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Strength loss in E-glass fibres after exposure to organic acids

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The corrosion of E-glass fibres has been investigated in aqueous solutions of selected organic acids. Although most organic acids have very little corrosive effect, oxalic acid and mesoxalic acid (2-oxopropanedioic acid) are extremely corrosive. The mechanism of the corrosion process appears to be related to three factors: relatively high acidic strength, formation of an insoluble calcium salt, and an ability to form stable complexes with cations present in the glass. This corrosion is extremely important when glass fibre composites are used in conditions where oxidative breakdown (e.g. by electric fields or ultraviolet radiation) of the resin material is likely to occur, as the two most corrosive organic acids are likely breakdown products.

1. Introduction

It has been well established that E-type glass fibre, the major reinforcing material used in glass fibre composites, is susceptible to chemical corrosion when exposed to strongly acidic environments [1–4]. Originally it was presumed that the corrosive effect was related to the acidic strength (expressed as hydrogen ion concentration) of the medium [1, 2] via an ion-exchange reaction. More recently it has been suggested that the anions associated with the hydrogen ions play a significant role in the corrosion process [4]. In particular, anions which can form neutral or negatively charged complex ions with the cationic species found in glass have a more corrosive effect that those which do not.

An interesting mechanism has recently been reported [5] for the failure of glass fibre composite materials used as insulators on high-voltage transmission lines, where the composite material is under electrical as well as mechanical stress. The mechanism proposes that degradation of the bonding resin occurs under the influence of partial discharge activity, forming low molecular weight organic acids and in particular oxalic acid, which then corrodes the glass fibre component, resulting in mechanical failure of the insulator. The discharge activity and glass fibre degradation could occur either in tiny air gaps within the composite material, where incomplete wetting of the fibre occurs, or at surface asperities in the rod. Normally the resin component is expected to play a protective role, shielding the glass fibre from the corrosive environment, but in this case the resin could contribute directly by providing the corrosive material.

The object of this work is to examine the mechanical properties of the E-type glass fibre after exposure to a series of organic acids. The acids investigated are those which are likely products of electrical or ultraviolet light-induced degradation of organic polymers of the type used in the manufacture of glass fibre reinforced composite materials. Polymer resins consist of carbon chains, and the ultimate products of degradation in an oxidizing atmosphere are carbon dioxide and water. However, in the intermediate stages of the degradation process the polymer backbone is broken at various places to give a mixture of organic acids of the type

$$\mathrm{HOOC\cdot(CH_2)_{\mathit{n}}\cdot COOH}$$

where $n = 0, 1, 2$, etc

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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 most highly oxidized of these, and hence the species expected to predominate next to carbon dioxide and water, is oxalic acid (where $n = 0$) although monocarboxylic acids such as formic and acetic acid are also likely to be present. It has been shown before that oxalic acid is produced in appreciable quantities from electrical discharge activity on polyethylene [6, 7] and epoxy resin used in glass-reinforced plastics [5]. The acids selected for this investigation were those combining relatively high acidic strength, aqueous solubility, the potential to form complex ions with the cationic species present in the glass, and which were likely products of resin degradation.

Some corrosion data are available for formic, acetic and mono-, di- and trichloroacetic acids but these refer only to leaching and not to strength retention [8]. These authors conclude that leaching is dependent on acidic strength, although they do speculate that films of aluminium salts, in an attempt to suppress the ion-inhibiting effect.

2. Experimental details

All chemicals used were analytical-grade reagents wherever possible, otherwise the purest grade available commercially was used. Glass specimens 200 mm long were cut from an E-glass fibre roving 2275 TEX of chemical composition shown in Table I. The procedure of immersion, washing, drying and tensile testing was identical to that described in a previous report [4]. The glass fibre was immersed in solutions of the organic acids listed in Table II made up in distilled water at $1\,\mathrm{mol\,dm^{-3}}$ concentration. Exposure lasted for 7 and 30 days, after which tensile testing was carried out. In a second series of experiments, glass fibre was immersed in oxalic and mesoxalic acid solutions of varying concentration (up to saturation) for a duration of 3 days in the former case and 5 days in the latter. Finally glass fibres were exposed for 3 days to oxalic acid solutions containing aluminium slats, in an attempt to suppress the ion-exchange reaction.

