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Microstructural observations in new matrix glass fibre reinforced cement

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Abstract

Glass fibre reinforced cement (GRC) durability is generally thought to be governed by weakening of the reinforcement by the alkaline matrix and/or precipitation of hydration products, particularly calcium hydroxide (CH), within and around the strands. Previous microstructural investigations of GRC have exclusively used scanning electron microscopy (SEM). This paper is concerned with the application of thin-section petrography (TSP) to GRC. TSP allows identification of CH and other phases associated with the strands and unlike SEM, sample preparation causes minimal interfacial disturbance. Three matrices were studied; OPC, OPC plus metakaolin and OPC plus calcium sulphoaluminate cement. It was found that the degree of composite degradation was unrelated to the amount of CH or other hydration products precipitated within the strands or at the interface. No significant loss of fibre section was observed in degraded composites. It is postulated that gradual enlargement of pre-existing fibre flaws causes strength loss in GRC. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Petrography; SEM; Degradation; Fibre reinforcement

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1. Introduction

Poor durability of glass fibre reinforced cement (GRC) is generally attributed to one or more of three mechanisms [1,2]: (i) corrosion of the fibres by hydroxyl ions from the hydrating cement matrix, (ii) precipitation of hydration products, especially calcium hydroxide (CH) within the reinforcing 'strands', thus reducing their flexibility, increasing bond strength and thereby changing the failure mode from fibre pullout to fibre fracture, (iii) densification of the matrix at the interface, reducing its compliance and increasing the bending stress induced in fibres bridging cracks. The relative significance of each of these mechanisms has not been fully resolved.

To overcome this degradation, improvements have been made to the alkali-resistant (AR)-glass fibres and new cement matrices have been developed [3–5]. The latter are mainly based on Portland cement with various additions of, e.g., ground granulated blast furnace slag, microsilica, metakaolin or calcium sulphoaluminate. These additions are intended to lower the pH of the pore solution and/or to reduce or eliminate the formation of calcium hydroxide during ageing. The superiority of these new matrices, with regard to retention of primary mechanical properties such as tensile strength and toughness after traditional accelerated ageing tests, has been clearly demonstrated in a recent project [6,7]. The variation in tensile strength and specific toughness (defined as the area under the stress–strain curve up to peak stress) with hot-water ageing time and temperature for GRC with matrices as described in Section 2.1 is given in Table 1.

To complement the findings of this project, microstructural investigations of the fibre/cement interfaces were undertaken to elucidate both the general degradation mechanisms in GRC and the microstructural features of the new matrix composites related to their improved durability, cf. Portland cement–GRC. Previous investigators have exclusively used the scanning electron microscope (SEM) in microstructural studies of GRC, e.g., Refs. [8–14]. Bentur [8] showed SEM micrographs of massive deposits, assumed to be CH, surrounding the AR-glass fibres after ageing in water and noted that the underlying fibre surfaces were smooth. It was considered that the interfilamental growth of hydration products was very effective in reducing mechanical properties via increases in bond strength and by the matrix densification/reduced

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Table 1
Variation of tensile strength (TS, MPa) and specific toughness (SpT, J/cm^3) with hot-water ageing time and temperature for three different GRCs (*Mean of quadruplicate tests*)

			20°C			65°C				
Matrix	Property	Unaged	28 days	182 days	365 days	7 days	14 days	28 days	182 days	365 days
O	TS	11.6	11.8	10.9	9.0	10.8	7.9	5.1	5.1	–[a]
	SpT	78.5	88.2	78.5	66.3	70.1	49.9	25.7	0.3	–[a]
M	TS	9.8	11.1	11.2	11.3	10.1	11.5	10.3	8.1	3.8
	SpT	63.6	71.4	81.9	89.2	71.4	68.1	65.8	46.0	5.0
C	TS	11.8	13.0	12.6	13.0	10.4	11.4	11.0	7.4	2.5
	SpT	87.6	89.0	109	95	58.3	72.0	61.7	48.5	0.02

[a] OPC not aged for 365 days at 65°C.

compliance mechanism quantified by Stucke and Majumdar [9]. Fibre corrosion was considered to play only a minor role in degradation of the composite. Cohen and Constantiner [10] noted that addition of silica fume at 20% w/w did not prevent CH 'stacking.' The same investigators also added alkalis to the cement in an attempt to promote AR fibre corrosion but detected none. Jaras and Litherland [11] also detected no AR-glass corrosion but significant matrix densification, after ageing for 5 years by immersion in water at 18°C. Diamond [12] emphatically dismissed fibre corrosion and again noted CH stacking, attributing degradation to the reduced flexibility of the filled strands. Yilmaz and Glasser [13] stated that where massive CH deposits impinged on fibres, localised fibre notching occurred and that the relative mechanical weakness of CH, cf. glass, was not relevant. They also found [14] that cracks running oblique to the fibres in massive adherent CH deposits may continue apparently unimpeded into the glass.

