by the grain size, provided the grain size is comparable to the flaws introduced during grinding. Hence the strengthening effect would be greatest when the grain size is much smaller than the transformed zone. However, a limitation in obtaining the optimum strengthening by reducing the grain size would come from the necessity of grinding to initiate the transformation. The depth of the machining flaws introduced into the surface (as well as the depth of the transformed zone) will depend on the severity of grinding.

Other factors that need to be considered are the volume fraction of transformable material and the compensating tensile stresses within the bulk of the material. If the volume of the transformable material is too large, agglomeration may occur and introduce significant microcracking. This phenomena would thereby alter the ratio of the initial flaw size to the depth of the transformed zone and hence reduce the strengthening effect. The tensile stress developed within the material, as indicated by Equation 3, depends very much on the thickness of the material and the magnitude of the surface compressive field. In addition, the severe stress gradients near the edge of the specimen may well significantly modify the static fatigue in corrosive environments from that of annealed materials. Previous studies by Hagan *et al.* [7] showed that a similar phenomena occurred in thermally tempered materials. In conclusion this work suggests that the optimum strengthening of ground ceramics containing metastable tetragonal zirconia may be obtained by reducing the ratio of the grain size or surface flaw size to the depth of the transformed zone.

Since writing this article, Claussen and Petzow [8] have presented further experimental evidence to support the above. They found in a hot-pressed alumina/metastable tetragonal zirconia system that the modulus of rupture could be doubled by grinding-induced tempering.

Acknowledgements

The author wishes to thank M. J. Bannister, R. C. Garvie and N. A. McKinnon for informative discussions and comments on the manuscript.

References

1. R. C. GARVIE, R. H. J. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
2. R. T. PASCOE and R. C. GARVIE, "Ceramic Microstructures 1976", edited by R. M. Fulrath and J. A. Pask (Westview Press, Boulder, 1977).
3. R. C. GARVIE, R. H. J. HANNINK and C. URBANI, Proceedings of the 4th CIMTEC meeting, St Vincent, Italy, May (1979).
4. M. V. SWAIN, to be published.
5. M. SUEZAWA and S. ISHIOKA, *Mat. Sci. Eng.* 37 (1979) 282.
6. B. R. LAWN and D. B. MARSHALL, *Phys. Chem. Glasses* **18** (1977) 7.
7. J. T. HAGAN, M. V. SWAIN and J. E. FIELD, *J. Mater. Sci.* **13** (1978) 189.
8. N. CLAUSSEN and G. PETZOW, Proceedings of the 4th CIMTEC, St Vincent, Italy, May (1979).

Received 28 September
and accepted 19 October 1979

M. V. SWAIN
CSIRO,
Division of Materials Science,
Melbourne,
Australia

Alkali resistance of fibres in cement

To efficiently use Portland cement as a construction material it is generally reinforced with various types of fibres. Widely used reinforcements are steel wires and asbestos. Other reinforcements recently tried as substitutes were polypropylene [1], carbon [2, 3], glass fibres [4, 5] and other organic fibres [1, 6].

Apart from compatibility and abrasion resistance due to mixing, fibre reinforced cement has to withstand the alkaline attack during hydration and, subsequently, under moist conditions. Portland Cement has a pH value of 12 to 13.

Commercially available A and E glass fibres lose their strength rapidly in an alkaline medium as a result of chemical attack [7]. Alkali-resistant glass fibres, with high zirconia content (CEM–FIL) developed recently, have been studied as a reinforcement over the last few years [8–10].

