

The microstructure and ageing of cellulose fibre reinforced cement composites cured in a normal environment

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Synopsis The correlations between microstructural changes after ageing and the mechanical performance of cellulose fibre reinforced cement composites were studied. Ageing conditions which promote carbonation (natural ageing and accelerated ageing in a CO₂ rich environment) result in densening of the matrix around the fibres and the petrification of the fibres, leading to an increase in strength and E-modulus. Accelerated ageing in a normal environment leads to densening of the matrix without fibre petrification, resulting in a reduction in strength. Both ageing environments led to a marked reduction in toughness. The processes leading to petrification and matrix densening are discussed with a view of explaining the changes in mechanical properties after ageing.

Keywords Fibre cement composites, cellulose fibres, ageing, microstructure, scanning electron microscopy, carbonation, mechanical properties, accelerated tests, fibre-matrix interface, cracking (fracturing), composite materials.

INTRODUCTION

Several mechanisms have been considered in cellulose cement products that may lead to changes in mechanical properties during ageing and could be associated with strength loss and embrittlement of cement reinforced with treated cellulose fibres or natural fibres [1-5]. These are summarised as follows:

- (a) Alkaline hydrolysis of cellulose molecules, causing degradation of molecular chains, thus leading to reduction in degree of polymerisation and lower tensile strength.
- (b) Dissolution of lignin and hemicellulose in the alkaline matrix breaking the link between individual cell fibres.
- (c) Increase in fibre-matrix bond that may lead to embrittlement, and, under certain conditions, to improved strength.
- (d) Microbiological attack that is more likely to occur in less alkaline matrix.

These ageing processes could depend on the matrix composition, and they could be quite different in autoclaved or normally cured composites. The type of the fibre used and its pretreatment may also exert a considerable influence in the long term performance.

This paper is part of a comprehensive study to evaluate the long term performance of normal cured cellulose cement composites intended for asbestos cement replacement, and to resolve the mechanisms which lead to changes in mechanical properties after exposure to various environmental conditions. Resolving the ageing mechanisms is particularly important for assessing the significance of accelerated ageing tests, and developing ways to improve the ageing performance of the composite.

It has been reported [6] that natural ageing resulted in a marked increase in strength and E-modulus of the product. These trends could be reproduced in accelerated tests in which the composites were subjected to drying and wetting cycles in a CO₂ rich environment. However, in a similar accelerated test, in a normal environment the changes in mechanical properties were different; there was a reduction in strength (in contrast to the increase in natural ageing and accelerated ageing in a CO₂ rich environment). These changes in the mechanical properties could not be correlated with changes in properties of the fibres, in which a mild reduction in degree of polymerisation was observed in all three cases. This is contrary to the trend of increase in strength

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and E-modulus observed after natural ageing and accelerated ageing in a CO₂ rich environment. It therefore appears that changes in the properties of the fibres cannot account for the ageing trends, and it is likely that microstructural changes at the fibre-matrix interface may be of greater significance in controlling the ageing characteristics of these composites. This is the subject of the study presented in this paper, for normally cured composites.

EXPERIMENTAL DETAILS

Details of specimen preparation, ageing and mechanical testing are given elsewhere [6]. The present work also included the study of an additional specimen with somewhat different composition which was aged for 25 years in a natural weathering environment in South Africa. This specimen consisted of a combination of asbestos and cellulose fibres. The purpose of investigating this specimen was to gain an insight into the reinforcing potential of the cellulose fibre component in the composite, and the changes it had undergone after prolonged natural ageing. Although this composite cannot be used for a direct comparison of the effect of ageing on a cellulose cement composite, it can be used as a bench mark for microstructural study of the cellulose fibre itself and the fibre-matrix interface.

The properties of the fibres before and after ageing were evaluated by determining degree of polymerisation, using a special technique described before [6].

The overall composition of the specimens was determined using X-ray diffraction (XRD) and a thermal gravimetric (TG) technique (Perkin Elmer TGS-2), using powdered specimens without prior drying, or after oven drying (105 °C for 24 hours). In addition, loss on ignition of the oven dried specimen was determined.

Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDXA) was used for microstructural study. The specimens were split and then dried at 50 °C for 2 days and subsequently coated for the SEM observation. The split plane was perpendicular to the main fibre orientation and parallel to the plane. The compositional analysis in the SEM was intended mainly to resolve the range of C/S* ratios. One should be aware of the limitations of such an analysis, which in the case of fractured rough specimens, is at best semi-quantitative in nature. A comprehensive discussion of the limitations and significance of the EDXA analysis of hydrated cement was given by Diamond et al. [7].

Some of the specimens were treated with a dilute 1:4 HCl solution prior to the SEM observations. The specimens were soaked with water before briefly immersing (1–15 seconds) their fractured surface in the acid. This treatment was carried out in order to remove the hydration products developed around the cellulose fibre and to expose its surface. The organic fibre is expected under these concentrations and exposure time to be insensitive to the acid treatment, while the cement will readily dissolve in it.

* Cement chemistry notation is used: C = CaO, S = SiO₂, A = Al₂O₃, Š = SO, Ć = CO₂, H = H₂O

TEST RESULTS

Overall matrix composition

Typical XRD patterns are presented in Figure 1, for the unaged composite and for specimens after different ageing treatments. The TG curves showed a distinct weight loss in the temperature range typical to CH and CC and the contents of these two components could be calculated. However, cellulose decomposes at the same temperature range of the CH, and adjustment for that had to be made in the calculation of the CH content. This was done by taking into account the content of the cellulose and its weight loss in this temperature range. The latter value was determined by running a TG test with fibres only. The calculated values of CH* and CC contents are provided in Table 1. The values are presented as percent of weight of the original cement, and for that purpose the loss on ignition value was used.