It should be noted however, that samples examined by SEM show exposed fibres and hence, the interfacial morphology has been disturbed to a significant degree during sample preparation. Even using EDXA equipped SEMs, it can be difficult to authoritatively identify interfilamental deposits (e.g., to distinguish between CH and calcite). On the other hand, preparation of petrographic thin sections should cause only minimal interfacial disturbance and would allow rapid identification of crystalline phases present. The absence of published thin-section petrographic studies of GRC in the literature has been previously remarked upon [15]. This paper presents the results of a petrographic examination of GRC composites exposed to accelerated ageing with supplementary SEM observations.

2. Experimental

2.1. Materials and specimen preparation

The cementitious materials for the matrices used in this study included:

Matrix O: an unblended Portland cement for control samples.

Matrix M: a blend of Portland cement with 20% w/w of a commercial metakaolin.

Matrix C: a commercial blend of a shrinkage compensated mining cement (PC + calcium sulphoaluminate clinker + anhydrite, 8:3:1 w/w) with 10% w/w metakaolin.

In order to reduce the number of variables and to avoid complicating XRD and DTA/TG analyses [6,7], no fine aggregate was added to the matrix. The water/solids ratio for all matrices was 0.4, with addition of sufficient quantities of a commercial naphthalene sulphonate superplasticiser for workability. CemFIL 2 AR-glass fibre was used as the reinforcement.

Boards were manufactured by a hand lay up process and cured for 28 days at 95% RH, 20°C. Continuous, unidirectional fibre reinforcement was used at a fibre volume fraction (V_f) of 1.5%. Samples were then either examined to provide unaged 'control' data or transferred to accelerated ageing environments, which included immersion in water at 20°C, 38°C and 65°C for various periods of time between 7 days and 1 year. Samples were vacuum-impregnated with epoxy resin, and petrographic thin sections (normal to the fibre alignment) prepared. Further details of materials and specimen fabrication may be found elsewhere [6,7].

2.2. Thin-section petrography (TSP)

Using a petrological microscope, the thin sections were examined between crossed polars to determine the nature of interfacial or interfilamental deposits and to examine the general nature of the fibre/cement interface. The microscope was fitted with a digital camera allowing rapid processing and analysis of the images. Diagnostics in TSP involves interpretation of the interference colours produced by the interaction of the crystals with polarised light. The images presented in this paper are necessarily monochrome with labels to help identify salient features although the original colour images may be observed on the World Wide Web [16].

Since both the glass fibres and the epoxy resin used for impregnation were non-crystalline and hence non-polarising, under ideal conditions they should both appear black in the images. In practice, residual stress in the resin caused the polymer molecules to become partially aligned, polarising the transmitted light and it appears bright rather than dark. Under the microscope, it can be readily distinguished by its non-uniform extinction and bluish-grey colour; in the micrographs, the distinction is less clear and it has been labelled where necessary. In a similar departure from ideal conditions, it was found that the significant difference in hardness between the fibres and the matrix resulted in slides of non-uniform thickness. The interference colour produced by a crystal phase is strongly dependent on the slide thickness, hence portlandite (CH — the phase of primary interest) sometimes appeared in different colours from the bright yellow expected in an ideal slide.

It was found useful during image capture to slightly 'uncross' the polars at about 70–80° so that the glass fibres transmitted sufficient light to be contrasted against the generally dark background of the matrix. This does not alter the colour diagnostic properties of crystals.

2.3. Scanning electron microscopy

SEM samples were prepared by artificially de-laminating small fragments of the test samples to expose lengths of in situ fibre. Samples were dried for 2 weeks over silica gel, mounted on aluminium stubs and sputter-coated with gold under vacuum. SEM was principally used to assess the extent of any fibre corrosion. The samples were taken from coupons aged to the extent that significant but not total degradation had occurred.

3. Results and discussion

3.1. Matrix O

A portion of a glass strand surrounded by hydrated cement components in unaged matrix O is shown in Fig. 1. The resin occupies the interfilamental spaces within the strand {R1} and is also present at the strand–matrix interface {R2}. This shows that in unaged composites, there is little significant penetration of matrix into the strand which therefore remains flexible.

