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Strength loss in E-glass fibres after exposure to hydrochloric, hydrobromic and hydriodic acids

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The corrosion of E-glass fibres by hydrochloric, hydrobromic, and hydriodic acids has been investigated by measuring the loss of mechanical strength of the fibres following immersion in solutions of the acids. Corrosion is greatest in hydrochloric acid and least in hydriodic acid. Curves of percentage strength retention against concentration show well-defined minima for hydrochloric and hydrobromic acids, but not for hydriodic acid. This phenomenon has been attributed to complex ion formation by metal ions in the glass with chloride or bromide ions in the corroding solution. Spectroscopic evidence suggests that ferric ions play an important role in the corroding process.

1. Introduction

Glass fibre reinforced composite materials have been used in a variety of applications, many of which involve exposure to strongly acidic environments. However it is becoming increasingly apparent that strong acids have a corrosive effect on such materials and several instances of corrosion related failures have been reported [1, 2]. The susceptibility of composites to corrosion-related failure is particularly severe when the material is under mechanical stress [1–7]. Investigations [1–4] of stress corrosion cracking of glass fibre composites have indicated that the glass fibre component of the composite is the constituent which breaks rather than the resin or resin–fibre interface, the resin in fact playing a protective role shielding the fibres from the corrosive environment. Several workers have described the effect of strong acids on glass fibres [8–10] and this has been attributed to the replacement of cationic species in the glass, such as sodium, calcium and aluminium, by the hydrogen ions from the acids according to the equation

$$\overline{\mathrm{M}^{n+}} + n\mathrm{H}^+ \rightleftharpoons \mathrm{M}^{n+} + n\overline{\mathrm{H}^+} \qquad (1)$$

where the bar denotes association of the species with the glass phase. As the hydrogen ions are much smaller in size than the cations replaced, tensile stresses are induced on the surface of the glass fibre and eventually these stresses initiate cracks [7]. The major cations replaced in E-glass, which forms the bulk of the material used for reinforcement, are calcium and aluminium, and it has recently been shown that a zirconia glass which does not contain either of these elements is not corroded to any extent when immersed in solutions of sulphuric acid [4].

A more recent investigation [11] in which the strength of E-glass fibres was determined after immersion in strong mineral acids, has suggested that in addition to the hydrogen ions, the anion present is also important in the corrosion process mainly for two reasons. Firstly, certain anions may associate with the leached metal cations to form insoluble salts, for example sulphuric acid corrosion in which calcium sulphate is formed, and effectively M^{n+} is removed from the right-hand side of the ion exchange equation (Equation 1), thus favouring the forward reaction. Secondly, anions which can associate with the leached metal cations to form complex neutral or anionic species will again favour the forward reaction

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and accelerate corrosion. The example quoted [11] was ferric ion during hydrochloric acid corrosion, which could form species such as $FeCl_4^-$ by the reaction

$$Fe_2O_3 + 8HCl \rightleftharpoons 2FeCl_4^- + 3H_2O + 2H^+ \quad (2)$$

This reaction is expected to be favoured at a particular concentration of hydrochloric acid, as increasing the hydrochloric acid concentration would favour the forward reaction but increasing the hydrogen ion concentration would favour the reverse. This would be shown by a well-defined minimum in a plot of corrosion rate against acidic strength, and has in fact been observed [11]. Although ferric oxide is only a minor component (0.39%) of E-glass, its removal was suggested to have a destabilizing effect on the glass structure which facilitated the removal of other cations [11].

This present work further investigates this hypothesis by examining the residual strength of E-glass fibre after exposure to hydrochloric, hydrobromic and hydriodic acids, which respectively have increasing acid strengths but decreasing ability to form complexes with ferric ions. (I^- is oxidized by Fe^{3+} and does not form complexes at all). The other halogen acid, hydrofluoric acid, attacks glass by a different and well-known mechanism involving attack of the silica lattice and was therefore not considered.

2. Experimental details

Glass fibre specimens 200 mm long were cut from an E-type roving 2275 TEX of chemical composition shown in Table I. Exposure of the glass fibres to aqueous solutions with varying concentrations of hydrochloric, hydrobromic and hydriodic acids was allowed to proceed for 72 h, after which the specimens were washed, air dried and subjected to tensile testing. The tensile procedure followed was identical to that described previously [11]. At least six specimens were tested for each data point and the mean and standard deviations of the peak loads calculated. Tests were repeated if the standard deviation was greater than 10% of the mean load. For less corroded (i.e. stronger) specimens, standard deviations were generally within 5% of the mean, but for more corroded specimens the standard deviations tended to increase, presumably because damage was not necessarily the same for each fibre nor uniform along the fibre length. The mechanical test results are presented in terms of percentage strength retention of corroded samples compared to control specimens.

