JOURNAL OF MATERIALS SCIENCE 24 (1989) 1005–1010

Diffusion of aqueous hydrochloric acid into polyester resins

Part 2 *Effect of an applied stress on diffusion behaviour*

B. D. CADDOCK, K. E. EVANS,
Department of Materials Science and Engineering, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK

D. HULL
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

The influence of an applied stress on the solubility and diffusivity of aqueous hydrochloric acid in polyester resins has been examined. A radioactive tracer method, involving the use of ^{3}H and ^{36}Cl, enabled the mobility of both the water and the acid in the solution to be followed simultaneously. The results obtained were in accordance with those obtained previously with unstressed resins and showed that whereas water would diffuse freely in stressed polymers, hydrochloric acid would not. The results have important implications in relation to the mechanism of crack propagation in E-glass/polyester composites.

1. Introduction

In a previous paper [1] a radioactive tracer technique was described to measure the extent to which aqueous hydrochloric acid diffuses into polyester resins. By using ^{3}H and ^{36}Cl as tracers it was found possible to monitor the mobility of both the water and the acid simultaneously in the polymers. The results obtained showed that water was able to diffuse freely and conformed with Fick's second law. Well-defined saturation levels were achieved at water contents in the range 0.5 to 3.5 wt %. The acid, however, was incapable of penetrating into the polymer network and it was concluded that the solubility of aqueous hydrochloric acid in the polyester resins examined was effectively zero.

Such a finding may have significant consequences for the mechanism of stress-corrosion crack propagation in glass-fibre reinforced composites made from such resins. With these composites it has been established [2, 3] that stress-corrosion cracking is primarily due to the weakening of the glass fibres by the corrosive action of the acid. Because the majority of the fibres in a composite are separated by polymer webs it is evident that the rate of crack propagation depends, *inter alia*, on the rate at which the acid can gain access to the fibres. The polymer is resistant to corrosion or short-term degradation by the acid and it is generally accepted that the acid can only reach the fibres by diffusion through the resin or by flowing through microcracks, voids, or crazes in the resin matrix. An understanding of the mechanism for crack propagation requires that both of these possibilities must be examined critically. The results described above favour flow through matrix cracks as the predominant acid transport mechanism.

An important consideration, however, is that a composite material experiencing stress-corrosion cracking is, by definition, in a condition of high local tensile stress, induced by the strain field of the incipient crack. This stress is the driving force for crack propagation in the composite [2, 4] and can have an important bearing on the failure process for two reasons. Firstly, it determines the extent to which fibre weakening must occur before the fibre will fracture. This, in turn, determines the minimum concentration of the acid that must accrue at the fibre surface in order to promote this weakening. Secondly, it determines the extent to which resin fracture and the associated development of microcracks in the resin at the crack tip will occur. If the stress field at the crack tip is not strong enough to cause local resin cracking it is still possible that fibre weakening could occur if the stressed resin became permeable to the acid. The concept of increased permeability in stressed resins has been shown to apply to water diffusion, which is enhanced by applying a stress [5, 6]. The effect, however, is relatively small, and has been shown to be correlated with the increase of the free volume of the polymer that results from the expansion of the polymer network as it is strained. No data are available on the effect of stress on hydrochloric acid diffusion in polyester resins; this deficiency is met by the present paper.

1.1. Diffusion data for unstressed resins

The crack propagation process is seen as one in which

0022-2461/89 $03.00 + .12

TABLE I Uptake of water and HCl by polymer rod specimens after 345 h exposure to molar hydrochloric acid, in the absence of an applied stress

Polymer type	wt % H_2O in resin	wt % HCl in resin
Crystic 272	1.87	0.000 63
25% Crystic 272 75% Crystic 586	2.41	0.001 05
50% Crystic 272 50% Crystic 586	3.21	0.002 04
Beetle 870	1.30	0.000 50
80% Crystic 272 20% NV 1080	2.07	0.000 43