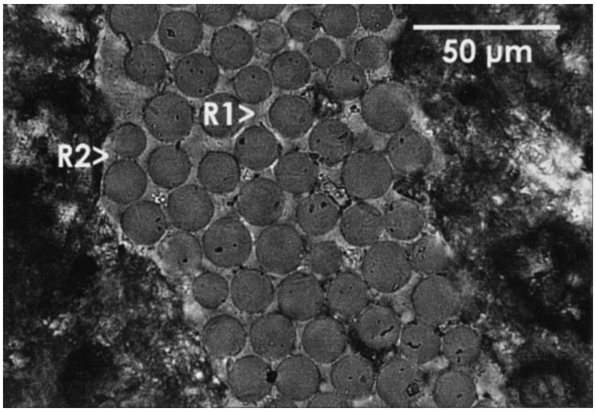

Fig. 1. Thin-section image (TSI), unaged matrix O GRC. Polars crossed at 75°.

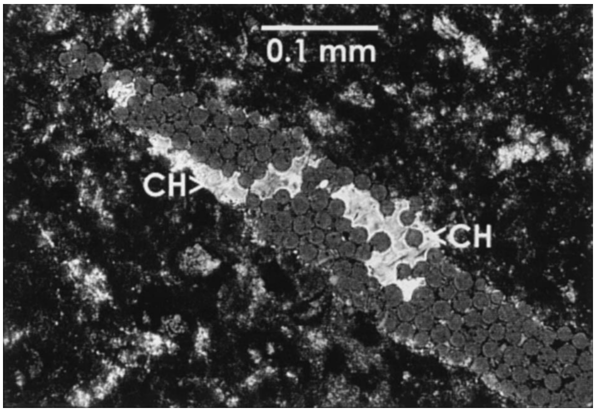

Fig. 2. TSI, matrix O GRC aged for 56 days at 65°C. Polars crossed at 77°.

Fig. 2 shows a strand after ageing for 56 days at 65°C. The composite was virtually completely degraded, judging by its primary mechanical properties. Deposits of calcium hydroxide {CH} can be seen associated with the strand. These deposits do not however uniformly and monolithically fill the interfilamental void space as suggested by other investigators [8,11,12]. There is some precipitation of CH at the fibre–matrix interface but only over a relatively small proportion of the perimeter. A broadly similar level of interfilamental and interfacial portlandite deposition was observed in composites aged for a similar period at 20°C, with no loss of mechanical performance.

3.2. Matrix M

In unaged matrix M composites (Fig. 3), material {Mx} morphologically similar to the groundmass of the surrounding matrix has penetrated some way into the fibre strands. The ingress material appeared to be interspersed with resin on a fine scale, indicating that it may have been porous. This ingress is not complete, as indicated by the remaining resin

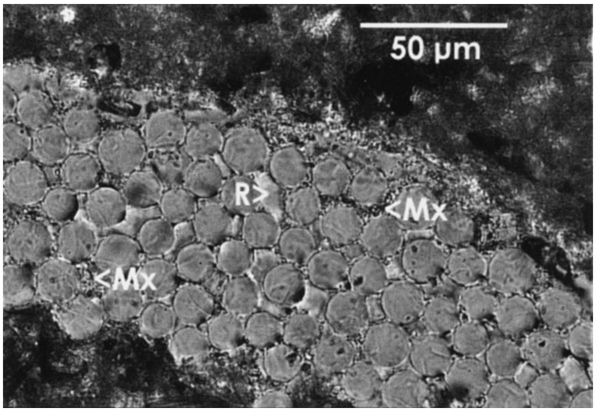

Fig. 3. TSI, unaged matrix M GRC. Polars crossed at 65°.

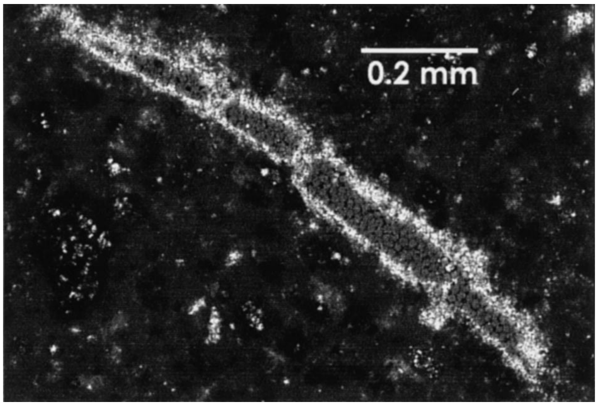

Fig. 4. TSI, matrix M GRC aged for 56 days at 20°C. Polars crossed at 80°.

