ELSEVIER

0958-9465(95)00041-0

Cement & Concrete Composites **18** (1996) 31–39
© 1996 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0958-9465/96/$15.00

Effect of Microsilica and Acrylic Polymer Treatment on the Ageing of GRC

Peter J. M. Bartos & Wenzhong Zhu

Advanced Concrete Technology Group, Department of Civil Engineering, University of Paisley, Paisley PA1 2BE, UK

(Received 4 August 1995; accepted 30 January 1996)

Abstract

Microsilica and acrylic polymer dispersions were used in different types of fibre treatments and matrix modifications. The effects of the various treatments/modifications on the flexural properties, the failure modes and the interfacial changes after different periods of ageing were investigated. The fibre treatment was found to be more effective in controlling the interfacial changes and properties of the aged composites, compared to the matrix modification. The relative effectiveness of the different fibre treatments, however, depended greatly on the bundle size of the fibre reinforcement used.

A new technique based on an unique micro-indentation apparatus was developed and used to carry out micro-strength testing in the fibre–matrix interfacial zone and particularly within the fibre bundle. Results suggested that a soft/flexible fibre bundle core combined with a strong bonding at the fibre–matrix interface was desirable for the optimal improvement of the long term performance of the composites.

Keywords: Glass fibres, fibre bundles, glass reinforced cement, acrylic polymer, microsilica, interfaces bond micro-fracture mechanics.

INTRODUCTION

Glass fibre reinforced cement (GRC) represents a typical case in which problems associated with ageing have been encountered in practice. A loss of tensile strength and/or ultimate strain capacity of the composite, and a significant reduction of toughness with time were observed for GRC products, particularly when exposed to weather. As a result the embrittlement of the aged composites remained a significant drawback to the full practical exploitation of this type of composite.

Various measures proposed to improve the ageing performance of the GRC composites have been reviewed by many authors.[1–6] These included changes of the chemical composition of the glass fibres, their surface treatment and the modification of the matrix. Two materials, namely, microsilica and acrylic polymer dispersions have been of particular interest and most extensively studied for different treatments and modifications in GRC. There is, however, a lack of agreement concerning the effectiveness of such measures and fundamental reasons for any improvements achieved. A series of studies conducted by Bentur *et al.*[7–9] indicated that both microsilica and acrylic polymer dispersions could be used more effectively in the fibre treatment than in the matrix modifications. Particularly, the fibre treatment by microsilica was found to be able to eliminate any loss in strength and to retain most of the initial toughness during accelerated ageing. One important reservation about their results is that the fibres treated and used were in a form of a roving which usually consists of 20–40 strands and is significantly different from the basic form of reinforcement (usually individual strands) in the GRC composites. Furthermore, little is known about the micro-mechanics of the actual fracture processes involved and the interfacial properties following different periods of ageing.

In this study, microsilica and acrylic polymer dispersions were used in different types of fibre treatments and matrix modifications. The

Table 1. Test series

Test series	*Matrix modifications*	*Fibre treatments*
Ref (7d, 7da, 21da, 42da)	None (plain OPC)	None (original AR-glass fibre)
Mmsi	By microsilica (10%)	None
Fmsi	None	Microsilica treated strands
Bfmsi	None	Microsilica treated bundles
Mfvf	By acrylic polymer (10%)	None
Ffvf	None	Acrylic polymer treated strands
Bffvf	None	Acrylic polymer treated bundles

effects of various treatments/modifications, including the use of different sizes of fibre bundle as the basic reinforcing element, on the flexural properties, the failure modes and the interfacial changes after different periods of ageing were investigated. Alkali-resistant glass fibres were used throughout the study.

EXPERIMENTAL

Materials and test series

A standard grade ordinary portland cement (Blue Circle) and an AR-glass fibre (Nippon Electric Glass) were used as the basic material for matrix and reinforcement, respectively. A microsilica slurry (Elkem Chemicals) and an acrylic polymer latex (Forton BV) were used for the fibre treatments and the matrix modifications.

Three different types of treatments/modifications were adopted. The first type used the original AR-glass fibre strands combined with modifications of the cement matrix. The second type used the treated fibre strands combined with plain OPC matrix. In the third type large fibre bundles containing ten original strands were treated and used in combination with plain OPC matrix, thus enabling the effect of the size of the fibre bundle to be investigated.

The matrix modifications were achieved either by adding 10% (by weight of cement) of polymer dispersion to the matrix, or by substituting microsilica for equal weight of 10% OPC in the matrix. The fibre treatments were carried out by cutting and separating a glass fibre roving (32 strands) into individual fibre strands and dipping the strands or bundles of strands into the slurry or dispersion for a period of time. The strands/bundles were then removed and left to dry. A fixed w/c ratio of 0·35 and a constant fibre volume content of about 0·4% were used throughout the investigation. Details of the test series are given in Table 1.

