

# The diffusion of hydrochloric acid in polyester thermosetting resins

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The possibility of diffusion of corrosive media in polyester resins is considered as a contributor to the process of stress corrosion cracking in glass reinforced polyester composites. It is shown that neither the saturation levels reached nor the rate of diffusion achieved for hydrochloric acid is sufficient for this mechanism to be considered a significant contributor to the process of low stress induced corrosion. It is believed that the corrosive medium will attack the fibres by a process of percolation through stress induced microcracks.

## 1. Introduction

Glass fibre reinforced polyester resin composites may be subject to failure by stress corrosion cracking under the simultaneous effects of low applied stresses and a corrosive environment [1]. The principal cause of failure is the weakening, by chemical corrosion, of the primary load bearing glass fibres [2]. Fibre failure leads to locally increased stresses and sharp crack propagation through the composite proceeding at an increasing rate as the stress intensity at the crack tip increases. Work with acidic environments has shown that [1, 3], at low loads, the resulting fracture surface is remarkably smooth. It is this low stress regime which is of particular interest to establish criteria for the long-term service life of pipes and vessels.

In such low stress regimes it is known [2, 4, 5] that failure of the glass reinforcement only occurs if the aggressive agent can gain access to the fibres. Two processes may be envisaged by which this can occur. Firstly, the existence of microcracks, or flaws, in the resin can allow passage of the corrosive medium to the fibres by a percolation process. This has been shown to be a possible mechanism, even in the absence of an applied load [6] and is particularly prevalent in cross-ply laminates due either to residual thermal stresses or to the swelling associated with the uptake of water by the polymer. The alternative possibility is that of diffusion of the corrosive environment through an undamaged, homogeneous matrix. It is to the question of the possibility of the latter mechanism to which this paper is addressed.

Having identified the alternative mechanisms by which the corrosive medium can gain access to the fibres in a composite it is necessary to ascertain whether the timescales and rates of such mechanisms are in agreement with the overall timescale and rate of stress corrosion cracking in the composite. In general

there are three important processes and their associated timescales to be considered.

1. Timescale needed for diffusion of the corrosive medium through the resin.
2. Timescale for resin cracking and percolation of the corrosive medium.
3. Timescale for weakening of the fibres, in contact with the corrosive medium, at a particular applied stress.

In this paper we consider the possibility of the first of these mechanisms.

In keeping with previous work [3] the corrosive medium used is aqueous hydrochloric acid acting on a number of polyester resins. Water alone is known to permeate polyester resins and has a maximum solubility between 0.5 and 2.5 wt % at room temperature [7, 8].

Various techniques have been applied for the measurement of water solubilities and diffusion coefficients, including the direct measurement of weight increase on exposure to water [8, 9] and the use of a radioactive tracer method to determine concentration profiles within an exposed specimen [7]. In an early study by Regester [10] an attempt was made to follow the penetration of both water and hydrochloric acid into an E-glass/polyester composite material with a gelcoat barrier layer. Regester showed that the composite was readily permeable to water but there was no detectable penetration of the hydrochloric acid through the barrier layer. A limitation of these measurements, however, was imposed by the relative insensitivity of the X-ray fluorescence method used for the chlorine determinations, which restricted the amount detectable to about 0.1 wt %. Sensitivity and sample handling problems also restrict the application of the energy-dispersive X-ray analysis (EDAX)

technique with the scanning electron microscope (SEM) for chlorine measurements in polyester resins.

In the present work a modified version of the radioactive tracer method [7] is used to examine the diffusion and solubility of molar aqueous hydrochloric acid in a range of resins, in an unstressed, room temperature environment. The objective is to ascertain whether the rate of diffusion and solubility of the acid in the bulk resin is sufficient to create an aggressive environment for fibre weakening to occur.

