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Acid corrosion analysis of fibre glass

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The scanning electron microscope and the energy dispersive X-ray based analytical techniques have been used to study the sulphuric acid corrosion resistance of standard "E" fibre glass and PPG developed and patented 1201 [1], an "ECR" acid-resistant fibre glass. While it is well agreed by the experts in the field that direct exposure of fibre glass to 0.5 M sulphuric acid is much too severe a condition to simulate service conditions of most filament wound fibre glass products, nevertheless, the above corrosive environment was used to demonstrate a significant superiority of PPG 1201 glass in acid resistance over the standard "E" glass regardless of the source of its origin. It is also demonstrated that not only boron oxide leached out during acid exposure but a significant amout of calcium, aluminium, and magnesium oxides also were depleted from the "E" glass composition during acid treatment. It is also demonstrated that heat treatment of "E" glass products reduced the rate of acid attack. It did not, however, eliminate it completely. Heat treatment affects the strength properties of this fibre glass adversely.

1. Introduction

Effects of corrosive environments, particularly mineral acids, on fibre glass reinforced composites have been studied extensively in the literature [2–18]. Various mechanisms have been proposed to explain the deterioration of fibre strengths during acid exposure. The most predominant is the diffusion controlled dissolution of selective leachable components [19] of glass composition in mineral acids. Hydrolysis of the glass–matrix interfacial bond is also suggested to be one cause of degradation. It has also been demonstrated that encapsulation of fibre glass in corrosion resistant matrix resins (such as epoxy, vinylester and cross-linked unsaturated polyester) reduces the acid attack on fibre glass or glass–matrix interface significantly. Most of the researchers [4, 10] in this field realize well that studying the corrosive deterioration of fibre glass in 0.5 M sulphuric acid is much too severe to simulate the field performance of fibre glass reinforced composites in most cases. Nevertheless, most of them have used this condition to determine the accelerated effects of acid attack to take remedial action, particularly in critical products where large liabilities are involved.

Scanning electron microscope (SEM) [2, 3] and energy dispersive X-ray (EDX) [4] analysis have been used in studying the corrosive morphological damage and elemental depletion analysis of fibre glass and the glass–matrix interface during acid exposure of composites. Use of direct current emission spectrometer has been reported in the literature for analysis of cations in the leachate solutions. In analysis of the standard "E" fibre glass and PPG experimental, acid resistant 1201 glass, we also used the above three techniques. Details of our experiments and the results and conclusions of our study are described in the following sections.

2. Experimental procedure

2.1. Instruments used

Scanning electron microscope	JEOL Model JSM-35C
Energy dispersive X-ray	Tracor Northern 2000
D.c. plasma emission spectrometer	Spectraspan V, Beckman ARL
Instron machine	For strength determination

2.2. Sample preparation

Two types of samples were prepared for acid exposure.

2.2.1. Vera specimens [5]

These were prepared by laying strands of fibre glass between the end tabs of catalysed vinylester resin saturated mat and were cured at room temperature. A typical example of this specimen is shown in Fig. 1. These end-tabbed specimens were immersed in 0.5 M sulphric acid solution for a specified period of time. After exposure, the specimens were removed, rinsed with water, air dried and tested, using each tabbed strand as one specimen, for residual strengths and then examined under SEM–EDX system.

2.2.2. Pultruded rod specimens

In order to develop better credibility in the EDX analysis of leached fibres, pultruded rods of desired fibre bundles were fabricated in catalysed vinylester

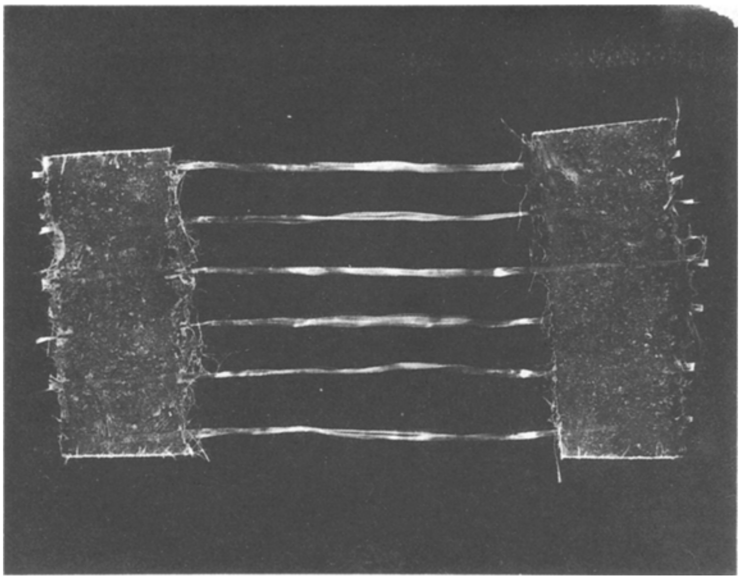

Figure 1 Typical VERA test specimen.

resin and cured at room temperature. Cross-sections of these cut rods were exposed to fresh acid by hanging the rods in acid containers making sure that no portion of the hanging rods touched any walls or bottom of the acid container. These sections were then removed, rinsed with water, air dried and coated with gold before being micrographed by SEM and X-ray analysed by EDX system. Results are discussed in the following section.