All the specimens had undergone a 7 day initial curing, after which selected numbers of specimens were stored in 60°C water to accelerate the ageing. Tests were conducted using specimens after 7 days of the initial curing, as well as after 7 days, 21 days, and 42 days of the accelerated ageing. The specimens were identified as 7d, 7da, 21da, and 42da, respectively.

Test methods and specimen preparation

The flexural behaviour of the different GRC composites was assessed using a four point bending test with a major span of 90 mm and loading rate of 1 mm/min. The test arrangement was closely related to that used by Bentur.[7] The specimens were $110 \times 20 \times 9$ mm in size and contained two parallel layers of glass fibres spaced equally across the 9 mm thick depth of the section. The fibre strands/bundles were evenly spaced across the 20 mm width of the specimen in each of the two layers, thus representing a continuous reinforcement. Two principal parameters were calculated from the load–deflection curves obtained: the post-crack maximum flexural stress and the post-crack energy absorption, which served as an estimate of the flexural strength and toughness of the composites, respectively. Parallel investigations of micro-fractural processes of the fibre composites were also carried out using a specially designed SEM tensile/pullout test stage. Specimens for these investigations were made from the same mixes and ageing procedures as the bending test specimens. Details about the specimens and the techniques are given in Refs 10 and 11.

In addition, investigations on the interfacial changes in the fibre–matrix interfacial zone and

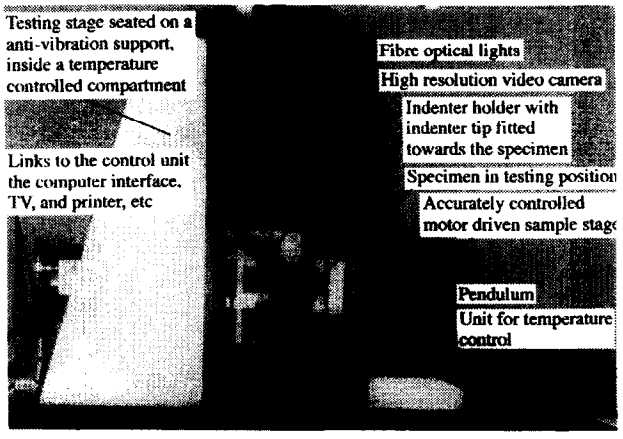

Fig. 1. Testing stage of the MicroTest 200 used for the measurement of micro-strength.

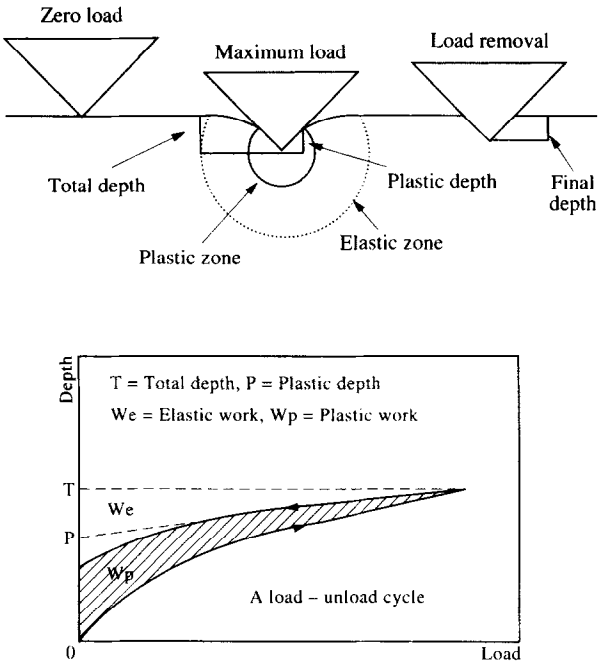

Fig. 2. Illustration of the principle using Continuous Depth Recording in the MicroTest 200 apparatus.

especially within the fibre strands/bundle due to the treatments and the modifications in the composites were carried out using an unique nano-technology based apparatus shown in Fig. 1. The apparatus 'MicroTest 200' is an instrument for continuous monitoring of a load–displacement relationship in the load range of 0–20 N and displacement range of 0–50 μm with resolutions of 0·7 mN and 1·7 nm, respectively. The instrument is specially configured for push-in and push-through testing on individual fibres to assess the actual magnitude of the interfacial bond. The fibre push-in test differs from the fibre pull-out test mainly in that the fibre is pushing into or through the matrix instead of pulling out from the matrix. In many cases, particularly for very small and brittle fibre filaments or fibre bundles, the push-in test offers a clear advantage over the conventional pullout test. Work on employing the push-in test to determine the bond values at the fibre–fibre and the fibre–matrix interfaces for GRC composites following different periods of ageing is currently in progress. In the first stage the apparatus was used for indentation testing on very small areas to assess the change of properties in the interfacial zone and within the fibre strand/bundle in this study.

