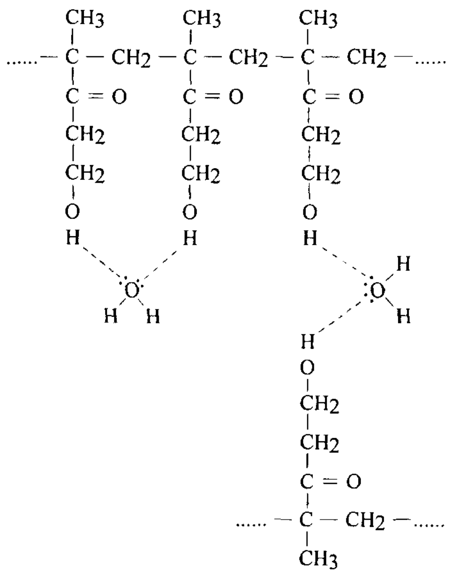

Figure 2 Hydrogen bonding formation between water molecules and the hydroxyl groups of PHEMA

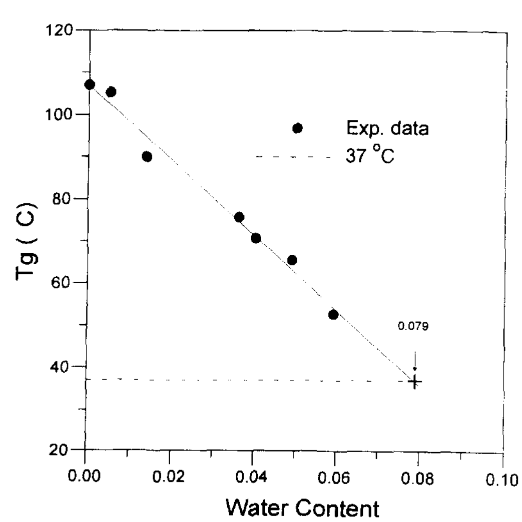

Figure 3 The relationship of the glass transition temperature (T_g) and the water content in PHEMA

This rationale implies that the amount of bounded water can be determined from the sorption isotherm data. The upper limit of the Henry's law sorption region from our data suggested that about 0.069–0.086 g of water could be bounded to the polymer chain in 1 g PHEMA (dry basis).

Sorption kinetics

It has been recognized that the sorption kinetics of solvents into glassy polymer changes with solvent activities and many non-Fickian anomalies have been reported for such systems[8,19]. The sorption kinetics of water vapour sorbed by PHEMA membrane is shown in *Figure 4*. The fractional weight increase (M_t/M_∞) was plotted against reduced time ($t^{1/2}/2L$, where L is the half thickness of the membrane). Two-stage sorption kinetics were observed for vapour activities lower than or equal to 0.51 where the equilibrium water contents were below $C_g(T)$ (*Figures 4a–c*). Sigmoidal sorption was observed for vapour activity of 0.72 where the equilibrium water content was above the $C_g(T)$ (*Figure 4d*). There are at least three different kinds of models which have been proposed to explain the two-stage sorption. The variable-surface concentration[20], diffusion–relaxation model[21,22], and diffusion–reaction models[23,24] were applied to analyse the data. All three models give satisfactory curve fitting to the experimental results and provide certain aspects of physical meaning. A detailed discussion of the mathematical modeling will be given in Part II of this series[25]. Only a brief introduction of these models is given here.

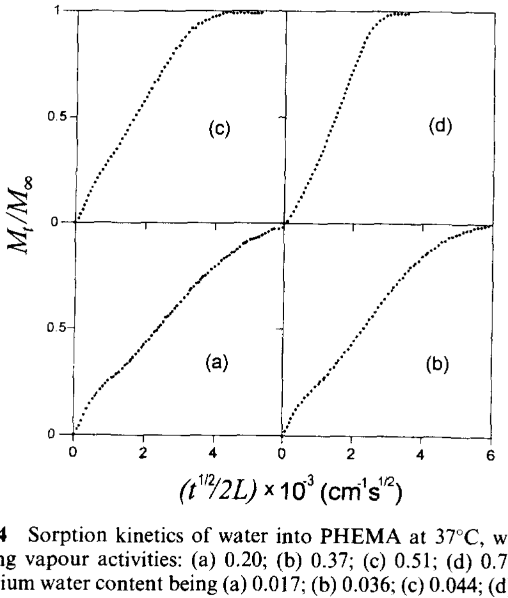

Figure 4 Sorption kinetics of water into PHEMA at 37°C, with the following vapour activities: (a) 0.20; (b) 0.37; (c) 0.51; (d) 0.72. The equilibrium water content being (a) 0.017; (b) 0.036; (c) 0.044; (d) 0.093 as found in *Figure 1*

Both the variable-surface concentration model and the diffusion–relaxation model mainly deal with the assumption that slow relaxation of polymer chains leads to time-dependent equilibrium states of sorption. In the variable-surface concentration model, the surface concentrations of penetrant attain their equilibrium values slowly, and the transport of penetrant within the membrane is still governed by Fick's law. In the diffusion–relaxation model, both diffusion and relaxation are considered to be two simultaneous and independent processes throughout the membrane, with two separated terms for expression of M_t/M_∞ to take account of their effects[21].

The diffusion–reaction model is close to the postulation we made in the previous discussion if we consider that the bounded water is reversibly immobilized by the hydroxyl groups within the polymer network[16,17] and only those unbounded water molecules contribute to diffusion, by Fick's law. The ratio of the pseudo-equilibrium of the first stage to the final equilibrium of the second stage is mainly determined by the equilibrium constant of the reversible immobilization reaction[24].