3. Results and discussion

A typical composition of "E" glass is found in many publications [2, 11, 14]. It contains 54.5% silicon dioxide, 14.5% aluminium oxide, 17.0% calcium oxide, 4.5% magnesium oxide, 7.5% boron oxide along with trace amounts of iron oxide, sodium oxide and potassium oxide. A typical 1201 composition is described in PPG US Patent 4 542 106.

Examination of the extended period (7 days), acid-exposed "E" glass specimens and experimental PPG 1201 glass specimens revealed that PPG 1201 glass (Fig. 2) remained practically unaffected in 7 days of 0.5 M H_2SO_4 acid exposure. The "E" glass, on the other hand, was severely attacked by acid (Fig. 3). The acid treated "E" glass fibres were exposed for one week. The untreated control "E" glass fibre is also shown in this figure for reference. The acid attack on filaments of "E" glass appeared to have initiated in a spiral cracking pattern (Fig. 4). Fig. 5 shows a collection of two SEM micrographs taken from the acid attacked "E" glass composite cross-sections. The top

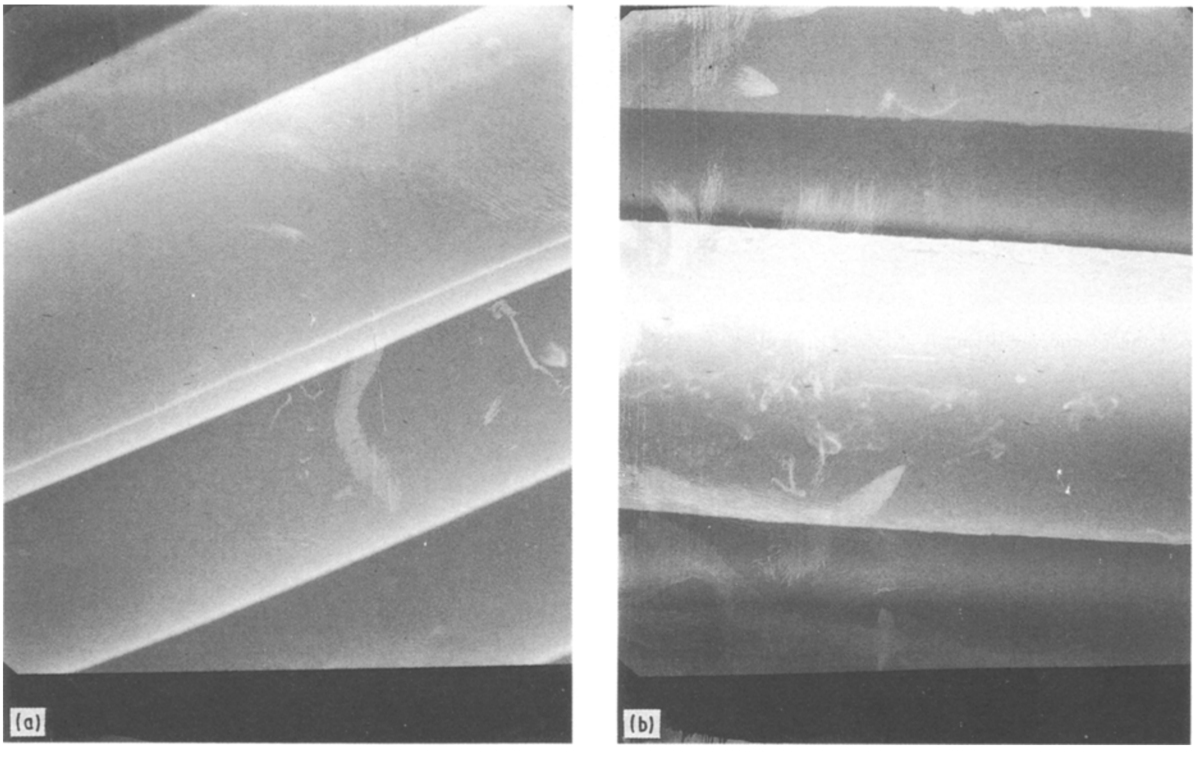

Figure 2 PPG 1201 acid resistant product. (a) 1201 control, 1800 × 3/5/84. (b) 1201 7 days in 5% sulphuric acid, 1800 × 3/5/84.