Two other fibres, basalt and jute, are available in abundance and from cheap sources – the former from a mineral rock and the latter from a vegetable source. Basalt rock is melted around

0022–2461/80/061579–06$02.60/0

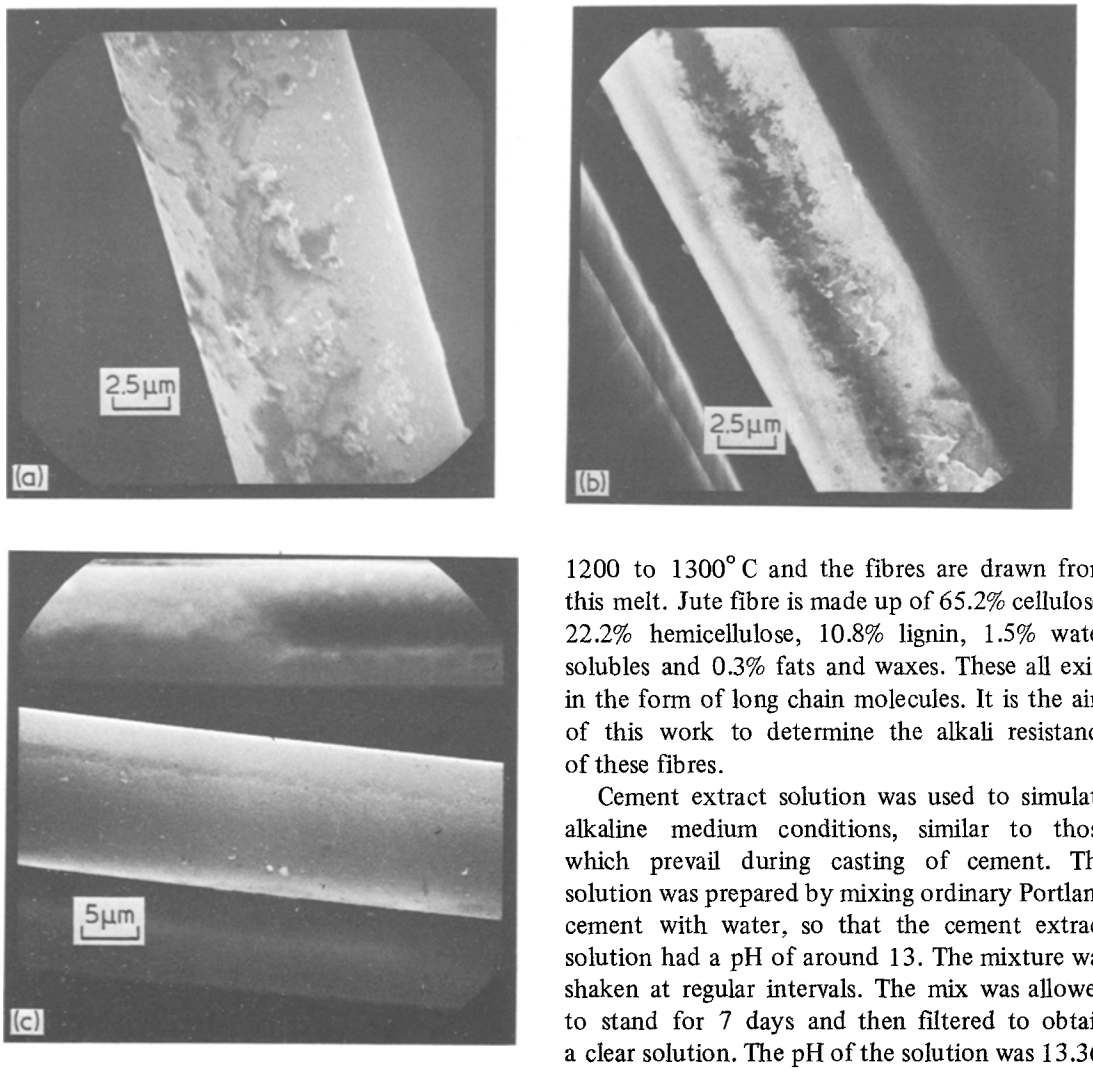

Figure 1 SEMs of glass fibres. (a) A glass after 30 days, (b) E glass after 30 days, and (c) CEM–FIL after 140 days, in the cement extract solution.