The XRD patterns and TG results indicate similar trends of relatively low CH values and a considerable amount of CC. In well hydrated cement, the CH content in the absence of carbonation should be about 20%, whereas in this case the values were much lower. These trends suggest considered tendency for carbonation, even in the composites which were not exposed to conditions which do not promote excessive carbonation. The marked increase in CC content could be particularly noticed in the accelerated ageing in a CO₂ environment and in a natural environment, where the CC content was more than twice as much as that in the unaged composite or the composite accelerated aged in a normal

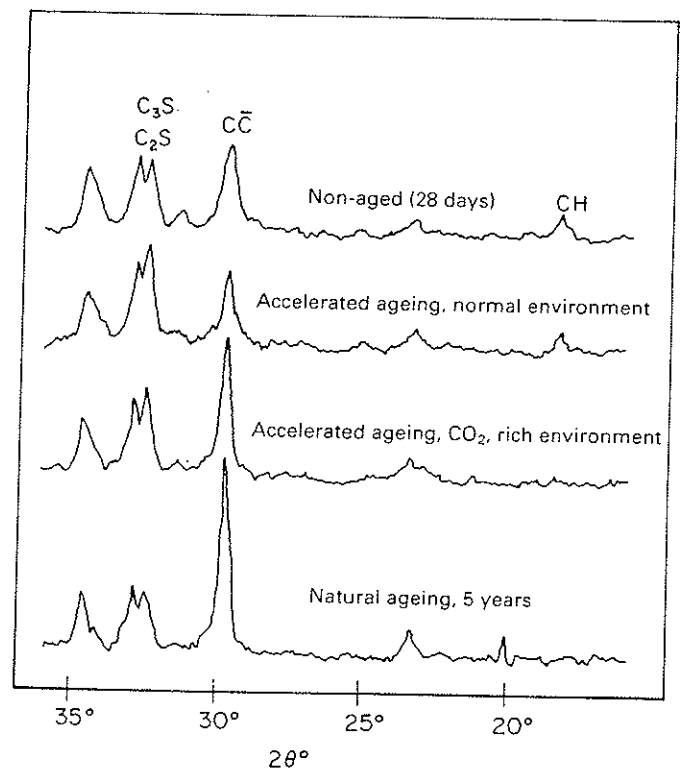


Figure 1 XRD patterns of cellulose-cement composites before and after ageing

Table 1 CH and CC content of cellulose cement composites cured in a normal environment, before and after ageing, as determined by TG analysis

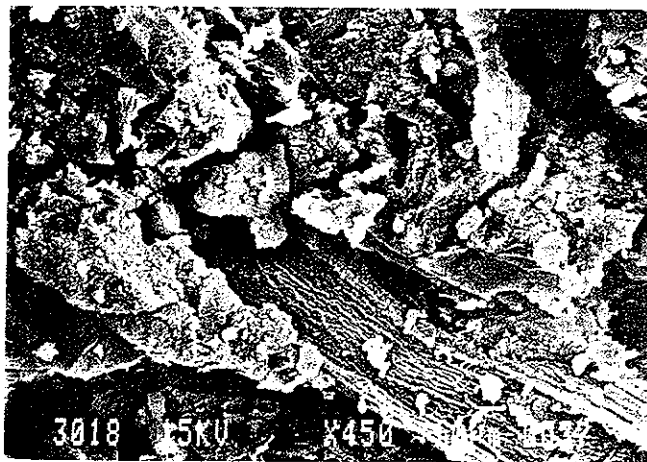
Ageing conditions	CH content % Wt.*	CC content % Wt.*
Unaged	4.9	8.9
Accelerated ageing, normal environment	7.4	8.0
Accelerated ageing CO ₂ rich environment	11.9	18.6
Natural ageing	7.0	18.4

* % Wt. of original composition

environment. The TG data indicated that this increase in CC content was not accompanied by an additional reduction in the CH content, but the XRD patterns reveal hardly any CH.

SEM observations of the interface

Unaged composites The dominant mode of failure was fibre pull-out (Figure 2a), and the matrix around the fibre was relatively porous (Figure 2b). The composition of the hydration products in these zones was typically that of CSH, even when analysing the more dense microstructure (Figure 2b – C/S ratio of 1.65 in point 1). When observing the microstructural characteristics along the fibres, large gaps and cracks in the matrix adjacent to the fibre surface could be frequently seen (Figure 3a, 4a), and fibre matrix debonding was evident in



(a)



(b)

Figure 2 (a) Typical pulled out fibre in an unaged composite; (b) The open matrix at the root of the fibre in (a). The C/S ratio in point 1 is 1.65



(a)



(b)

Figure 3 (a) Open matrix along a fibre in an unaged composite; (b) Higher magnification around a crystalline matrix zone in (a)