3. Results

The chemical structures and dissociation constants of the acids tested are listed in Table II, together with the strength retention of the glass fibre after immersion in the particular acid solution. Very little corrosion was observed after 7 days except in the cases of oxalic acid and mesoxalic acid, where the corrosive effect was severe. In these two cases precipitates were observed which were shown to be calcium oxalate and calcium mesoxalate respectively by comparison of their infrared spectra with those of authentic materials. In the case of mesoxalic acid, crystals of calcium mesoxalate slowly formed on the glass fibres which made washing

TABLE II Acid solutions and their effects

Acid	Structure	pK_a*	Strength retention (%)	
			7 days	30 days
Oxalic	COOH | COOH	1.26	3.7[‡]	–
Maleic	HCCOOH ‖ HCCOOH	1.91	89	77
Mesoxalic	⁄COOH CO \COOH	2.00[†]	5	8
Malonic	⁄COOH CH_2 \COOH	2.81	76.7	21
Glyoxylic	CHO | COOH	3.46	82	52
Formic	HCOOH	3.75	77.6	86
Succinic	CH_2COOH | CH_2COOH	4.22	76.3	84
Glutaric	⁄CH_2COOH CH_2 \CH_2COOH	4.34	79.5	82
Acetic	CH_3COOH	4.76	83.7	82

*Values obained from [9]. The most acidic pK_a only is given for the dibasic acids.

[†] Determined in this laboratory by potentiometric titration.

[‡] 3 days exposure.

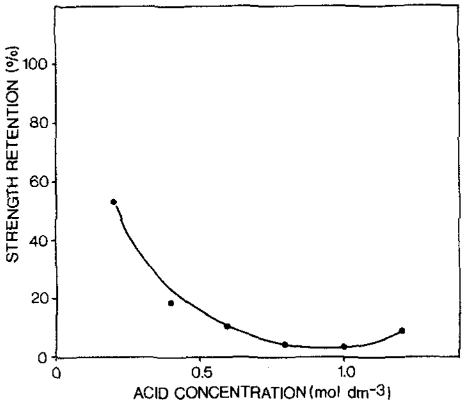

Figure 1 Strength retention against acid concentration for fibres exposed for 72 h to oxalic acid solutions.

and weighing difficult. Mass loss data were therefore not meaningful in this case. In other cases, degree of corrosion was directly related to mass loss after immersion. Figs. 1 and 2 show the strength retention against concentration for the two corrosive acids, and both show strength retention minima at a particular concentration.

Table III shows the strength retention of glass fibres exposed to oxalic acid solutions containing aluminium salts. In all cases the strength retention is increased compared to oxalic acid alone and is particularly high in the case of aluminium chloride.

4. Discussion

Strong mineral acids are known to have a corroding effect on E-glass fibres although acid strength does not appear to be the sole contributing factor [4]. On the basis of the acid strength, the relatively weak organic acids would not be expected to have much corrosive effect and indeed for many organic acids this is the case. However two organic acids, oxalic and mesoxalic, have a particularly severe corrosive effect on E-glass fibres. The corrosive effect of oxalic acid has been implicated in the failure of composite insulators [5], where electrically induced oxidation of the resin in the composite produces oxalic acid which then corrodes the glass fibre core. Mesoxalic acid is also a likely product of resin oxidation and this also may play a role in insulator failure.

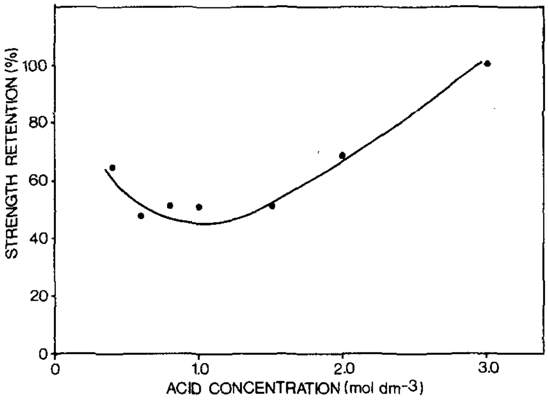

Figure 2 Strength retention against acid concentration for fibres exposed for 72 h to mesoxalic acid solutions.

