

# A High-Temperature Polyimide Reinforced with Silica Fibre

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*Received 2 September 1966*

Poly-[N,N'-(4,4' oxydiphenylene) pyromellitimide] has been reinforced with unidirectionally aligned silica fibre. A partial pre-cure of the basic laminate before lay-up in the mould successfully prevented porosity and strength degradation in the final composite structure.

Samples heated for periods up to 100 h and temperatures up to 400° C in circulating air retained 50 to 90% of their original strength. For all the samples, the dynamic modulus of elasticity was in the range 4.55 to 4.95 × 10<sup>6</sup> lb/in.<sup>2</sup> (3.20 to 3.48 × 10<sup>5</sup> kg/cm<sup>2</sup>), the fibre content being 43 to 47.5% by volume. This material incurred a 5% weight loss on heating in air at 350° C for 100 h.

## 1. Introduction

Modern technology requires strong, low-density and temperature-resistant materials. Fibre-reinforced resin is now being used extensively to replace metal parts where the weight of a component has to be minimised. At present, most commercial resins have an upper limit of 250° C when used continuously. It is apparent that any increase in temperature resistance of the resin would result in reinforced resins being considered for many more applications.

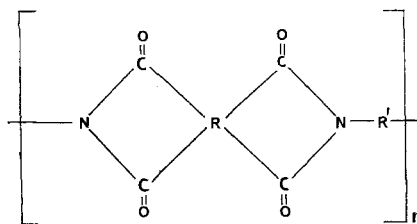
In recent years, a new generation of heat-resistant polymers has been developed. These polymers have aromatic or heterocyclic ring systems incorporated in the molecular chains. Aromatic systems have optimum chemical resistance at high temperature, and confer rigidity on the constituent macromolecules, thereby preventing serious degradation of the mechanical properties on heating. These polymers retain useful mechanical properties in the region of 350 to 500° C for appreciable periods of time [1].

Many of these polymers are both insoluble and infusible. Although these are most desirable properties, they cause difficulty in the method of fabrication.

A polyimide was selected for the present work because its synthesis is performed in two steps

and involves a soluble, high-molecular-weight polymer intermediate.

Polyimides are one particular group of polyaromatic polymers having the general formula



where R and R' are both aromatic groups.

Freeman and his coworkers [2] have reported on the relative thermal stabilities of many polyimides, and from this information poly-[N,N'-(4,4' oxydiphenylene) pyromellitimide] was selected as a suitable material for this investigation.

This polymer is produced by the condensation of pyromellitic dianhydride (I) and 4,4'-diaminodiphenyl ether (II) as represented in fig. 1. The reaction producing the intractable polyimide (IV) proceeds in two stages by way of an intermediate amide-acid polymer (III) which is soluble in several polar solvents.

So far, attempts to produce glass fibre/polyimide structures with good, high-tem-

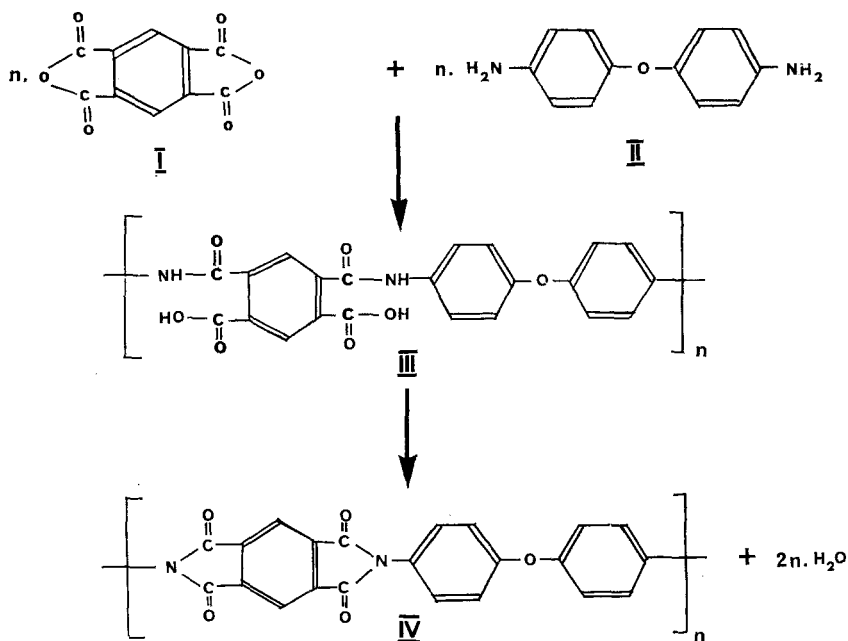


Figure 1 The reaction scheme for polyimide formation.

perature strength properties have not succeeded [3]. The polymer is only tractable in the polyamide-acid stage and polyimide is produced from this material by heating to remove the elements of water. This water can both degrade the polymer by hydrolytic chain scission and weaken the structure by making it porous.

