Polymethyl methacrylate plus water: sorption kinetics and volumetric changes

D. T. Turner
Dental Research Center, University of North Carolina, Chapel Hill, NC 27514, *USA*

(*Received* 26 *February* 1981; *revised* 6 *August* 1981)

Sheets of polymethyl methacrylate were weighed periodically in water and, after surface mopping, in air. A case was made for dual mode sorption kinetics with 40–60% of the water accommodated in microvoids and the remainder taken up by swelling. The kinetics of sorption departed from Fick's laws in ways which appeared to be mutually inconsistent. For example, the value of the diffusion coefficient appeared to increase not only in the course of sorption but also in desorption. This inconsistency was interpreted as an artifact due to a retarded swelling component of dual mode kinetics.

Keywords Kinetics, sorption, volume; polymethyl methacrylate; swelling; desorption

INTRODUCTION

Water sorption by polymethyl methacrylate (PMMA) has been reviewed in the broader context of sorption of a variety of penetrants by glassy polymers[1–4]. The present work is a contribution to the already extensively investigated subject of the kinetics of sorption but is novel in the way it emphasizes the relatively neglected aspect of accompanying changes of volume. Previously in analyses of the sorption kinetics of the system PMMA/H_2O it was simply assumed that the volumes of polymer and water are additive.

Sorption studies are usually made by stepwise equilibration of polymer samples in contact with vapour, in order to learn from boundary conditions which can be imposed by control of the pressure variable[5–7]. Such studies indicate conformity with Fick's laws of diffusion only at lower pressures[5,6] and, therefore, ideal behaviour is not to be expected for sorption of liquid water. Notwithstanding, only minor departures from Fick's laws were reported by Kovacs, the diffusion coefficient apparently increasing slightly with increasing uptake of water[8]. More remarkably, Braden subsequently found conformity with Fick's laws both in sorption and desorption[9]. This report of ideal behaviour under such simple experimental conditions motivated the present work. However, Braden worked with proprietary PMMA materials of unspecified composition and here it was preferred, following Kovacs, to use 'Plexiglas' which is known to be a simple homopolymer of methyl methacrylate.

Initial experiments pointed to a need to establish whether water is taken up solely by swelling or whether there is a dual mode mechanism, with a component accommodated in pre-existing 'microvoids', of the kind accepted to account for the sorption of gases by glassy polymers such as polyethylene terephthalate[10] and polystyrene[11]. In respect of a swelling component, there is decisive evidence that the linear dimensions of dental prostheses made of PMMA increase on wetting and decrease on drying[12]. But, because of complex geometry, it does not seem possible to calculate whether such changes are in quantitative agreement with the simple 'rule' of additivity of volumes. Bueche addressed this question directly by recognizing that sorption in voids should result in a significant increase in density whereas, in contrast, sorption accompanied by swelling should cause relatively little change. He concluded, from limited experimental data, that in sorption 'the volumes are nearly additive'[6].

EXPERIMENTAL

Samples were taken from sheets of PMMA of high molecular weight ($>10^6$) retaining only small amounts of residual monomer (Plexiglas, Rohm and Haas Company, Philadelphia). A sawn massive sample (~ 5.2 g) had a mean thickness of ~ 0.5 cm. Other samples were machined to dimensions $\sim 7.5 \times 2.5$ cm from sheets of nominal thickness 0.07 cm; a mean thickness was calculated from measurements of surface area, weight, and density. In a few experiments these samples were examined directly and were conditioned in the laboratory at a relative humidity in the range 40–60%. Generally samples were dried in air at room temperature over anhydrous calcium sulphate (Drierite, W. R. Hammond, Ohio). A few samples were heated gradually, in 8 h, in vacuum up to 95°C. They were maintained at this temperature in vacuum, some 5°C below T_g, for one week and then gradually cooled back to room temperature. Finally the samples were conditioned in dry air at room temperature. Finally the samples were conditioned in dry air at room temperature. The main purpose of this treatment was to expel residual monomer and to ensure rigorous drying. The heat treatment is described in detail lest it affect microstructure.