## 2. Experimental method

The radioactive tracer method was selected for use in these studies for the following reasons. Firstly, it is possible to achieve very high sensitivity as the radioisotopes used do not occur naturally. This sensitivity can be used to the full without interference from contaminants in the samples or the environment. Low diffusion rates can be measured without the need for excessively long exposure times or inconveniently large specimens. Secondly, since the source of the diffusing material is uniquely tagged it provides unambiguous evidence of the movement of material from the diffusant solution into the polymer. Finally, it enables the diffusion of different molecular species to be followed simultaneously. This is of interest because the diffusion and solubility characteristics of aqueous solutions of hydrochloric acid in resins are complicated by the fact that the water and the hydrochloric acid are almost certain to have different solubilities and diffusion rates. If penetration of the polymer structure is a thermally activated process occurring at the molecular level the diffusion rates would be expected to be significantly temperature dependent and the relative proportions of acid and water would vary with diffusion depth. On the other hand the permeation of the resin by an acid solution through cracks or pores in the material could lead to the transport of the acid solution through the resin without change in concentration and with only a relatively small effect of temperature on the rate of movement of the acid through the material. In seeking to explore these different possibilities it was therefore of interest to consider, in some of our experiments, a method in which the movement of both the water and the hydrochloric acid through the resins could be followed simultaneously. This was found to be possible by using two different beta-emitting isotopes to label the two compounds. The water was traced with tritium ( $^3\text{H}$ ,  $t_{1/2} = 12.3$  years,  $E_{\text{max}} = 0.018$  MeV) whilst the hydrochloric acid was traced with  $^{36}\text{Cl}$  ( $t_{1/2} = 300 \times 10^3$  years,  $E_{\text{max}} = 0.714$  MeV) where  $t_{1/2}$  is the half-life of the radioactive isotope,  $E_{\text{max}}$  is the maximum energy of the emitted beta particle. The energy difference between the two isotopes is very large and it is easily possible to resolve the counts from the two isotopes by beta spectrometry, using a liquid scintillation counter (Tracor model 6892).

Results from recent published work [7–9] show that water diffuses through polyester resins in accordance with Fick's law at room temperature with diffusion coefficients of the order of  $10^{-9}$  cm<sup>2</sup> sec<sup>-1</sup>. The specific activity of the tritiated water used for the present

experiments was about 10 Ci ml<sup>-1</sup> and that of the  $^{36}\text{Cl}$ -labelled hydrochloric acid about 1 Ci ml<sup>-1</sup>.

The diffusant solution was molar hydrochloric acid and it was estimated that at this activity level a concentration of 0.001 M HCl in the fluid dissolved in 40 mg polymer samples saturated with diffusant could be detected and measured.

### 2.1. Solubility and diffusion measurements

The method used was required to provide accurate values of both solubilities and diffusion coefficients. The total uptake method [11] was found to be best suited to meet these requirements, since it gives a direct measure of both the solubility and the diffusion coefficient of each diffusant in the polymer. In using this method a number of nominally identical polymer specimens were prepared, weighed and exposed to the radioactive diffusant for various times. After exposure the uptake of diffusant in each specimen was measured by radioactive assay and the results were used to construct uptake against time profiles. The flat portions of these profiles represent the situation where the specimen is saturated with diffusant and are a direct measure of diffusant solubility. Diffusion coefficients are calculated from the rise time of the curve as discussed by Ellis and Found [8], who have shown that for thin flat plates the half-saturation time,  $T_{1/2}$ , is related to the diffusion coefficient  $D$  by the equation  $D = 0.049L^2/T_{1/2}$  where  $L$  is the plate thickness. For cylindrical specimens, which have been used to minimize edge effects,  $D = 0.063a^2/T_{1/2}$  where  $a$  is the cylinder radius.

The two types of specimen used in the present work were (a) thin plates, approximately 36 mm × 8 mm with thicknesses varying from 0.08 mm to 0.25 mm; (b) cylindrical rods 25 mm long with radius 0.6 mm. All the specimens were prepared by casting catalysed liquid resins which were allowed to cure overnight at room temperature prior to postcuring in the usual way. Exposure to the radioactive diffusant was achieved by immersing the specimens in 2 ml of radioactive molar hydrochloric acid.

### 2.2. Radioactivity measurements

On completion of the exposure to the radioactive diffusant it was imperative to wash the excess liquid from the specimen surface after removal from the solution. This is potentially a serious source of error since the amount of this surface material can exceed that which has diffused into the specimen. A suitable procedure was developed in which the specimen was washed by momentarily dipping it in three separate baths of inactive 0.01 M HCl. Tests on blank specimens showed that this procedure freed them from surface contamination.

