# Radioisotope techniques for the study of diffusion in polymers

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Radioisotopes can serve as a suitable tool for the study of diffusion in polymers. Two different methods have been used for this purpose: radiometric measurements, which enable us to determine the total amount of substance diffused into polymers and to compute diffusion coefficients, and autoradiographs, which can yield the distribution of substances in polymer and also the local concentration of diffused substances.

**(Keywords: polyesters; diffusion; radioisotopes; autoradiography; optical densities; corrosion)**

## INTRODUCTION

The diffusion of various substances in plastics is of great practical importance and many methods have been devised for investigating it. One of these is the method of radioactively labelled atoms and compounds, which not only is highly sensitive but also has a particular advantage. It can detect the local distribution of water diffused into plastics, which can hardly be detected by any other method. This is important because most of the solutions employed in industry are aqueous solutions.

In our laboratory we use radioactive isotopes for the following purposes:

1. qualitative estimation of distribution of aggressive substances diffused in plastics;
2. determination of the content of these substances;
3. determination of diffusion coefficients;
4. determination of penetration depths of substances in plastics;
5. determination of local concentrations of aggressive substances (mainly water) in plastics.

In cases 2 and 3 we employ the radiometric method and in cases 1 and 3–5 autoradiography.

The theoretical relations used in our paper are based on Crank's monograph[1]. The solution of the diffusion equation for the first stage of diffusion under the present initial conditions can be written as:

$$M = 2CP\sqrt{Dt/\pi} \qquad (1)$$

where:

$M$ = mass of substance diffused (kg)
$C$ = concentration of substance in liquid ($\mathrm{kg\,m^{-3}}$)
$P$ = diffusion area ($\mathrm{m^2}$)
$t$ = diffusion time (s)
$D$ = diffusion coefficient ($\mathrm{m^2\,s^{-1}}$)

The tracer method is based on the proportionality of radioactivity to mass. From this it follows that:

$$I = 2I_1P\sqrt{Dt/\pi} \qquad (2)$$

where $I$ is the radioactivity of the polymer (Bq) and $I_1$ is the specific radioactivity of the substance diffused.

## EXPERIMENTAL

### *Radiometry*

The plastic specimens were placed in a solution labelled with the relevant radioisotope, e.g. water labelled with $^3$H, sulphuric acid labelled with $^{35}$S, for a given time at a given temperature (both specified below). The specimens were taken out of the solution, dried and placed in measuring vials of the Tricarb Liquid Scintillation System (Packard Instruments), where the diffused substance labelled with radioisotope was extracted and its radioactivity measured.

### *Autoradiography*

This method is based on the fact that the radiation from a radioactive substance can be detected by a photosensitive material (e.g. on a film). A special autoradiographic film, namely ORWO AF 4, GDR, was used for this purpose.

A scheme of an autoradiographic method is shown in *Figure 1*. The specimens are cut from a plate of the polymer under test and a small plastic tube is affixed to the surface of the specimen so that a cell is formed. The radioactively labelled substance is pipetted into the cell, and the cell inserted in a temperature-controlled oven, where the surface of the specimen is exposed to the aggressive substance at a given temperature. After a given time the cell is taken out of the oven, the substance poured out and the tube removed.

The specimen prepared in this way was cut into slices using the method suggested by Kimma and Choi[2], and the diffusion profile measured.

Because of the easy evaporation of water during cutting and the very low energy of beta particles of tritium in the case of water diffusion tested, cutting had to be performed in a stream of liquid nitrogen. Such cutting on a lathe can be seen in *Figure 2*.

The slices were placed on films at a temperature of −22°C. The autoradiographs were evaluated by the Joyce–Loebl Mark III microdensitometer. The penetration depths of diffusion were determined by the standard method described in our previous paper[3].