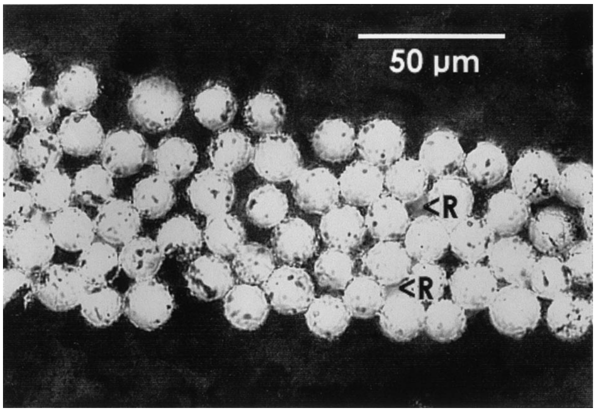

Fig. 6. TSI, unaged matrix C GRC. Plane polarised light.

{R}. While it was not possible to identify this product, it is assumed to be rich in metakaolin since this material has a very fine particle size and a platy morphology allowing it to penetrate the fibre bundles.

After ageing for 56 days at 20°C, striking 'halos' were observed around the strands (Fig. 4). These halos were mainly crypto-crystalline CH interspersed with a small amount of calcium carbonate. The halo of CH did not generally enter the interfilamental spaces. This ageing period had no detrimental effect on the mechanical properties suggesting that such precipitates are not deleterious. It should be noted that while this matrix has a reduced concentration of CH (cf. OPC), it is not completely absent.

Fig. 5 shows part of a similarly aged strand under higher magnification. Matrix penetration {Mx} is more pronounced than in the unaged composite (Fig. 3) and some of the porous matrix penetrant has been replaced by an opaque, homogenous material {My}. It has been reported that CH is attracted to and preferentially precipitates on AR-glass in preference to other glassy substrates [10,17]. It would appear that in the case of matrix M composites, the first CH formed is attracted to the fibres and reacts with material which has already penetrated the strand to form the dense hydration product {My}. This acts as a barrier to further CH ingress and consequently, it precipitates at and around the strand matrix interface, rather than within it as in the case of matrix O (Fig. 2).

3.3. Matrix C

Fig. 6 shows an unaged matrix C composite. The matrix material has virtually completely filled the strand. Only small, isolated areas of resin {R} remain. Compared with the other matrices, a greater proportion of the anhydrous cementitious material (i.e., the calcium sulphoaluminate and anhydrite) very quickly reacts on wetting; the calcium sulphoaluminate also hydrates far quicker than other matrix components [18]. The solution penetrating the strands is therefore far richer in ions that can form hydration products and interfilamental material is precipitated quickly.

Fig. 7 shows the same composite after ageing for 1 year at 65°C. The composite was completely degraded yet there were no discernible changes in the interfacial or interfilamental morphologies.

3.4. Fibre morphology

The delamination procedure used to expose the fibre surfaces tended to remove any monolithic interfilamental material. The linear features seen on all the fibres are the

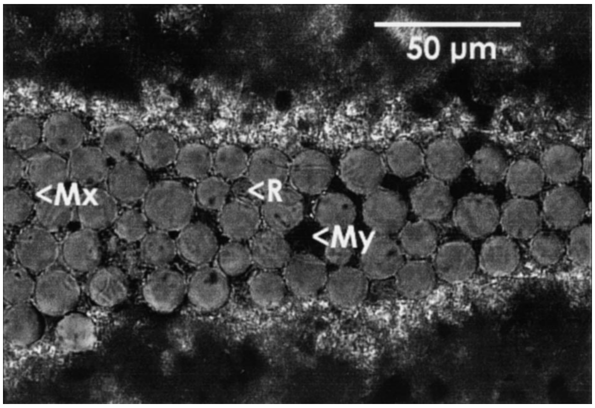

Fig. 5. As in Fig. 4, higher magnification, polars crossed at 67°.