This paper primarily describes the development of a technique to fabricate a fibre-reinforced polyimide structure without degrading the high-temperature resistant properties of the polymer. The success of the method is evaluated by the strength at temperature measured on standard test-pieces.

Silica fibres were used to reinforce the polyimide and were filament wound to produce unidirectionally reinforced composites. Silica fibres have superior resistance to strength loss on heat ageing than commercial silicate glasses [4].

## 2. Experimental Techniques

### 2.1. Specimen Preparation

The preparation of polyamide-acid solutions and the subsequent conversion to polyimide has been described [5, 6]. To obtain maximum thermal stability in the resulting polyimide, impurities in the starting materials should be minimal.

The pyromellitic dianhydride was purified by

recrystallisation in acetic anhydride under an atmosphere of dry nitrogen to yield a product melting at 287 to 288° C.

4, 4'-diaminodiphenyl ether had a melting point of 191 to 192° C after recrystallisation in ethyl acetate.

N, N'-dimethylformamide, which was used as a solvent for the reaction, was distilled under reduced pressure in a dry, nitrogen atmosphere after shaking with phosphorus pentoxide and then potassium hydroxide pellets.

The resin solution was prepared in a dry atmosphere by addition of an equimolar amount of finely powdered pyromellitic dianhydride to a solution of the amine in N, N'-dimethylformamide. The reaction vessel was cooled to absorb any heat of reaction which might cause degradation of the polyamide-acid [7]. The prepared solution contained 17% by weight of solids and was stored in sealed flasks at 0° C.

The silica fibre was produced continuously by drawing down a silica rod to a diameter of 0.0017 in. using an oxy-coal gas flame. This fibre was then precisely wound onto a 12 in. diameter drum, coated with Teflon sheet. A Douglas coil-winding machine was used to give an interfibre spacing of 0.0026 in. (1.0 in. = 25.4 mm).

To prevent mechanical damage to the silica, it was coated with a thin, protective layer of

polyimide before it passed over the guides of the winding machine. This was achieved by passing the fibre through a 0.01 in. gap between two Teflon capillaries. A resin solution containing 35% by weight of acetone was fed, under pressure, via the capillaries onto the fibre, and the coating was then quickly dried by passing through a furnace maintained at 400°C. The coating of about 0.0001 in. thickness was smooth and uniform and permitted the precision winding of coated fibre at 320 ft/min without excessive mechanical damage (1.0 ft = 30.5 cm).

This winding was sprayed with the resin solution diluted with N, N'-dimethylformamide and dried by a cold air blast. The resulting unidirectionally reinforced sheet was stripped off the drum and partially cured by heating to 200°C over a period of 100 min in a nitrogen atmosphere.

The sheet was sprayed again with polyamide-acid solution diluted with solvent to give an interlaminar bonding surface and dried by an air blast.

3.5 in. × 0.5 in. strips were cut from one sheet and bonded together by moistening with solvent and pressing at 1000 lb/in.<sup>2</sup> (70 kg/cm<sup>2</sup>). Release from the mould was facilitated by using Teflon mould liners and removing the excess solvent under a vacuum. Forty strips were used for each sample, giving a final thickness of 0.07 in.

The samples were then clamped between flat, stainless-steel plates to prevent blistering caused by the evolution of volatiles on curing. For the curing cycle, the samples were heated from room temperature to 350°C at a carefully programmed rate (5°C/h) in an atmosphere of nitrogen.

To evaluate the relative heat resistance of the polyimide/silica composites, panels of two, commercial, high-temperature composite materials were fabricated.