Preliminary experiments compared three methods for following volumetric changes during water sorption: dilatometry, microscopic changes in the diameter of spherical beads, and the displacement method of Archimedes. The latter method was chosen because it was both more precise and convenient. Samples were immersed in distilled water at laboratory temperature (23.5 ± 0.5°C). The weight in water (W_w) was determined, by suspending the sample from a silk fibre (0.4 mg), using a Mettler Digital Balance of precision ± 0.05 mg. The weight in air (W_a) was determined after wiping the sample

0032-3861/82/020197-06$03.00

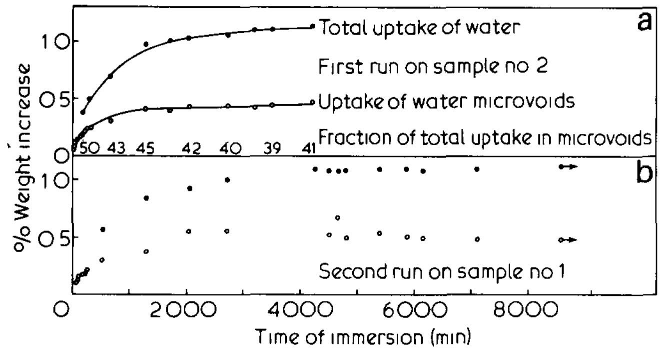

Figure 1 Total water sorption and filling of microvoids (samples conditioned in laboratory).

dry, within one minute, before re-immersion in water. The total uptake of water was expressed as a weight percentage and, analogously, the uptake in microvoids calculated from the expression $100(W_{w,t}-W_{w,0})W_{a,0}^{-1}$, where the second subscript refers to time of immersion. The fraction of the total water uptake which is accommodated without any expansion of the sample, in microvoids, was calculated as $(W_{w,t}-W_{w,0})(W_{a,t}-W_{a,0})^{-1}$.

Desorption measurements were made by following weight changes of samples momentarily removed from dry air. No attempt was made to monitor volumetric changes during desorption.

RESULTS AND DISCUSSION

Volumetric changes

A practice run was made on a sample which had been conditioned in the laboratory. It was then left to dry to constant weight in the laboratory and a second run made (*Figure 1a*). Within an immersion period of one week the total uptake levelled off near 1.2%; about one-half of the water was accommodated in microvoids. The trend of these results was determined more precisely in a first run on a second sample (*Figure 1b*). After a few hours the fraction of water accommodated in microvoids was 0.5, declining to 0.4 in the course of a few days and then remaining constant.

The results given above are for samples which, conditioned at room humidity, contained about 0.6% water prior to immersion. Subsequently the second sample was dried in air in presence of anhydrous calcium sulphate. After such conditioning the total uptake of water was 1.7% and the fraction accommodated in microvoids declined from an initial value of 0.5 to 0.45 (*Figures 2a* and *b*).

Finally a sample which had been heat-treated, as detailed previously, was found to give similar results (*Figure 3a*) except that the fraction of water accommodated in microvoids was initially somewhat higher, declining from 0.6 to 0.48 (*Figure 3b*). These results were obtained in a second run, after drying. The first run gave similar results for total uptake but the uptake in microvoids was not monitored.

Further information about the mode of sorption of water by PMMA can be deduced from the relationship between density and moisture content. To this end consider a unit volume of an initially dry polymer, of density ρ_0, which takes up w wt% water. Suppose that a fraction, f, of the water contributes to an increase in volume. The density of the moist polymer is given by equation (1), in which ρ_w is the density of water:

$$\rho=\frac{\rho_0(1+w/100)}{1+wf/100\rho_w} \qquad (1)$$

Plots of ρ/ρ_0 vs. w can be derived from equation (1) for various values of f ranging between the extreme cases in which the water contributes all its volume to the polymer ($f=1.0$) to that in which it contributes nothing ($f=0$). Experimental data are available for comparison due to Ender[13] and to Kimmel and Uhlmann[14]. The latter authors gave a graph summarizing the relationship between density measurements, made at 23°C, and moisture content. Data read off this graph will be seen to approximate the case in which about half the water is accommodated in microvoids, i.e. $f=0.5$ (*Figure 4*). This deduction is consistent with the results of the present work.

