polymer reports

# Sorption and diffusion of solvents in highly oriented polyethylene

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(*Received* 16 *July* 1981)

Measurements have been made of the sorption and diffusion coefficients of various solvents in oriented linear polyethylene pipe produced by hydrostatic extrusion. In all cases the equilibrium sorption is a factor of about ten less than that for isotropic linear polyethylene, and the diffusion coefficients are a factor of about a hundred less.

**Keywords** Measurement; sorption; diffusion; polyethylene; pipe; oriented; hydrostatic extrusion

## INTRODUCTION

Although it has been concluded from a number of studies, in particular nitric acid etching[1], that the chemical resistance of oriented linear polyethylene is superior to that of isotropic polymer, there is a need for definitive information regarding the sorption or diffusion of chemical reagents in such materials, especially in the form of large solid sections, where oriented polyethylene may be used to practical advantage. The present note reports some recent results of such measurements on oriented linear polyethylene pipe, produced by hydrostatic extrusion.

## EXPERIMENTAL

### *Preparation of oriented pipe*

The hydrostatic extrusion process has been described in a number of previous publications, one of which gives a detailed account of the preparation of oriented tubular sections[2]. For the present experiment, a tubular billet was prepared from Rigidex 006-60 grade linear polyethylene ($\bar{M}_w = 135000$ $\bar{M}_n = 25500$). This billet was then hydrostatically extruded through a 15° semi-angle die and over a fixed mandrel. The high pressure fluid was castor oil and the extrusion temperature was 100°C. The overall exit diameter was 23.8 mm, which combined with a mandrel head diameter of 21.8 mm to give tubes of 1 mm wall thickness. The extrusion ratio was 10, which gave a product with a room temperature tensile modulus of 11.2 ±0.6 GPa. The bursting pressure of the pipe was 2.4 MPa (compared with ~3.5 MPa for isotropic tube) and the pipes showed no measurable change in dimensions after immersion in boiling water for six hours.

### *Measurement of sorption and diffusion coefficients*

The changes in weight of 5 cm long pipe samples in various solvents* at 50°C were monitored with time. The samples and solvents were placed in polypropylene bottles suspended in stirred water baths with temperature control to ±0.1°C. The samples were removed from the bottles, wiped to remove surface liquid and weighed rapidly in a closed container on an Oertling analytical balance capable of a resolution of ±0.1 mg. The samples were then returned to the bottles. Equilibrium was considered to have been achieved when no further change in weight was observed over a period of approximately 500 hours, and testing was then discontinued.

## RESULTS AND DISCUSSION

Sorption data at 50°C for the oriented pipe are compared with those for isotropic pipe in *Figure 1*. The results are presented in the form of weight percentage uptake as a function of $t^{1/2}/l$ where $t$ is the time in seconds and $l$ the

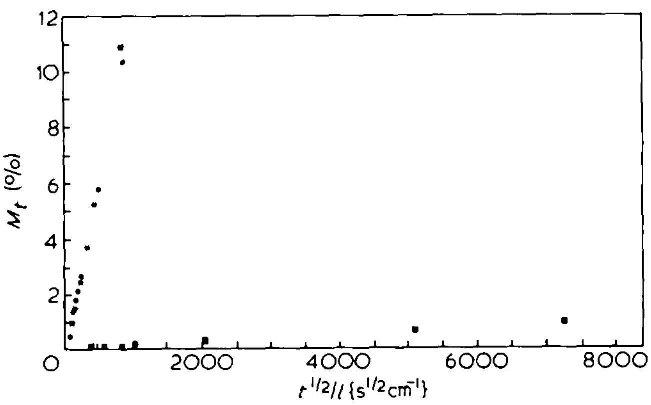

*Figure 1* Sorption data for toluene in polyethylene at 50°C ($M_t$ = amount taken up in time $t$, sample thickness $l$) *, isotropic pipe; ●, isotropic sheet; ■, oriented pipe

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* Tetrahydrofuran (THF); toluene; methanol; 4-methyl pentan-2-one (MIBK)