crack growth accelerates with increasing crack length for a given applied load, progressing slowly at first, but eventually very rapidly. Price and Hull [4] measured crack propagation rates in glass-fibre composites, using a series of resins that exhibited a range of fracture toughness. Typically, the crack propagation rate during the slow growth stage of the process was found to lie in the range 10^{-6} to 10^{-10} m $\sec^{-1}$. This measured rate is important in that it sets the timescale for events occurring at the crack tip during propagation. Diffusion data have been obtained on all these resins in both the stressed and unstressed conditions. For convenience in comparing results, Table I lists acid and water solubility data obtained in previous work on unstressed resins [1], together with new data on the flexible resin Crystic 272 + 20% NV1080. Three of the materials listed in Table I are based on Crystic 272 resin, which is a cross-linked unsaturated polyester resin. It is made by condensing isopthalic acid and maleic anhydride with propylene glycol. Additional cross-linking is obtained by further reaction with styrene. The flexibilizing additives, Crystic 586 and NV 1080, are both rubbery materials. Beetle 870 is another polyester resin made from a chlorinated acid (HET acid: hexachloroendomethylenetetrahydrophthalic acid).

It can be seen that the new data for the flexible resin are consistent with the earlier results. None of the resins, when tested in an unstressed condition, exhibited a significant solubility for hydrochloric acid.

2. Experimental details

The data in Table I were all obtained by immersing resin specimens in the liquid diffusant. The specimens were not subjected to an externally applied stress, although there may have been internal stresses in the specimens [7], due to either residual thermal stresses, or to swelling associated with the uptake of water. A method for measuring the influence of high stresses or strains on acid solubility and diffusivity in the polymer was required, to determine their importance in stress corrosion. A test method was developed that uses an initially curved, unstressed thin plate of resin, which was then flattened between two microscope slides (see Fig. 1). An appropriate expression for the tensile stress generated on the concave side of the plate, when flattened is

$$\sigma \simeq ED/2\varrho \tag{1}$$

where D is the sample thickness, ϱ the radius of curvature, E the modulus, and σ the surface stress. It is therefore possible to obtain different tensile stresses by varying either the sample thickness or the radius of curvature. In practice, both were varied, so that a range of surface stresses were obtained when different curved plates were fully flattened during the subsequent tests.

The stress field is equivalent to that for an initially flat plate deformed in four-point bending to the same radius of curvature. The surface tensile stress will fall with increasing depth from the initially concave surface, tending to zero halfway through the thickness of the plate. Thereafter an equivalent compressive stress develops which reaches a maximum at the initially convex surface of the plate. An "O"-ring seal was used to define a constant area within which the radioactive diffusant was confined on the flattened plate surface.

2.1. Specimen preparation

To prepare the initially curved plates, tubes were manufactured by introducing a measured amount of catalysed, accelerated resin into a pipe, which was then spun about its longitudinal axis. The pipe acted as a mould and the resin formed a constant thickness layer on the inside surface of the pipe. When the resin

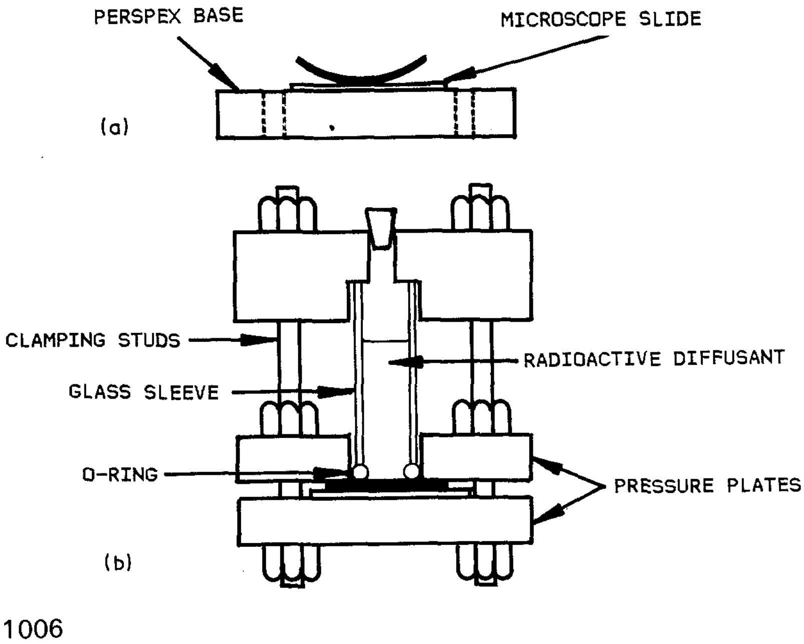

Figure 1 Rig for exposing stressed plates to radioactive diffusant. (a) Unstressed curved plate prior to assembly. (b) Stressed plate in assembled rig.