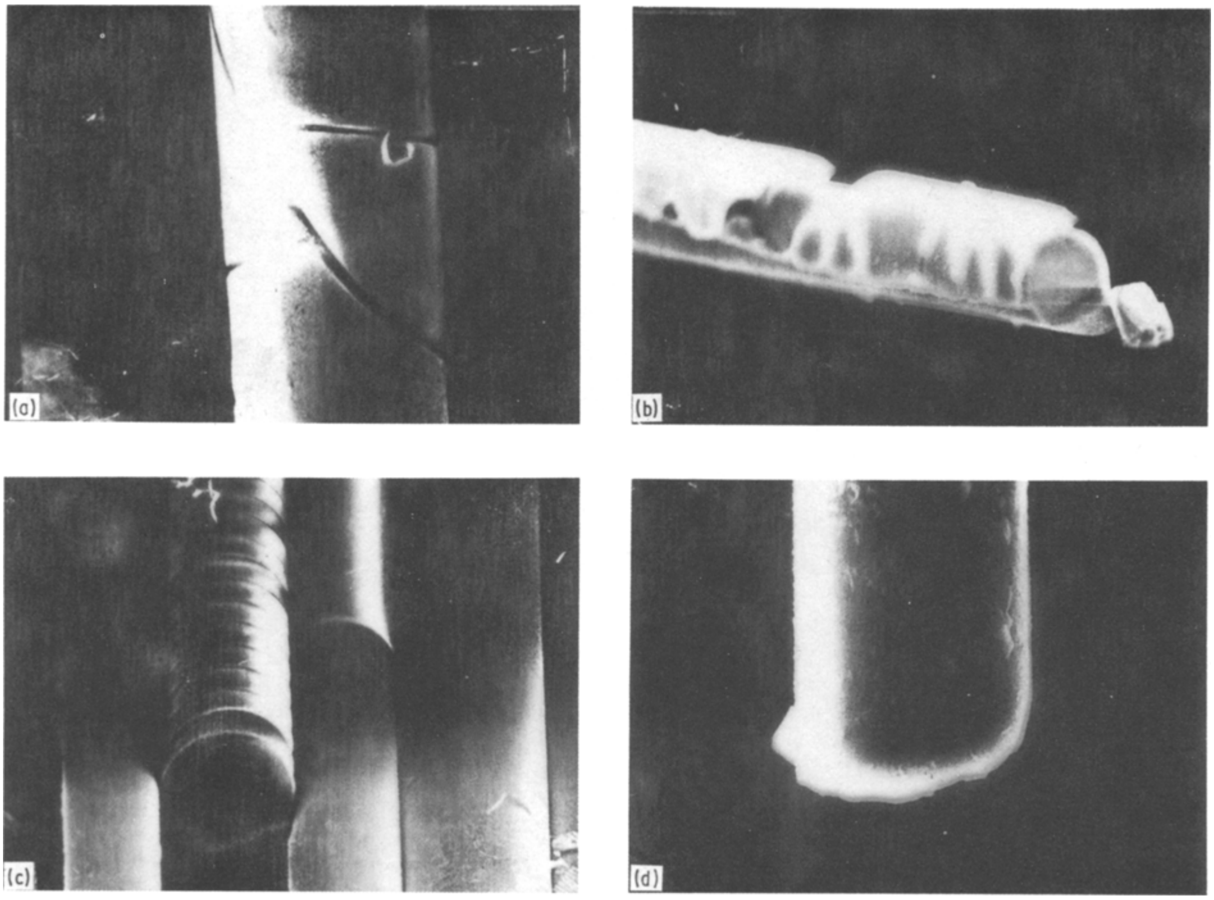

Figure 3 (a), (b) and (c) "E" acid treated. (d) "E" untreated.

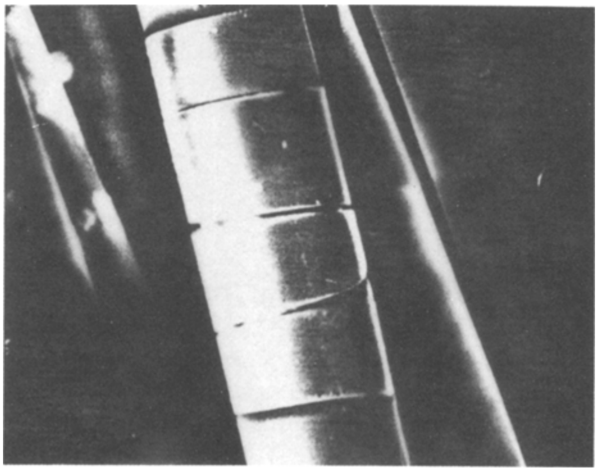

Figure 4 Spiral cracking of non-heat-treated specimens.

micrograph was taken at 0° tilt angle and the bottom micrograph was taken at 30° tilt angle. The severity of the acid attack is more vividly seen at 30° tilt. These pictures at two tilt angles are shown to highlight the usefulness of different tilt angle viewing in electron microscopy.