1200 to 1300° C and the fibres are drawn from this melt. Jute fibre is made up of 65.2% cellulose, 22.2% hemicellulose, 10.8% lignin, 1.5% water solubles and 0.3% fats and waxes. These all exist in the form of long chain molecules. It is the aim of this work to determine the alkali resistance of these fibres.

Cement extract solution was used to simulate alkaline medium conditions, similar to those which prevail during casting of cement. The solution was prepared by mixing ordinary Portland cement with water, so that the cement extract solution had a pH of around 13. The mixture was shaken at regular intervals. The mix was allowed to stand for 7 days and then filtered to obtain a clear solution. The pH of the solution was 13.36.

The fibres mentioned in Table I were dipped separately into the cement extract solution, in a closed flask to prevent evaporation and absorption

TABLE I Typical chemical composition of some reinforcements available as fibre (wt.%)

Reinforcements	SiO_2	Al_2O_3	B_2O_3	MnO	MgO	CaO	$Na_2O + K_2O$	ZrO_2	Li_2O	TiO_2	Fe_2O_3
A Glass*	72.2	1.8	–	–	3.5	9.5	13	–	–	–	
E Glass*	52.4	14.4	10.4	–	5.2	16.6	0.8	–	–	–	
Basalt†	49.1	13.8	–	0.21	5.25	9.43	4.0	–	–	3.16	13.98
Asbestos‡											
($3MgO\ 2SiO_2\ 2H_2O$)	40.0	0.65	–	–	42	–	–	–	–	–	–
Alkali-resistant glass*	71.0	1.0	–	–	–	–	11.0	16	1	–	–

*From [15]
†Obtained from Prof. R. V. Subramanian, Department of Materials Science and Engineering, Washington State University, Pullman, USA.
‡From [16].