set, a hollow tube was left which, on release from the mould, was cut to make the required curved plates. Moulds for making resin tubes were made from lengths of 25 and 40 mm diameter aluminium pipe. These pipes were split axially to enable a ground joint to be made between the two halves. After grinding, the two halves were clamped together and the outside and inside surfaces were re-machined to restore the circular cross-section of the moulds. A slot was also provided to assist in mould separation and specimen release.

To use the moulds it was necessary to have a very smooth surface finish on the inside walls. Every time a mould was used the inside wall was treated with a mould release wax and the surface was buffed to give a mirror finish. The moulds were sealed by coating the ground joint with silicone rubber sealant. The seal was made by clamping the treated mould together at 50 to 60° C for 1 to 2 h before use. After introducing the measured quantity of resin, the mould ends were sealed with rubber bungs. The whole assembly was spun in a lathe for 4 h and finally the resin was post-cured at 80° C for 4 h. By varying the amount of polymer added to the moulds, tubes with wall thicknesses in the range 0.3 to 2 mm were produced without difficulty, with a very uniform thickness. The curved plates were obtained by cutting the tubes on a mandrel with a jeweller's saw, and the cut edges were ground to remove any asperities. The pieces used for the tests were approximately 16 mm wide and 20 mm long.

2.2. Estimation of stress levels in flattened plates

It was found that the tube sections retained their shape when cut axially, indicating that there were no major residual stresses in the cut plates. Standard three-point bend tests were conducted, using an Instron 1185 tensile test machine, to see if measured values of flexural strength and modulus agreed with the estimates derived from the simple beam formula given in Equation 1.

Using specimens cut from cast Crystic 272 sheets, with thicknesses of 2.2 and 1.2 mm, the standard flexure test method [15] was used to obtain a simple average value for the flexural failure stress, σ_b^*, and the flexural modulus, E_b, from four tests, giving $\sigma_b^* = 114 \pm 11$ MPa and $E_b = 3.58 \pm 0.26$ GPa.

As a consistency check, a scale sketch of one of these four plates was made just prior to failure. The measured failure stress of this particular plate was 128 MPa. From the sketch the radius of curvature of the deformed plate at the instant of failure was obtained. Using this value and the above average value of the modulus, Equation 1 was used to calculate the surface stress at failure as 143 MPa. This value compares well with the measured value, obtained from the standard flexure test, of 128 MPa. Equation 1 was therefore considered to be an effective measure of the reverse situation of estimating the stress in an initially curved plate when flattened.

2.3. Measurement of diffusion in stressed plates

The design of the rigs for the measurement of stress-induced diffusion is shown in Fig. 1. A number of these rigs were made to enable several tests to be carried out simultaneously.

In use, the curved specimen rests on a microscope slide, sited between two Perspex pressure plates. A glass sleeve passes through a central hole in the upper plate and bears on an "O"-ring, thus forming a small enclosure for the radioactive diffusant. A third Perspex plate serves to compress this "O"-ring seal by means of the clamping bolts. Great care was needed when tightening up the clamping bolts to avoid specimen fracture. In trying to achieve loads in excess of 0.75 of the fracture strength, uneven loading of the plates and strength variability led to a failure rate during assembly of about 50%. Assembly was much easier at lower loads.

After assembly, the rigs were charged with radioactive diffusant by means of a Pasteur pipette. At the end of each exposure the same pipette was used to remove the excess diffusant. The specimens were recovered by dismantling the rigs, and were cleaned of surface contamination by blotting dry the exposed surface with absorbent paper. Counting was carried out by the methods described in an earlier paper [1].

