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Methanol transport in crosslinked poly(methyl methacrylate)

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Methanol transport in crosslinked poly(methyl methacrylate) (PMMA) was studied. Four thicknesses were considered: 0.6, 1.0, 1.5 and 1.9 mm. The front velocity is independent of thickness. The front velocity obeys the Arrhenius equation and the activation energy is 20 kcal mol^{-1}. Comparing the crosslinked and uncrosslinked PMMA, the front velocity of the crosslinked PMMA is smaller than that of uncrosslinked PMMA. The saturated amount of methanol increases with temperature and obeys the van't Hoff plot. The process of mass transport is endothermic and the heat of mixing is 2.65 kcal mol^{-1} regardless of thickness.

(Keywords: poly(methyl methacrylate); methanol transport; crosslinking)

Introduction

Transport of small molecules in a polymer is well known but not well understood. It can be classified as case I or case II. Case I flows from high concentration to low concentration based on diffusion. Case II moves with constant velocity controlled by swelling. Swelling is not important for very small molecules or low solubility so their transport is controlled by diffusion. However, swelling plays a significant role for large molecules or high solubility. Usually, the process behaviour is a mixture of case I and case II. Thomas and Windle[1–4] described swelling and transport in poly(methyl methacrylate) (PMMA) and proposed a model where diffusion and viscosity flow control kinetics. Both terms are dependent on concentration.

Kwei and co-workers[5–9] proposed an equation to combine the transport of case I and case II. Harmon *et al.*[10,11] modified the Kwei equation to apply to a specimen of finite size of PMMA. The solvent-induced crack healing of PMMA was studied and it was found that the crack closure rate arising from solvent transport was controlled by case II[12,13]. The change of opacity in amorphous PMMA arising from solvent transport was investigated by Lin *et al.*[14,15]. The crack closure rate during crack healing in polycarbonate treated by solvent was controlled by case I[16]. This prompted us to study methanol transport in crosslinked PMMA.

Experimental

Crosslinked PMMA (Electroglas) contact lens buttons were obtained from Glasflex in Sterling, NJ, USA. They were of standard size, 12.5 mm (0.5 in) diameter and 4.75 mm (0.187 in) thickness. These buttons were mounted in a bench lathe and thinned to 0.6, 1.0, 1.5 and 1.9 mm. Samples were polished on 600 and 1200 grid carbimet papers. Final polishings with 1 and 0.03 μm aluminium slurries followed. The samples were then annealed for 24 h in a vacuum chamber at 130°C and furnace cooled to room temperature. The sample was preheated to the desired temperature of methanol transport. Then each specimen was immersed in methanol and kept in a thermostatted water bath at 40–60°C. The sorption study was conducted by measuring weight gain of the specimen periodically. Samples were weighed on a Kern 870 digital balance and immediately returned to the water bath for another period. Data are the average of three samples.

Results and discussion

Methanol transport in crosslinked PMMA of various thicknesses is displayed in *Figure 1* where A_0 is the unit area (1 cm^2) of the cross-section. The initial slopes are found to be independent of thickness. The initial slopes of *Figure 1* are estimated as 2.5×10^{-3}, 4.7×10^{-3}, 8.6×10^{-3}, 1.2×10^{-2} and 1.7×10^{-2} g cm^{-2} h^{-1} corresponding to 40, 45, 50, 55 and 60°C, respectively. The density of the methanol is 0.7914×10^{-3} g cm^{-3}. The front velocities (initial slope of *Figure 1* divided by the density of methanol) are 0.9×10^{-6}, 1.6×10^{-6}, 3.0×10^{-6}, 4.3×10^{-6} and 5.9×10^{-6} cm s^{-1}, corresponding to 40, 45, 50, 55 and 60°C, respectively. The front velocity satisfies the Arrhenius equation and the activation energy is 20 kcal mol^{-1}. The velocity front was observed by naked eye in the uncrosslinked PMMA[15] but not in the crosslinked PMMA. In order to compare the front velocities of both crosslinked and uncrosslinked PMMA, the sharp front in the uncrosslinked PMMA was also analysed. *Figure 2* shows the distance between the sharp front and the original surface (see inset in *Figure 2*) as a function of time, where the sample size is 40 mm × 6.3 mm × 1 mm. The deviation of the curve from a line increases with increasing temperature. The front velocities calculated from the initial slope of *Figure 2* are 3×10^{-6}, 3.8×10^{-6}, 4.5×10^{-6}, 5.5×10^{-6} and 6×10^{-6} cm s^{-1} corresponding to 40, 45, 50, 55 and 60°C, respectively. Comparing both crosslinked and uncrosslinked PMMA, the front velocity of crosslinked PMMA is smaller than that of uncrosslinked PMMA.