EDX X-ray intensity scans of the leached surface areas of control "E" glass and leached fibres are shown in Figs 6 to 8. While Fig. 6 is the EDX scan of an unleached fibre, Figs 7 and 8 are the surface area scans of leached fibres for 15 h and 4 days, respectively. In these EDX scans, the X-ray counts for gold originates

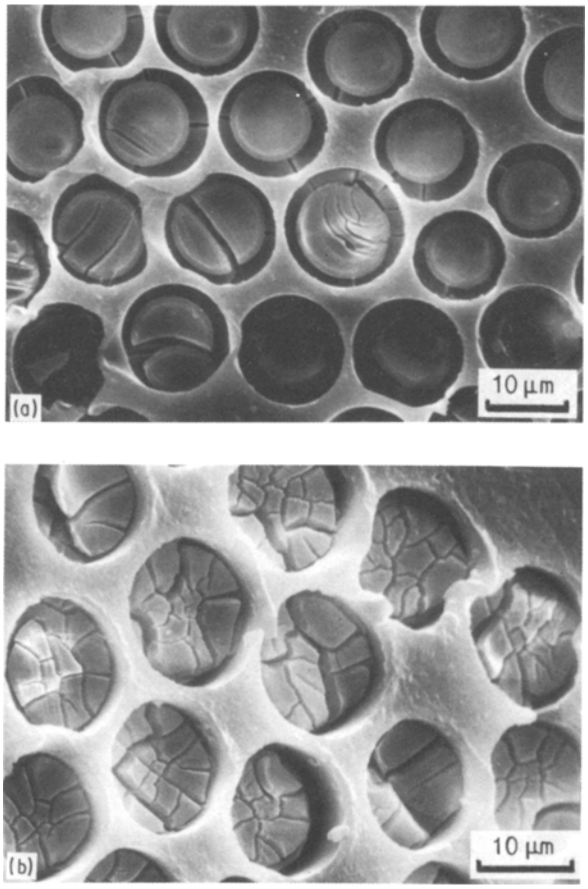

Figure 5 Acid-treated pultruded rods. (a) "E", 7 days, 0° tilt. (b) "E", 7 days, 30° tilt.

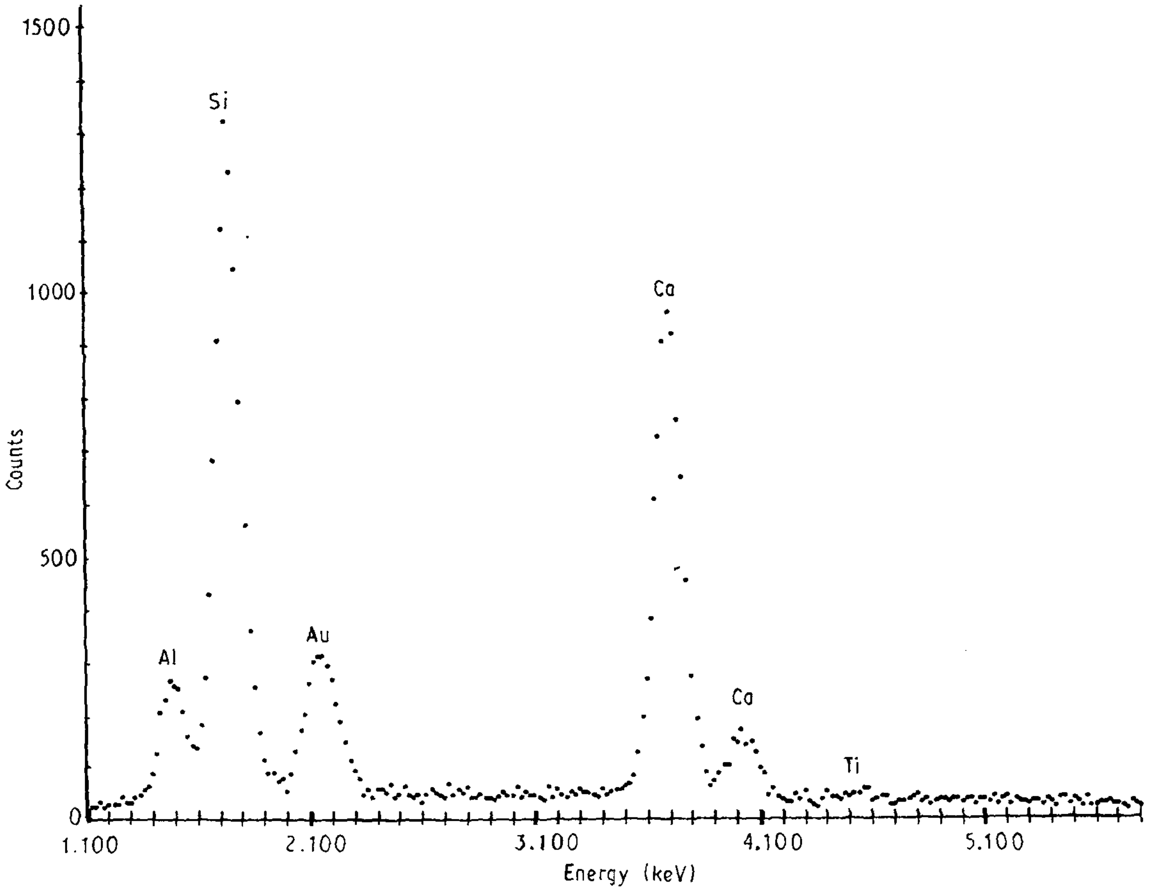

Figure 6 "E" control area scan.