2.4. Effect of stress gradient on solubility and diffusivity.

The method of stressing the specimens described above generates a tensile stress which is a maximum at the initially concave surface. Quantitative interpretation of the effects of stress on solubility and diffusivity is complicated by the presence of a stress gradient through the thickness of the plate. The current objective, however, was to establish qualitatively whether or not acid solubility and diffusivity were influenced at all by the application of a tensile stress. This was done by making comparative tests, in which the ^{3}H and ^{36}Cl uptake of stressed plates was compared with that found with unstressed plates. To achieve this comparison, initially curved plate specimens were tested alongside initially flat plates, which were not under stress when installed in the rigs.

Unreinforced resin specimens, when subjected to an applied load, are prone to creep. The effect of this is that the initial surface tensile stress produced by flattening a curved plate decays with time as creep

TABLE II Comparison of ^{36}Cl and ^{3}H uptake by stressed and unstressed Crystic 272 plates. Slow extraction measurements [1] after 212 h exposure to the radioactive diffusant

Specimen	Radius of curvature (mm) r	Thickness (mm) t	Net counting rate (counts min^{-1})		Surface stress (% of max)
			^{3}H	^{36}Cl	
SR1	flat	1.24	19 975	23	0
SR2	12.5	0.40	13 534	81	50

occurs. It was therefore reasoned that the best chance of observing a stress effect on solubility or diffusivity would be at relatively short exposure times. This also ensured that the diffusion, if any, would be occurring in that region of the specimen where the tensile load was highest, i.e. near to the concave surface. The experiments described below involve a range of exposure times, to cover this situation.

The efficacy of the blotting method for removing gross contamination of the specimen surface by excess diffusant was checked in a separate experiment, in which one of the initially flat plates was exposed to the radioactive diffusant for only a few seconds. It was found that the method effectively decontaminated the exposed surface.

3. Results

3.1. Crystic 272 resin

In the first experiment with Crystic 272, a curved plate, cut from a 25 mm diameter tube was used. The wall thickness was 0.40 mm and the ^{3}H and ^{36}Cl uptakes of this plate were compared with that from a flat plate with a thickness of 1.2 mm. The results are given in Table II. The actual ^{3}H and ^{36}Cl counts were obtained by the slow extraction method [1] and were corrected for the background counting rate. The surface stress was estimated using Equation 1 and is given as a fraction of the surface tensile stress at failure for a dry plate.

As can be seen from Table II, there is no large increase in the ^{3}H uptake by the stressed specimen SR2, compared with the unstressed specimen SR1. Although there is a rise in the ^{36}Cl uptake with the stressed specimen, this is very small compared with the count rate associated with the build-up of a significant acid concentration in the fluid diffusing into the resin. Using the methods described in [1] it is estimated that the ^{36}Cl counts expected for 1 M HCl diffusion would be 2960 counts min^{-1}. The acid uptake is thus considered to be negligible. The small increase in the uptake of ^{36}Cl detected with the stressed specimen could easily be a consequence of surface cracking.

In a similar experiment, two more specimens were cut from a slightly thicker tube of Crystic 272. This produced an increased surface stress when the plates were flattened. The water and acid uptakes of these plates were again compared with those from unstressed plates. In these experiments the exposure time was shortened, to maximize tensile stress effects, and the measurements were made by the reverse diffusion method [1]. The results are given in Table III.

Again, the results for the ^{36}Cl uptake are very low in relation to the level expected for the diffusion of the molar acid. Unchanged diffusion of the acid would have given 1671 counts min^{-1} for SR10 and 1230 counts min^{-1} SR11. The flat plate, SR8, gave the highest ^{36}Cl count rate in this group of specimens. The rate corresponding to the uptake of molar acid by this specimen is 3500 ^{36}Cl counts min^{-1}. It was noticed that the exposed surface of SR8 had been scratched during sample preparation. The increase pick-up by the scratched surface emphasizes the importance of surface condition in these measurements.

To obtain data at higher stress levels, use was made of resin tubes made with a wall thickness of 1 mm in a 40 mm diameter mould. The results obtained are given in Table IV. Again, insignificant changes in the ^{36}Cl concentration are observed under stress. In all the long-term experiments involving stressed resin specimens, significant creep was observed, evidenced by a change in the curvature of the plates on load release. From the reduction in curvature seen in these tests it was estimated that the stress was approximately halved after an exposure of 200 h. Specimen SR17 had been deliberately scratched on the exposed surface. The adverse effect of this treatment can clearly be seen in the results.