In order to give a broader view of volumetric changes during the sorption of water, previous results will be cited

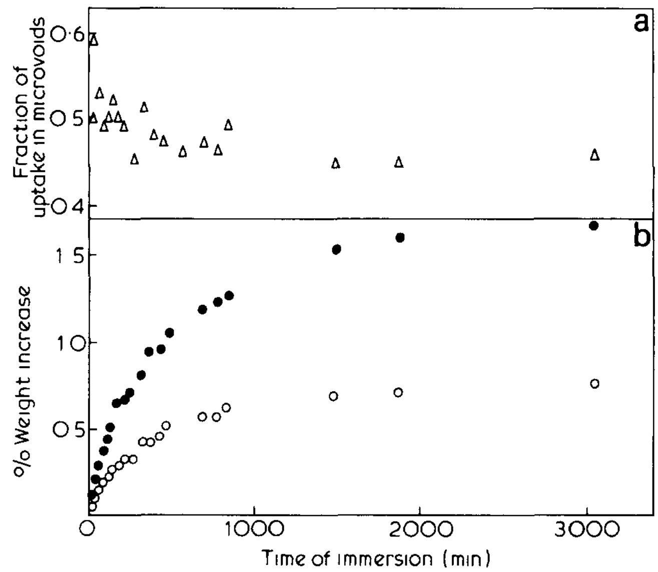

Figure 2 Total water sorption and filling of microvoids (dried sample). ●, Total uptake of water; ○, uptake in microvoids; △, fraction of total uptake in microvoids

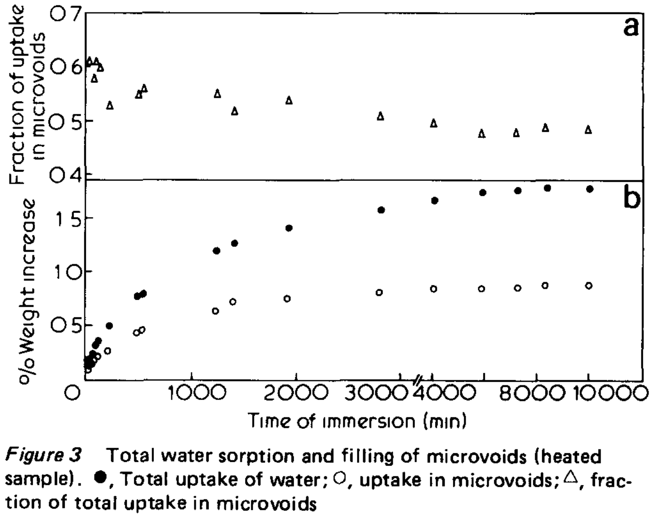

Figure 3 Total water sorption and filling of microvoids (heated sample). ●, Total uptake of water; ○, uptake in microvoids; △, fraction of total uptake in microvoids

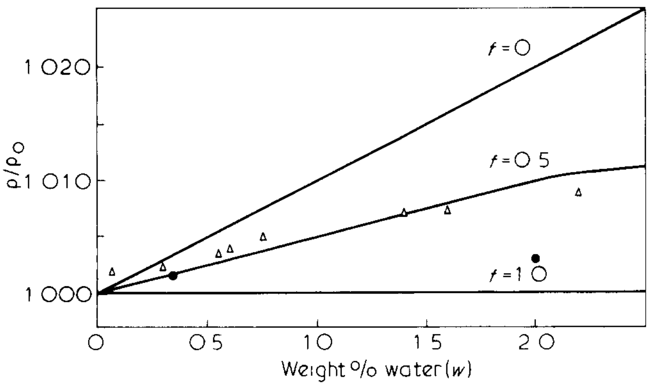

Figure 4 **Relationship between density ratio of PMMA and moisture content; equation (1). △, Ref. 14; ●, ref. 6**

for other glassy polymers. It was reported that 'the volume of the system cellulose–water vapour was found to be much smaller than that given by the components cellulose and condensed water as long as the amount of adsorbed water was below 4%'. It was suggested that water was chemisorbed, in internal surfaces, with an effective density of 2.4 g cm^{-3} (ref. 15). For polyvinyl alcohol ($T_g \sim 85$ °C) it was stated that in the concentration range studied, $\geqslant 1$ wt%, the partial molar volume of water remained constant near 18 cm^3 mol^{-1}. It was concluded that 'swelling occurs to the extent predicted by approximate additivity of volumes'[16]. More recently, extensive work has been done on the sorption of water and other penetrants by polyarylates[17]. Results on water sorption were reported for a polycondensate of phenolphthalein and terephthalic acid[18]. The density obtained using mercury was 1.310 g cm^{-3} as compared to a value of 1.280 g cm^{-3} gauged in an aqueous density gradient column. The difference in these values was attributed to the accommodation of water in pores to the extent of 0.018 cm^3 g^{-1}. In other experiments the total uptake of water was determined gravimetrically as 0.021 cm^3 g^{-1} and, therefore, the fraction of water accommodated in pores was 0.86[18]. This previous work shows that in some cases glassy polymers can take up water, partially, without a corresponding increase in volume.