The measurement of the  $^{36}\text{Cl}$  activity of the specimens was relatively easy since they were sufficiently thin to avoid self-absorption problems. However, the very low energy of the  $^3\text{H}$  beta particles causes very severe problems with self-absorption and the only satisfactory method of measurement by liquid scintillation counting is one in which the radioactive material is uniformly dissolved in the liquid phosphor. This

means that the water that has diffused into the polymer must be extracted and dissolved in the counting medium. Three different ways of achieving this were explored and the results were self-consistent:

i. Combustion of the washed specimens in a stream of air in a quartz tube containing a section packed with quartz chips and maintained at 1000°C. This treatment drove the diffusants out of the polymer, which was oxidized to  $\text{CO}_2 + \text{H}_2\text{O}$ . The radioactive water and hydrochloric acid was condensed in a cold trap together with the water of combustion and was subsequently dissolved in 20 ml of liquid phosphor.

ii. Slow extraction of the diffusants from the polymer specimens into 15 ml of liquid phosphor containing 0.2 ml of 0.01 M aqueous HCl. By carrying out this extraction directly in a counting vial the  $^{36}\text{Cl}$  assay could be made immediately since virtually all the high energy beta particles escape from the specimen into the scintillation medium. The  $^3\text{H}$  counts slowly increase with time as the radioactive water in the specimen equilibrates with that in the liquid phosphor. The massive excess of inactive water in the phosphor leads to essentially complete recovery of the  $^3\text{H}$  into the phosphor after about one week at room temperature.

iii. Reverse diffusion by immersing the washed resin samples in 2 ml inactive aqueous 0.1 M HCl. After 1 week the specimen was removed and placed in a second 2 ml of 0.1 M HCl. Each 2 ml of solution produced in this way was dissolved in 15 ml of liquid phosphor and counted. The counts from two to three extractions on each specimen were combined to give the total specimen counting rate, although in fact 95% of the activity was recovered in the first extract.

It was straightforward to find pulse discrimination settings that enabled  $^3\text{H}$  to be counted in one channel of the counter and  $^{36}\text{Cl}$  in the other. Quenching control and quantitative estimations of the amount of radioisotope present in each sample were achieved by counting matched liquid phosphor solutions containing known amounts of the radioisotope in question [12].

From the recorded counts on each specimen and the measured specific activities of the diffusant solutions it was easily possible to calculate the total uptake per unit weight for each specimen, and these data were used to construct the required uptake against time

### 3. Results

#### 3.1. Thin plate specimens

Solubility and diffusion data were obtained using the following polyester resins: (a) Scott-Bader Crystic 272; (b) blends of Scott-Bader Crystic 272 with Crystic 586 and (c) Beetle 870. These resins were chosen for study because from previous work [1, 3] detailed measurements were available of stress corrosion crack propagation rates for a range of E-glass composites made from them. Beetle 870 is a het-acid polymer and is relatively brittle. Crystic 272 is made from isophthalic acid and is less brittle. Crystic 586 is a resin modifying agent which makes Crystic 272 even less brittle.

Measurements were made first on thin plate specimens of Crystic 272 weighing about 50 mg. These were exposed to aqueous molar HCl labelled with  $^{36}\text{Cl}$  for periods varying from 1 h to 3 months. In all a total of 50 specimens were tested and were counted by the combustion and slow extraction methods described earlier. Examination of the results obtained showed that the uptake of  $^{36}\text{Cl}$  by the resin was very low in relation to the expected solubility of water in the resin. If the molar HCl had permeated the resin without change of concentration it would be expected that when the water uptake reached its saturation value in the resin the corresponding chlorine content would be about 0.06 wt %. The results obtained had a mean value of 0.0018 wt %. Moreover, the results showed much scatter, did not gradually increase with time and did not show a trend to level out at an equilibrium level representing the saturation solubility. It is believed that the acid may not be diffusing into the resin at all but is becoming absorbed on the specimen surface or entering surface microcracks, particularly at the cut edges of the specimens. Further experiments were made with Crystic 272 plate specimens of varying thickness which were exposed to the  $^{36}\text{Cl}$  labelled diffusant. In a parallel experiment a similar set of thin plate specimens of varying thickness were exposed to tritium-labelled aqueous molar hydrochloric acid for 310 h. These latter specimens were counted by the reverse diffusion method. From the radioactivity measurements on all these specimens the HCl and  $\text{H}_2\text{O}$  uptakes were calculated and the results obtained are given in Table I.