3.2. Crystic 272 with NV 1080

Measurements were also made on the most flexible resin used by Price and Hull [4] for crack propagation measurement, i.e. Crystic 272 + 20% NV1080, designated resin 1080. The results obtained with stressed plates of resin 1080 are shown in Table V. As can be seen there is again insignificant diffusion of HCl into the resin. Once again it was noted that after exposure to the diffusant under stress for a period of one week, severe creep of the curved plates was apparent. With this resin the effect seemed to be more severe than with Crystic 272, as expected.

4. Discussion

It is clear from the results obtained that the application of a tensile surface stress in the range 50 to 80% of the fracture stress in tension does not substantially enhance the ability of HCl to penetrate the polymer network for Crystic 272, even when the resin is flexibilized with NV 1080. Neither the stress at short times, nor the yielding and permanent strains associated with the creep that occurs at long times, appears to alter the very low or zero solubility of the acid in the resin.

Water, however, diffuses as freely with stress as without, although no significant difference between the two cases was seen. This is in accord with the work of Marom and Broutman [5]. They have related a small increase in water solubility, observed in certain stressed resins, with an increase in the free volume of the polymer. This free volume increase is a direct

TABLE III Comparison of ^{36}Cl and ^{3}H uptake by stressed and unstressed Crystic 272 plates. Results for 169 h exposure

Specimen	Radius of curvature (mm) r	Thickness (mm) t	Assay method	Net counting rate (counts min^{-1})		Surface stress (% of max)
				^{3}H	^{36}Cl	
SR8	flat	1.84	rev diff	15979	154	0
SR10	12.5	0.52	rev diff	7640	42	65
SR11	12.5	0.48	rev diff	5625	65	60

TABLE IV ^{36}Cl and ^{3}H uptake by stressed and unstressed Crystic 272 plates of the same thickness. Results for 336 h exposure

Specimen	Radius of curvature (mm) r	Thickness (mm) t	Assay method	Net counting rate (counts min^{-1})		Surface stress (% of max)
				^{3}H	^{36}Cl	
SR12	20	1	slow ex	13 305	40	78.5
SR13	20	1	rev diff	13 470	25	78.5
SR14	20	1	rev diff	13 079	0	78.5
SR15	flat	1	slow ex	15 709	60	0
SR16	flat	1	rev diff	12 557	0	0
SR17	flat	1	rev diff	16 695	357	0

consequence of polymer strain. However, they have estimated the maximum increase in water solubility, even at high stress levels, to be only of the order of 2% of the total amount of water present.

The acid does appear to be taken up by surface imperfections in the resin, and it was not found possible to prepare specimens without these imperfections. However, the characteristic features of a diffusion process are the gradual build-up of the diffusant in the specimen, culminating in the attainment of a saturation level, representing the solubility of the diffusant in the resin. These features are clearly evident in the results obtained for water diffusion in polyester resins [1], but not in those concerned with acid diffusion. The absolute sensitivity of these solubility measurements depends on the specific activity of the tagged diffusant, the background counting rate and the stability of the liquid scintillation counter. Taking these factors into account it was estimated that the count rates observed above for ^{36}Cl were equivalent to a maximum concentration of 0.005 M in the aqueous fluid diffusing through the resin. This effective concentration is substantially lower than that needed to weaken E-glass in a composite subjected to stress-corrosion cracking [8].

A possible explanation for the very different behaviour of the water and HCl is the ionic character of the acid in aqueous solution, where it exists as hydrated hydrogen ions (hydroxonium ions, H_3O^+) and chloride ions. Because the resin is a non-ionizing environment, the chloride and hydroxonium ions have a much higher affinity for water than for the resin, and would not be expected to enter the dry resin. Water, on the other hand, is predominantly covalent in character, and is readily able to enter and move through the holes and spaces in the resin network as uncharged molecules. This is clearly what happens when moisture diffuses into the resin from the vapour phase. The implication of this model is that the ionized acid can only enter the polymer if sufficient water is taken up to establish a continuous liquid network, in which the acid can dissolve. In a sense this is a limiting case of cavitation or cracking occurring in the matrix to produce interconnected ligaments of liquid extending through the resin. Thus acid diffusion cannot occur if water diffusion involves the random movement of individual covalent water molecules in a general way through the resin network. Because insufficient water molecules are present at 2% concentration to form a continuous phase, the movement of the ions is prevented.