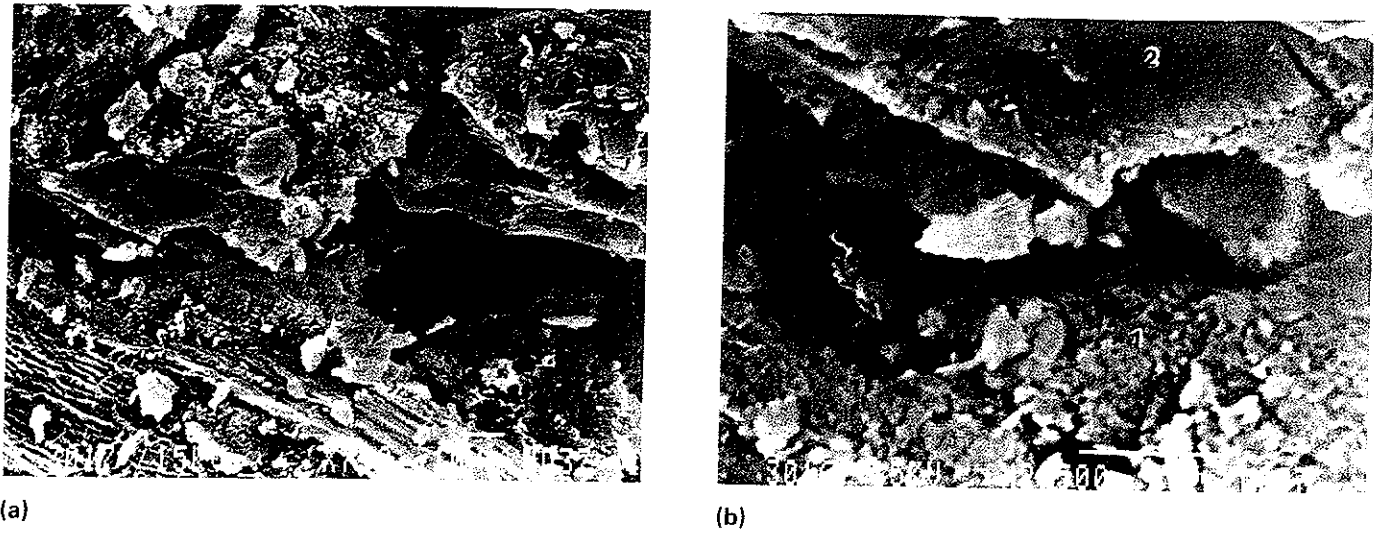


Figure 4 (a) Open and porous matrix along a fibre in an unaged composite; (b) Higher magnification along (a) showing porous and dense hydration product. The C/S ratios of points 1 and 2 are 2.08 and 3.51, respectively

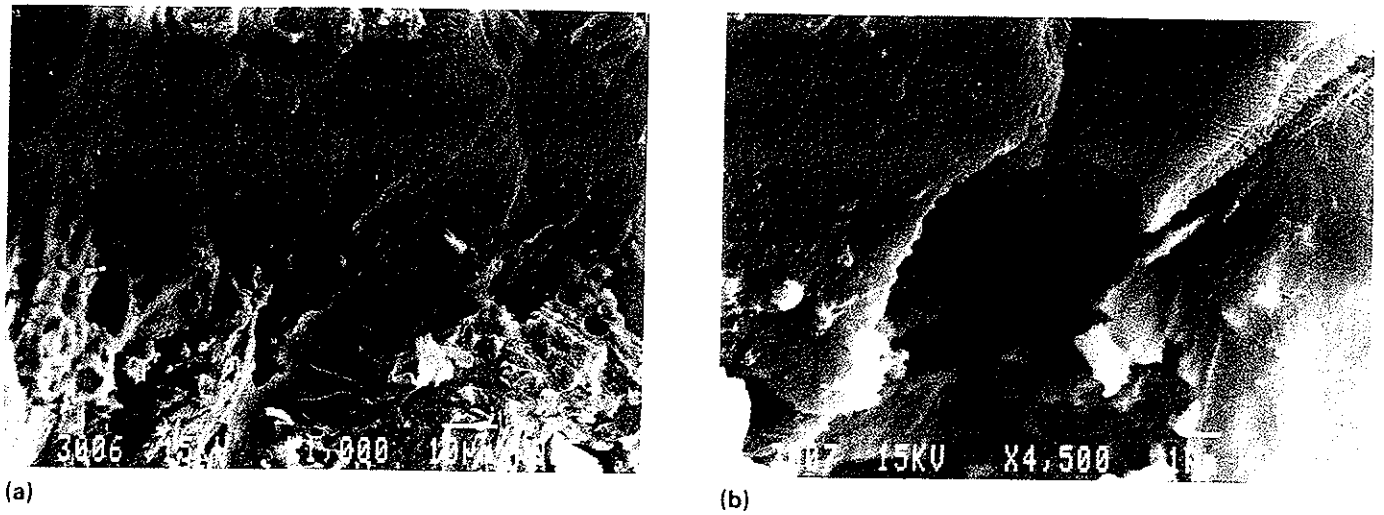


Figure 5 (a) The groove left after removal of a cellulose fibre in an unaged composite; (b) Higher magnifications of the thin film in (a); (c) Higher magnification of (b)

many locations. Although the hydration products were usually non-crystalline in nature, with C/S ratio less than 2 (Figure 2, Figure 4b), some crystalline lamellar structure typical to CH could sometimes be seen (Figures 3b, 4b). However, the C/S ratio in such zones was not extremely high (2 to 4), suggesting either impure CH or more likely a mixture of CH crystals and CSH. In such zones, the microstructure of the products engulfing the fibres was dense, but even here debonding and matrix cracking could be seen.

In some cases, the impression left by the fibres on the matrix could be observed. This was in zones where the fibre was removed after splitting the specimen, revealing the groove below it. One such groove can be seen in the central portion of Figure 5a. Higher magnification of the fractured zone of the groove (Figure 5b) shows the presence of a thin film ($=1\ \mu\text{m}$ thick) with a

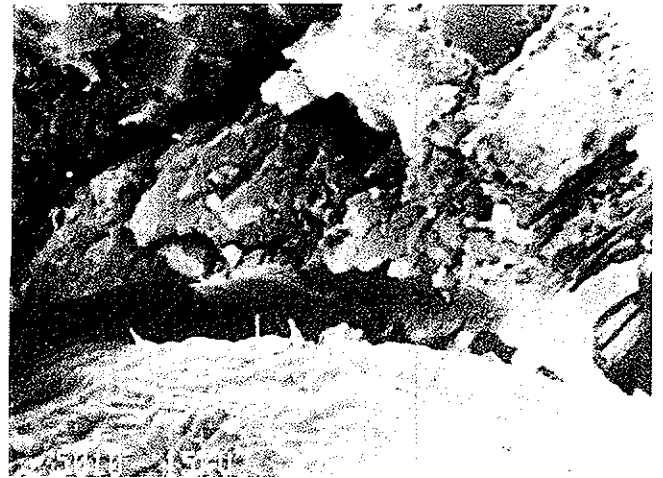
relatively smooth surface, which was apparently in contact with the fibre. Below it there is a vacant space, extending several microns, where some hydration products could be seen (Figure 5b). It was difficult to resolve the nature of these products because of their location below the surface, but higher magnifications of some zones (Figure 5c) suggested that they were not crystalline, and were somewhat open in nature.

