Water sorption of poly(methyl methacrylate): 3. Effects of plasticizers

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(Received 24 February 1987; accepted 27 March 1987)

Plasticized poly(methyl methacrylate) was made by γ-irradiation of mixtures of monomer and various phthalates. Samples were immersed in water and uptake and diffusion coefficients determined. More reliance was placed on determinations made in desorption because these did not involve complications due to loss of components by dissolution. As expected, plasticizers reduced water uptake simply due to their more hydrophobic nature. An additional reduction was attributed to the filling, by plasticizer, of microvoids which otherwise would have been able to accommodate water. The diffusion coefficient of water increased with plasticizer content and there was an indication that this increase was greater above the glass transition temperature.

(Keywords: water sorption; diffusion; plasticizers; glasses; polymethacrylates; glass transition temperature)

INTRODUCTION

Relatively little has been done on the influence of plasticizers on the water sorption of glassy polymers and such work has been concentrated mainly on copolymers of vinyl chloride. Doty studied the permeation of water vapour through a copolymer of vinyl chloride and vinyl acetate containing 25% plasticizer. He was able to draw interesting conclusions from conventional analyses of temperature dependence[1]. This approach, at a single plasticizer content, was pursued by Kumins *et al.*[2] They expected that plasticizer would cause a 'physical loosening of bonds' and thereby result in a decrease in activation energy followed by a rapid increase in diffusion above T_g. A decrease in activation energy was observed but a rapid increase in diffusion was obtained at a much higher temperature than expected. It was suggested that the copolymer had a second higher value of T_g at which the change occurred but, in retrospect, this suggestion seems unlikely.

No systematic studies have been reported of the influence of variations in plasticizer content on the water sorption of a glassy polymer. However such studies have been reported in respect of the permeability of poly(vinyl chloride) (PVC) to gases. It has been reported that plasticization of PVC results in an increase in permeability whereas antiplasticization results in a decrease[3]. In an extension of this work, Raucher and Sefcik reported that the apparent diffusion coefficient for CO in plasticized PVC reached a minimum value with about 10% tricresyl phosphate. The main-chain relaxation rate, determined from ^{13}C n.m.r. spectra, reached a minimum value with about 15% tricresyl phosphate. This correlation was interpreted as evidence for a rate-determining step in which the jumping of CO molecules is determined by cooperative motions of the polymer main chains[4], as had been described in detail by Pace and Datyner[5].

The purpose of the present work is to investigate the influence of plasticizers on the water sorption of poly(methyl methacrylate) (PMMA). Use was made of a technique in which specimens were made by high-energy irradiation of mixtures of methyl methacrylate and plasticizer. Previously this technique was found to give specimens with values of T_g which conformed to theoretical predictions of the Kelley–Bueche free-volume theory[6]. Also it has been reported that inclusion of up to about 10% dioctyl phthalate resulted in a pronounced decrease in water uptake which was attributed to the filling of microvoids which otherwise, in the absence of the plasticizer, would be available to water[7]. A first aim is to pursue this topic further. A second aim is to find whether, consistent with a 'physical loosening of bonds', there would be simple increases in the rate of water diffusion in the glassy state, i.e. up to T_g. An alternative possibility is that more complex behaviour might be observed which would parallel antiplasticization effects, as inferred from measurements of tensile properties of PMMA plasticized with phthalates[8].

From a more applied point of view the results are of interest because plasticized glassy polymers are used in dental applications. Braden was surprised to find that the diffusion coefficient for water in proprietary PVC compositions was not very different from that in an unplasticized polymer[9]. In studies of proprietary plasticized acrylic polymers, estimation of values of diffusion coefficients was complicated by leaching out of plasticizer[10].

EXPERIMENTAL

Mixtures were made of methyl methacrylate (MMA) (Aldrich, Wisc., USA) with both diethyl phthalate (DEP) (Aldrich Corporation) and dioctyl phthalate (DOP), i.e. di(2-ethylhexyl) phthalate. Mixtures of methyl methacrylate and plasticizer in various proportions were polymerized by 6 h exposure to a ^{137}Cs γ-ray source (dose rate = 0.8 Mrad h^{-1}; ambient temperature = 35°C) in a nitrogen atmosphere. The plasticizer content was

0032-3861/87/101749-04$03.00

calculated as a volume per cent, as described in previous work[6]. The polymerized products, cylindrical in shape, were cut under a stream of water with a high-speed diamond band saw to provide samples of the following dimensions: diameter = 1.4 cm; thickness = 0.1 cm. With up to 25% plasticizer the products generally were transparent and appeared to be homogeneous. However, with 30% or more of DOP, products were slightly turbid. Samples were immersed in distilled water, usually at 50°C, until equilibrated with water: they were dried at room temperature over anhydrous calcium chloride, and weighed periodically. The water uptake was determined relative to the dry weight of the sample[11,12]. The equilibrium water uptake of the plasticizers at room temperature (25°C) was determined by Karl Fischer analysis.