5. Conclusions

A radioactive tracer method has been developed to enable the solubility and diffusivity of water and hydrochloric acid to be measured simultaneously in stressed specimens of polyester resin. The stress is applied by flattening initially curved plates in a rig, in which the radioactive diffusant is contacted with the flattened surface in an area defined by an "O" ring. The only limitation to the level of the initial stress that can be applied to the specimens is that they do not fracture during the initial application of the stress. It was noted that significant creep occurred during the tests, so that the surface stress initially applied to the specimens decayed with time, leading to a situation of permanent strain at long times. Measurements have been obtained by this method on a group of resins that exhibit a range of flexibility and fracture toughness. The results show that the application of a tensile stress, to within 75% of the fracture load of the resin, does not make the resin permeable to the acid. In accordance with

TABLE V ^{36}Cl and ^{3}H uptake by stressed and unstressed resin 1080 plates. Reverse diffusion results for 168 h exposure to molar HCl

Specimen	Radius of curvature (mm) r	Thickness (mm) t	Net counting rate (counts min^{-1})		Predicted ^{36}Cl counting rate for M HCl diffusion
			^{3}H	^{36}Cl	
SR18	flat	1.40	18 370	33	1934
SR19	flat	1.40	7 948	30	1837
SR20	12.5	1.00	10 171	119	2350
SR21	12.5	1.00	9 600	44	2218
SR22	12.5	1.00	8 796	24	2032
SR23	12.5	1.00	10 338	18	2349
SR24	flat	1.6	9 135	19	2085
SR25	flat	1.6	7 904	16	1804
SR26	12.5	1.6	11 328	47	2586
SR27	12.5	1.6	10 784	24	2473
SR28	12.5	1.6	10 037	50	2291
SR29	12.5	1.6	9 502	66	2169

previous work on unstressed resins, it was found that water was readily taken up by the stressed resin specimens. The resulting acid concentrations are too low to cause fibre failure during stress corrosion in composites. Matrix voids, microcracking, crazing or similar mechanisms are required, therefore, to allow transport of the acid to the fibres.

References

1. B. D. CADDOCK, K. E. EVANS and D. HULL, *J. Mater. Sci.* **22** (1987) 3368.
2. P. J. HOGG and D. HULL, in "Developments in GRP Technology-1", edited by B. Harris (Applied Science, London, 1983) p. 37.
3. B. A. PROCTOR, "Glass Current Issues", in Proceedings of Nato Advanced Study Institute, Puerto de la Cruz, Tenerife, April 1984 (Martinus Nijhoff, Dordrecht, Netherlands, 1985) p. 524.
4. J. N. PRICE and D. HULL, *J. Mater. Sci.* **18** (1983) 2798.
5. G. MAROM and L. J. BROUTMAN, *Polymer. Compos.* **2** (3) (1981) 132.
6. S. NEUMANN and G. MAROM, *J. Mater. Sci.* **21** (1986) 26.
7. J. KABELKA, "Developments in reinforced plastics-3", edited by G. Pritchard (Elsevier, London, 1984) p.189.
8. B. D. CADDOCK, PhD thesis, University of Liverpool (1987).
9. J. N. PRICE and D. HULL, *J. Mater. Sci.* **22** (1987) 331.
10. B. NOBLE, S. J. HARRIS and M. J. OWEN, *ibid.* **18** (1983) 1244.
11. C. LHYMN and J. M. SCHULTZ, *ibid.* **18** (1983) 2029.
12. F. R. JONES and P. A. SHEARD, "Fibre reinforced composites conference", Liverpool, 1986 (Institute of Mechanical Engineers, London, 1986) p. 63.
13. F. R. JONES, J. W. ROCK and J. E. BAILEY, *J. Mater. Sci.* **18** (1985) 1059.
14. L. N. McCARTNEY, *Proc. Roy. Soc. Lond.* **A409** (1987) 329.
15. BS 2782, part 10, Method 1005 (1977).

Received 4 March
and accepted 25 July 1988