Accelerated aged composites in normal environment

The fractured surface observed invariably broken fibres with their hollow nature clearly shown in Figure 6a. In some cases, the fibres seemed to be breaking in flexure (Figure 7). In most cases the matrix around the fibres was quite dense, as seen at higher magnifications in Figures 6b, 7b. The C/S ratio in such



(a)



(b)

Figure 6 (a) A broken fibre in a composite after accelerated ageing in a normal environment; (b) Higher magnification of the upper part of the interface in (a). The C/S ratio of this zone is 4.87



(a)



(b)

Figure 7 (a) A fibre broken in flexure in a composite after accelerated ageing in a normal environment; (b) Higher magnification of the dense matrix around the fibre in (a). The C/S ratio of this zone is 1.61

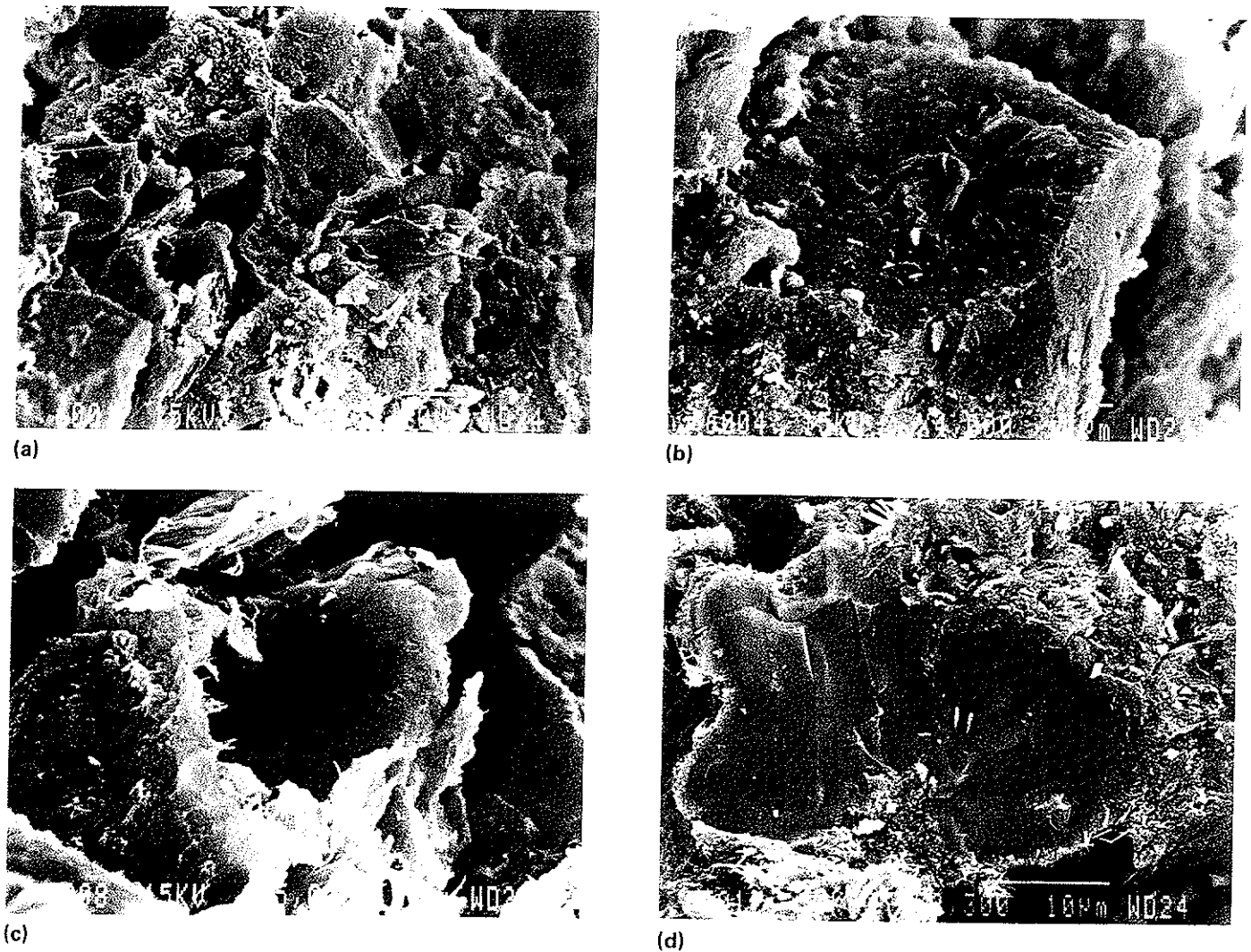


Figure 8 (a) Brittle fracture in a composite after accelerated ageing in a CO₂ rich environment; (b) Higher magnification of one of the fibres in (a) showing the circular morphology filled with dense, massive material ('brittle petrified'). The C/S ratio of the centre is 2.0; (c) Higher magnification of one of the fibres in (a), showing the circular hollow fibre ('brittle cellular'); (d) The dense matrix around a petrified fibre

zones was usually less than 2, which is in the range typical to CSH. Higher C/S ratios, like 4.87 in Figure 6b were less frequent.