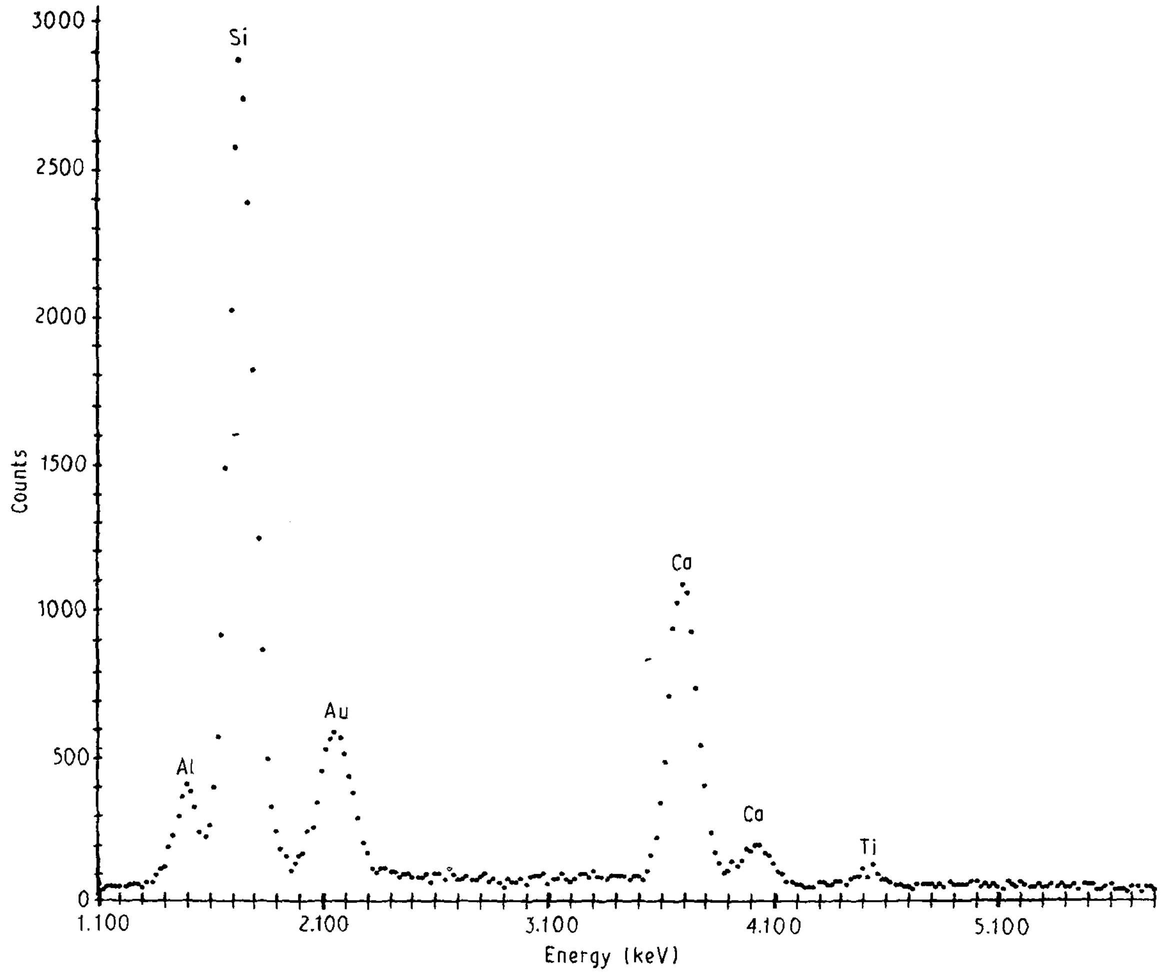

Figure 7 "E" 15 h area scan.