There is a big conceptual jump in proceeding from the cautious statement ending the preceding paragraph to adoption of a hypothesis as specific as microvoid filling. Initially this jump is justified by analogy with acceptance of the dual mode hypothesis to account for previous results on gas sorption. Eventually, however, retention of this hypothesis will require demonstration of the existence of microvoids by characterization of properties such as size. One source of information is in published data on sorption isotherms but this presents problems of analysis. Thomas analysed his data by the *BET* method and deduced that each sorption site in saturated PMMA accommodates about five molecules of water[5]. One objection to this procedure is that water sorption data are more appropriately analysed by de Boer–Zwikker–Bradley polarization theory (ref. 19). Sorption isotherms may also be analysed by reference to Kelvin's equation to estimate a void size distribution[20]. This has not been done for PMMA and judging from the plots presented by Thomas and also from plots of the data tabulated by Brauer and Sweeney[7] this approach would be dubious because the isotherms approximate to the less tractable type III class (ref. 21). A less conventional approach is by analysis of small angle X-ray scattering data. Recently Morosoff and Stannett used this method to estimate a total void fraction of 7×10^{-3} in certain samples of polyacrylonitrile which had been shown to have unusual transport properties[22]. In principle, this method can be extended to include void size as a parameter but its discrimination is expected to decrease as molecular dimensions are approached[23].

Kinetics of water sorption

The samples studied in the present work approximate to thin flat sheets in which diffusion through the edges may be neglected (the range of applicability of this approximation has been studied experimentally for the water sorption of PMMA by Kovacs[8]). The solution to Fick's laws for sorption is given by equation (2), in which M_t and M_∞ are the masses of penetrant at times t and infinity, respectively; $2\,l$ is the thickness of the sheet; D is the diffusion coefficient. For desorption, the masses refer to loss of penetrant[24]. Conformity to Fick's laws may be diagnosed by showing that initial experimental data fit a single straight line, according to equation (3), which is an approximation of equation (2), for samples differing in thickness and also in modes of both sorption and desorption. Such conformity was found by Braden[9] who, additionally, with the value of D derived thereby, demonstrated a good fit to equation (2) up to the maximum value of M_t/M_∞ of unity.

$$\frac{M_t}{M_\infty}=1-\frac{8}{\pi^2}\sum_{n=0}^{n=\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2Dt}{4l^2}\right] \tag{2}$$

$$\frac{M_t}{M_\infty}=2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{3}$$

Results for the massive sample, plotted according to equation (3), are compared with Braden's most extensive set of data (*Figure 5* and inset). The slope drawn gives a diffusion coefficient of $D=0.67\times10^{-8}$ cm^2 s^{-1} which is similar to Braden's value of 0.54×10^{-8} cm^2 s^{-1}. Thus, on a summary view, the present results might be judged to be in rough agreement with previous work but to include minor discontinuities which, however, are considerably

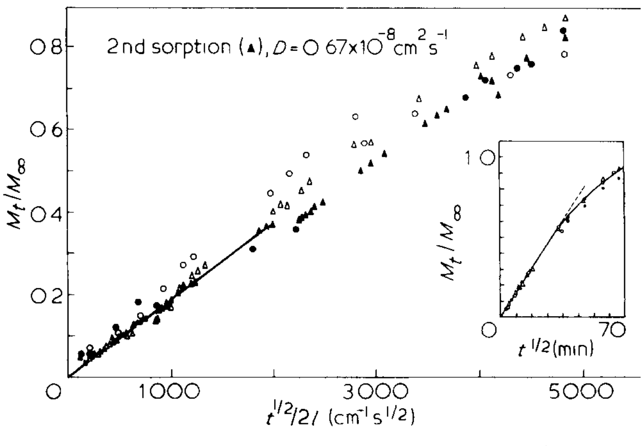

Figure 5 **Sorption and desorption kinetics; equation (3) (massive sample). ●, 1st run (sorption from laboratory conditioning to ultimate uptake of 1.17%); ○, 2nd run (desorption by drying to loss of 1.91%); ▲, 3rd run (sorption to 2.14%); △, 4th run (desorption to 2.00%). Inset[9] : ●, 1st run (sorption); △, 2nd run (desorption); ○, 3rd run (sorption)**