The saturated amount S of methanol as a function of temperature is shown in *Figure 3* where the unit of the saturated amount is the weight of pure PMMA. At the

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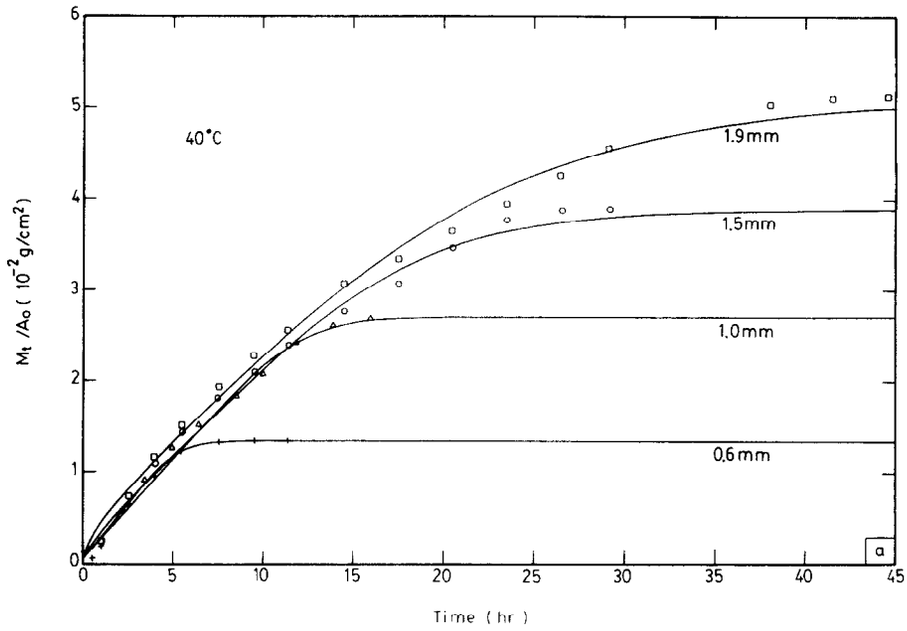
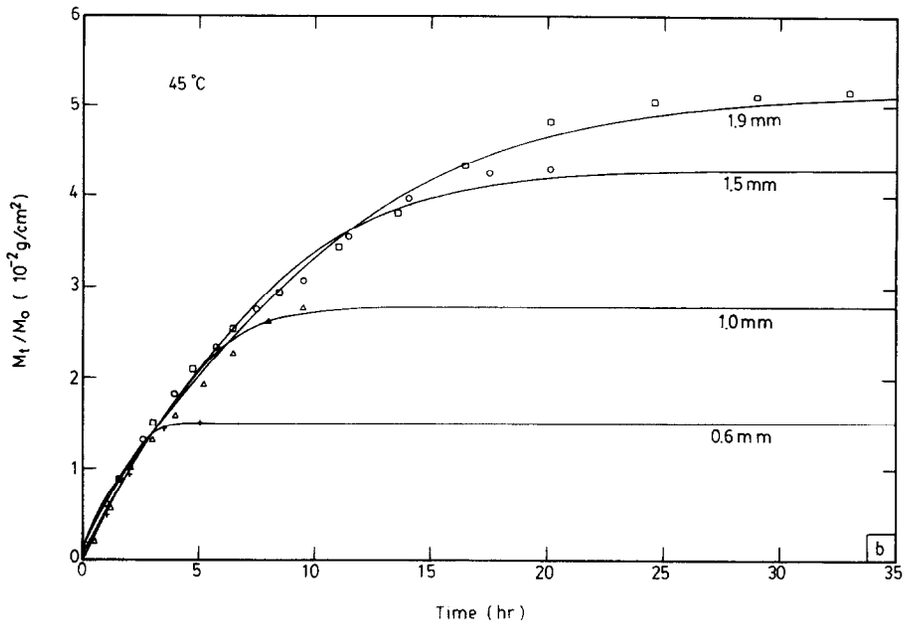
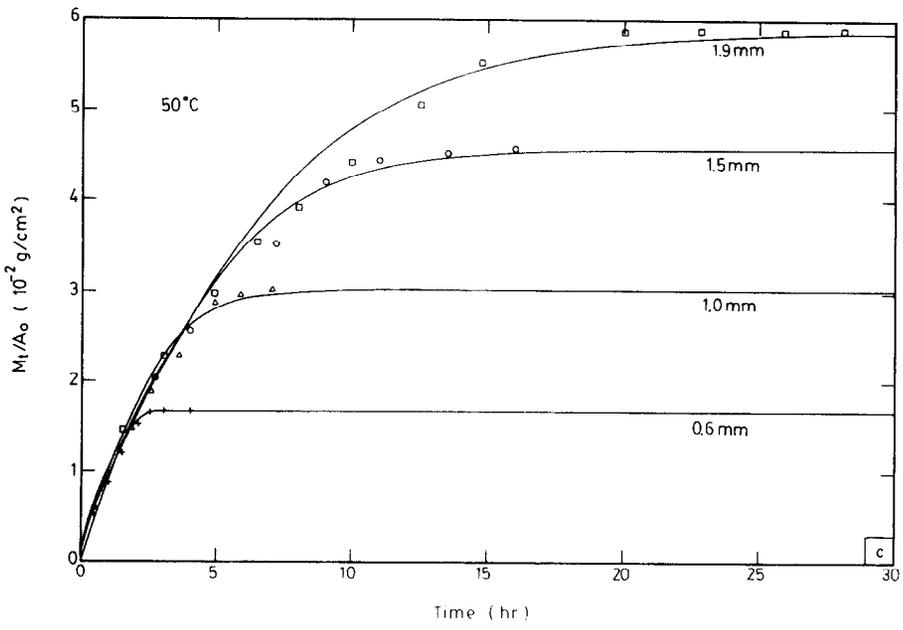