As shown in Fig. 2, an indenter tool (usually a diamond tip) was moved to be just in contact with the surface of a selected area. The indenter was then pushed against the specimen until a designated maximum load was reached before being unloaded to zero. A complete load–displacement curve was recorded during the test by a Continuous Depth Recording measuring system. A special material micro-mechanical parameter, namely Micro-strength, as defined in eqn (1) could be calculated from the indentation curves.

$$\text{Micro-strength} = L_m/(k*P^2) \quad (1)$$

where L_m = maximum load; P=plastic depth of the indentation; k=indenter tool geometry factor.

The indenter tool geometry factor k in eqn (1) is a constant independent of the depth for an ideally perfect indenter tool geometry. In the case of imperfect tool geometry, k becomes a function of the depth, and calibrations have to be made to determine the values of k at different depths. To avoid the determination of k in the absence of information about the indenter tool geometry, relative micro-strength values can be easily calculated instead by comparing one load–depth curve with another obtained from a reference sample at the same plastic depth. In this study a 90° diamond (i.e. corner of a cube) was used as the indenter tool, and a homogeneous plexiglass material was used as the reference for the determination of relative micro-strength values.

By definition the micro-strength value is closely associated to the Vickers microhardness number in the conventional microhardness testing. However, the determination of the Vickers microhardness number requires the diagonal lengths of the indentation to be measured opti-

cally. This is a very difficult task when applied to a small/porous area and usually, the required deep/large indentations are not practicable.

Preparation of specimens for the micro-strength testing was carried out in four stages, namely: (1) cutting a slice from the sample of the four point bending test perpendicular to the fibre axis; (2) embedding the slice in a moulding resin to form a disc specimen; (3) grinding and polishing the specimen with silicon carbide papers and diamond particles to obtain a flat and very smooth surface finish; (4) cleaning the specimen in an ultrasonic bath to remove the dust and diamond particles left in the voids or porous areas after the polishing.

RESULTS AND DISCUSSION

Mechanical properties and failure modes

The effect of fibre treatments/matrix modifications by the microsilica on the composite flexural properties is shown in Fig. 3(a) and (b). The results for the acrylic polymer modifications/treatments are presented in Fig. 4(a) and (b).

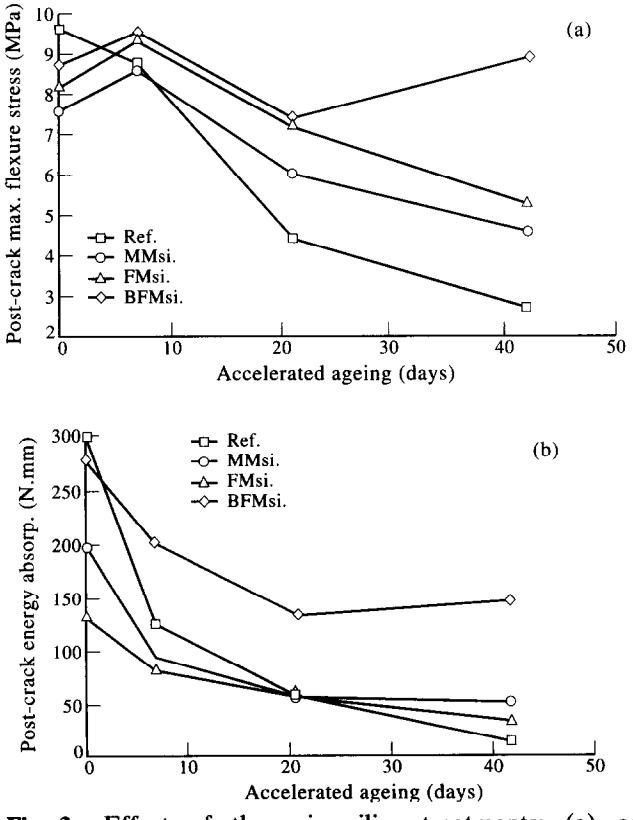

Fig. 3. Effect of the microsilica treatments: (a) on strength and (b) on toughness.

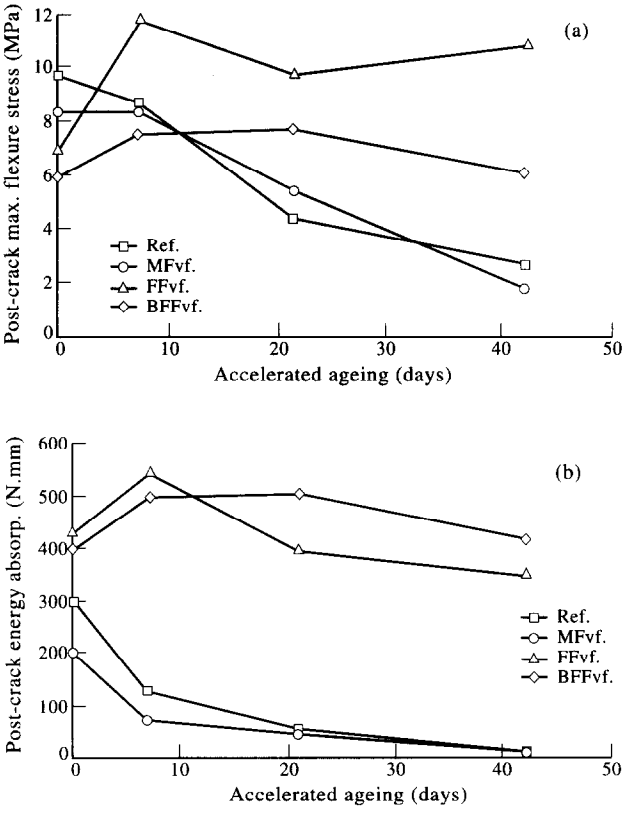

Fig. 4. Effect of the acrylic polymer treatments: (a) on strength and (b) on toughness.