One panel was prepared from "Narmco Imidite 1850" laminate. This comprised a standard, 181-style glass fabric impregnated with a polybenzimidazole-based resin. The panel was formed from the laminate by pressing (200 lb/in.<sup>2</sup>) for 3 h at 370°C. It was then post-cured in a nitrogen atmosphere for 24 h at 315, 343, 370, and 400°C successively and finally 8 h at 430°C.

An epoxy-novolak panel reinforced with predominantly unidirectionally aligned, E glass fibres was fabricated from "Scotchply XP 253" laminate. This was pre-cured for 20 min at

125°C and pressed at 165°C. It was then cured by heating at 180°C for 4 h and post-cured at 200°C for 2 h.

A sample of unreinforced film was prepared by coating a thin layer of polyamide-acid solution onto a glass plate. This was dried using an air blast and then cured by heating in nitrogen from room temperature to 300°C in 100 min.

## 2.2. Testing

For microphotographic examination, a sample was cut through its midpoint along a plane perpendicular to the fibre axis, and mounted in a block of acrylite casting resin. The cross-section was then ground, polished, and photographed. Two typical photomicrographs are shown in fig. 2.

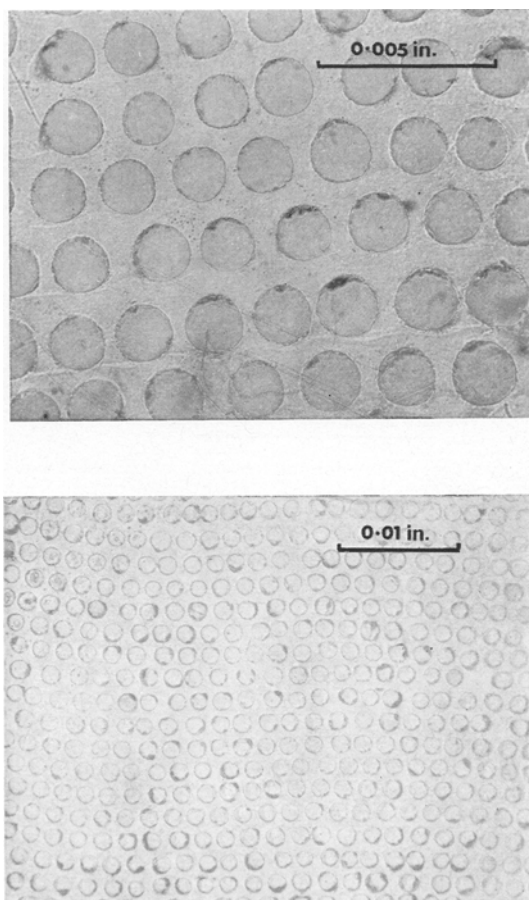


Figure 2 Photomicrographs of typical silica/polyimide composites (1.0 in. = 25.4 mm).

The fundamental resonant frequency of the samples after curing was determined using a Bruel and Kjaer complex modulus measurement apparatus as described previously [8].

The percentage fibre by weight in each sample was determined by ignition to 1000° C in air to burn off all the resin.

The samples were heated for selected periods of time at temperatures of 350, 375, and 400° C in circulating air, the percentage weight losses being recorded at intervals.

For tensile testing, the samples were filed to the dimensions shown in fig. 3 and end-pieces cemented on with an epoxy adhesive. They were then stressed to fracture in an Instron tensile tester. Standard, Instron, serrated grips were used, the Duralumin end-pieces ensuring that the samples did not fracture in the grips.

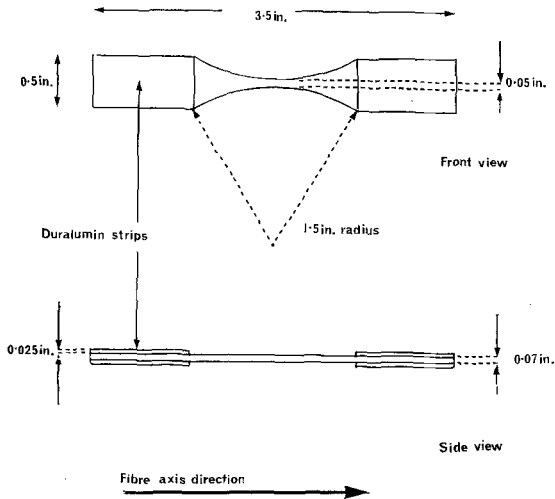


Figure 3 Test sample for determination of ultimate tensile stress (1.0 in. = 25.4 mm).