Values of T_g were estimated by differential scanning calorimetry, as described previously[6].

RESULTS

Samples immersed in water increased in weight and reached values which are stationary in the sense that apparently constant values were attained over a period of several days. Such stationary values are used in the present work but it should be noted that on prolonged immersion a slow decrement in weight was detected, presumably due to leaching out of plasticizer. This effect may also be a factor in accounting for the observation that estimates of water uptake by desorption are generally greater than values estimated by sorption (*Table 1*). In the present work, uptake of water is estimated, more reliably, from desorption data.

The water uptake decreased markedly with increasing plasticizer content up to about 10% (*Figure 1*). At higher plasticizer contents, decreases were less marked presumably because of replacement of PMMA by the more hydrophobic plasticizer. Decreases were greater for DOP than for DEP, which is consistent with a difference in water uptake: DOP, 0.18 wt%; DEP, 0.92 wt%.

Water uptake increases with temperature up to about 50°C (*Figure 2*).

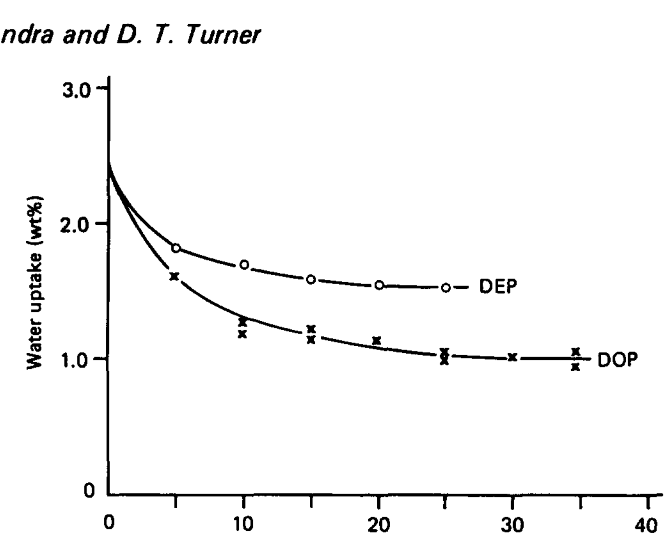

Figure 1 Influence of plasticizers on uptake of water at 50°C

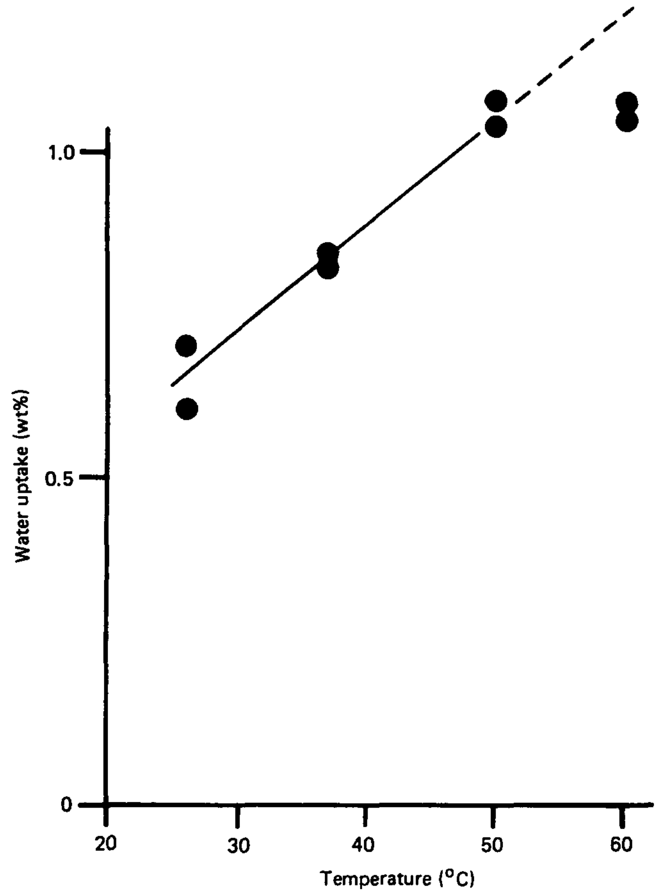

Figure 2 Influence of temperature on water uptake: DOP, 20%; PMMA, 80%

The rate of desorption and sorption was analysed by reference to conventional solutions by Fick's laws of diffusion for plane sheet geometry[13]:

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

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

where M_t and M_∞ are the masses of water sorbed, or desorbed, at times t and ∞, respectively; and $2l$ is the thickness of the specimen.