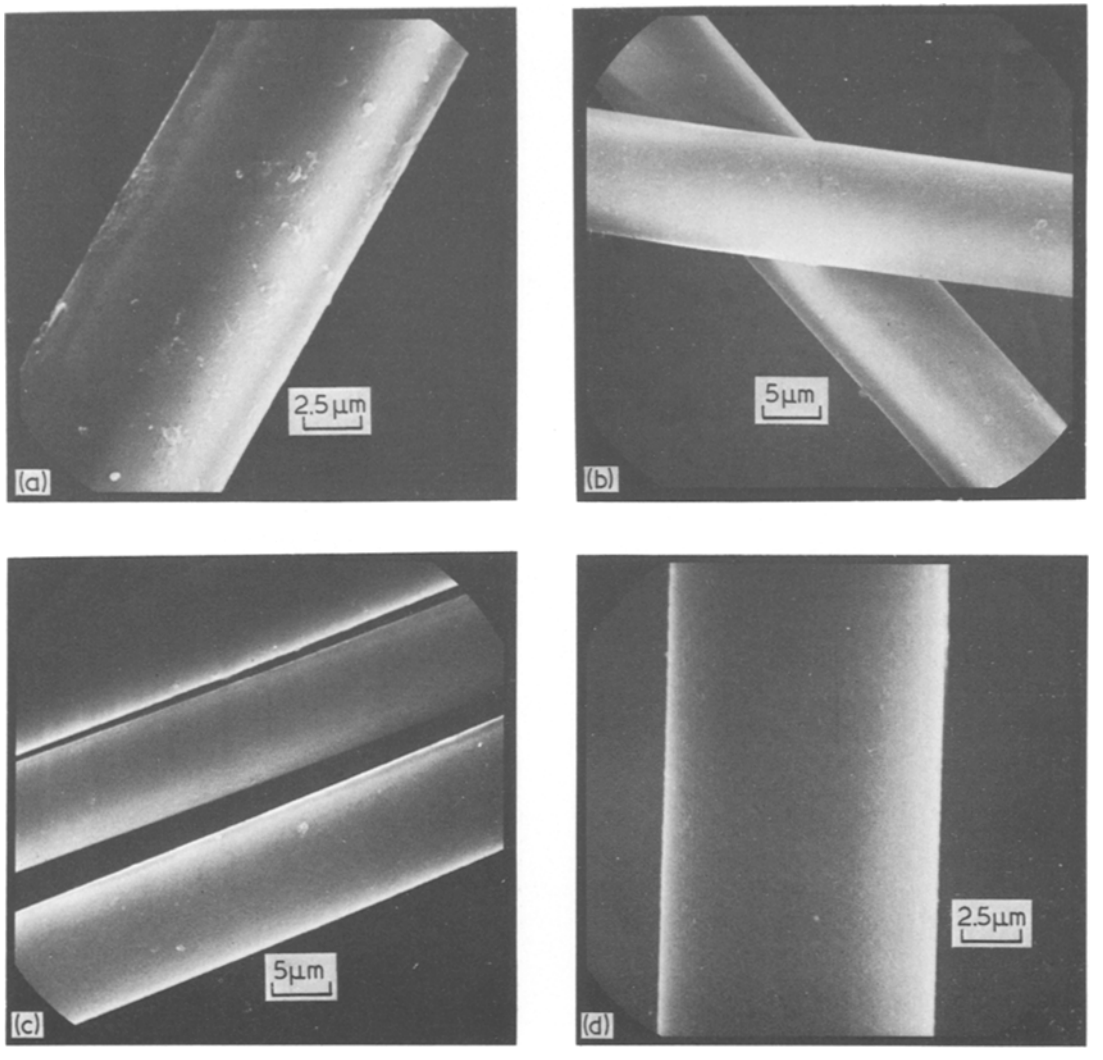

Figure 2 SEMs of Basalt fibres. (a) Untreated, (b) 7 days, (c) 30 days, and (d) 180 days, in the cement extract solution.

of CO_2. The flasks were kept at room temperature (27° C) and periodically shaken. They were removed after 1, 7, 30 and 140 days. They were washed gently with warm water to remove any reaction products, dried at 50 to 60° C and their surfaces studied under the SEM. The mechanical properties before and after 30 days dipping were determined on single fibres of 2 cm gauge length using an Instron testing machine employing a strain rate of 0.05 cm min^{-1}. In the case of CEM–FIL fibres, the gauge length was 1 cm. In each batch 25 to 30 fibres were tested and the average strength and modulus were computed. The strengths of basalt and CEM–FIL were also determined after 260 days exposure in the solution to ascertain their superiority. In the case of jute fibre, the strengths could not be measured due to total fibre collapse.

It is well known that A and E glass fibres are chemically attacked by alkali. Alkali attacks directly the silica network and completely dissolves the glass. The hydroxyl ion of the alkali breaks the Si–O–Si linkages according to the equation $\equiv Si-O-Si\equiv + OH^- \rightleftharpoons \equiv Si-OH + \equiv Si-O^-$. Fig. 1a and b show the attack of A and E glass fibres after 30 days in the cement extract solution, respectively. Fig. 1c indicates the excellent resistance of CEM–FIL fibre to alkali attack even after