The tests were performed at room temperature, 350, 375, and 400° C. The samples tested at elevated temperatures were heated by a 1 in. long, cylindrical furnace with a split, aluminium core to effect good heat transfer. This core had a recess to fit the profile of the samples and carried a thermocouple.

For flexural testing, test-pieces measuring 1 in. × 0.1 in. × 0.08 in. were cut from the samples. The flexural strengths were determined in a four-point bending apparatus as described by Mallinder and Proctor [9]. The sample was placed in a rectangular slot passing through two pulleys, which were mounted on bearings (fig. 4). Rotation of the pulleys, caused by

applying a tension to the load wire, exerted a bending moment on the sample.

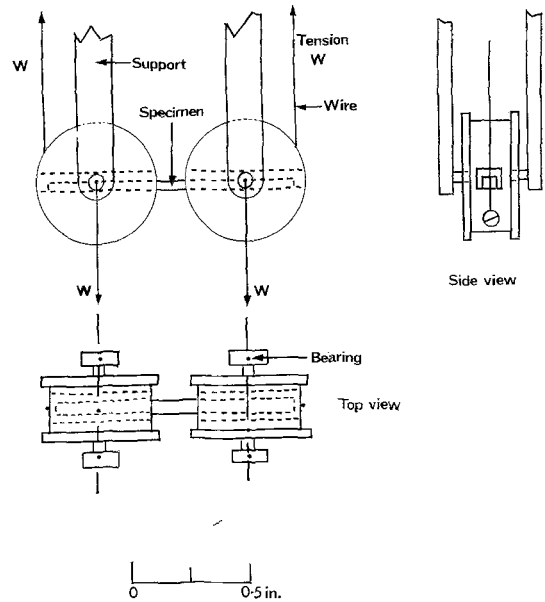


Figure 4 Design of grips for flexural strength testing of samples broken on four-point bending (1.0 in. = 25.4 mm).

The grip pulleys and supports were made from stainless steel and mounted in graphite bearings to permit complete insertion of these parts in a furnace for high-temperature testing.

### 3. Experimental Results

The dynamic modulus  $E$  of the sample was calculated from [10]

$$E = \frac{0.002438 w l^4 F^2}{bd^3}$$

where:  $l$  is the length of the sample;  $w$ , the mass per unit length;  $b$ , the breadth;  $d$ , the thickness; and  $F$ , the fundamental vibration frequency. For all the samples, the  $E$  values were in the range 4.55 to 4.95 × 10<sup>6</sup> lb/in.<sup>2</sup> (3.20 to 3.48 × 10<sup>5</sup> kg/cm<sup>2</sup>). Individual values were consistent with those predicted by assuming a rectilinear relationship between the dynamic modulus and the volume percentage of fibre.

The volume percentage of fibre in each sample was calculated from a knowledge of the densities of silica (2.2 g/cm<sup>3</sup>) and polyimide (1.42 g/cm<sup>3</sup>). The average fibre content was 45.6% and all individual values lay in the range 43.0 to 47.5%.

The percentage weight losses on prolonged heating in circulating air at 350, 375, and