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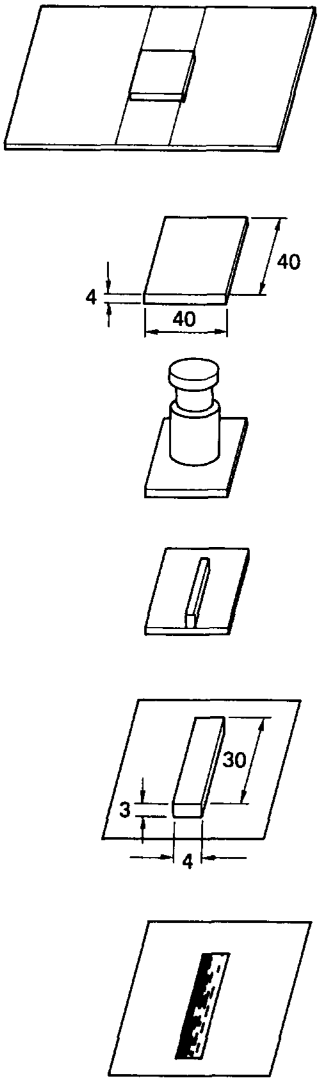


**Figure 1** Scheme of autoradiographic method

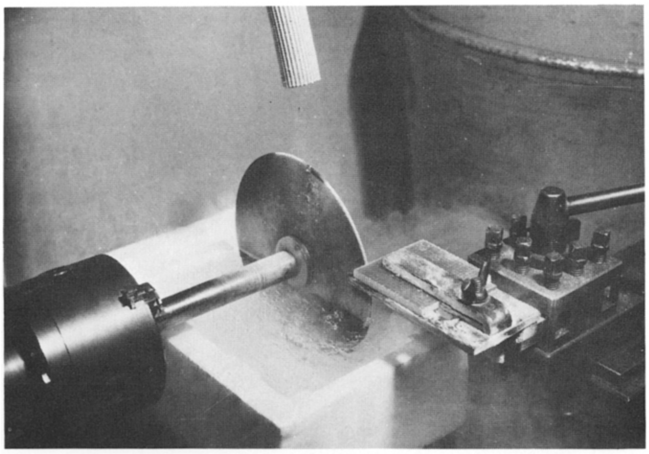


**Figure 2** Cutting under liquid nitrogen

## RESULTS AND DISCUSSION

### *Radiometry*

The principal results obtained by the radiometric method are summarized in *Table 1*.

Statistical tests have shown that the vinylester resins are significantly more water resistant than the isophtal polyester resins.

From Equation (2) the diffusion coefficients were found to be $3.9\times10^{-13}\,m^2\,s^{-1}$ and $5.6\times10^{-11}\,m^2\,s^{-1}$ for the isophtal polyester resin at temperatures of 20 and 80°C, respectively.

### *Autoradiography*

The results obtained from autoradiographs and from their evaluation on a microdensitometer are useful for the technology of plastics. Typical examples of these results are:

*Difference between polymers. Table 2* gives data on diffusion depths into various resin types. From this table it can be seen that water and water solutions diffuse deeper into the orthophtalic polyester resin than into isophtalic polyester resin.

*Effect of post-curing.* The post-curing of polyester resin improves its resistance to corrosion. This is illustrated in *Table 3*.

*Effect of glass fibre reinforcement.* There are two stages in the water corrosion of polyester resin reinforced with glass fibres. *Figure 3* shows the first stage, the distribution of water diffused into the laminate after 2 day's exposure

**Table 1** Radiometric results

| | Substance/polymer | | | | |
|---|---|---|---|---|---|
| | water/iso[a] | water/iso | HCl/iso | water/vinyl[b] | HCl/vinyl |
| Time (days) | 6 | 26 | 26 | 26 | 26 |
| Temperature (°C) | 40 | 40 | 40 | 40 | 40 |
| Substance content (%) | 0.25 | 0.63 | 0.43 | 0.20 | 0.27 |
| S.s.d.[d] (%) | 0.09 | 0.13 | 0.21 | 0.03 | 0.12 |

[a] Iso, isophtal polyester resin
[b] Vinyl, vinylester resin
[c] S.s.d., sample standard deviation

**Table 2** Water diffusion depths into various resin types

| Resin type | Number of measurements | Diffusion dpeth (mm) | S.s.d. (mm) |
|---|---|---|---|
| Orthophtalic | 62 | 2.29 | 0.46 |
| Isophtalic | 37 | 1.95 | 0.26 |

**Table 3** Influence of post-curing on diffusion depth

| Post-curing | Number of measurements | Diffusion depth (mm) | S.s.d. (mm) |
|---|---|---|---|
| No | 18 | 2.24 | 0.28 |
| Yes | 15 | 1.92 | 0.35 |