Effect of ageing

For the reference series (Ref), the results in Fig. 3(a) and (b) showed that both the post-crack flexural strength (post-crack maximum flexural stress) and the flexural toughness (post-crack energy absorption) decreased sharply with the accelerated ageing. The composite lost almost all the improvement in toughness and retained less than one third of the initial post-crack maximum flexural stress. This occured after 42 days of the accelerated ageing, which is approximately equivalent to 30–35 years of outdoor exposure in the UK.

Investigations using the SEM tensile/pullout test demonstrated that the embrittlement of the composite was associated with a change of the failure mode from a pullout failure of a complete fibre strand (Fig. 5(a)) to a complete fracture of the whole strand (Fig. 5(d)), through intermediate failures showing partial pullout/fractures of the strand (Fig. 5(b)–(c)). The fibre strand which is the basic reinforcing element in

the GRC composite consists of 204 fibre filaments loosely bonded together by a coating or 'size'. It is indicated that the improvement of toughness in such a brittle matrix composite reinforced with brittle fibres relies mainly on the pullout of the fibres and the resulting pseudo-ductility. The work of fracture of the fibres alone is very small and contributes little to the total composite energy absorption.

Effect of the microsilica

The improvement of flexural properties of the aged GRC due to the microsilica treatment/modification appeared to be very much dependent on the types of treatments/modifications used. When the microsilica was used in the matrix modification (Mmsi) or in the treatment of fibre strands (Fmsi) the rate of the decrease in post-crack flexural stress with ageing was slower than that of the reference sample (Fig. 3(a)) but the loss of toughness due to ageing remained the same as in the series Ref (Fig. 3(b)). The use of large fibre bundles treated by the microsilica (Bfmsi), however, turned out to be the most effective in improving the ageing performance of the composite. The results indicated that the post-crack flexural strength of the composite after a substantial ageing remained as high as that of the young composite. A much higher toughness was also retained. The SEM pullout test revealed that the telescopic pullout became a typical failure mode throughout the ageing periods for the composite samples using the microsilica treated fibre strands/bundles as shown in Fig. 6. The telescopic failure which showed a gradual fracture of the outer filaments and the pull out of the inner core filaments from the treated fibre bundle, as introduced by Bartos,[12] is actually a