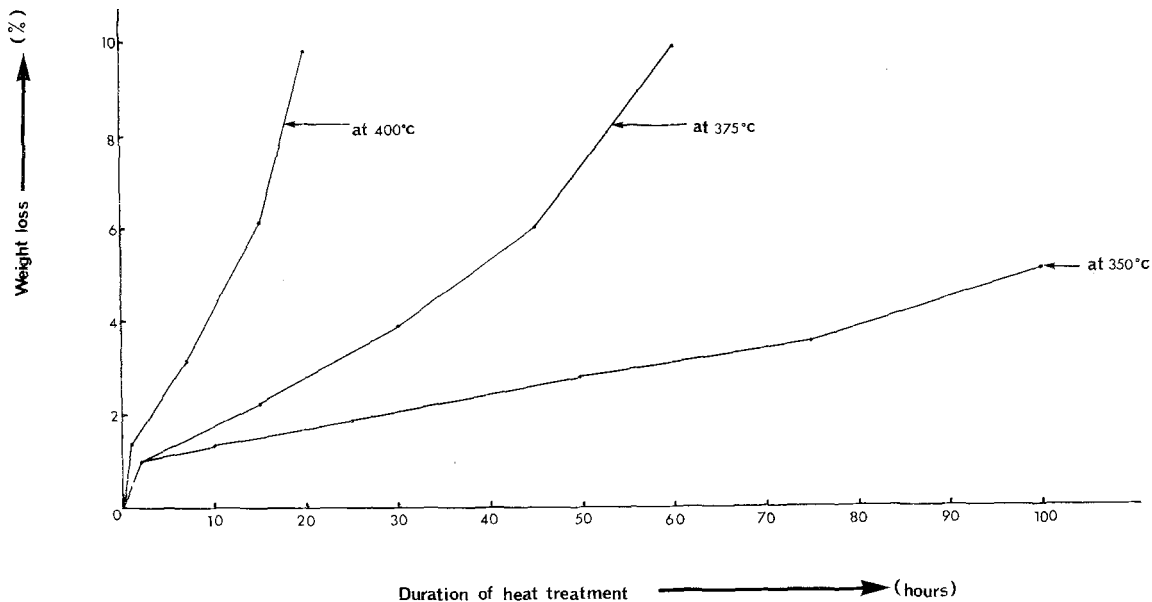


Figure 5 Percentage weight loss on prolonged heating in circulating air.

400° C are shown in fig. 5. Extensive surface degradation of the resin matrix caused mechanical loss of fibre from the surface of the samples. This resulted in increased rates of weight loss at longer exposures.

The tensile and flexural strengths of the polyimide/silica composites after heat treatment are summarised in table I. Duplicate results were obtained for each tensile value and four samples tested for the flexural values.

The flexural strengths at room temperature of the two commercially available composites after heating in circulating air are shown in table II.

#### 4. Discussion of Results

The interlaminar bond developed in the fabrication technique was non-porous and only faintly discernible on the photomicrograph. The samples produced were used to assess the high-temperature performance of non-porous polyimide structures, all previous data being related to porous structures.

When tested in tension, silica is the main stress-bearing component in the composite on account of its much greater elastic modulus. In the composites tested, the tensile stresses at fracture were in the range  $1.15$  to  $2.30 \times 10^5$  lbt

TABLE I The effect of heat treatment in air on the strength properties of silica/polyimide composites ( $1 \text{ lb/in.}^2 = 7 \times 10^{-2} \text{ kg/cm}^2$ ).

Heat treatment in air flow		% wt loss	Test temperature (°C)	Ultimate tensile stress $\times 10^{-3}$ (lb/in. <sup>2</sup> )	Ultimate flexural stress $\times 10^{-3}$ (lb/in. <sup>2</sup> )
Duration (h)	Temperature (°C)				
—	—	—	R.T.	102.4	95.2
—	—	—	350	80.7	73.1
50	350	2.74	350	64.8	86.9
100	350	5.09	350	79.1	60.6
100	350	5.09	R.T.	79.0	71.4
—	—	—	375	82.7	72.0
30	375	3.86	375	75.6	63.8
60	375	9.91	375	65.8	51.2
60	375	9.91	R.T.	56.0	66.4
—	—	—	400	75.6	70.3
10	400	4.13	400	66.5	68.6
20	400	9.80	400	76.7	55.6
20	400	9.80	R.T.	79.0	63.9

TABLE II The effect of thermal ageing on two commercial composites ( $1 \text{ lb/in.}^2 = 7 \times 10^{-2} \text{ kg/cm}^2$ ).

	Heat treatment in air flow		% wt loss	Ultimate flexural stress $\times 10^{-3}$ (lb/in. <sup>2</sup> )
	Duration (h)	Temperature (°C)		
"Imidite 1850"	—	—	—	73.2
	10	350	3.98	17.2
	50	350	12.2	0
	10	400	12.0	0
"Scotchply type XP 253"	—	—	—	220.4
	1	300	0.74	207.6
	20	300	3.56	139.3
	50	300	5.31	121.1
	20	350	12.32	0

in.<sup>2</sup> ( $0.81$  to  $1.62 \times 10^4 \text{ kg/cm}^2$ ) of silica. This compares with values of  $8.00$  to  $9.50 \times 10^5 \text{ lb/in.}^2$  ( $5.63$  to  $6.68 \times 10^4 \text{ kg/cm}^2$ ) for freshly drawn silica fibres. It is therefore evident that the reinforcement has been weakened during the fabrication procedure.