The sigmoidal sorption of *Figure 4d* at higher activity is the result of a glassy to rubbery transition during the process of sorption as the final equilibrium water content goes beyond $C_g(T)$. In this case, the diffusion rate and the relaxation/reaction rate are much faster than those at lower activities. The characteristic knee of two-stage sorption disappears. By applying the above mathematical models, experimental data are still well reproduced except those in the later part of the curve.

The sorption rates of the membrane also depend on the vapour activities. The higher the surrounding water vapour pressure (activity) is, the fast the sorption reaches equilibrium. The reduced times of 80% sorption $(t^{1/2}/2L)_{0.8}$ are 4.03, 3.75, 2.73 and 2.14 × 10^3 cm^{-1} $s^{0.5}$ for *Figures 4a–d*, respectively. These results are attributed to the plasticization effect of water sorption. From the sorption isotherm, the equilibrium water contents of the polymer are higher for those with higher vapour activities. The more water sorbed, the greater free volume is available for diffusion, and in turn, the faster the sorption rate.

Desorption kinetics

The desorption of water from the PHEMA membrane is shown in *Figure 5*. It is interesting to see the dependence of desorption kinetics on the original water content in the sample. Pseudo-Fickian desorption is found for samples with water contents close to or less than $C_g(T)$ (*Figures 5a* and *b*), while most of the sorbed water can be classified as bounded water. Obviously, the desorption is limited by the reverse immobilization reaction or the slow relaxation process. For those samples containing water content above $C_g(T)$, the desorption curves become slightly sigmoidal (*Figures 5c–f*). In addition to the bounded water, the water in the polymer matrix can be either interfacial or free bulk water depending on the level of water content. The transport mechanisms within this range are much more complicated and are not explained by any available theories despite the desorption being just a reverse process of sorption. The diffusion and the states of water, the relaxation and the rubbery-to-glassy transition of polymer, and the interaction (reaction) between water and polymer all influence the desorption and their coupled effects cannot be ruled out. Further investigation is needed to fully explain these data.

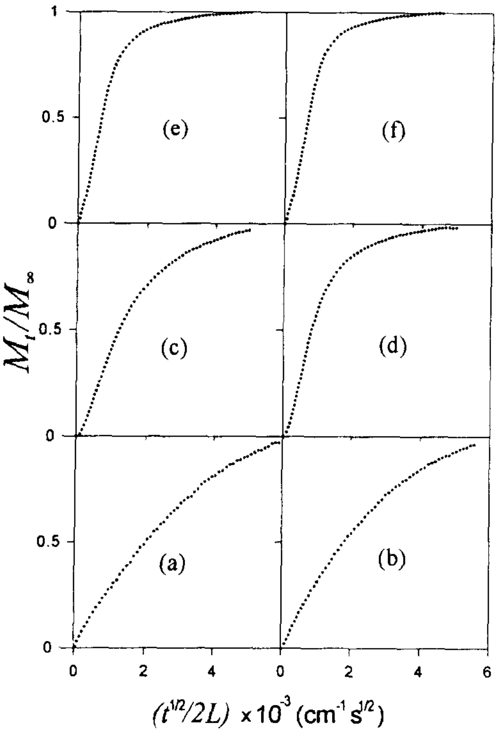

Figure 5 Desorption kinetics of water from PHEMA at 37°C, with the following original water contents: (a) 0.053; (b) 0.075; (c) 0.140; (d) 0.243; (e) 0.374; (f) 0.413

The desorption rate is proportional to the original water content. The higher the water content is, the faster the desorption rate. The reduced times for 80% desorption $(t^{1/2}/2L)_{0.8}$ are 3.90, 3.62, 2.57, 1.66, 1.19 and 1.12× 10^3 cm^{-1} $s^{0.5}$ for *Figures 5a–f*, respectively. Although the transport mechanisms are not clear at this time, the data suggested that the desorption rate is dependent on the states of water, the free bulk water being easiest and the bounded water the most difficult to remove from swollen PHEMA, while median desorption rate might be obtained for interfacial water.

CONCLUSIONS

In this paper, we examined the sorption and desorption of water vapour into and from a hydrophilic PHEMA membrane. There are some unique results summarized as follows: (1) The sorption isotherm of water in PHEMA at 37°C follows Henry's law at lower activities and Flory–Huggins type sorption at higher activities. The water content at the transition region between the Henry's law sorption and the Flory–Huggins sorption coincides with $C_g(T)$, the water content which leads to a glassy-to-rubbery transition at the isotherm temperature. (2) In the range of Henry's law sorption, the sorption of water molecules is postulated by the hydrogen bonding formation between one water molecule and two hydroxyl groups in the polymer. The stoichiometric calculation supports the postulation; however, other techniques may be required for further confirmation. (3) The sorption of water consists of a two-stage behaviour or a sigmoidal behaviour when the equilibrium water content is lower or higher than $C_g(T)$, respectively. The anomalies can be modelled by using Fickian law and taking either a slow relaxation process or a reversible immobilization reaction into consideration. (4) Due to the limitation of the slow relaxation process or the rate of the reverse immobilization reaction, the desorption of water is pseudo-Fickian for the PHEMA membrane in which the water contents are close to or less than $C_g(T)$. If the water content is higher than $C_g(T)$, the desorption curve is close to sigmoidal. The diffusion and the states of water, the relaxation and the rubbery-to-glassy transition of polymer, and the interaction between water and polymer all participate in the desorption process, the kinetics being too difficult to be described by a simple model, and the mathematical modelling remains to be solved in future studies.

ACKNOWLEDGEMENT

This work was supported by research grant NSC-81-0402-B-155-501 from the National Science Council of the Republic of China.

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