It was typical to observe debonding between the cellulose fibre and the matrix around it. Separations of 1 µm or greater could be measured between the fibre and matrix (Figures 6, 7).

Accelerated aged composites in CO₂ rich environment

The mode of fracture of these specimens was brittle, with most of the fibres being broken at the fractured plane (Figure 8a). Very frequently, the circular cross section of the broken fibre was filled up with what seemed to be dense hydration products (Figure 8b). The C/S ratio in these dense zones was 2 or less. It should be noted that in these 'filled' fibres no perimeter debonding could be seen. This microstructure will be referred to as 'brittle petrified'.

In fewer instances the fractured fibres were hollow inside, revealing the usual structure of the cellulose fibre (Figure 8c). In a few cases one could see the holes left in the matrix around fibres which probably pulled out (Figure 8d). The matrix was usually dense, similar to that observed around the zones where the fibres were still present on the fractured surface.

In one case (Figure 9), the perimeter of a cellulose fibre could be seen slightly below its broken surface, and within its perimeter, there appeared to be dense and porous hydration products filling the circular space. This was a rare observation, and cannot be considered typical. Observations of this kind may suggest that the morphology defined previously as petrified fibres, was originally a cellulose fibre which became filled with reaction products. In order to verify this hypothesis, the specimens were treated with hydrochloric acid, which can dissolve the reaction products, without damaging the cellulose fibres. Observations after brief etching are

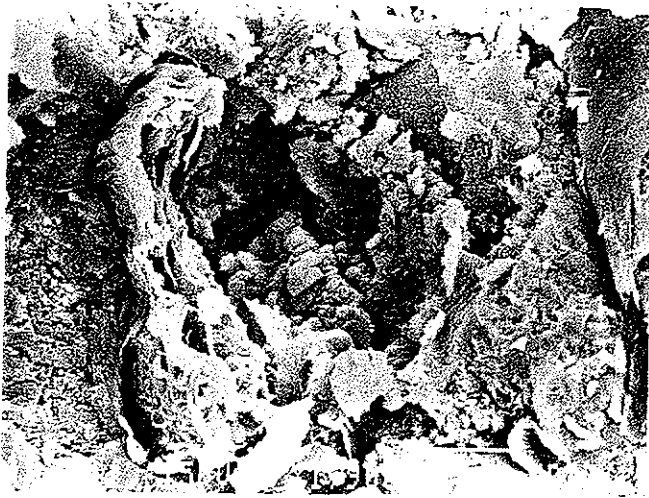


Figure 9 Brittle failure of a partially 'petrified' fibre in a composite after accelerated ageing in a CO₂ rich environment

presented in Figure 10 and micrographs of specimens after more intensive etching are shown in Figure 11.

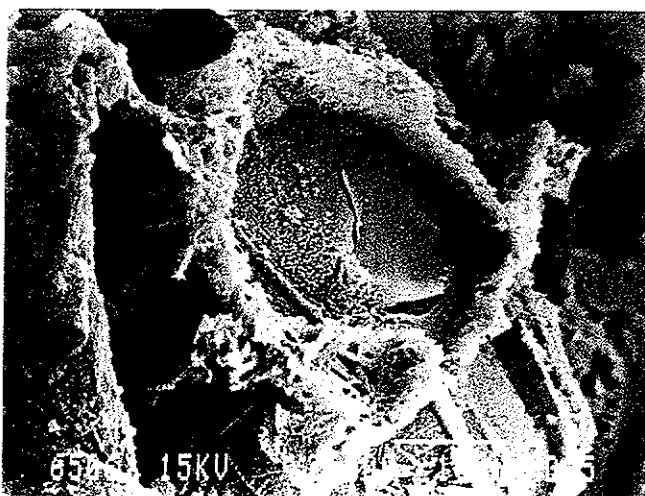
Brief etching clearly revealed the typical structure of the cellulose fibres. In some cases the core of the fibre was vacant, but often the perimeter of the fibre wall could be seen, and within it the etched hydrated material which dissolved only partly on the surface (Figure 10). Higher magnification of the centre of such zones clearly revealed the etched nature of the surface (Figure 10b). The C/S ratios in such zones were about 1.30 which is indicative of the composition expected in slightly etched CSH. These micrographs clearly indicate that the petrified morphology, which was so typical to the accelerated ageing in CO₂ rich environment, was indeed

the result of filling of the vacant core of the cellulose fibre with reaction products.

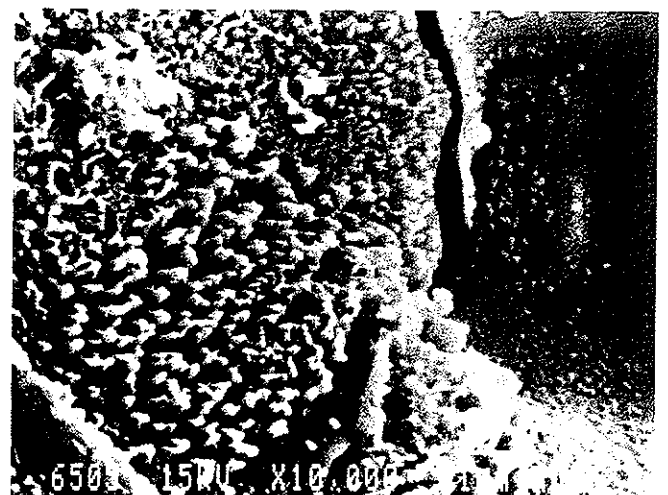
The more extensive etching removed completely the reaction products within the cellulose fibres and around them. The frequent observation of the circular cross-section of the cellulose, is a manifestation of the brittle fracture of the fibre. The hollow and fibrillar characteristics were clearly seen in etched specimens (Figure 11), but were absent in the unetched specimens, where the fibres were impregnated with reaction products leading to the formation of the petrified morphology. EDXA of the extensively etched fibre walls gave a weak signal of Ca and Si with the C/S ratio being about 0.20. The fact that such a signal could be obtained may indicate that the walls of the cellulose fibre contained some calcium silicates and the signal observed was that of the remnants of such etched material. Acid treatment of the calcium silicate is expected to dissolve most of them and leave behind a residue of silica gel, which may account for the low C/S ratio observed.