This loss in strength has been investigated by observing the effect of heat treatment and polyimide coating of single filaments of silica [11]. These results are summarised in fig. 6.

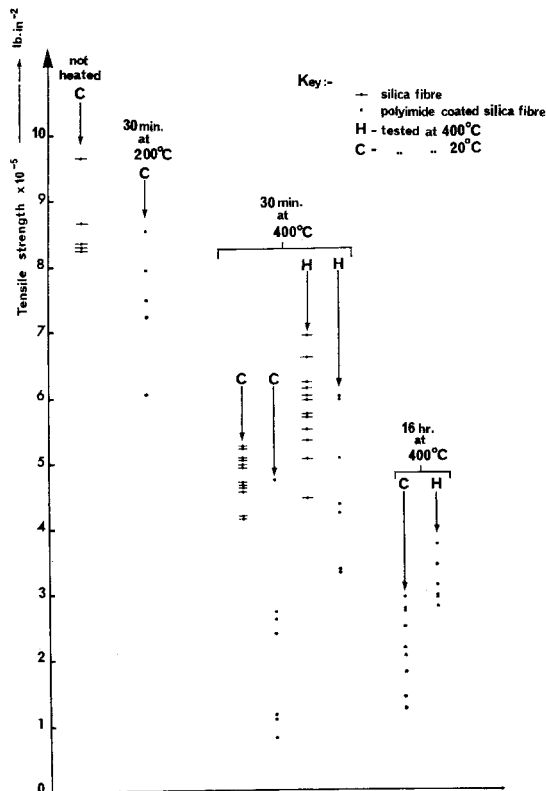


Figure 6 Tensile strengths of single filaments after heat treatment ( $1 \text{ lb/in.}^2 = 7 \times 10^{-2} \text{ kg/cm}^2$ ).

Polyimide coating of the fibre involved heating for 30 min at  $200^\circ \text{C}$  and caused only a slight loss in strength. However, drastic strength reductions were apparent on subsequent heat treatment of these coated filaments at  $400^\circ \text{C}$ . Most of the damage occurred after 30 min at  $400^\circ \text{C}$  and did not increase significantly after 16 h at this temperature.

Uncoated fibres show similar trends in strength loss on heating, but the presence of polyimide enhances this degradation.

Silica is extremely susceptible to surface damage [4] and it is possible that the differential thermal contraction between polyimide and silica might cause extra surface damage.

All composite tensile fractures were fibrous (fig. 7), indicating weakness in the fibre resin bond. Samples tested after heat treatment in air at both  $375$  and  $400^\circ \text{C}$  had longer fibre "pullout". In general, the surfaces of the exposed fibres were clean, but in several places flakes of loosely adhering resin were observed. This indicated some adhesion had been developed in the fabrication technique. Adhesion between resin and silica might have been reduced by shrinkage stresses which occur during the cure of the laminate or on subsequent heat ageing [12].

On flexural testing, most samples exhibited normal composite fracture, consistent with failure of the reinforcing fibres. However, several samples failed in shear along a plane between the laminae. Examination of the fracture surface showed that two different types of failure had occurred. In parts, the inter-laminar band had failed, and elsewhere the fracture occurred at the silica/resin boundary, leaving fibre exposed in the fracture face. This suggests that the flexural strengths of the