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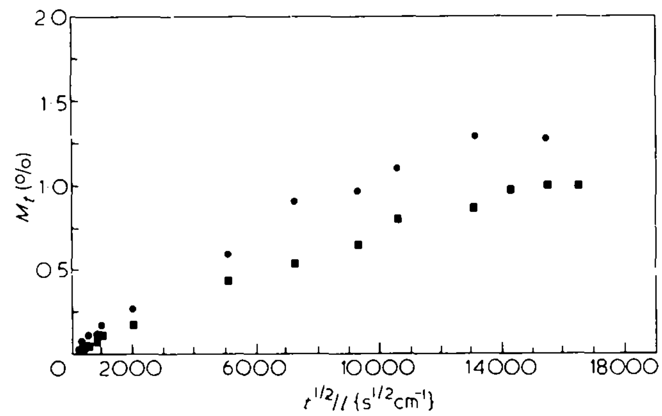

*Figure 2* Sorption data for THF and toluene in oriented polyethylene pipe at 50°C: ■, THF; ●, toluene

sample thickness in cms. Data is shown for toluene only, the pattern for THF absorption being analogous.

It can be seen in both cases the initial sorption is Fickian, but with the oriented material showing a much lower rate of absorption.

*Figure 2* shows extended time data for oriented polyethylene in both THF and toluene and diffusion coefficients may be calculated from this data.

For short times—i.e. in the initial region of the curves, $D$ can be calculated, to a good approximation, from the expression[3]

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2}$$

where $M_t$ = amount of diffusant taken up in time $t$
$M_\infty$ = equilibrium sorption value
$D$ = diffusion coefficient
$l$ = sample thickness

Results for the two solvents are summarized in *Table 1*. It can be seen that there is a large reduction in both the equilibrium sorption and the diffusion coefficient for the oriented pipe compared with the isotropic material.

Limited sorption data were also obtained for MIBK and methanol. Again the oriented material showed far greater resistance to these solvents. Equilibrium sorption for MIBK was found to be 0.1% for oriented aterial compared with 4.0% in isotropic samples. No appreciable methanol absorption could be measured in ~1350 hours in the oriented pipes, whilst the isotropic pipes increased in weight by ~0.3% in an equivalent time period.

*Table 1* Summary of results

| | | Equilibrium sorption (weight %) | Diffusion coefficient (cm$^2$ s$^{-1}$) |
|---|---|---|---|
| Isotropic pipe | Toluene | 12 | $1.3 \times 10^{-7}$ |
| | THF | 10 | $1.1 \times 10^{-7}$ |
| Oriented pipe | Toluene | 1.5 | $1.6 \times 10^{-9}$ |
| | THF | 1.0 | $1.9 \times 10^{-9}$ |

The results compare well with those reported previously for the sorption of organic vapours in drawn polyethylene sheet by Peterlin and co-workers, and with more recent results obtained at Leeds University. For example, Peterlin, Williams and Stannett[4] report a diffusion coefficient for methylene chloride of $\sim 8 \times 10^{-10}$ cm$^2$ s$^{-1}$ from sorption measurements on narrow tapes of linear polyethylene ($\bar{M}_w = 80\,000$, $\bar{M}_n = 5\,500$) drawn to draw ratio 10. Holden *et al.*[5] have recently obtained a value of $8.1 \times 10^{-8}$ cm$^2$ s$^{-1}$ for methylene chloride in isotropic linear polyethylene ($\bar{M}_w = 312\,000$, $\bar{M}_n = 33\,000$), reducing to $1.3 \times 10^{-9}$ cm$^2$ s$^{-1}$ by draw ratio 9, and $4.9 \times 10^{-10}$ cm$^2$ s$^{-1}$ by draw ratio 17.5.

All these results confirm that there is a dramatic reduction in the diffusion coefficient between isotropic material and draw ratio ~10, when the transformation from the initial spherulitic texture to a drawn structure has taken place, with further significant but smaller reductions on further drawing. These measurements are interesting in confirming that the measurement of diffusion can provide additional insight into the structure of these oriented materials.

With the advent of hydrostatic extrusion and other solid phase forming techniques, the prospect of solid tubular sections also provides the possibility of being able to make use of these dramatic improvements in sorption and diffusion resistance in practical applications.

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