Natural ageing for 5 and 25 years

The typical mode of fracture was brittle in nature, with the fibres breaking at the fractured plane, or being pulled out slightly before being fractured (Figure 12). The hollow nature of the fibres was usually not present, and as in the case of accelerated aged specimens in a CO₂ environment, the circular cross-section of the fibre was characterised by a dense microstructure (Figure 13). Only in a few instances could the remnants of the hollow nature of the fibre be seen at the broken surface. Also, only seldom was a fibre pulled out of the matrix during fracture. Regardless of the mode of fracture, the matrix around the cellulose fibres was quite dense (Figure 14a). Only in a few instances could one see some more porous matrix around the fibres, as demonstrated, for example,

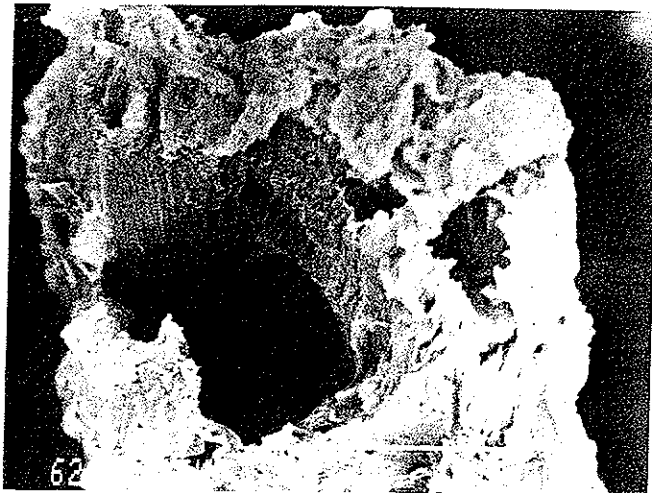


(a)

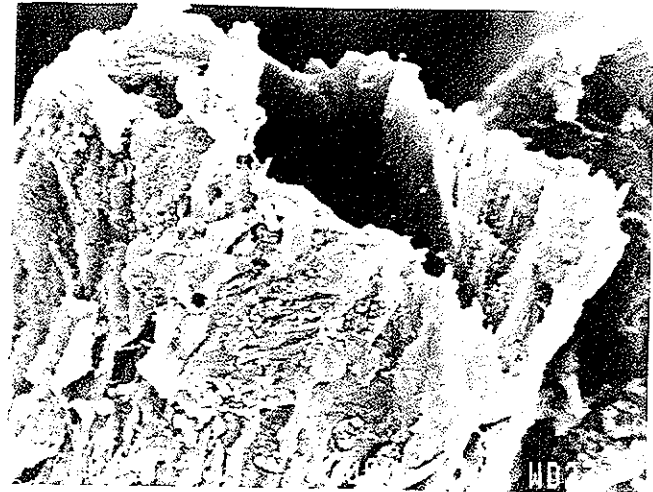


(b)

Figure 10 Fibres revealed after brief etching of a composite after accelerated ageing in a CO₂ rich environment; (a) General view of a fibre, showing the fibre with dense material deposited in the core surrounded by the fibre wall; (b) Higher magnification of the centre of (a), showing the etched nature of the material. The C/S ratio at the centre is 1.37



(a)



(b)

Figure 11 (a) Fibre revealed after more intense etching of a composite after accelerated ageing in a CO₂ rich environment; (b) The C/S ratio of the cell wall in (b) is 0.20

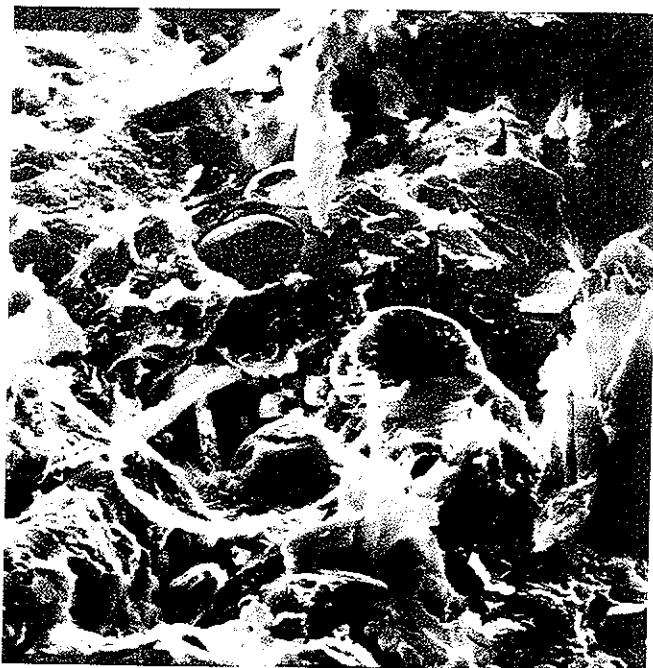


Figure 12 Brittle fracture in a composite after ageing for 5 years in natural weathering