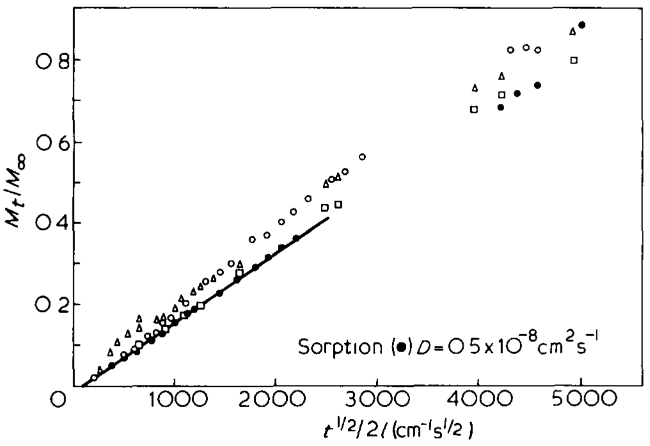

Figure 6 Sorption and desorption kinetics; equation (3) (heated sample). Data from *Figure 3*. ●, 1st run (sorption); △, (microvoid filling, equation 4); ○, 2nd run (desorption); □, 3rd run (sorption)

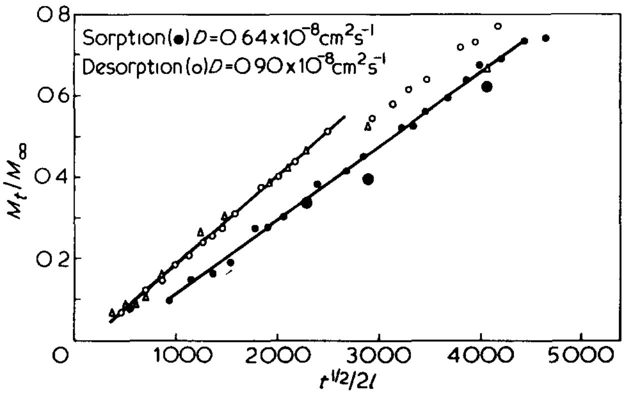

Figure 7 Sorption and desorption kinetics; equation (3) (samples conditioned in laboratory). Data from *Figure 1*. ●, 1st run (sorption); △, (microvoid filling, equation 4); ○, 2nd run (desorption). ●, 1st run (sorption of a second similar sample)

larger than experimental error. The cause has not been elucidated but it is suspected that the discontinuities are the result of swelling forces. In any event, they are less pronounced in thinner samples (*Figures 6* and *7*). For possibly related phenomena in sorption isotherms of various ceramics and metals, where data points were collected in unusually small intervals (see ref. 25).

Kinetic data can also be derived about the filling of microvoids, from changes of weight of samples maintained in water, by reference by equation (4) which contains terms defined in an earlier section:

$$\frac{M_t}{M_\infty}=\frac{W_{w,t}-W_{w,0}}{W_{w,\infty}-W_{w,0}} \tag{4}$$

In explanation of equation (4) the specimen when initially immersed in water weighs $W_{w,0}$ (i.e. in water). After immersion for a time t the weight, in water, increases to $W_{w,t}$. It is assumed that this increase in weight is due to accommodation of water in microvoids. Note that water taken up by swelling does not, according to the rule of additivity of volumes, influence the weight in water because of the exactly compensating upthrust. The rate of microvoid filling, generally similar to the rate of desorption, eventually exceeds the rate of total sorption (*Figures 6* and *7*).