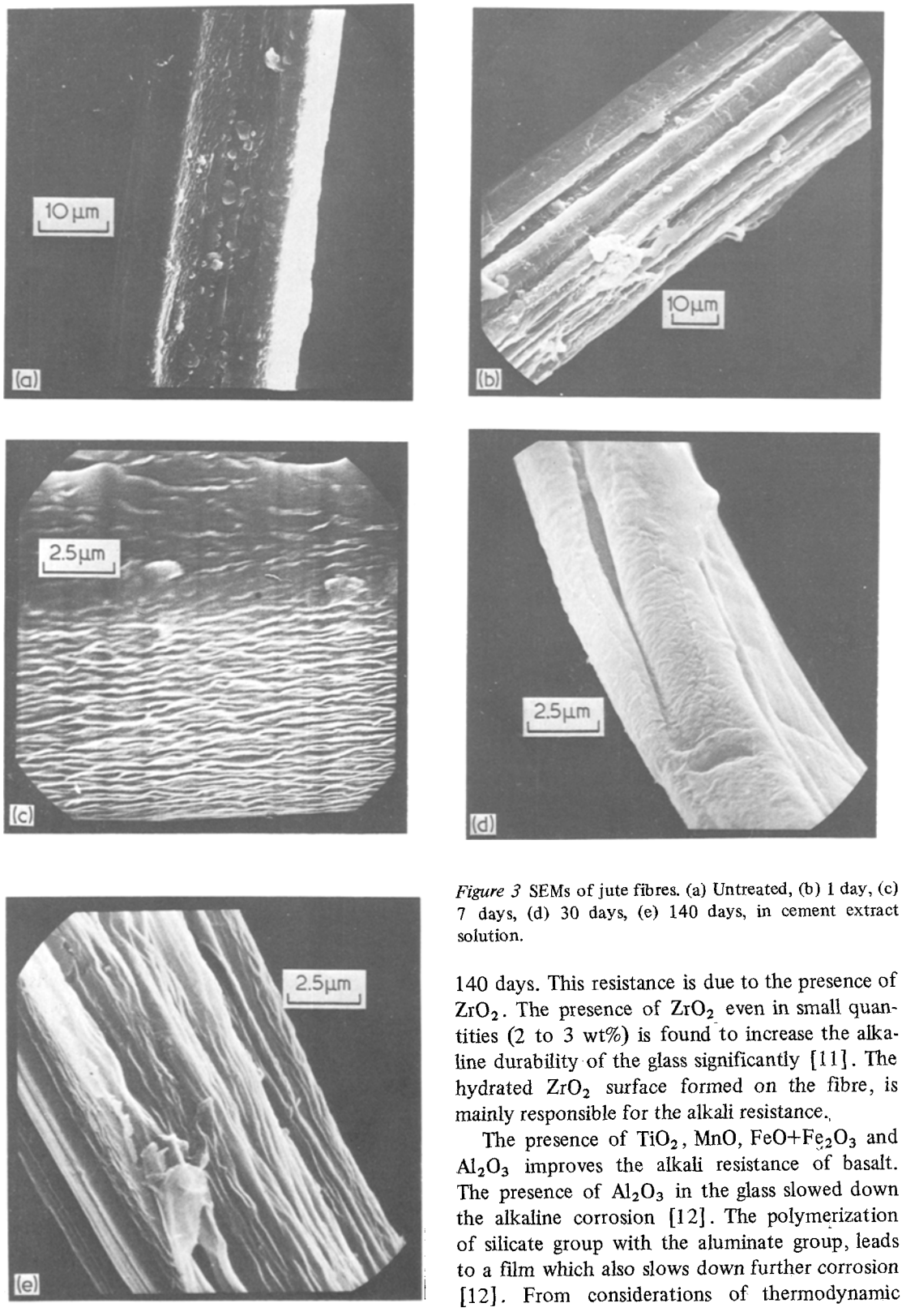

Figure 3 SEMs of jute fibres. (a) Untreated, (b) 1 day, (c) 7 days, (d) 30 days, (e) 140 days, in cement extract solution.

140 days. This resistance is due to the presence of ZrO_2. The presence of ZrO_2 even in small quantities (2 to 3 wt%) is found to increase the alkaline durability of the glass significantly [11]. The hydrated ZrO_2 surface formed on the fibre, is mainly responsible for the alkali resistance.

The presence of TiO_2, MnO, $FeO+Fe_2O_3$ and Al_2O_3 improves the alkali resistance of basalt. The presence of Al_2O_3 in the glass slowed down the alkaline corrosion [12]. The polymerization of silicate group with the aluminate group, leads to a film which also slows down further corrosion [12]. From considerations of thermodynamic