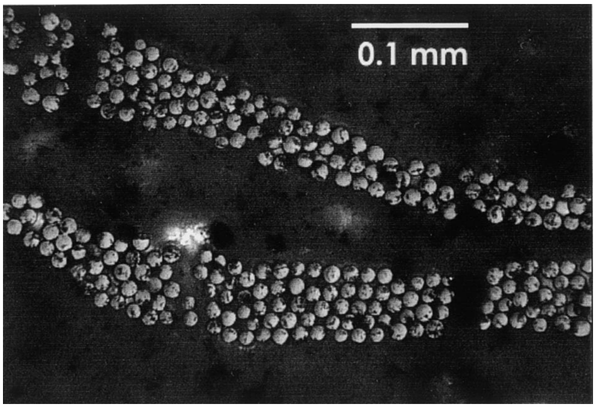

Fig. 7. TSI, matrix C GRC aged for 1 year at 65°C. Polars crossed at 75°.

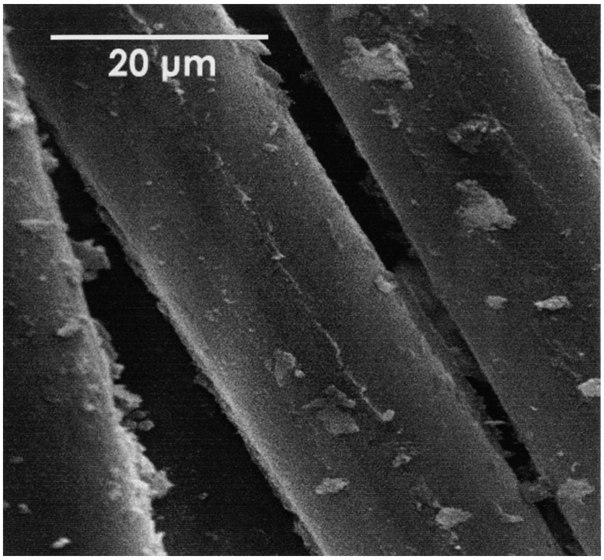

Fig. 8. SEM image, exposed fibres in matrix O GRC aged for 28 days at 65°C.

remains of the channels of matrix that the fibres were embedded in, clear lines providing evidence of an intimate interface. Thus, these SEM micrographs are only intended to convey the state of the fibre surfaces.

Fig. 8 shows the fibre surface in a matrix O composite aged for 28 days at 65°C. The composite was significantly degraded. Small particles of matrix can be seen on the fibre. The underlying fibre surface appears smooth and uncorroded. This is in agreement with observations made by other investigators [10,11,13] and contrasts with the significant loss of section observed in 'E' glass fibres under similar conditions [8,10,11].

Figs. 9 and 10 show fibre surfaces in matrix M and C composites, respectively, after ageing for 6 months at 65°C. Again, the composites were significantly degraded yet no gross fibre corrosion was observed. Rather more matrix material was adherent to the fibres than in Fig. 8, which might be expected considering the longer period of ageing.

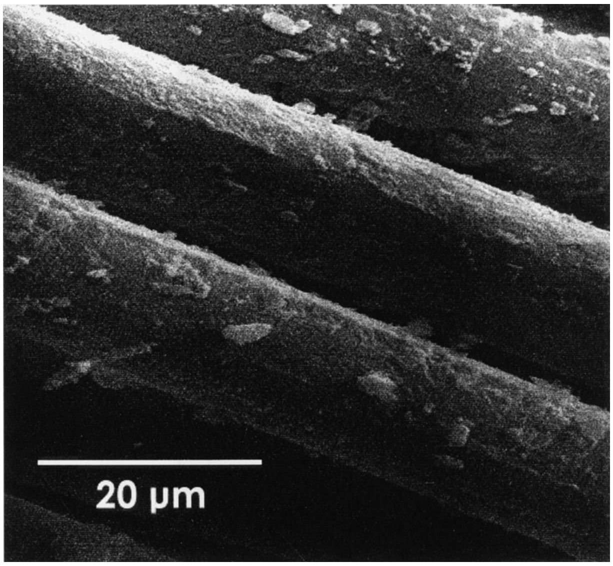

Fig. 9. SEM image, exposed fibres in matrix M GRC aged for 6 months at 65°C.