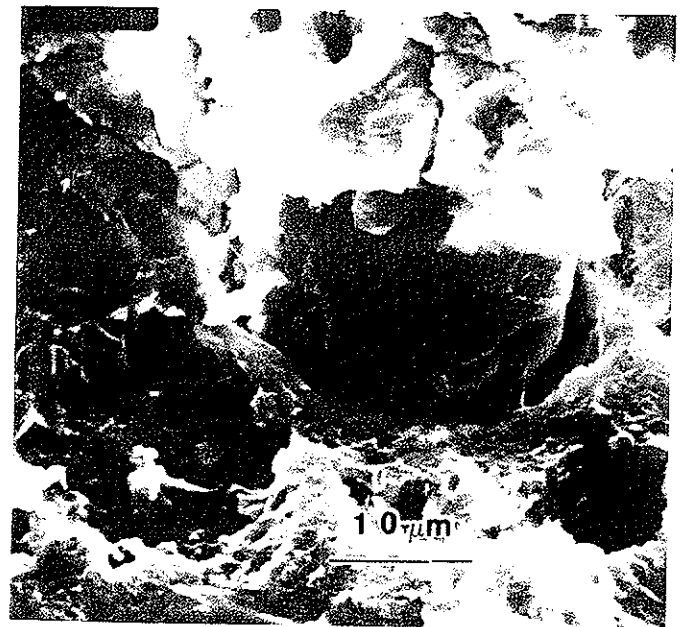


Figure 13 Brittle petrified fibre in a composite after ageing for 5 years in natural weathering (left fibre in the micrograph)

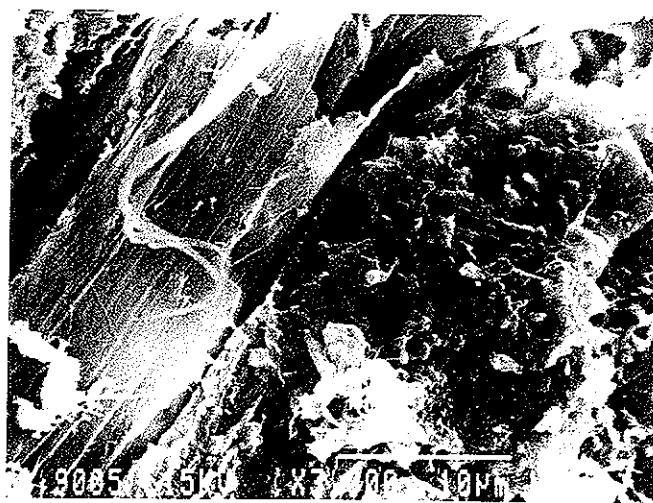
in Figure 14b. Usually, the C/S ratio of the matrix surrounding the fibres was about 2 or less. Only in a few points was the C/S ratio greater than 3 and, even then, no crystalline morphology was evident. On rare occasions one could see the presence of dense crystalline zones, typical to CH, where the C/S ratio was higher than 7 (Figure 14c).

It should be noted that in the places where the fibres were broken in a brittle manner, revealing a dense,

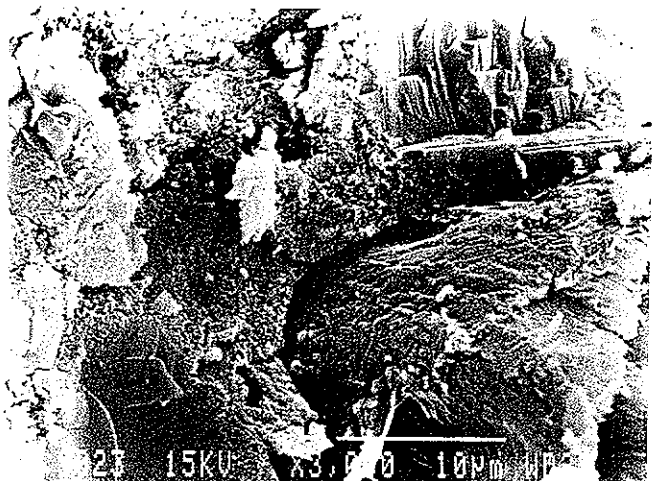
petrified, microstructure in the fibre cross-section (Figure 13), no bond separation at the perimeter of the fibre could be seen.

The typical matrix microstructure away from the fibres was dense, similar to that around the fibres, and the C/S ratio typical to these areas was about 2.

The observations outlined here were also evident in the cellulose fibre component of the 25 years old cellulose-asbestos composite.



(a)



(b)



(c)

Figure 14 The matrix around the fibre in a composite after ageing for 5 years in natural weathering; (a) Dense matrix; (b) Porous matrix; (c) Dense matrix, with some crystalline material at the right side with C/S ratios of 10.5

DISCUSSION OF TEST RESULTS

Overall composition of the composite

In all the specimens, the CH content was very small, much less than would be expected in cast pastes and concretes. The calcium carbonate (CC) content was quite high, even in the specimens that were normally cured for 28 days. A marked increase in the CC content was observed after natural ageing and after accelerated ageing in a CO₂ rich environment. This increase was not necessarily accompanied by a marked change in the CH content, which was already low to start with. This may suggest that the CSH had carbonated and part of it was converted to CC and hydrated silica gel. These trends were consistent in the results of the XRD and TG analysis. Also, in the SEM observations, it was rare to come across a zone with crystalline CH morphology and a high C/S ratio.

The tendency for carbonation and the low CH content accompanying it may be associated with the relatively small thickness of the composite.