Data both in sorption and desorption conformed experimentally to equation (2) (*Figures 3–5*). A higher rate of desorption is similar to that reported previously in studies of PMMA alone, at room temperature, and interpreted as due to a dependence of the diffusion coefficient on water content[14]. This same complexity is recognized for values of D obtained in the present work. Furthermore there is a tendency for plots to remain linear beyond the validity of the approximation in equation (2), i.e. at $M_t/M_\infty > 0.5$, which may indicate a time

Table 1 Influence of temperature on uptake of water and diffusion coefficients of PMMA specimens with 20% DOP

Temperature (°C)	26	37	50	60
Uptake by desorption	0.71	0.83	1.05	1.04
(%)	0.60	0.84	1.08	1.07
Uptake by sorption	0.71	0.53	0.91	1.04
(%)	0.61	0.63	0.87	1.00
Diffusion coefficient, by desorption, D_d	4.90	6.5	11.1	23.8
($cm^2\ s^{-1} \times 10^8$)	5.1	6.5	9.0	19.7
Diffusion coefficient, by sorption, D_s	5.6	7.7	9.6	20.6
($cm^2\ s^{-1} \times 10^8$)	4.5	5.9	9.4	26.0

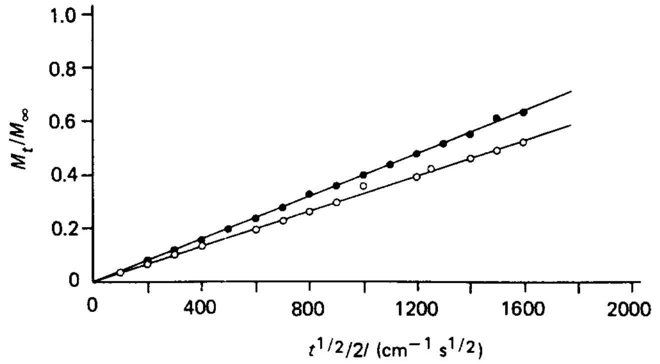

Figure 3 Kinetics of sorption (○) and desorption (●) of PMMA alone at 50°C

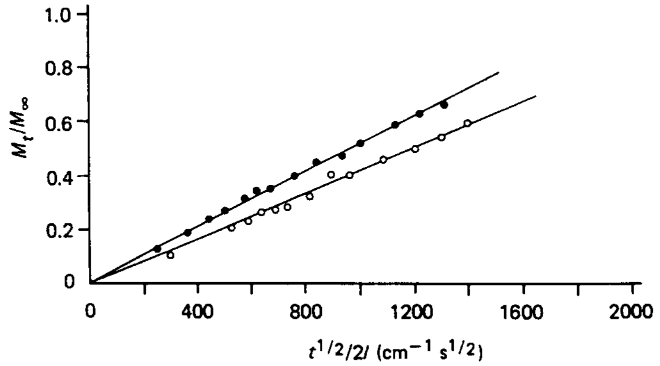

Figure 4 Kinetics of sorption (○) and desorption (●) of PMMA with 5% DEP at 50°C

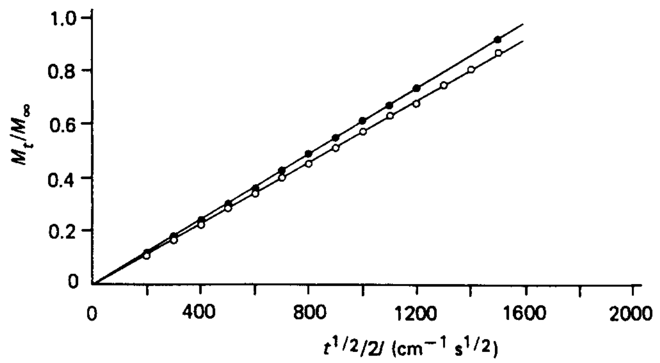

Figure 5 Kinetics of sorption (○) and desorption (●) of PMMA with DOP (15%) at 50°C

dependence of swelling on uptake of water[15]. In view of these departures from ideal behaviour it should be noted that use of equation (2) provides apparent values of the diffusion coefficient, but these suffice to give a preliminary overview of trends. More reliance is placed on values of D calculated from desorption data up to 37°C, for which duplicate runs agreed with a few per cent, but at higher temperatures results were less reproducible (*Table 1*). Nevertheless, most measurements were made at 50°C in order to reduce the time of testing. The influence of plasticizer content on D is shown in *Figure 6*.