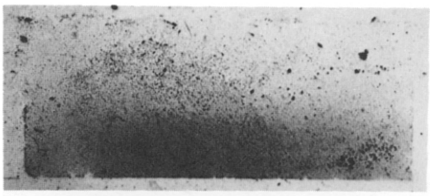
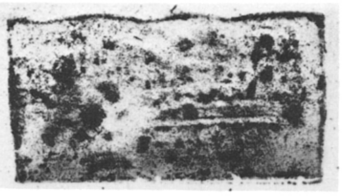


**Figure 3** Diffusion of water into laminate – first stage



**Fiugre 4** Diffusion of water into laminate – second stage

**Figure 5** Diffusion of water containing 10% HCl into laminate

at 40°C. Water diffused about 2 mm into the surface. The distribution of diffused water was slightly inhomogeneous. From mechanical tests, which were carried out simultaneously, it follows that the flexural modulus is about the same as that before diffusion.

*Figure 4* shows the distribution of diffused water in the same material after 26 days exposure at the same temperature, i.e. at 40°C. It can be seen that water in this case diffused through the whole specimen and concentrated in certain areas of it. Optical densities of autoradiographs are very inhomogeneous. Mechanical tests showed that at this stage of corrosion the flexural modulus decreased with time.

*Effect of hydrochloric acid.* The same material as that shown in *Figure 3* was exposed for 2 days at 40°C to a 10% solution of hydrochloric acid labelled with tritium. An example of an autoradiograph of this case is shown in *Figure 5*. The surface layer is decomposed. The tritium concentration is high, but nevertheless the diffusion depth is nearly the same as in the previous case. From comparison of the two cases it follows that diffusion of water is not affected by the decomposition of the surface layer by the hydrochloric acid.

*Calibration for quantitative work.* The autoradiographs described above and their microdensitometric curves make possible both the quantitative evaluation of water diffusion into plastics and, especially, the determination of local concentration of water diffused into plastics. As examples, *Figures 6* and *7* show photometric curves of autoradiographs of laminates with diffused pure water and diffused water with 10% HCl, respectively. The original calibration in terms of optical density is on the left-hand side.

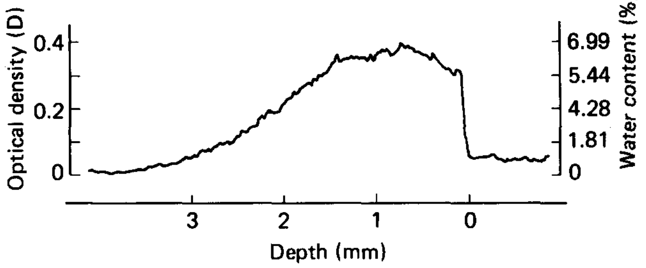


**Figure 6** Local concentration of water after diffusion

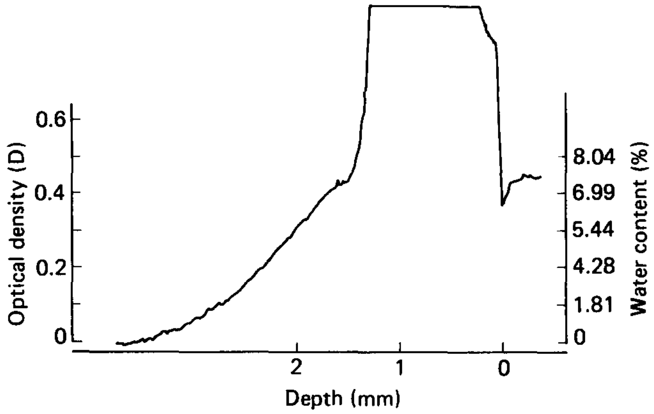


**Figure 7** Local concentration of water after diffusion of 10% HCl

The curves can be calibrated in terms of water concentration (content) if autoradiographs of the standard are made simultaneously. The optical densities of autoradiographs of specimens can be compared with those of the standard. If we know the so called densitometric curve of the film used and the specific activity of diffused water we can compute the dependence of optical density on water content. The corresponding values are shown on the right-hand sides of *Figures 6* and *7*; the water content scale is logarithmic.

## REFERENCES

1 Crank, J. 'The Mathematics of Diffusion', Clarendon Press, Oxford, 1968
2 Kimma, M. A. and Choi, S. S. Proc. 21st Tech. Man. Conf. RPD SPI, Chicago, 1966
3 Jokš, Z., Krejči, M. and Menclovà, B. *Radioisotopy* 1979, **20**, 533