TABLE II Fibre properties before and after 30 days treatment

Fibres	Diameter (μm)	Tensile strength (10^3 psi*)		Modulus (10^6 psi*)	
		Before treatment	After treatment	Before treatment	After treatment
A Glass	9–11	240 (217–251)	160 (151–175)	9–10	5–10
E Glass	9–10	225 (212–243)	176 (164–180)	9–10	5–7
Basalt	11–13	190 (183–196)	170 (162–188)	7–8	7–8
Alkali-resistant glass	12–14	280 (262–297)	260 (251–268)	8–9	8–9
Jute	variable Av. 40–60	50 (40–82)	12 (11–28)	4–5	1–2

Tensile strength is expressed as mean of 25 to 30 values.
The figure in brackets indicate the minimum and maximum of the test results.
*10^3 psi $\equiv$ 6.89 N mm^{-2}.

activities, manganese and iron oxides always improve the alkaline durability [13]. The presence of TiO_2 also contributes to the resistance of a fibre to alkali, titania also forms insoluble complexes with silicates and thereby protects the fibre [14]. It is expected that the fibre should have good alkali resistance. This fact has been well substantiated by the SEM pictures. Fig. 2a to d show the basalt fibre surface before the treatment after 7, 30 and 180 days, respectively. The undamaged surface is a clear indication of its resistance. There is no significant variation in the diameter before and after the treatment.

From the Fig. 3a to e it is clear that jute fibres are unsuitable as a reinforcement in cement, and may be suitable only after special surface treatments. It is observed that lignin, which binds the cellulose and hemicellulose fibres, is itself preferentially leached out during the early stages. Fig. 3b and c, photographs of the fibre after 1 and 7 days of dipping, substantiate the break down of the lignin matrix. After the removal of lignin the jute structure is exposed to the alkaline environment. The hemicellulose and cellulose molecules are now prone to attack. This leads to fibrillation. Fig. 3d depicts the typical fibrillation stage, after 30 days, and Fig. 3e shows the total structural collapse after 140 days with the possible removal of hemicellulose.

The observations made under the SEM on these fibres are further substantiated by the change in mechanical properties. Physical observation after 140 days revealed that basalt fibre retained its flexibility, whereas jute had become brittle and, on handling, fragmented. Table II compares the strength and modulus values before and after 30 days. There is a considerable reduction in tensile and modulus values in the cases of A and E glass fibres and jute fibres.

Basalt fibre compares very well with the presently available alkali-resistant fibre. In both the fibres the loss of tensile strength is very marginal.

References

1. S. GOLDFEIN, *Modern Plastics* **42** (8) (1965) 156.
2. J. WALLER, "Fibre Reinforced Concrete", ACI Special Publication SP 44 (1974) p. 143.
3. M. A. ALI, A. J. MAJUMDAR and D.L. RAYMENT, Proceedings, Conference on the properties of Fibre composites, Teddington 1971 (IPC Science and Technology Press, Guildford, 1972) pp. 27–28.
4. A. J. MAJUMDAR and J. F. RYDER, *Glass Technol.* 9 (3) (1968) 78.
5. B. R. STEELE, "Glass fibre reinforced cement in prospects for reinforced construction materials" (Building Research Station, London, 1971) pp. 29–36.
6. A. D. FAIRWEATHER, Proceedings International Building Exhibition Conference on "Prospects for Fibre Reinforced Construction Materials", London, 1971 (Building Research Station, Watford, 1972) pp. 41–43.
7. F. J. GRIMER and M. A. ALI, *Mag. Concr. Res.* **21** (1969) 28–30.
8. A. J. MAJUMDAR, J. M. WEST and L. J. LARNER, *J. Mater. Sci.* **12** (1977) 927.
9. M. S. STUCKE and A. J. MAJUMDAR, *ibid.* **11** (1976) p. 1019.
10. M. A. ALI, A. J. MAJUMDAR and B. SINGH, *ibid.* **10** (1976) 1732.
11. V. DIMBLEBY and W. E. S. TURNER, *J. Soc. Glass Technol.* **10** (1926) 304.
12. W. A. WEYL, *ibid.* **35** (1951) 462.
13. A. PAUL and A. YOUSSEFI, *J. Mater. Sci.* **13** (1978) 97.
14. T. BAAK, C. F. RAPP, H. T. HARTLEY and B. E. WIENS, *Amer. Ceram. Soc. Bull.* **47** (1968) 727.
15. A. J. MAJUMDAR and R. W. NURSE, "Glass fibre reinforced cement" Current paper, CP 79/74 (Building Research Establishment, August 1974).