40°C
1.9mm
1.5mm
1.0mm
0.6mm
a
M_t/A_o (10^{-2} g/cm^2)
Time (hr)


45 °C
1.9 mm
1.5 mm
1.0mm
0.6 m m
b
M_t/M_o (10^{-2} g/cm^2)
Time (hr)


50°C
1.9mm
1.5mm
1.0 mm
0.6 mm
c
M_t/A_o (10^{-2} g/cm^2)
Time (hr)

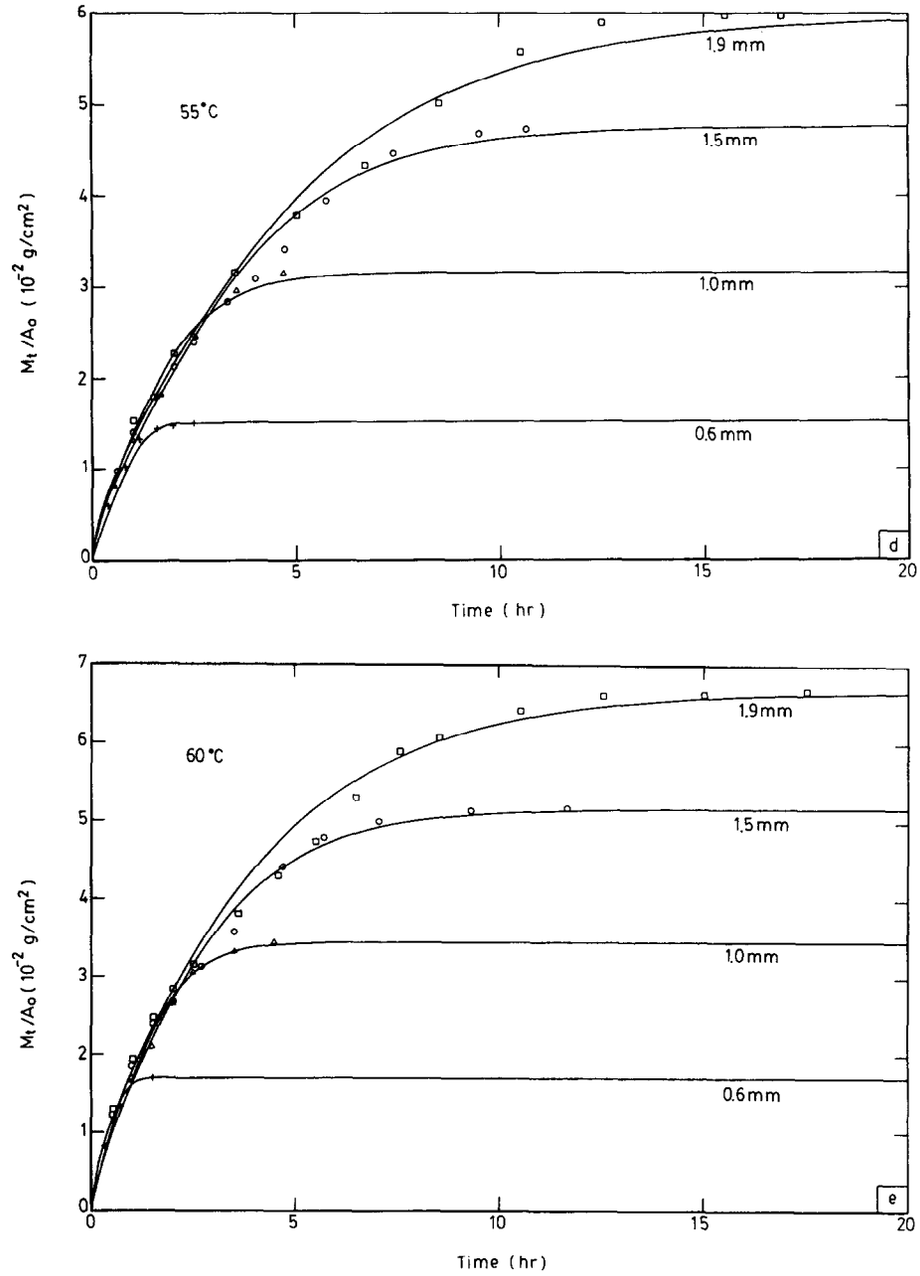


Figure 1 Methanol transport in crosslinked PMMA discs of different thicknesses at temperatures (a) 40°C, (b) 45°C, (c) 50°C, (d) 55°C, and (e) 60°C

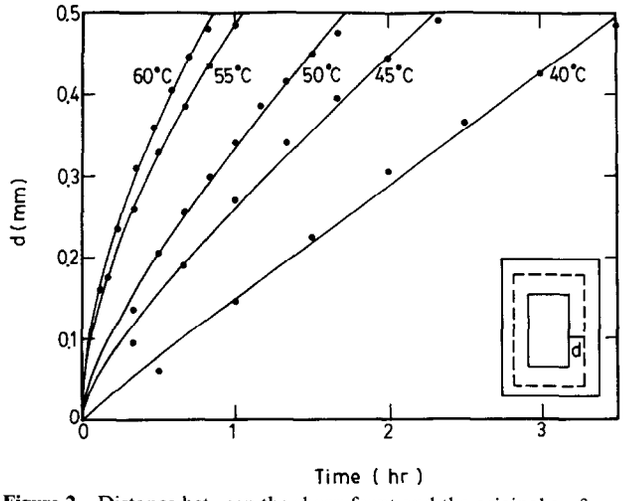


Figure 2 Distance between the sharp front and the original surface as a function of time at various temperatures. The dashed line in the inset is the original surface and the inner and outer solid lines represent the sharp front and the swollen surface, respectively

same temperature the saturated amount of methanol increases with increasing thickness and satisfies the van't Hoff equation. The