TABLE I Percentage composition of E-glass fibres

SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	B_2O_3
52.10	14.86	23.90	1.78	0.39	1.02	1.06	4.29

The tests in hydrochloric acid were then repeated in the presence of 1 mol dm^{-3} ferric chloride in order to determine the effects of ferric ion on the corrosion process.

Further experiments were performed in which the hydrogen ion concentration was varied in the presence of constant chloride concentration, and in which the chloride ion was varied in the presence of constant hydrogen ion concentration. The solutions were prepared using appropriate amounts of hydrochloric acid, sodium chloride and nitric acid. The object of this experiment was to test the effect of the complexing anion.

Results are presented in terms of percentage strength retention of corroded samples compared to control specimens. Hydrogen ion activities for hydrochloric and hydrobromic acids are presented as Hammett acidity functions, H_0, which allow for incomplete dissociation in concentrated solutions and which are a better representation of acidic strength than molar concentrations [12]. Acidity functions for hydriodic acid have not been found in the literature, but the pK_a values in aqueous solution for hydriodic, hydrobromic and hydrochloric acids are -10, -9 and -7 respectively [13], indicating decreasing acid strengths and hence decreasing acidity functions for a given concentration.

3. Results

3.1. Strength retention after exposure to the acids

Fig. 1a shows strength retention against hydrogen ion concentration for each of the three acids. Fig. 1b shows strength retention against acidity function for hydrochloric and hydrobromic acids.

After 72 h, percentage strength retentions in hydrochloric and hydrobromic acids show marked minima at [HCl] = 3 mol dm^{-3} ($H_0 = -1.0$) and at [HBr] = 2 mol dm^{-3} ($H_0 = -0.6$), the strength loss in hydrochloric acid being

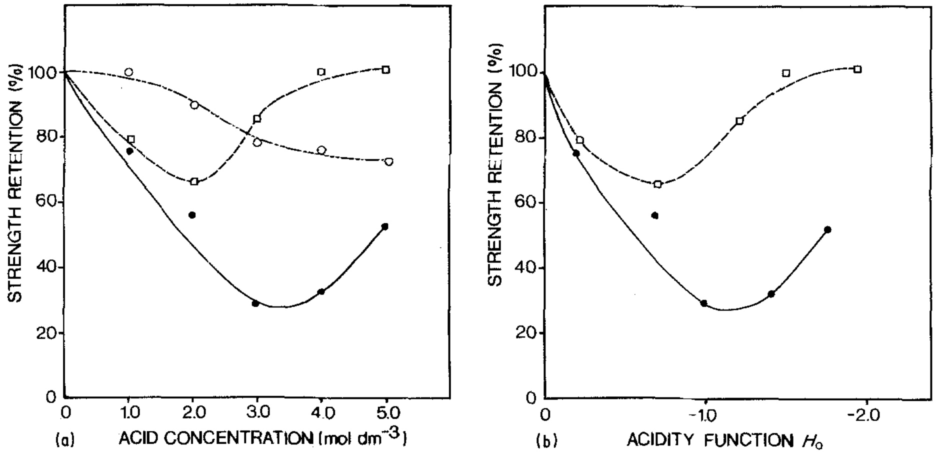

Figure 1 Strength retention against (a) acid concentration and (b) acidity function, for fibres exposed for 72 h to; ● hydrochloric, □ hydrobromic and ○ hydriodic acid solutions.

greater than that in hydrobromic acid. In contrast the corresponding curve for hydriodic acid shows no such minimum, and strength retention decreases more or less steadily with increasing concentration. Mass loss (Table II) is inversely related to strength retention in all cases, showing maxima in the cases of hydrochloric and hydrobromic acids (again at [HCl] = 3 mol dm^{-3} and [HBr] = 2 mol dm^{-3} respectively) and is almost negligible in the case of hydriodic acid. In the case of hydrochloric acid, the acid solutions became yellow after 72 h contact with the glass fibre, the colour showing a maximum intensity at [HCl] = 3 mol dm^{-3} (H_0 = -1.0), corresponding to maximum mass loss and minimum strength retention. The ultraviolet and visible absorption spectrum of the solution shows a maximum at a wavelength of 342 nm, which corresponds to that of neutral ferric chloride $FeCl_3$ [14]. This would be formed by the reaction