16. W. E. SINCLAIR, "Asbestos: Its origin, Production and Utilisation" (Mining Publications Ltd, London, 1959).

V. VELPARI
B. E. RAMACHANDRAN
T. A. BHASKARAN
B. C. PAI*
N. BALASUBRAMANIAN
Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

Received 3 January and accepted 24 October 1979.

*Present address: Department of Metallurgy, The University of Sheffield, UK

Enhancement of the fatigue life of PMMA through prior crazing

In a previous paper [1], it was demonstrated that the low-stress-level fatigue life of polycarbonate could be increased several fold by prior tensile deformation. In that case, the material was loaded to 90 to 95% of its macroscopic yield stress prior to fatigue in equal tension/compression, constant load amplitude testing. The fatigue life at low cyclic stress levels was increased by nearly an order of magnitude, relative to virgin material. The life enhancement was attributed to the relative "softness" [2, 3], at low stress levels, of large crazes. At high cyclic stress levels, where the crazed material is highly extended, the fatigue life was decreased by tensile treatment. The present communication extends these observations to another glassy polymer, PMMA.

The material used was Plexiglas® "G" sheet. The specimen shape is as described in [1]. Specimen blanks 0.63 cm × 2.5 cm × 20.3 cm were milled to produce a non-uniform gauge section bounded by 7.6 cm circular arcs. The minimum width was 0.63 cm. In order to standardize the material, all specimens were air-annealed at 120° C before testing. Pre-crazed specimens were prepared by drawing to 335 kg, 95% of the macroscopic yield load (352 kg), after annealing and prior to cyclic testing.

The fatigue frequency used was the highest that could be used without significantly heating the specimen. Fig. 1 shows the surface temperature (determined using a thermocouple attached with epoxy glue to the specimen surface) against cycling time at seven different frequencies. A frequency of 10 Hz causes thermal failure (see, for example, [4]), whereas 5 Hz causes only an asymptotic 10° C

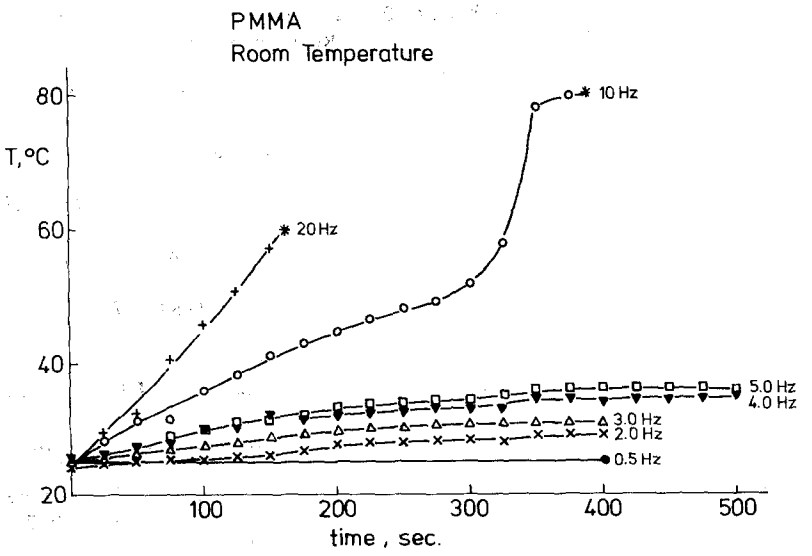

Figure 1 Temperature versus cycling time during equal tension/compression amplitude loading at ± 24.8 × 10^5 kg m^{-2}.

0022–2461/80/061584–02$02.20/0