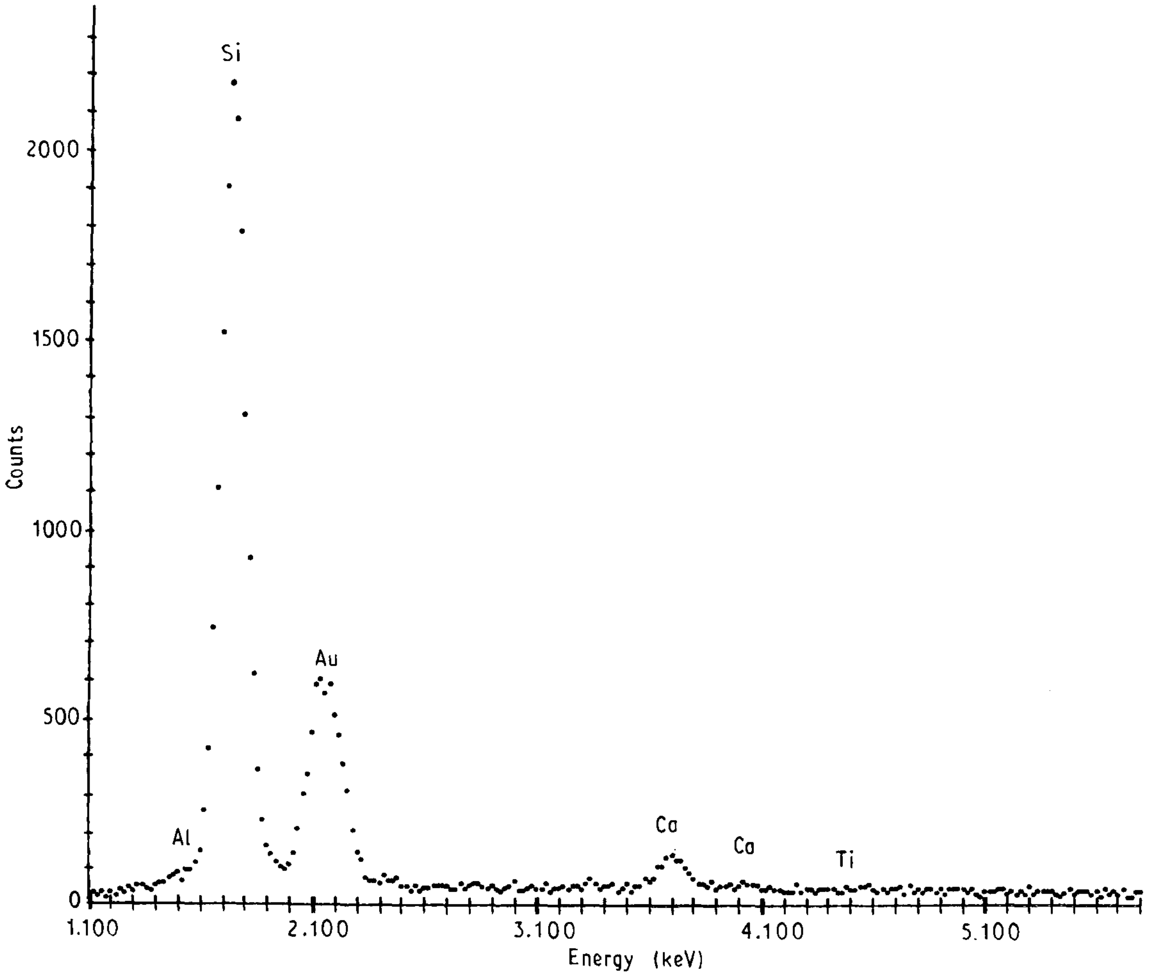

Figure 8 "E" 4 days area scan.

from the gold coating used for examining these fibres under SEM–EDX systems. It should also be mentioned here that EDX analysis, using Tracor Northern 2000 system, cannot detect X-rays generated by boron. Hence, absence of X-rays for boron from the control in Fig 6 should not be surprising. Based on the d.c. plasma analysis of the leachates, however, it was known to us that, along with boron, the complexes of other cations such as aluminium, calcium, and magnesium also leached out in acid from "E" glass fibre. A more interesting observation to us was, however, that even the EDX X-ray intensity scans showed the depletion of these elements qualitatively. Going from Fig. 6 to Fig. 8, one can observe the intensity of calcium and aluminium X-ray counts progressively decreasing as the acid leaching time increased. This is shown more dramatically in Figs 9 and 10 where the decay ratios of Ca to Si and Al to Si, respectively, were plotted against the leaching time for a typical "E" glass fibre product. It thus became obvious that approximately 40% weight loss, observed in one week of 0.5 M acid leaching, was due not only to loss of the boron phase, but also to the loss of complexes of aluminium, calcium, sodium, magnesium, iron and potassium in an undefined complicated manner.

PPG 1201 experimental glass did not deteriorate at all when exposed to 0.5 M sulphuric acid solution for an extended period of time. Fig. 11 is a comparison of tensile strength retention of PPG 1201 glass roving

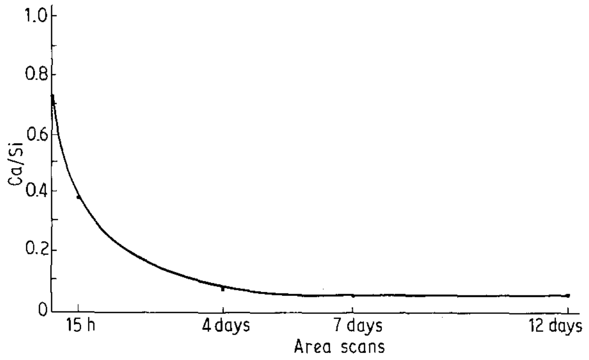

Figure 9 Comparison of Ca to Si ratio in E glass leached fibre surface.