Data for the influence of temperature on values of D for PMMA with 20% DOP were plotted according to the Arrhenius equation (*Figure 7*). Up to 50°C, the activation energy for water diffusion is 20.5 kJ mol^{-1}.

Data for the influence of plasticizer content on T_g were reported previously and plotted in a manner suitable for comparison with free-volume theory[6]. For more direct comparison with water sorption data, a plot is given of T_g vs. content of plasticizer (*Figure 8*).

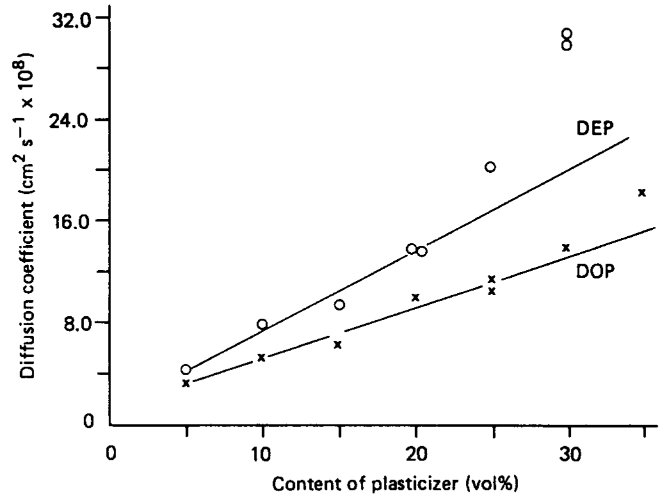

Figure 6 Influence of plasticizer content on diffusion coefficient, in desorption at 50°C

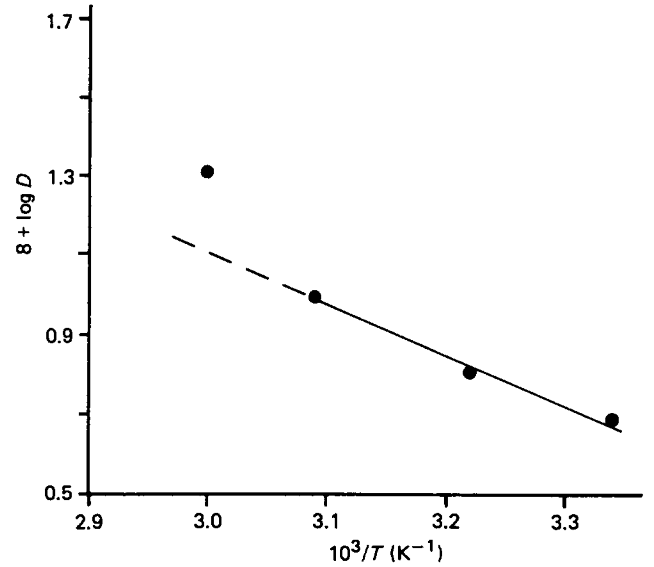

Figure 7 Influence of temperature on diffusion coefficient, in desorption: DOP, 20%; PMMA, 80%