TABLE III The effect of aluminium salts

Medium	Strength retention (%)
1 M oxalic acid + 1 M $Al_2(SO_4)_3$	70.2
1 M oxalic acid + 1 M $AlCl_3$	96.2
1 M oxalic acid + 1 M $Al(NO_3)_3$	86.9
1 M oxalic acid	3.7

It appears from these and other observations [4] that although acid strength is important, other factors influence the corrosion process. Both oxalic and mesoxalic acids have insoluble calcium salts and this will assist the leaching of calcium ions from the glass by the protons in solution. The generally accepted mechanism is the ion exchange reaction

$$\overline{M^{n+}} + nH^+ \rightleftharpoons M^{n+} + n\overline{H^+}$$

where the bar denotes species associated with the glass phase. Formation of insoluble reaction products on the right-hand side of the equation effectively removes M^{n+} and promotes the forward reaction. This effect has been observed with sulphuric acid [3, 4], which also has an insoluble calcium salt.

Complex ion formation has also been suggested [4] as a factor and it is well known that oxalic acid forms very stable complexes with aluminium and iron(III) ions [9], as well as having an insoluble calcium salt. Although very few data are available for mesoxalic acid as a complexing ligand it is likely, owing to the favourable orientation of the two carboxyl groups (Fig. 3a), that this too will form complexes particularly with trivalent ions such as Fe^{3+} and Al^{3+}. Other dicarboxylic acids are also known to form similar complexes [9]. Mesoxalic acid is also relatively strong for an organic acid

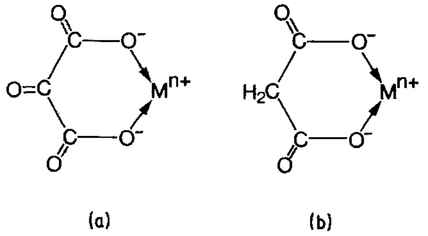

Figure 3 Structure of complexes formed with metal ions from (a) mesoxalic and (b) malonic acid. Each metal ion can bind up to three acid molecules.

and it too has a calcium salt of low solubility. Malonic acid, similar in structure to mesoxalic acid (Fig. 3b), is known to form complexes, but is insufficiently dissociated to provide the hydrogen ion concentration necessary for rapid leaching of the glass cations, although severe corrosion does occur after prolonged exposure. Maleic acid, although fairly strong, does not form an insoluble calcium salt and the carboxyl groups are too close together for favourable complex formation. Glyoxylic acid, although a relatively weak monocarboxylic acid, is similar in structure to oxalic acid and is likely to form similar, if weaker, bidentate complexes (Fig. 4). The corrosive effect of this acid is only apparent after prolonged exposure of the glass fibre. All the others are too weak to provide the hydrogen ion concentration necessary to favour the ion-exchange reaction to any large extent.

The strength retention against concentration curves for oxalic and mesoxalic acids show well defined minima (Figs. 1, 2). This is interpreted as an indication of complex formation. At low acid concentration the ion-exchange reaction is not favoured because the hydrogen ion concentration is too low; at high acid concentration the anions present bind to certain metal cations on the surface of the glass and prevent their dissolution. This passivating mechanism has recently been observed [10] in hydrochloric acid solutions, the chloride ion being the complexing agent in this case.

The incorporation of aluminium salts in the corroding medium shows interesting features. Firstly the presence of aluminium will tend to reverse the ion-exchange reaction and prevent leaching of aluminium ions from the glass. This is evident from the high strength retention figures in all three cases (Table III), compared to that in oxalic acid alone. Secondly, strength retention is greatest when aluminium chloride is used, again illustrating the passivating effect of complexing ions, in this case chloride. Thirdly, strength retention is least when sulphate is the associated anion and as both calcium sulphate and calcium oxalate are insoluble, leaching of calcium ions from the glass is facilitated.

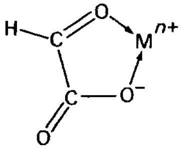

Figure 4 Structure of complexes formed from glyoxylic acid and metal ions.

5. Conclusion

Of several organic acids tested two, namely oxalic and mesoxalic, were found to have severe corrosive effects on E-glass fibres. The mechanism by which the glass is corroded involves three factors; relatively high hydrogen ion concentration, formation of an insoluble calcium salt, and the ability to form complexes with ions such as Fe^{3+} and Al^{3+}.

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