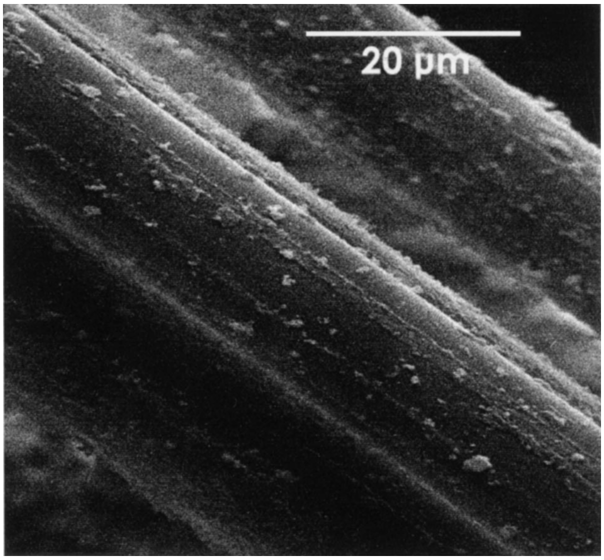

Fig. 10. SEM image, exposed fibres in matrix C GRC aged for 6 months at 65°C.

4. General discussion

The above observations emphasise the usefulness of TSP in addition to SEM for microstructural observations. It is particularly evident when trying to compare the extent of interfilamental precipitation under different ageing conditions.

The bundle filling mechanism usually invoked by authors who dismiss fibre corrosion as a cause of degradation in GRC [8,12] does not seem to be relevant to these composites. In matrix O composites, bundle filling is sporadic and samples aged for similar times at different temperatures show similar amounts of portlandite precipitation yet totally different levels of degradation. Progressive bundle filling with amorphous matrix material was observed in matrix M samples aged at 20°C with no loss of mechanical properties. In matrix C composites, complete bundle filling with matrix material is observed even in unaged samples with no apparent detriment to the primary mechanical properties. Similarly, the interfacial morphology in fully aged, completely degraded samples is indistinguishable from that in the unaged composite or those aged at immersion temperatures which caused no degradation.

In matrix M composites, the initially porous strand/matrix interface becomes densified as the void space fills with CH deposits, forming the halos, with no detrimental effect on the mechanical properties. The matrix C interface appears fully dense from the outset. Hence, the matrix densification mechanism also appears to be inadequate.

Composite strength loss as a result of gross fibre corrosion (i.e., loss of section) can be discounted as a degradation mechanism in AR-GRC, both from the results of this study and those referred to previously. However, it is possible that a reduction in the strength of the fibres could occur via a stress corrosion mechanism, normally termed 'static fatigue.' This mechanism involves sub-critical propagation of flaws when fibres are subjected to a stress in a corrosive environment and is a well known phenomenon [19–21]. These stresses may be small in magnitude and while the tensile test coupons studied were not under any primary stress during ageing, it is possible that internal stresses were generated by a number of mechanisms. The thermal coefficient of expansion of cement paste [22] is about twice that of AR-glass fibres [1], 15 and 7.5 $\mu\ ^{\circ}\mathrm{C}^{-1}$, respectively, and hence, it is possible that a stress was induced in the fibres by hot-water ageing. Other possible mechanisms include leaching of the components from the glass surface [21] and nucleation of CH in the vicinity of surface flaws.

Observation of these sub-critical flaws using the SEM is very difficult. This is partly because they are considered to be very small (<0.5 μm) and may also be obscured by the sizing agent applied during production [23]. Other techniques such as atomic force and scanning tunnelling microscopy have been applied with variable success [24]. In practise, mechanical testing of fibres combined with fracture mechanics theory is used as an indirect technique to determine the probable nature and behaviour of such flaws and the influence of surface coatings, e.g., Ref. [25].

A preliminary model of strength loss in GRC due to the enlargement of sub-critical, manufacture-induced flaws, possibly aggravated by the growth of CH crystals, has been postulated [6] and its extension will form the basis for a forthcoming paper.

5. Conclusions

Thin-section petrography is an effective complementary method to SEM for observing and characterising interfacial and interfilamental features in GRC. The extent to which OPC–GRC strands are filled with CH is particularly clearly indicated.

With regard to the previously proposed processes of degradation, similar levels of strand filling were observed in aged OPC–GRC samples whether degraded or not and monolithic strand filling was never observed. Significant strand filling with non-CH material was observed in metakaolin modified GRC and complete strand filling in calcium sulphoaluminate modified GRC without detriment to their mechanical properties. Strand filling is not necessarily detrimental to GRC. Similarly, interfacial densification was also observed without detriment to the mechanical properties.

General fibre corrosion was not observed in any of the significantly degraded GRC composites. Strength loss would appear to be due to the enlargement of sub-critical flaws introduced into the glass filaments during composite manufacture.

Acknowledgments

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