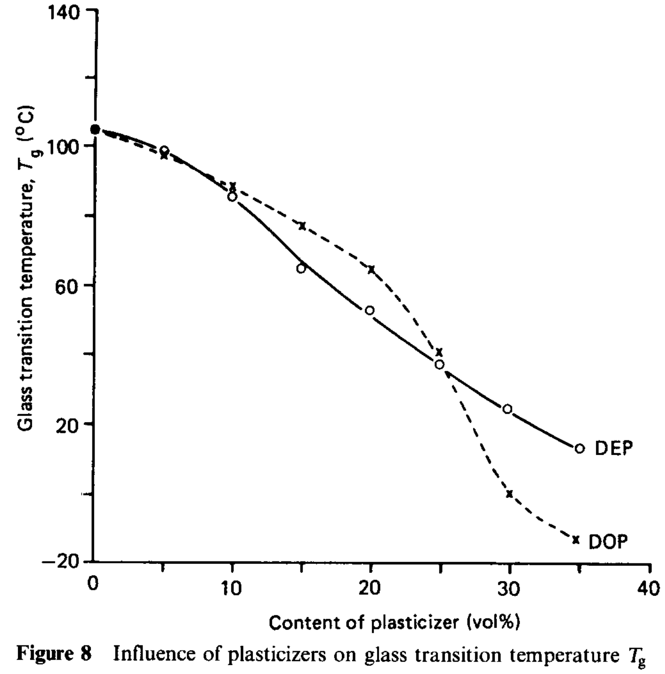

Figure 8 Influence of plasticizers on glass transition temperature T_g

DISCUSSION

The influence of plasticizer on the uptake of water may be analysed into two regions (*Figure 1*). Above about 10% the influence is small and consistent with the replacement of polymer by the more hydrophobic plasticizer. Previously the unexpected efficacy of smaller proportions of DOP was attributed to microvoid filling. This interpretation was based on evidence that PMMA, without plasticizer, takes up about 2 wt% water but swells by only 1%. It was suggested that about one-half of the water is accommodated in microvoids. It was further suggested that DOP can also fill microvoids and thereby exclude uptake of water. This explanation is now extended to include DEP, which is judged to be less effective as a microvoid filler. Perhaps DEP is more soluble in PMMA and its partition into microvoids less favoured. In broader perspective, similar ideas about the influence of liquid in reducing water sorption by rigid polymers can be traced back to Sheppard's work on cellulose and its derivatives[16].

The uptake of water in one plasticized composition (20% DOP) was found to increase with temperature (*Figure 2*). It has been reported that water uptake by unplasticized PMMA ($T_g = 100°C$) increases above 70°C, but quantitative data are not available for comparison[3]. In the present work, the water uptake appears to level off in the temperature range 50–60°C (*Figure 2*). For the binary composition under consideration $T_g = 66°C$ (*Figure 8*) but this would be depressed by 1% water ($T_g = -140°C$)[17] to $T_g = 61°C$, according to the Fox equation[18]. Thus it appears that the levelling off occurs near the glass transition temperature.

A number of factors might be expected to complicate the influence of plasticizer content on the diffusion of water through PMMA. First, differences in microvoid filling might affect results up to about 10%. Secondly, antiplasticization might affect results at higher contents. In this latter respect it has been reported that the tensile strength of PMMA at 26°C exhibits minimum and maximum values with 7% and 26% dibutyl phthalate, respectively. Notwithstanding such potential complexities, there is a relatively simple monotonic increase in the diffusion coefficient with increasing plasticizer content (*Figure 6*). In the absence of any theoretical guidance, a least-squares straight line was drawn through diffusion values for all plasticized compositions judged to be in the glassy state by reference to values of T_g, i.e. with $\leqslant 20\%$ plasticizer (*Figure 8*). On this basis it appears that the value of D increases more rapidly above T_g. This upturn is less marked in the case of DOP but additional evidence of a change in mechanism was obtained in experiments on temperature dependence (*Figure 7*). These indicate a higher rate of diffusion at temperatures above 50–60°C, which is near the T_g value for this composition, i.e. 61°C. The activation energy for diffusion in the glassy state is 20.5 kJ mol^{-1}. This is lower than the value reported for unplasticized PMMA (43.5 kJ mol^{-1})[14].

In summary, there are several factors which might influence the way in which a plasticizer affects water transport in a glassy polymer. One factor is that the plasticizer molecules might increase transport by decreasing the attractive forces between segments of the macromolecules. This would have the effect of decreasing the activation energy for diffusion, as observed in the present work. Such an effort would also be consistent with the observed monotonic increase in the diffusion coefficient up to T_g. The more marked increase in the diffusion coefficient above T_g would be consistent with transport into holes formed by main-chain motions, of the kind generally adduced to account for gas transport in glassy polymers[4,5]. A second factor is that transport might be affected by plasticizer molecules occupying space, here termed 'microvoids'. Evidence for such occupancy has been presented but any effect on transport does not complicate the simple picture as presented above.

CONCLUSIONS

The uptake of water by PMMA is reduced by inclusion of either dioctyl phthalate or by diethyl phthalate in a way which has been interpreted to involve the filling of microvoids which, in the absence of such additives, can accommodate water.

The diffusion coefficient of water in PMMA increases monotonically with increasing contents of either dioctyl phthalate or diethyl phthalate. The diffusion coefficient increases less markedly when the plasticized polymers are in the glassy state.

ACKNOWLEDGEMENTS

This investigation was supported by USPS Research Grant No. DE 06201 and General Research Support No. RR 0533. We thank Mr Oleg Zur for preparation of samples.

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