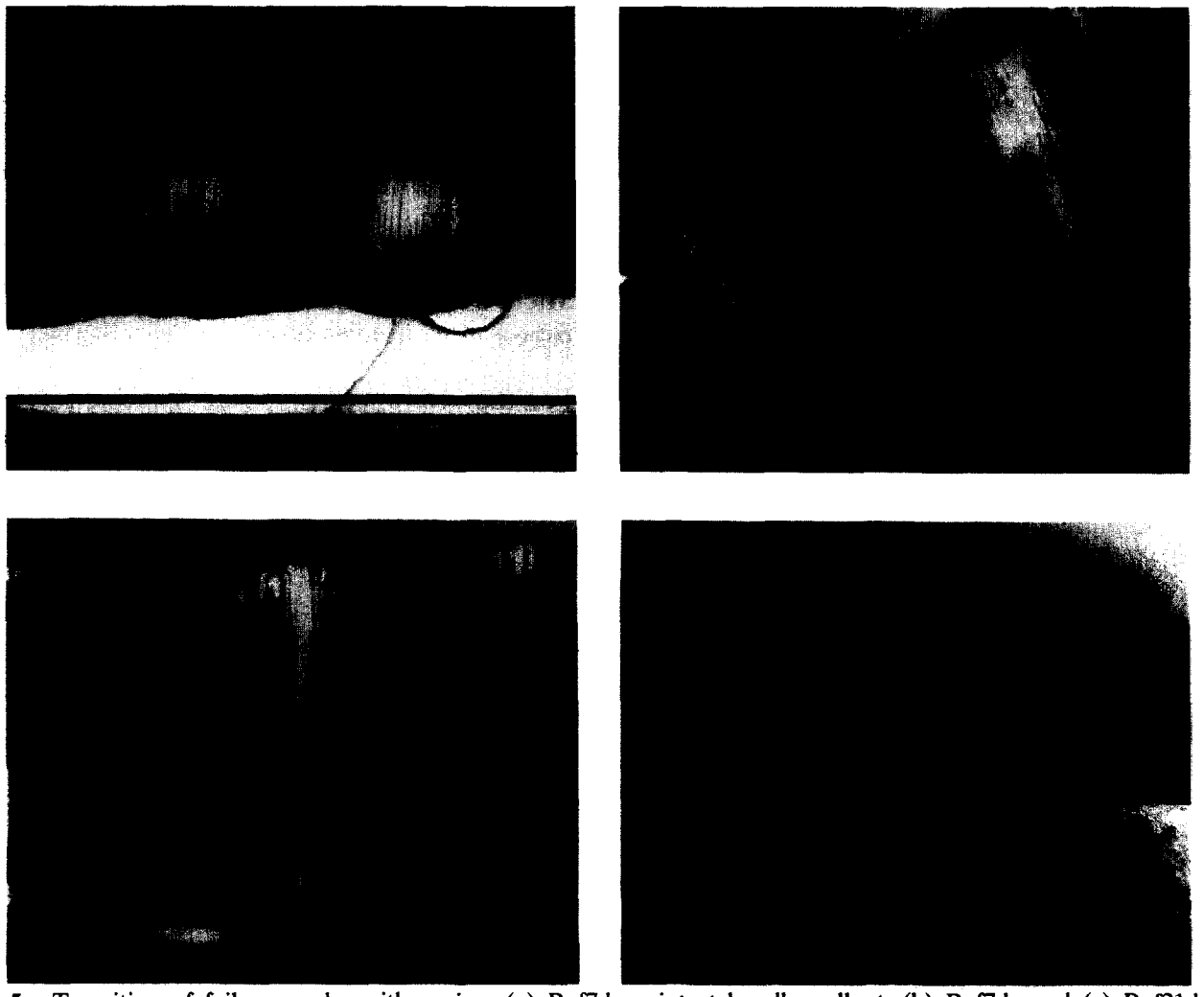

Fig. 5. Transition of failure modes with ageing: (a) Ref7d — intact bundle pullout, (b) Ref7da and (c) Ref21da — partial fracture/pullout and (d) Ref42da — complete tensile fracture.

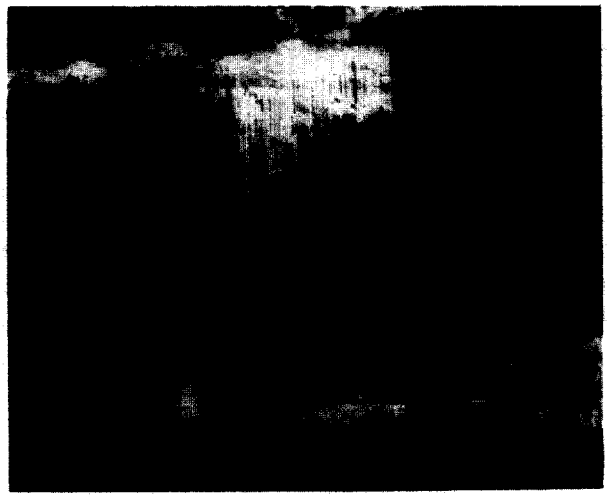

Fig. 6. Telescopic pullout (typical failure mode associated with microsilica treatment).

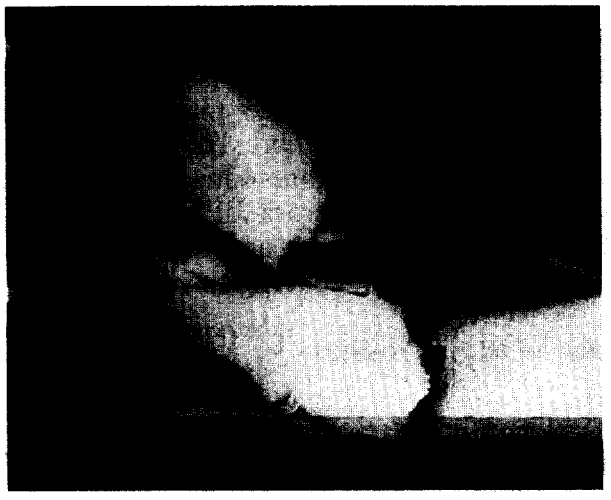

Fig. 7. Matrix failure between fibres (associated with polymer treatment).

special type of intermediate mode of failure. The use of large treated fibre bundles usually leads to a complete pullout of a substantial inner core of the bundle, while in the case of the treated single strands the inner cores of the fibre strand gradually ruptured and even the innermost filaments failed to show intact pullout for the aged composites.