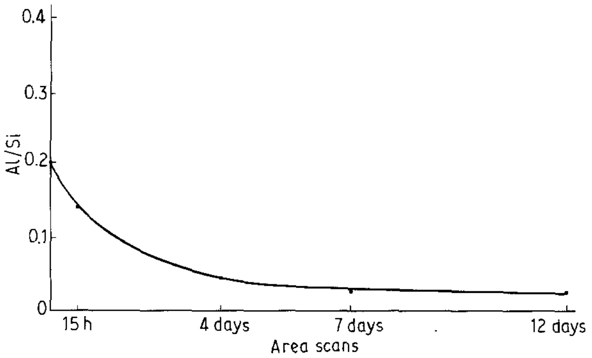

Figure 10 Comparison for Al to Si ratio in E glass leached fibre surface.

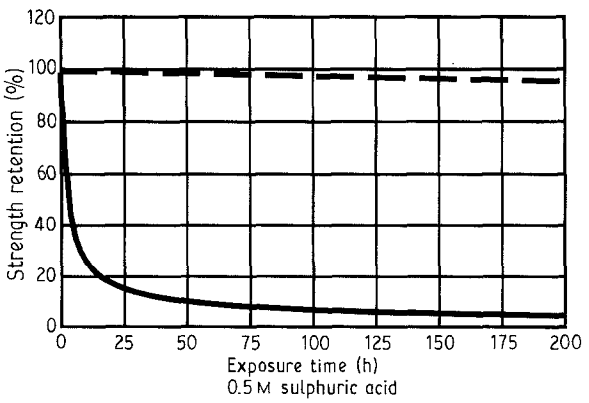

Figure 11 Acid resistance of fibre glass roving tensile strength retention. (—— E glass, --- 1201 glass).

against a typical "E" fibre glass roving in acid solution. While "E" glass lost its strength drastically in a week, 1201 remained practically unaffected. EDX analysis of the seven-day acid leached as opposed to unleached control had shown no difference in its elemental X-ray scans. It is not, however, being presented in this publication to protect the proprietary nature of this technology.

4. Effect of heat treatment on "E" glass products

In the hope that heat treatment of "E" glass products would give a permanent improvement in acid durability [20], various experiments were performed. A sizeable amount of "E" glass roving was initially exposed to heat (1000 °F) (537.8 °C) for various lengths of time (1, 4, 8, and 24 h). After cooling the strands, Vera test specimens, shown in Fig. 1, were prepared. Duplicate sets of 12 specimens were made for each condition of heat treatment. One set from each heat treatment was immersed in 2 l of 0.5 M H_2SO_4 solution separately. After 16 h of acid exposure, specimens were removed from acid, rinsed with water, and air dried before each strand test specimen was tested for its residual strength. The control specimens were also tested for initial strength. The acid solutions with leachate ions were filtered and analysed for Fe, Si, Mg, Na, Al, Ca, and B in parts per million (p.p.m) using d.c. plasma emission. Results are shown in Table I. The control 0.5 M H_2SO_4 solution was also analysed for these ions. A review of these data indicates that heat treatment at 1000 °F dropped the tensile strength significantly (from 97 to 32 lb per strand in 1 h of heat treatment) (1 lb = 0.453 µg). But, concentrating on the leachate analysis, one sees that the heat treatment for one hour did reduce the rate of leaching of Al, Ca, and B significantly. The control values for these three ions were 8.3, 19.7 and 1.9 p.p.m, respectively, which dropped to 2.8, 6.3, and 0.6 p.p.m, respectively, in 1 h. If the initial strength of 1 h per heat-treated control specimen can be assumed to be 32.6 lb per strand, then 16 h of acid leaching reduced it to 31.5 lb per strand. The non-heat-treated control dropped from 96.8 to 57.9 lb per strand in the same time period of acid exposure. Spiral cracking was evident in SEM micrographs of non-heat-treated glass (Fig. 4), but the 1000 °F heat-treated glass showed no spiral cracking after 16 h acid treatment (Fig. 12).