$$Fe^{3+} + 3Cl^- \rightleftharpoons FeCl_3 \qquad (3)$$

A similar effect is observed in the case of hydrobromic acid; in this case the ultraviolet intensity maximum occurs at a wavelength of 410 nm. the spectrum is identical than that of a solution of ferric ions in 2 mol dm^{-3} hydrobromic acid, although the complex formed in this case is more likely to be the $FeBr_2^+$ species. This is suggested by observations made in this laboratory based on ether solubility of the coloured species, which is low at [HBr] = 2 mol dm^{-3} and intense at [HBr] = 5 mol dm^{-3}. The neutral species $FeBr_3$ is soluble in ether, whereas the ionic species $FeBr_2^+$ is not. The reaction in this case would be

$$Fe^{3+} + 2Br^- \rightleftharpoons FeBr_2^+ \qquad (4)$$

TABLE II Percentage mass loss for E-glass fibres exposed for 72 h to solutions of hydrochloric, hydrobromic and hydriodic acids

Treatment	Concentration (mol dm^{-3})					
	0.5	1.0	2.0	3.0	4.0	5.0
Hydrochloric acid	–	5.94	11.1	11.5	11.4	10.7
Hydrobromic acid	–	3.46	8.45	5.00	1.89	0.94
Hydriodic acid	–	1.65	0.32	0.11	0.00	0.00
Hydrochloric acid plus ferric chloride	4.08	5.67	4.08	2.66	2.70	2.20

3.2. Strength retention in hydrochloric acid and ferric chloride solution

Fig. 2 shows the strength retention of fibres exposed to varying concentrations of hydrochloric acid containing 1 mol dm^{-3} ferric chloride. Results indicate a suppression of corrosion, with no well-defined minimum. If anything, corrosion tends to increase as the hydrogen ion activity decreases.

3.3 Strength retention with varying hydrogen and chloride ion concentrations

The strength retention of fibres immersed in solutions of varying hydrogen and chloride ion concentration are shown in Figs. 3 and 4. Both curves show well-defined minima around 3 mol dm^{-3} hydrogen ion and 3 mol dm^{-3} chloride ion concentration. All solutions

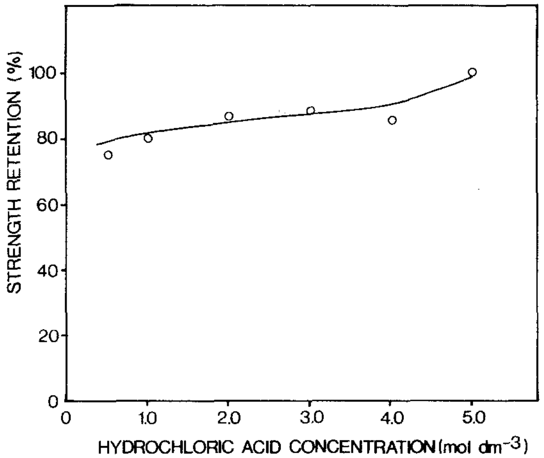

Figure 2 Strength retention against hydrogen ion concentration for fibres exposed for 72 h to hydrochloric acid solutions containing 1 mol dm^{-3} ferric chloride.

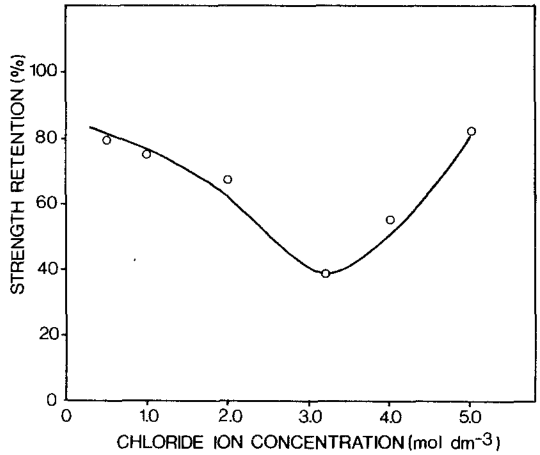

Figure 4 Strength retention against chloride concentration for fibres exposed for 72 h to a solution of constant hydrogen ion concentration. $[H^+] = 3$ mol dm^{-3}.

developed the yellow colour characteristic of the $FeCl_3$ species, as measured by ultraviolet and visible spectroscopy, with intensity maxima corresponding to strength-retention minima.