Effect of the acrylic polymer

Effect of the treatments/modifications by the acrylic (Forton) polymer differed from that of the microsilica. As the results in Fig. 4(a) and (b) show, the matrix modification (Mfvf) did not improve the ageing performance of the composite. Using the polymer treated fibre strands (Ffvf), however, did greatly enhance the performance of the aged composite. Both the flexural strength and toughness were increased and maintained at a very high level after the accelerated ageing. Compared to the series Ffvf, the use of the polymer treated large fibre bundles (Bffvf) seemed to have reduced the reinforcing efficiency of the fibres although it did improve the ageing performance of the composite. Microscopic observation of the polymer treated fibre strands/bundles revealed that the polymer particles penetrated into the space between the filaments within the strand/bundle and bonded all the filaments together. A relatively thick polymer coating (10–30 μm) was formed, which covered the strand/bundle overall. As a result, the whole fibre strand/bundle behaved like a single reinforcing fibre of a very large size. Investigations using SEM pullout test (Fig. 7) suggested that another kind of failure usually appeared in the aged composite specimens with the polymer treated fibre strands/bundles. It appeared that the crack was deflected to a zig-zag path and then led to the crushing of the matrix and spalling between the fibre strands/bundles during the SEM tensile testing. Such a micro-fracture mechanism may have contributed to the very high energy absorption observed in test series Ffvf and Bffvf.

Micro-strength distributions in the interfacial zone and within the fibre bundle

For the reference composite specimens, Fig. 8 shows the effect of ageing on the micro-strength distribution pattern in the interfacial area. The negative distance values in the graph indicate that the centre of the indentation had fallen

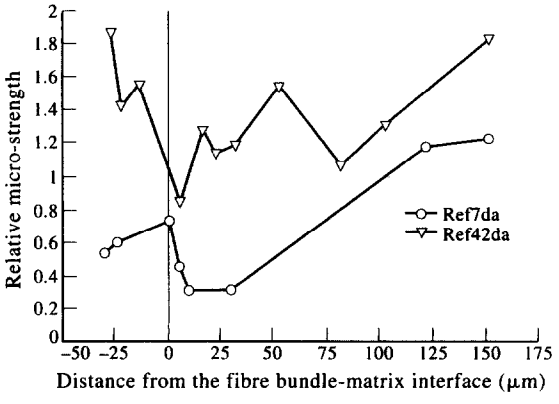

Fig. 8. Effect of ageing on micro-strength distribution.

within the overall cross section of the fibre bundle/strand. A single indentation measurement using the tool within the fibre bundle usually affected an area containing 20–30 fibre filaments. The micro-strength distribution curves in Fig. 8 show a 'valley' or 'trough' at a small positive distance from the fibre–matrix interface indicating a porous/weaker area. The micro-strength values at all the distances increased with the ageing (comparing Ref7da and Ref42da). These are well in agreement with the phenomenon observed in aggregate/matrix interfaces, e.g. by Mehta and Monteiro[13] who reported that the microhardness value of the interfacial film increased about 25% from a 30-day old to 1-year old concrete sample.

The most significant change in the micro-strength distribution pattern due to ageing happened within the fibre strand (positions: -50–0 μm). Results shown in Fig. 8 indicated that the micro-strength value decreased slightly when the indentation point moved toward the centre of the strand for a young composite (Ref7da). This decrease in micro-strength suggested that the centre of the fibre strand/bundle was more porous or there was weaker bonding between fibre filaments than at the fibre–matrix interface.

For the aged composites (Ref42da), however, the micro-strength values within the fibre strand/bundle became much higher compared to Ref7da, and it increased considerably when the test position moved from the strand–matrix interface towards the centre of the bundle. This would indicate that the porous fibre–fibre interfacial zone in the young composite was gradually filled up during ageing and the individual filaments became strongly bonded to each other. As a result the strand lost its original flexibility.

The effects of the microsilica and the acrylic polymer treatments on the micro-strength distribution patterns of the aged composites are shown in Figs 9 and 10, respectively. As shown in Fig. 9, it is apparent that the matrix modification by the microsilica (series Mmsi42da) proved to have little effect on the overall micro-strength pattern compared to that of the reference series Ref42da. However, for the systems with microsilica treated fibre strands (Fmsi42da) and with treated large bundles (Bfmsi42da), the micro-strength distribution patterns within the fibre strand/bundle were significantly different from those of Ref42da. In

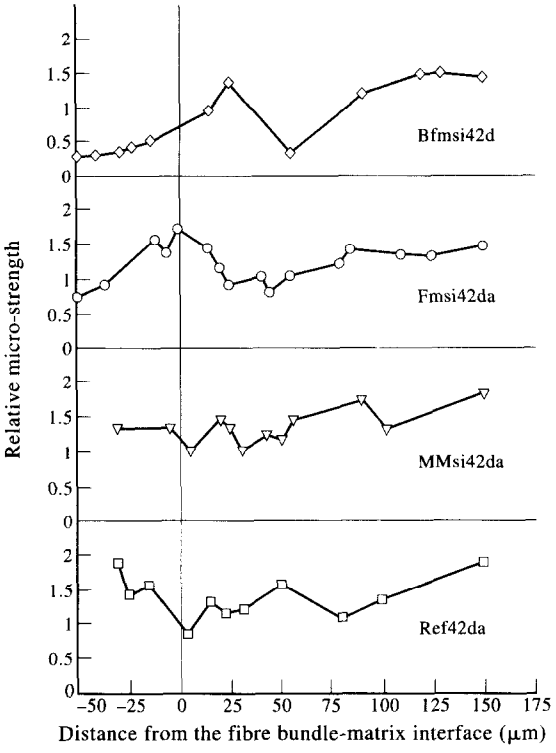

Fig. 9. Effect of microsilica on micro-strength distribution for the aged composites.