process of mass transport is endothermic and the heats of mixing are 2.7, 2.7, 2.6 and 2.6 kcal mol^{-1} corresponding to thicknesses of 0.6, 1.0, 1.5 and 1.9 mm, respectively. Heats of mixing, E_h, are close to each other in the range from 0.6 to 1.9 mm. This implies that the saturated amount of methanol is not influenced by thickness. The value of E_h in the present study (2.65 kcal mol^{-1}) is larger than the value obtained by Harmon *et al.*[10] (1.6 kcal mol^{-1}) owing to the ageing effect, and slightly less than the values obtained by Hopfenberg *et al.*[17] (2.8 kcal mol^{-1}) and Thomas and Windle[1] (3.0 kcal mol^{-1}).

Acknowledgement

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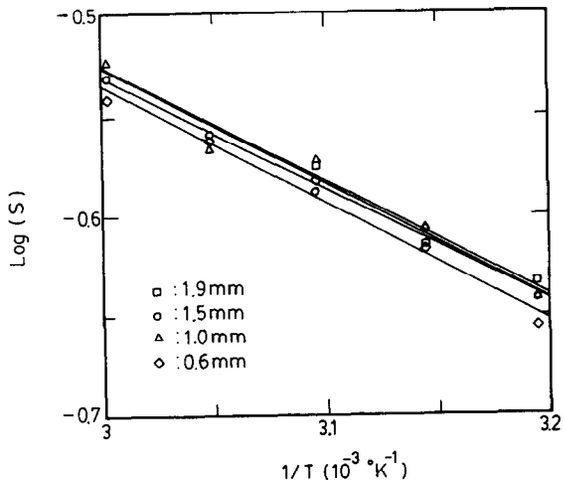

Figure 3 The van't Hoff plots

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