4. Discussion

It appears from these results that the corrosion of E-glass fibres by hydrochloric, hydrobromic and hydriodic acid is not solely dependent on the strength of the acid, since the stronger hydriodic acid is less corrosive than the comparatively weaker hydrochloric acid. The observed minima in the hydrochloric and hydrobromic acid strength retention against acidic strength curves imply some sort of complex formation, and as ferric ion is the only ion in the glass capable of forming complexes with halide ions in aqueous solutions at the acid strength used, this albeit minor component appears to play a critical role in the corrosion process. When ferric chloride is present in the hydrochloric acid solution, the extent of corrosion is suppressed (Fig. 2), which further supports the involvement of ferric ion. Spectroscopic studies of iron(III) chlorocomplexes in hydrochloric acid [14] indicate that formation of $FeCl_3$ is most favourable at around $[HCl] = 3$ to 4 mol dm^{-3}, which corresponds to the minimum in the hydrochloric acid strength-retention curve. No published data are available for the hydrobromic acid case, but solubility studies carried out during the present investigation indicate an optimal concentration of 2 mol dm^{-3} hydrobromic acid for the formation of $FeBr_2^+$, again corresponding to the minimum in the hydrobromic acid strength retention curve. Although it would seem more likely that the formation of neutral or anionic species would facilitate leaching of the ferric ions in the glass, by driving the ion exchange reaction (Equation 1) over to the right, as is the case with ferric chloride, a cationic species, $FeBr_2^+$, appears to serve the same purpose in the hydrobromic acid case (Equation 4).

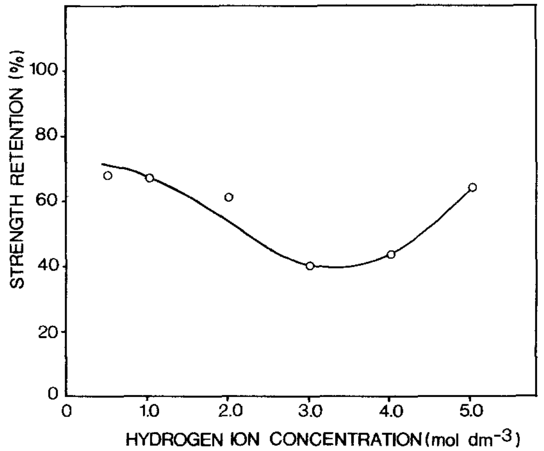

Figure 3 Strength retention against hydrogen ion concentration for fibres exposed for 72 h to a solution of constant chloride ion concentration. $[Cl^-] = 3$ mol dm^{-3}.

The reduced corrosion at high acid concentration has been explained [11] by a suppression of the ion exchange reaction (Equation 1), as a high hydrogen ion concentration would favour the reverse reaction. An alternative explanation is that as the anion concentration increases there will be a tendency for the anions to associate with the ferric ions on the surface of the glass, thus inhibiting the leaching by hydrogen ions. This mechanism would only be effective for ions which can form complexes, and strength-retention minima would not be expected for ions which do not, as is the case with nitric and sulphuric acids [11]. Because of their smaller size, more chloride ions than bromide ions would be necessary to prevent leaching of ferric ions, which would explain the positions of the respective minima in the hydrochloric and hydrobromic acid strength retention curves. Because of the lower tendency of bromide to form complexes, the minima in the hydrobromic acid case is not as pronounced as that for hydrochloric acid.

Such a mechanism would also explain the minima in the curves for hydrogen and chloride ion variations (Fig. 3). At constant hydrogen ion concentration, low chloride concentration would reduce the possibility of complex formation, whereas at high chloride concentration leaching is suppressed by a passivating mechanism involving complex formation on the glass surface. At constant chloride concentration, low hydrogen ion concentration would not favour the forward ion exchange reaction (Equation 1), whereas at high hydrogen ion concentration reassociation of hydrogen and chloride ions would suppress complex formation by reducing the chloride ion concentration.

The process becomes optimal at $3\,\mathrm{mol\,dm^{-3}}$ hydrogen ion and $3\,\mathrm{mol\,dm^{-3}}$ chloride concentration. Suppression of corrosion by ferric chloride can also be accounted for by high chloride concentration, as well as high ferric ion concentration.

5. Conclusion

Corrosion of E-glass fibre in hydrochloric, hydrobromic and hydriodic acids is inversely related to acidic strength and is directly related to the complexing ability of the conjugate anion. Ferric ion appears to play a critical role in the case of hydrochloric and hydrobromic acid corrosion, but not hydriodic acid. A possible mechanism for this is that owing to complex formation, ferric ions are leached relatively rapidly from the glass matrix, thus initiating the corrosion process and facilitating removal of other cationic species. This corrosion can be inhibited to some extent by the presence of ferric ion in the corroding medium. In addition, an excess of the complexing anion, e.g. chloride or bromide ion, appears to have a passivating effect, protecting the surface of the glass from the corroding solution. Again this can be attributed to complex formation, in this case with ferric ions on the surface of the glass rather than in solution.

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