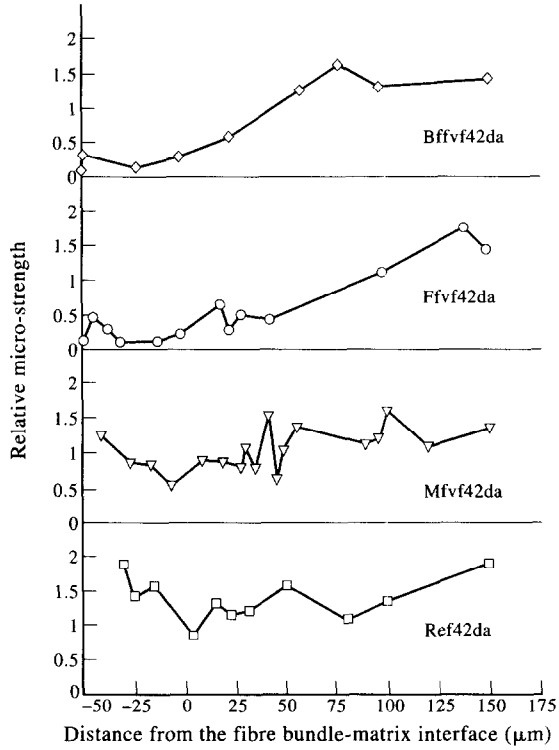

Fig. 10. Effect of acrylic polymer treatment on micro-strength for aged composites.

both series Fmsi42da and Bfmsi42da the micro-strength values at the centre of the strand/bundle were much lower and increased gradually towards the fibre–matrix interface (−50–0 μm), which was quite similar to the case for the young composite (i.e. Ref7da). The telescopic failure mode associated with the fibre treatment by microsilica may be explained by such a gradual change of the micro-strength within the fibre strand/bundle. For a fibre strand/bundle to fail in a telescopic manner, a high bond at the fibre–matrix interface and a descending value of fibre–fibre bond (adhesive and/or frictional) within the fibre strand/bundle, with the lowest bond value at the centre of the bundle, would be required.

The effect of the acrylic treatment on the micro-strength distribution appeared very similar to that of the microsilica treatment. The results shown in Fig. 10 suggest that the matrix modification by the polymer did not change significantly the micro-strength values and their distribution pattern for the aged specimens. The micro-strength values within the fibre strand/bundle and near the interface (−50–25 μm) for the series Ffvf42da and Bffvf42da were generally similar, but considerably smaller than those of Ref42da. The micro-strength value at the centre of the strand/bundle was lower and increased at a slower rate toward the matrix–fibre interface compared to that for the case of series Fmsi42da and Bfmsi42da. The very low value of micro-strength in such cases, however, does not necessarily mean that the bond at the fibre–fibre and fibre–matrix interface has to be poor. This is because the micro-strength of the polymer itself was found very low compared to the cement hydrates but it does suggest a compliable interfacial layer and a more flexible fibre strand/bundle.

The change of micro-strength due to ageing as well as the various treatments could be expressed more clearly by presenting the micro-strength values at the centre of the fibre strand/bundle relative to those of the aged reference composites (series Ref42da), as shown in Fig. 11. For the young composites (Ref7da and Mfvf7da) the micro-strength at the centre core of the fibre strands was less than 30% of the aged composites (Ref42da). The matrix modifications using microsilica or polymer only modestly reduced or delayed the increase of the micro-strength at the centre of the strand/bundle. The fibre treatments were more effective in

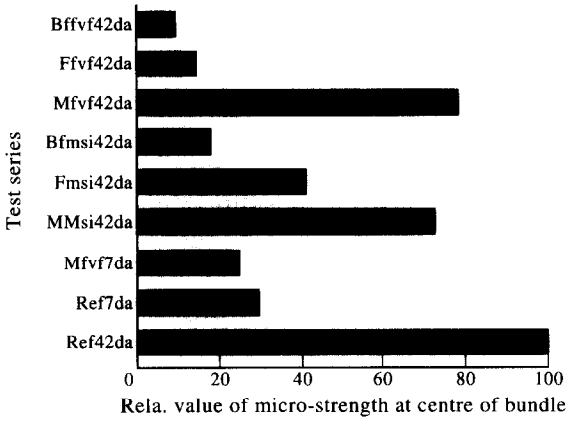

Fig. 11. Relative micro-strength values at the centre core of the fibre strands/bundles.

reducing the micro-strength within the strand/bundle for the aged composites. In the case of the fibre treatment by microsilica the fibre bundle size used appeared to affect considerably the micro-strength value in the aged specimens.

