Variation in Polymer Film Structure and Thickness-Dependent Permeability

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Fick's laws have been applied to permeation processes in polymer films, and in Fickian permeation flux and film thickness vary inversely,[1] thus allowing prediction of film performance at various thicknesses. In a film having a porous asymmetric structure (a porous core bounded by compact surface zones), the relative proportions of the various zones in the barrier and indeed the pore structure of each zone may vary during a change in film thickness, thus resulting in non–Fickian permeation. This aspect was investigated in the present study.

An acrylate-methacrylate copolymer (ERI-100, Rhom Pharma, Darmstadt) was used to form films of various thicknesses by casting the polymer solution on PTFE molds.[2] The films contained a plasticizer, glycerol triacetate (GTA) or glycerol tributyrate (GTB), 16.6%. Film permeability was determined after Abdel-Aziz and others (1975)[2] at 30°C using 10% urea or sodium chloride as permeant. Film lower surface (in contact with mold during casting) was upstream in the permeation experiments. Permeability coefficient P was calculated from the quasi-steady-state equation[1]

$$\log \frac{2\,C_t - C_0}{C_0} = \frac{0.87\,Pt}{LV}$$

Where C_0 and C_t are the concentrations initially and at time t in the donor fluid. L is film thickness, and V is the volume of each compartment. Film pore structure was determined by electron microscopy[2]; the plasticizer leached from the films under conditions of the permeation experiment was determined by a gas-liquid chromatographic (GLC) method.[3]

Permeability coefficients increased linearly with increase in film thickness when urea was used as permeant (Fig. 1). The effect was most pronounced in the GTB-plasticized film and least pronounced in films from which the plasticizer GTA had been leached prior to permeation experiments; for instance, the overall increases in permeability coefficients for each 10 μm increase in film thickness were 0.963, 0.233, and 0.041 $\times$ 10^{-7} cm^2 s^{-1} for the GTB, GTA, and deplasticized GTA films, respectively. The use of sodium chloride as permeant resulted in a decrease in film permeability with increase in film thickness; observed values of the permeability coefficient were 0.025, 0.014, 0.004, and 0.002 $\times$ 10^{-7} cm^2 s^{-1} obtained with films of thickness 19.8, 39.4, 59.4, and 79.8 μm, respectively.

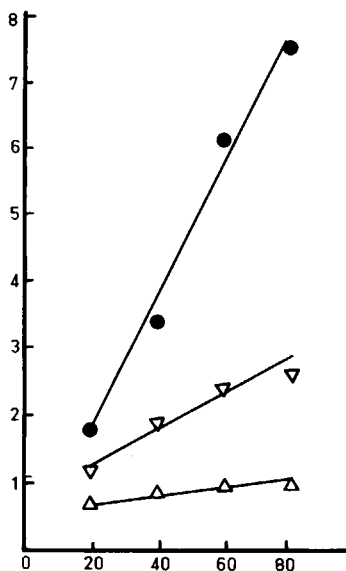*Present Address: Department of Pharmaceutics University of Benin, B/City Nigeria

Fig. 1.   Variation in permeability coefficient (ordinate, $cm^2S^{-1} \times 10^{-7}$) with increase in film thickness (abscissa, μm) in gtb ● gta ▽ and deplasticized gta △ films; permeant was urea 10%W/V.

The amount of plasticizer GTA released through the film upper surface declined from 48 and 44% to 38% as film thickness was increased from 39.4 and 59.4 μm to 79.8 μm, respectively, and the release through the film lower surface became progressively higher from 49 and 54% to 56%. This finding suggests an increasing compactness of pore structure in the upper surface zone of thicker films. The lower permeability coefficient of sodium chloride in thicker films may be associated with this effect. Sodium chloride
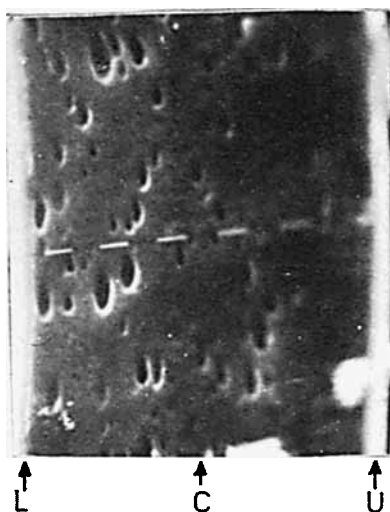

Fig. 2.   Electromicrograph of film section (magnification, 1250) showing the porous core zone (c) and the compact lower (L) and upper (u) surface zones.

causes film shrinkage, whereas urea causes slight film swelling[3] with a tendency to offset the effect of the upper surface compactness.

An electron micrograph of the film section (Fig. 2) shows the loose porous structure in the film core bounded by the more compact upper and lower surface zones. Thicknesses of both surface zones were virtually equal, each 4 ± 0.2 μm S.D. and remained constant during variation in overall film thickness from 19.8 to 79.8 μm; the core zone thickness increased from 11.8 to 70.4 μm. The increase in the proportion of the more permeable core zone together with film swelling account for the increase in permeability coefficients when urea was used as permeant. GTB-plasticized films are more readily swellable than the GTA-plasticized films,[3] hence, the greater increase in permeability coefficients in the former film.

The results permit a conclusion that asymmetric polymer films do not lend themselves to Fickian permeation as a result of variation in film structure during a change in film thickness. In the design of controlled-release devices with this type of water-swellable polymer, film thickness may be increased to obtain mechanical strength without a significant sacrifice to the desired release rate.

References

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