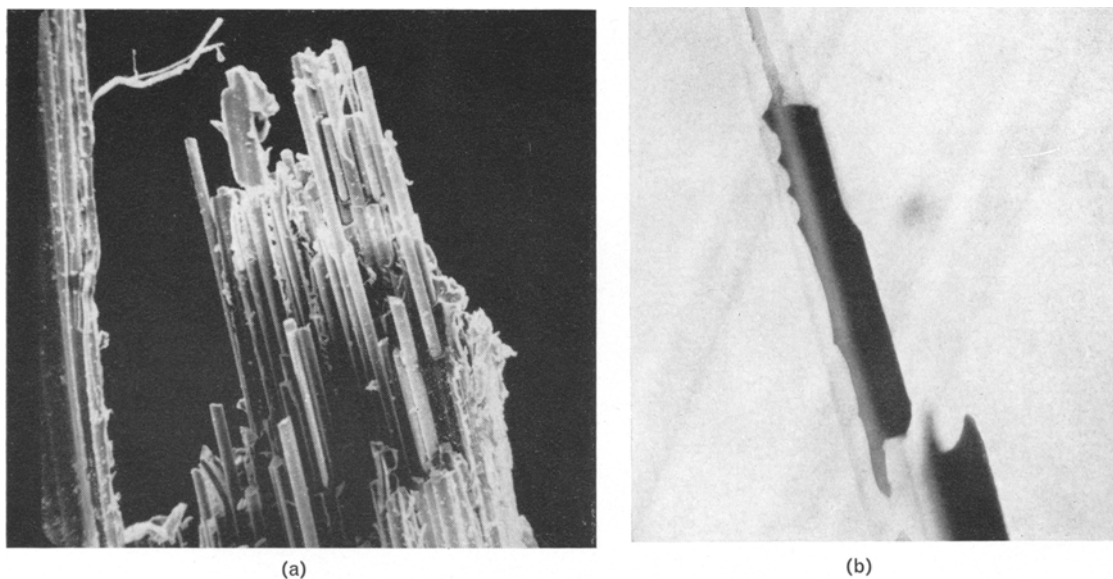


Figure 7 The tensile fracture surface: (a) overall view ( $\times 160$ ); (b) individual fibre with a flake of loosely adhering resin ( $\times 25$ ).

composites would not be improved by solely strengthening the reinforcement. Both the inter-laminar resin bond and the fibre/resin bond would have to be improved.

From experience of epoxy laminates, a coupling agent applied to the silica fibre might enhance the fibre/resin bond. However, a coupling agent with suitable high-temperature capabilities would probably be required.

Freeman *et al* [2] using a different fabrication technique produced glass-cloth-reinforced polyimide structures. Four different coupling agents were used on the cloth, the highest strength composites resulting from phenolic or  $\gamma$ -aminopropyl end groups. Composites produced without a coupling agent were slow to cure and did not maintain strength at temperature.

However, fused silica does not absorb water and develop a hydrolytic surface to the degree exhibited by ionic glasses. Thus no curing problem was encountered with fused-silica-fibre-reinforced polyimide structures, even without a coupling agent, since the silica surface is relatively inert.

The efficacy of coupling agents depends on their ability to link, by hydrolytic reaction, to the surface of the fibre. Since the silica surface is relatively inert, this property of coupling agents is not of advantage. Also, the coupling agents do not have good high-temperature properties. It is therefore unlikely that the mechanical

strengths of the composites would have been improved by the use of a coupling agent, even though the fibre-polyimide adhesion is obviously barely sufficient for effective load transfer.

The flexural and tensile strengths of the composites were not seriously reduced by the heat treatments in air. In comparison with the flexural strengths of the two, commercial, laminating materials, polyimides had much superior heat resistance. Both the polybenzimidazole and the epoxy-novolak composites were unsuitable for long-term use at  $350^{\circ}\text{C}$  as shown in fig. 8.

When the weight loss on heating approached 10%, excessive shrinkage of the matrix caused fine cracks to appear in the surface of the samples and the heat ageing was terminated.

After heating in air, much greater weight losses were observed for the polyimide film than for the composites (fig. 9). It is therefore most probable that the degradation is dependent upon the surface area of the sample. A metal coating might reduce the weight loss of the composite and extend the high-temperature capability of this resin.

## 5. Conclusions

A successful technique for the production of unidirectionally reinforced polyimide samples has been evolved. The strengths in flexure and in tension were determined after heat ageing in