The water uptake results on plates 8 to 10 show that saturation is reached by the resin with the

TABLE I Crystic 272 solubility experiments at 20°C with thin specimens

Plate no.	Exposure time (h)	Weight (mg)	Thickness (mm)	HCl uptake, wt % from $^{36}\text{Cl}$ assay	$\text{H}_2\text{O}$ uptake wt % from $^3\text{H}$ assay
1	2280	0.098 58	0.25	0.001 36	
2	2280	0.098 17	0.25	0.001 29	
3	310	0.096 73	0.25	0.000 752	
4	2280	0.049 28	0.12	0.002 82	
5	2280	0.047 82	0.12	0.003 39	
6	310	0.028 84	0.08	0.003 00	
7	1968	0.025 92	0.08	0.004 10	
8	310	0.099 04	0.25		1.79
9	310	0.046 52	0.12		1.86
10	310	0.030 80	0.08		1.84

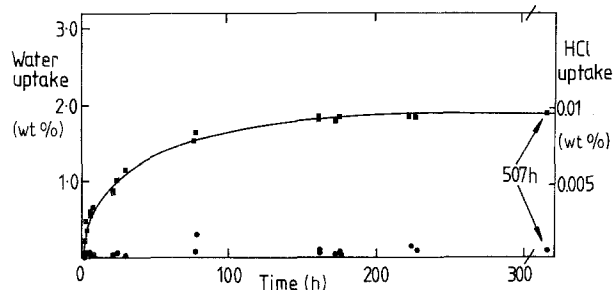


Figure 1 Diffusion of water and HCl into Crystic 272 at 20°C. (■) Water uptake by resin; (●) HCl uptake by resin (expanded scale). Largest measurements taken at 507 h.

exposure time of 310 h and that measured solubility is independent of sample thickness. The water uptake is reversible, since the counts were obtained by the reverse diffusion method, and the results are therefore consistent with the known Fickian diffusion of water into polyester resins.

In contrast to this the HCl uptake on plates 1 to 7, as measured by the  $^{36}\text{Cl}$  uptake of the resin samples, was extremely low and erratic. This clearly indicates that the samples do not saturate within the timescale of the experiments. In fact the best correlation appeared to be with the surface areas of the specimens.

### 3.2. Rod specimens

To demonstrate further the difference in the solubility and diffusivity of water and HCl in polyester resins dual labelling with  $^3\text{H}$  and  $^{36}\text{Cl}$  was used. High aspect ratio polymer rod specimens were used to minimize end effects and the results obtained are shown as a cumulative uptake curve in Fig. 1. These data were obtained at a laboratory temperature of 20°C and the points represent measurements made by the combustion and slow extraction procedures. The curve through the water uptake points is that for Fickian diffusion. It can be seen that water is diffusing into the polymer according to Fick's law and that the saturation solubility is 1.82 wt % with a diffusion coefficient of  $3 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ . The  $^{36}\text{Cl}$  data reflect very low or zero bulk diffusion into the polymer.

Complete diffusion profiles for the other polymers of interest were not measured at 20°C. It was considered sufficient to show that, on exposure to molar HCl, water diffused into the polymers to reach a saturation level whereas a negligible uptake of HCl occurred. Results for other polymers are given in Table II and relate to experiments with polymer rods exposed to the dual-tagged molar HCl for 2 weeks.

TABLE II Uptake of water and HCl by polymer rod specimens

Polymer	Water content, wt % after 345 h exposure	HCl content, wt % after 345 h exposure
Crystic 272	1.87	0.00063
25% Crystic 272 } 75% Crystic 586 }	2.41	0.00105
50% Crystic 272 } 50% Crystic 586 }	3.21	0.00204
Beetle 870	1.30	0.00050

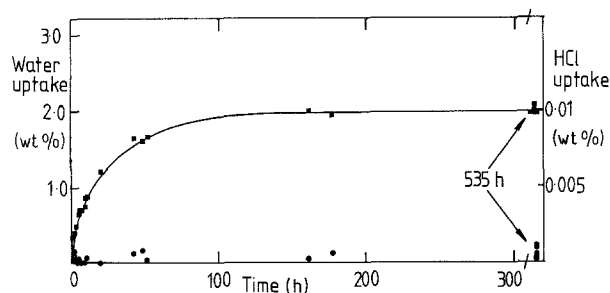


Figure 2 Diffusion of (■) water and (●) HCl into Crystic 272 at 25°C. Final group of measurements represent readings taken at 317, 362, 367 and 535 h with no consistent increase with time.

Although these data show a trend for HCl content to correlate with water content the measured levels are still extremely low in relation to the value of 0.07%, which would be obtained from Crystic 272 at saturation if the acid diffused without change of concentration.

The effect of temperature on the solubility and diffusion of water and HCl into these polymers was studied further and in Figs 2 and 3 curves for water and HCl uptake from molar HCl into Crystic 272 and Beetle 870 at 25°C are presented. Again the uptake of HCl is either seen to be very low or is confined to surface occlusion or adsorption.