A major departure from ideal behaviour is that, away from the extremities bounded by $t=0$ and $t=\infty$, the rate of desorption is greater than the rate of sorption (*Figures 5* to *7*). This trend is similar to that reported by Kovacs and by Bueche, for a baked out film, at a relative humidity of 92%. Bueche displayed his data using another approximation to equation (2) which applies at higher values of t:

$$\log_e\left(1-\frac{M_t}{M_\infty}\right)=\log_e\left(\frac{8}{\pi^2}\right)-\frac{\pi^2 Dt}{4l^2} \tag{5}$$

Data, for the most comparable, heat-treated, sample (*Figure 6*) are replotted according to equation (5) and shown to be similar to Bueche's findings (*Figure 8* and inset). Thomas, under apparently comparable conditions, reported just the reverse relationship, i.e. desorption rate <sorption rate. The reason for these discrepancies is unknown.

A second major departure from equation (2) is to be seen in the increasing initial slope of kinetic plots for both total sorption and desorption (*Figures 6* and *7*). This might be interpreted to mean that D is not a constant but, instead, increases in value. Such an interpretation was made by Kovacs by reference to values of D calculated from approximations of equation 2 viz. equation (3) ($M_t/M_\infty \leqslant 0.5$) and equation (6) ($M_t/M_\infty \geqslant 0.36$).

$$D=\frac{-l^2}{4t}\left[0.0851+0.933\log_{10}\left(1-\frac{M_t}{M_\infty}\right)\right] \tag{6}$$

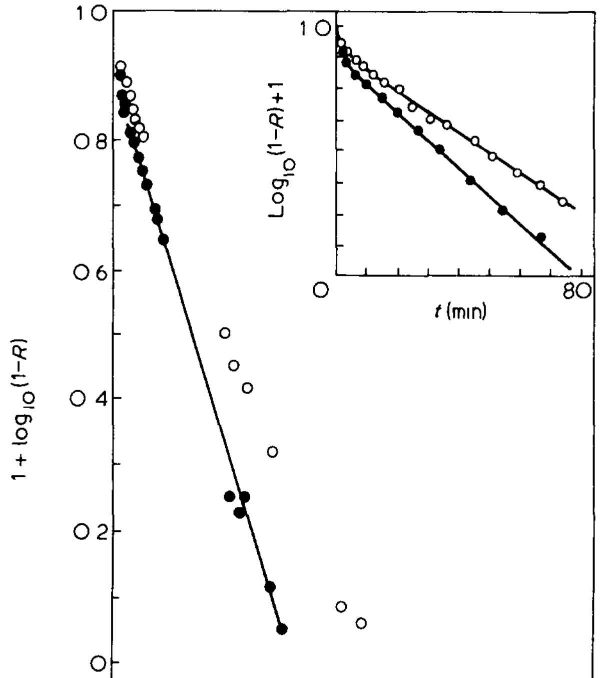

Figure 8 Sorption and desorption kinetics; equation (7) (heated sample). Data from *Figure 3* and ref. 6 (inset). ○, (sorption); ●, (desorption); $R = M_t/M_\infty$

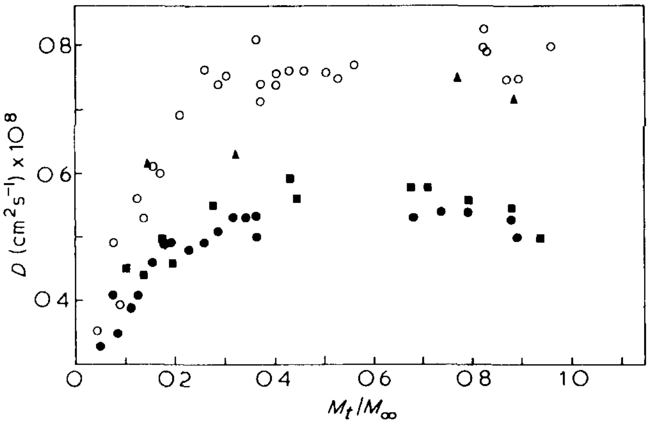

Figure 9 Values of D (equations 3 and 6) *versus* M_t/M_∞ (heated sample). Data from *Figure 6*. ●, (sorption); ○, (desorption); ▲, (sorption data of Kovacs transposed from 18° to 24°C, using an activation energy[5,31] of 10.1 kcal/mole[6])