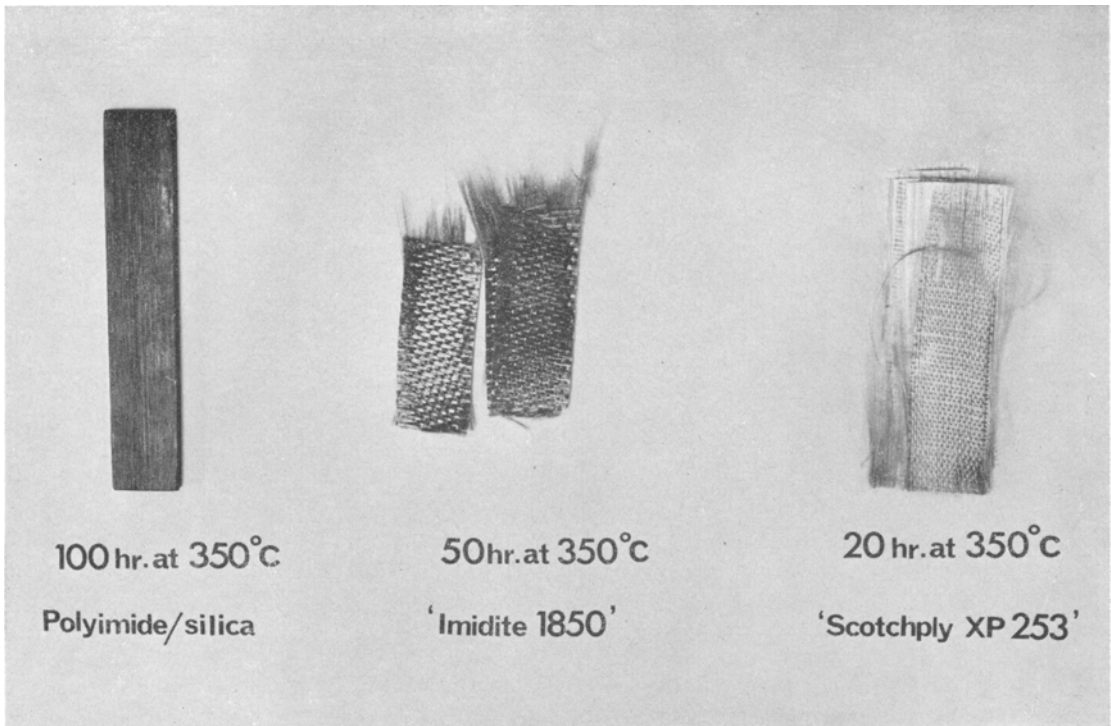


Figure 8 Composites after prolonged heating in air at 350° C.

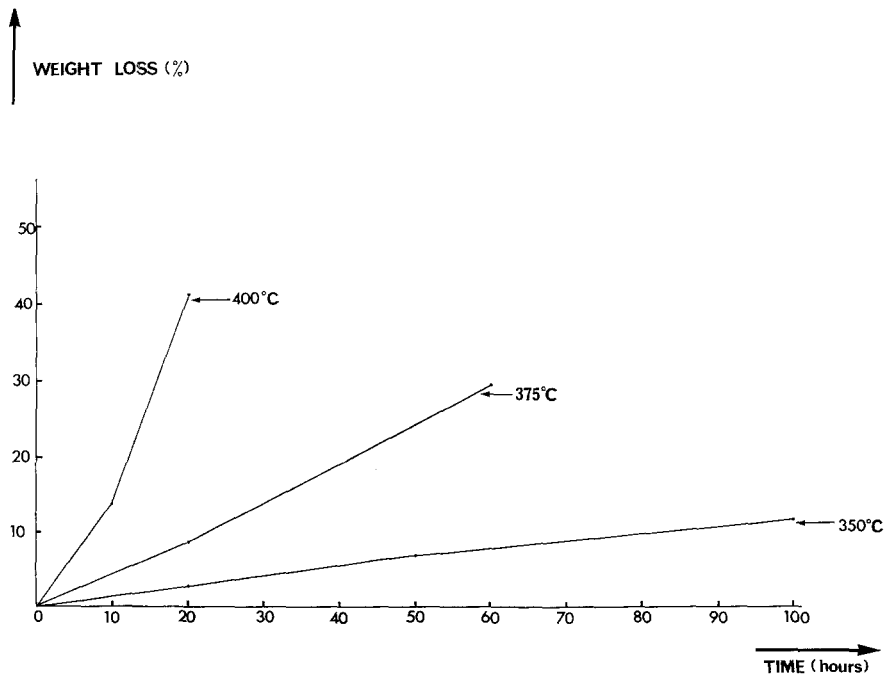


Figure 9 Percentage weight loss of polyimide film on heat ageing in air.



circulating air. Flexural strength retentions in the range of 54 to 63% of the original, obtained for samples aged for 100 h at 350° C, 60 h at 375° C, and 20 h at 400° C, are much superior to those for commercial resins.

### Acknowledgements

We wish to thank Rolls-Royce Ltd for permission to publish this paper and Mr J. R. Gould for much of the sample preparation and testing.

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