### 4. Discussion

The results obtained for unstressed polymer resins show that, while water diffuses freely in the resin ( $D = 3 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$  at 25°C), achieving a relatively high saturation concentration ( $S = 1\text{--}2 \text{ wt } \%$ ), hydrochloric acid is unable to achieve such values. Strictly speaking the experimental data show that chloride ions will not diffuse through the polymer network and it is assumed that the need to overcome electrostatic attraction forces will preclude the diffusion of solvated protons into the polymer. We consider this to be a reasonable assumption since it would be necessary to provide energy to drive a charge separation process and it is unlikely that this would occur spontaneously. Register [10] attempted to measure hydrogen ion diffusion experimentally through polyester composites exposed to 5%  $\text{H}_2\text{SO}_4$  and 15% HCl at 100°C. No evidence of such diffusion was found after an exposure period of six months and Register concluded that  $\text{H}^+$  ion mobility is restricted by the anion mobility to preserve electrical neutrality within the laminate.

Although the very small uptake of chlorine observed

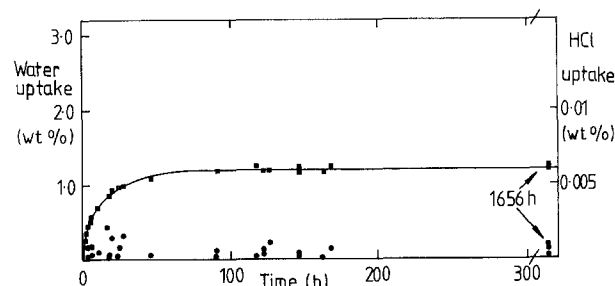


Figure 3 Diffusion of (■) water and (●) HCl into Beetle 870 at 25°C. Final group of measurements were taken at 812, 1007 and 1656 h with no consistent increase with time.

with the resin samples at room temperature is believed to be a surface effect it was possible to estimate an upper bound for a hypothetical diffusion coefficient. This was done by taking the largest observed uptake for Crystic 272 and assuming that the resin would eventually saturate to give an acid concentration of 0.1 M in the aqueous fluid diffusing through the resin. Interpreting the data in this way gives the maximum feasible diffusion coefficient for HCl as  $3.4 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ . This value can be used to compare the time available for diffusion in a composite during crack propagation with that required to build up a significant acid concentration at the surfaces of unbroken fibres at the crack tip.

Price and Hull [3] found with aligned E-glass/Crystic 272 composites in 0.6 M HCl that planar stress corrosion cracks would propagate at stress intensities in the range of 2 to  $6 \text{ MNm}^{-3/2}$ . A typical crack propagation rate was  $10^{-8} \text{ msec}^{-1}$ . Assuming that the average distance between the fibres is  $5 \times 10^{-6} \text{ m}$  the average time for the crack front to progress from fibre to fibre is about 10 min. Confirmation of this value has been obtained from the results of acoustic emission experiments [13].

Calculation shows that within this timescale the maximum acid concentration achievable by diffusion over the distance separating the fibres is less than  $10^{-6} \text{ M}$ . Such a low concentration is considered to be incapable of weakening the fibres sufficiently for progressive fibre breakage to occur.

We thus conclude that diffusion of hydrochloric acid cannot provide sufficient corrosive medium quickly enough to lead to fibre failure in stress corrosion cracking. In fact, from the results obtained it is highly unlikely that any significant diffusion of HCl occurs at all.

If stress effects cause an increase in acid diffusivity within the resin it would be necessary for this concentration to increase by 4 or 5 orders of magnitude for fibre weakening to become significant. It is very unlikely that stress effects would lead to such a magnification, although experiments are in hand to check this possibility.

## 5. Conclusions

A radioactive tracer method capable of measuring simultaneously the uptake of water and hydrochloric acid into unstressed polymers exposed to aqueous molar HCl has been developed. The results obtained with this method show that water diffuses into polyester resins in accordance with Fick's Law to reach

a saturation solubility in the range 0.5 to 3 wt % at or near room temperature. Hydrochloric acid, measured by chloride ion mobility, does not diffuse into or dissolve in unstressed polyester resin at or near room temperature to a sufficient extent to account for the fibre weakening that leads to stress corrosion crack propagation.

In stress corrosion cracking situations it is of course possible that high stresses at the crack tip are capable of opening up the polymer network for HCl diffusion, especially with ductile resins that are capable of yielding in the high stress field at the crack tip. This possibility is being examined in current work in which the radioisotope method is being used to quantify both diffusion and percolation processes in stressed resins.

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