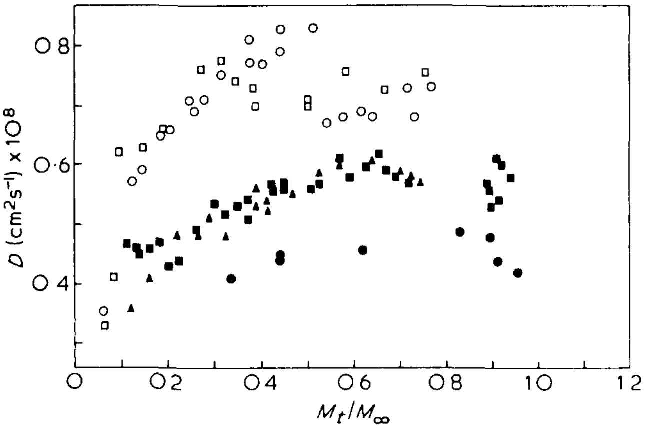

Figure 10 Values of D (equations 3 and 6) *versus* M_t/M_∞ (samples initially conditioned in laboratory). Data from *Figures 2* and *3*. ●, ■, ▲, (sorption); ○, □, (desorption)

Analysis of the data in *Figures 6* and *7* confirm a similar trend in plots of D *versus* M_t/M_∞. More precisely, values of D increase initially and then tend to level off in both sorptive and desorptive modes (*Figures 9* and *10*).

In an attempt to explain the trend described above, consider a likely course of events when a dry sample of PMMA is immersed in water. The zone immediately adjacent to the surface takes up water both by the filling of microvoids and by a process which involves swelling. The latter process, because of retarded contributions from components with long relaxation times[26,27], continues to contribute to the take up of water even after the wetting front has moved on. As a result there is an acceleration in the rate of sorption which continues until the swelling in the surface zone reaches an equilibrium value. Thereafter, on the simplest view, the swelling zone and the wetting front keep pace and a constant value is derived for D until such time as the fronts from the two surfaces of the sample meet. An increase in the rate of desorption may be visualized in a similar manner although in this case the increment in rate is to be attributed to water slowly lost from a contracting zone behind the 'dry' front (*Figure 11*).

The features described above appear to correspond to a small contribution to Fickian sorption by Case II sorption (ref. 28).

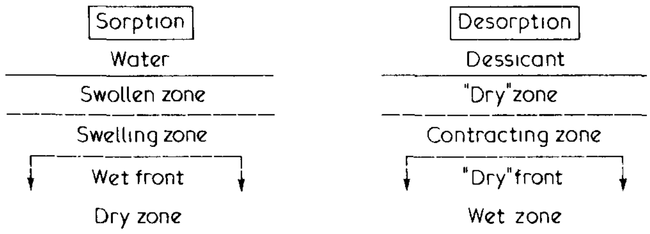

Figure 11 Retarded contribution to M_t from the swelling (or contracting) zone

More easily analysed data revealing the true dependence of D on M_t/M_∞ were obtained by Barrie and Platt in stepwise experiments in which water vapour was allowed to diffuse into samples of PMMA having initially uniform concentrations of water. It was shown that D decreases as the concentration of water is increased and this trend was attributed satisfactorily to decreasing mobility as the water molecules participate increasingly in cluster formation[29,30].

CONCLUSION

The object of finding a simple system which conforms to Fick's laws was not realized. Instead, along with minor discontinuities in plots of kinetic data, two major departures from Fick's laws were confirmed. Possibly the closeness to ideality of Braden's results are due to some difference between proprietary materials which he studied and simple PMMA. In this respect it should be noted that such proprietary materials commonly include a particulate phase of linear PMMA in a crosslinked matrix. Proceeding methodically to an intermediate level of complexity, studies have been initiated, in collaboration with Ms. A. K. Abel, to find whether copolymers of methyl methacrylate and ethylene glycol dimethacrylate conform to Fick's laws.

The observation that the diffusion coefficient appears to increase in the course of both sorption and desorption, could be explained qualitatively by invoking a retarded swelling component of dual mode sorption. Evidence consistent with dual mode sorption was obtained by analysis of changes of density during sorption. A further step in this work is to find whether the existence of microvoid components can be validated by a characterization of their size. To this end experiments are in progress, in collaboration with Dr N. Morosoff, to apply the small angle X-ray scattering technique to dry PMMA.

ACKNOLLEDGEMENTS

Advice from Professor V. Stannett, Dr N. Morosoff, and Dr E. E. LaBarre is gratefully acknowledged. This investigation was supported by USPHS Research Grant No. DE02668 from the National Institute of Dental Research and by General Research Grant No. RR05333 from the National Institute of Health.