Recalling the results of the four point flexural testing shown in Figs 3 and 4, it is interesting to observe that the trend of the change of ageing performance (strength and toughness) of the composites due to the different modifications/treatments can be closely related to and is well in agreement with relative magnitudes of the micro-strength at the centres of their fibre strands/bundles. This implies that the fibre–fibre interface within the fibre bundle in GRC composites plays a much more important role than has been previously assumed in controlling the performance of an aged GRC.

CONCLUSIONS

The effect of various treatments/modifications using microsilica and acrylic polymer dispersions on the ageing performance of GRC was investigated. The results confirmed that when the GRC composites lost part of their tensile/flexural strength and almost all of their toughness due to ageing the failure mode changed from that of the complete, intact pull-out to the complete tensile fracture of fibres.

The microsilica and the acrylic polymer did not significantly improve the ageing performance of GRC when used as a modification of the matrix. The same materials were more effective in improving the properties of the aged composites when used as fibre treatments. The size of the fibre bundle used was found to

affect strongly the effectiveness and reinforcing efficiency of glass fibre in the GRC composites with treated fibres. Large bundles consisting of multiple fibre strands were found to perform better in the case of a microsilica treatment but single strand fibres proved to be more efficient following a treatment by the acrylic polymer.

Results of the micro-strength test indicated that the embrittlement of the aged composites was closely associated with the significant increase of micro-strength values and the change of their distribution pattern close to the fibre–matrix interface, particularly within the fibre strand/bundle. These findings also suggest that in order to understand better the ageing mechanisms of the GRC composite, its basic reinforcing element, i.e. the fibre strand/bundle, should be treated as a composite itself.[14]

ACKNOWLEDGEMENTS

The financial support from the UK Engineering and Physical Sciences Research Council (grant GR/499769) and contributions from Fibre Technology (UK) Ltd and Forton BV are gratefully acknowledged.

REFERENCES

1. Bentur, A. & Mindess, S., *Fibre Reinforced Cementitious Composites*. Elsevier Science Publishers, Amsterdam, 1990.
2. Majumdar, A. J. & Laws, V., *Glass Fibre Reinforced Cement*. BSP Professional Books, Oxford, 1991.
3. Leonard, S. & Bentur, A., Improvement of the durability of glass fibre reinforced cement using blended cement matrix. *Cement and Concrete Research*, **14** (1984) 717–28.
4. Litherland, K. L. & Proctor, B. A., The effect of matrix formulation, fibre content and fibre composition on the durability of glass fibre reinforced cement, In *Proc. Durability of GFRC Symp.*, ed. S. Diamond. Pre-stressed Concrete Institute, Chicago, 1985, pp. 124–35.
5. Bijen, J. D., A survey of new developments in glass composition, coatings and matrices to extend service lifetime of GFRC, *ibid.*, pp. 251–69.
6. Hayashi, M., Sato, S. & Fuji, H., Some ways to improve durability of GFRC, *ibid.*, pp. 270–84.
7. Bentur, A. & Diamond, S., Effects of direct incorporation of microsilica into GFRC composites on retention of mechanical properties after ageing, *ibid.*, pp. 337–51.
8. Bentur, A., Treatment of glass fibre strands in polymer and silica fume dispersions to improve the ageing performance of glass fibre reinforced cements. *Advances in Cement Research*, **1** (1988) 147–54.
9. Bentur, A., Silica fume treatments as means for improving durability of glass fibre reinforced cements. *Journal of Materials in Civil Engineering*, **1** (1989) 167–83.
10. Zhu, W. & Bartos, P., Effects of combined fibre treatments and matrix modifications on toughness of aged GRC, In *Proc. 9th Biennial Int. Congr., GRCA*, June 1993, Copenhagen, pp. I·4·1–10.
11. Zhu, W. & Bartos, P., Effect of ageing on durability and micro-fracture mechanism of GRC, In *Proc. 3rd Beijing Int. Symp. on Cement and Concrete,* 1993, ed. Z. Wu, *et al.* International Academic Publishers, Beijing, pp. 943–48.
12. Bartos, P., Brittle matrix composites reinforced with bundles of fibres, In *Proc. The First Int. RILEM Congr., From Materials Science to Construction Materials Engineering*, ed. J. C. Maso, Vol. 2. Chapman and Hall, London, 1987, pp. 539–46.
13. Mehta, P. K. & Monteiro, P. J. M., Effect of aggregate, cement, and mineral admixtures on the microstructure of the transition zone, In *Proc. Materials Research Society Symp.*, ed. S. Mindess & S. Shah, 1988, Vol. 144, pp. 65–75.
14. Zhu, W., Effect of ageing on durability and micro-fracture mechanism of fibre reinforced cement composites, PhD Thesis, University of Paisley, Paisley, UK, 1995.