TABLE I "E" Glass leachate analysis (16 h in 0.5 M H_2SO_4)

	Residual strength (lb)				
	Control (0)	1 h	4 h	8 h	24 h
Heat treated at 1000 °F	96.8	32.6	24.6	13.8	9.4
Heat treated at 1000 °F + 0.5 M H_2SO_4 exposure for 16 h	57.9	31.5	21.6	13.3	10.7

Leachate ions, p.p.m	0.5 M H_2SO_4 control	Heat treated for specified hours at 1000 °F and leached for 16 h				
		Control (0)	1 h	4 h	8 h	24 h
Fe	0.13	0.35	0.2	0.3	0.5	0.5
Si	0.03	2.2	0.8	1.1	1.0	0.6
Mg	0.09	0.3	0.1	0.1	0.1	0.1
Na	0.14	0.8	0.3	0.5	0.3	0.3
Al	0.02	8.3	2.8	3.1	2.2	1.7
Ca	0.30	19.7	6.3	6.9	4.7	3.7
B	< 0.01	1.9	0.6	0.7	0.5	0.3

It was thought that less severe heat treatment would significantly reduce the loss in initial strength due to heat treatment. Rovings of "E" glass without sizing were heat treated for 15 min at 700 °F (371 °C) and 500 °F (260 °C) and were exposed to 0.5 M sulphuric acid solutions for 16 h. No spiral cracking was observed. Figs 13 and 14 are the respective SEM micrographs of these two heat-treated and acid-leached fibres. The residual strengths of these two mildly heat-treated controls were not, however, much better than the 1000 °F heat-treated fibres. The initial strengths of the 700 °F and 500 °F heat-treated, unsized fibres were in the low and mid 40 lb per strand range, respectively. Leachate analysis results did indicate a reduction in the rate of leaching (Table II) compared to the control products (both vacuum dried and wet). In seven days

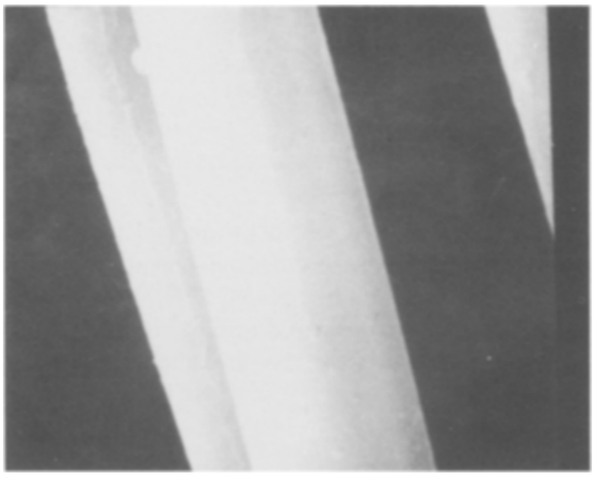

Figure 12 Effect of 1000 °F heat treatment on acid durability (no cracking).

Figure 13 Effect of 700 °F heat treatment on acid durability (no cracking).

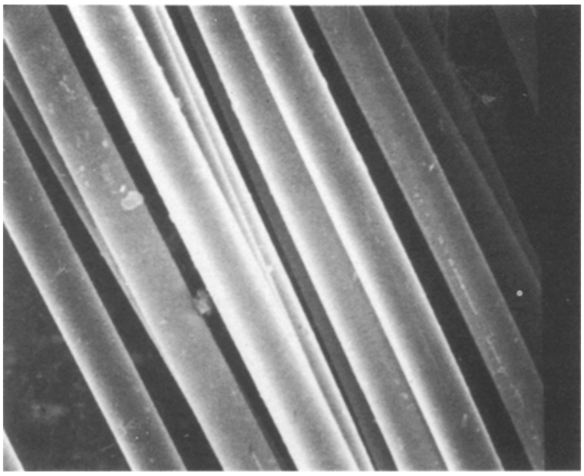

Figure 14 Effect of 500 °F heat treatment on acid durability (no cracking).

TABLE II Effect of heat treatment on acid resistance (0.5 M H_2SO_4) of "E" glass

Elements, p.p.m	Leached for 16 h			
	Room temperature vacuum dried	Wet strand	15 min heat treated at	
			500 °F	700 °F
Fe	0.59	0.42	0.39	0.38
Mg	0.61	0.61	0.37	0.51
Na	1.44	1.45	1.07	1.06
Al	14.6	13.1	7.90	10.0
Ca	34.1	30.2	18.2	23.2
B	3.8	3.0	1.7	2.7

of acid exposure, however, all products deteriorated so drastically that the advantage due to heat treatment in reducing the leaching rate ceased to retain any benefit. In applications where acid durability is more important than strength, mild heat treatment of "E" glass products may, however, be of some value.

5. Conclusions

The conclusions are as follows.

1. Acid resistance of PPG 1201 experimental fibre glass was found to be greatly superior to any commercial "E" glass product.
2. Heat treatment did improve the initial acid durability of "E" glass products for a short period of time (48 h in 0.5 M sulphuric acid solution) by reducing the rate of acid leaching.
3. Heat treatment reduced the rate of acid leaching at the cost of initial strength reduction. In applications where acid durability is more important than strength retention, a mild heat treatment would, therefore, be of some value.
4. Leaching losses of large amounts of aluminium, calcium, and magnesium ions, in addition to boron, suggest that the acid attack process goes beyond the soluble borate phase. It also attacks complexes of calcium, aluminium, magnesium, and other elements in an unknown manner.

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