REFERENCES

1 Fujita, H *Fortschr. Hochpolym.-Forsch* 1961, **3**, 1
2 Rogers, C. E. in 'Physics and Chemistry of the Organic Solid State', (Eds D. Fox, M. M Labes and A Weissberger), Interscience, 1965, New York, pp 509–635
3 Barrie, J A in 'Diffusion in Polymers', (Eds. J Crank and G S

Park), Academic Press, 1968, London, p 259

4 Molyneux, P in 'Water: Vol 4', (Ed. F. Franks), Plenum Press, 1975, New York, Ch 7, pp 703–721

5 Thomas, A. M. *J. Appl. Chem* 1951, **1**, 141

6 Bueche, F. *J. Polym. Sci.* 1954, **14**, 414

7 Brauer, G. M. and Sweeney, W. T. *Modern Plastics* 1955, **32**, No. 9, p 138

8 Kovacs, A. *J. Chim. Phys.* 1948, **45**, 258

9 Braden, M. *J. Prosthet. Dent.* 1964, **14**, 307

10 Michaels, A. S., Vieth, W. R. and Barrie, J. A. *J. Appl. Phys.* 1963, **34**, 1

11 Vieth, W. R., Frangoulis, C. S. and Rionda, Jr., J A. *J. Colloid Sci* 1966, **22**, 454

12 Woelfel, J. B., Paffenbarger, G C. and Sweeney, W. T., for a convenient review see Souder, W and Paffenbarger, G. C., 'Physical Properties of Dental Materials', NBS Circular **C433**, 1942, pp 165–169

13 Ender, D H. *ScD Thesis*, Dept. of Mechanical Engineering, Massachusetts Institute of Technology, 1967 (as cited in ref. 14)

14 Kimmel, R. M. and Uhlmann, D. R. *J. Appl. Phys.* 1970, **41**, 2917

15 Filby, E. and Maass, O. *Can J. Res.* 1932, **7**, 162

16 Long, F. A. and Thompson, L. J. *J. Polym. Sci.* 1955, **15**, 413

17 Tsilipotkina, M. V., Nechayeva, O. V., Bessonov, Yu. S., Sidorov, N A., Tager, A. A. and Shtarkman, B. P. *Vysokomol. Soedin.* 1975, **A17**, 1591 (Engl. transl. *Polymer Sci. USSR* 1975, **17**, 1833)

18 Tikhonova, N. I., Kazantseva, V. V., Teies-Akun'ya, G., Rudakova, T Ye. and Askadskii, A. A. *Vysokomol. soyed.* 1978, **A20**, 1543 (Engl. transl. *Polymer Sci. USSR* 1979, **20**, 1740)

19 Ling, G. N. in 'Water Structure at the Polymer–Water Interface', (Ed. H. H. G. Jellinek), Plenum Press, 1972, New York, pp 4–13

20 Sheppard, S. E. and Newsome, P. T. *J. Phys. Chem.* 1929, **33**, 1817, *et seq.*

21 Gregg, S. J. and Sing, K. S. W. 'Adsorption, Surface Area and Porosity', Academic Press, 1967, London, pp 6–9 *et seq.*

22 Morosoff, N. and Stannett, V. *J. Macromol. Sci.—Phys.* 1980, **B17(1)**, 157

23 Morosoff, N., private communication

24 Crank, J. 'The Mathematics of Diffusion', Clarendon Press, 1957, Oxford, Ch IV

25 Brunauer, S. 'The Adsorption of Gases and Vapors', Princeton Press, 1943, London, pp 346–348

26 Bagley, E. and Long, F. A. *J. Am. Chem. Soc.* 1955, **77**, 2172 *et seq.*

27 Newns, A. C. *Trans. Faraday Soc.* 1956, **52**, 1553

28 Barrie, J. A. and Platt, B. *Polymer* 1963, **4**, 303

29 Alfrey, T., Gurnee, E. F. and Lloyd, W. G. *J. Polym. Sci.* (*C*) 1966, **12**, 249

30 Barrie, J. A. and Machin, D. *Trans. Faraday Soc.* 1971, **67**, 244, 2970

31 Zhurkov, S. N. and Ryskin, G. Ya. *Zhur. Teknicheskoi Fiz.* 1954, **24**, 797