Modes of fibre failure

The microstructural analysis here and the in-situ flexural testing reported by Akers et al. [8] describe the fracture mechanisms of cellulose products. Using these observations and the results in this paper the following modes of fibre failure may be described:

- (i) Ductile pull-out – in which the fibre pulled out of the matrix to a considerable length and the matrix around the fibres was relatively porous. This mode was typical of the unaged composite.
- (ii) Brittle-hollow – in which the fibres broke close to the fractured surface, revealing the hollow nature of the fibre. Fibre-matrix separation or debonding at the interface could be seen, but the matrix at the interface was quite dense, consisting mainly of CSH, in contrast to interfacial CH which is more common in steel and glass fibre reinforced cements [9, 10]. This mode was typical of accelerated aged composites in a normal environment.
- (iii) Brittle petrified – in which the fibres broke at the

fractured surface, revealing circular cross section filled with dense reaction products. The matrix was as dense as in the brittle-hollow case, but no interfacial separation or debonding could be seen. This mode was typical of composites exposed to ageing in conditions which promoted carbonation, i.e. natural ageing and accelerated ageing in a CO₂ rich environment.

Ageing mechanisms

In the unaged composite the failure was characterised by pull-out of the fibres. This resulted in a ductile composite, with modulus of rupture and tensile strength values considerably higher than those of the matrix. The matrix around the fibres was not extremely dense, and cracks could be observed in the matrix in the vicinity of the pulled out fibres. A somewhat weak matrix in the vicinity of the fibre, which can yield or crack, can be favourable from the point of view of the ductility of the fibre composite. It was shown theoretically and experimentally [11–13] that in composites with a brittle matrix and randomly oriented fibres, the inclined fibres bridging the crack tend to bend locally. As a result, a dense matrix in such a zone can lead to the development of localised flexural stresses which could result in premature failure of the fibres; in a weaker interface these stress concentrations can be relaxed by cracking of the matrix.

In the aged composites, the prevailing mode of failure was a brittle one, with fibres breaking at or close to the fractured surface and only a few of them pulling out. The densening of the matrix around the fibres, which was observed after all of the ageing treatments, could be a factor contributing to the reduction in toughness, by reducing the flexibility and deformation capacity of the fibres. A change of this kind can be accompanied by a reduction in strength, or an increase in strength, depending on the nature of the fibres and the effect of the ageing conditions on the properties of the fibres themselves. It was observed that, after accelerated ageing in a normal environment, the composite became brittle and lost strength, and the mode of failure of the fibres was brittle-hollow. After natural ageing and accelerated ageing in a CO₂ rich environment, the composites showed a reduction in toughness but their strength and E-modulus increased by 80% or more. In these cases the more typical mode of fibre failure was 'brittle-petrified', and brittle-hollow failure was less frequently observed. Thus, there appears to be a correlation between the changes in the properties of the composite after ageing and the fibre failure mode: brittle-hollow mode occurred in the composite that lost strength and brittle-petrified in the composites that gained strength. In both cases a reduction in toughness was observed. In the following paragraphs possible explanations for these effects will be discussed.

Dry/wet cycles (in a normal environment) and brittle-hollow fibre failure mode may be associated with weakening of the fibres, or with premature fibre failure in flexure, or with both. The weakening of the fibre may be the result of chemical or physical changes. On wetting

and drying, the cellulose is expected to exhibit considerable cyclic dimensional changes which may lead to cracking and strength loss. The debonding and the gap observed between the fibre and the matrix after this ageing treatment is the result of the volume instability of the fibre. Premature fibre failure in flexure, like that observed in Figure 7, may be the result of the densening of the matrix around the fibres, in accordance with the processes described in references [11–13].

The reduced toughness and strength gain of the composites, which were exposed to ageing conditions where carbonation took place (accelerated ageing in a CO₂ rich environment and natural ageing), may be associated with the brittle-petrified fibre failure mode. The filling of the core of the fibre with hydration products and possibly its cell wall is expected to result in an increase in its strength and stiffness. In addition to that, it seems that the 'petrified' fibres are more stable dimensionally; no separation and debonding between them and the matrix could be observed. Thus, as a result of the increase in the density of the matrix around the fibres and the reduction in the tendency of the fibre to shrink away from the matrix, the bond between the two will become greater. The increase in fibre-matrix bond, and the increase in fibre strength and stiffness may account for the marked increase in the strength and E-modulus of the composite, and in its reduced toughness.

Stronger, more rigid and brittle fibres, and improved bond strength, are known to lead to higher strength and lower ductility. The strengthening of the fibres due to petrification may compensate for weakening effects such as premature flexural failure due to matrix densening which was observed after accelerated ageing in a normal environment, or changes in the degree of polymerisation of the fibres.

The question to be addressed at this point, is how the fibres become 'petrified' and why it occurs more readily in the conditions which promote carbonation. The penetration of CO₂ into a partially wet portland cement matrix is associated with reduction in the pH and increase in the tendency of the hydration products (CH and CSH) to dissolve, and to be transported to more porous zones, and then to redeposit [15, 16]. Such effects, which have been discussed extensively in relation to carbonation shrinkage, may account for the deposition of hydration products within the cellular fibres, leading to the formation of the petrified morphology. This may account for the fact that the petrified morphology occurred more frequently in the composites with more advanced carbonation.

CONCLUSIONS

1. The cellulose fibre reinforced cement tends to carbonate readily.
2. The dominant mode of fibre failure in the unaged composite was pull-out or a combination of pull-out and fracture. The matrix around the fibres was not extremely dense.

3. After accelerated ageing in a normal environment, the dominant mode of fibre failure was brittle, with the fibres breaking at or close to the fracture plane, revealing their hollow cross-section. It is suggested that fibre debonding from the matrix, and possibly a reduction in fibre strength due to physical damage associated with expansion shrinkage, led to loss in strength and toughness of the composite.
4. After natural ageing and accelerated ageing in a CO₂ rich environment, the dominant mode of fibre failure was brittle. Most of the fibres were 'petrified', i.e. their core was filled with hydration products. It is suggested that the increase in the strength and rigidity of the petrified fibres, and the increase in their bond strength due to matrix densification and to elimination of shrinkage-debonding from the surrounding matrix, can account for the increase in strength and E-modulus of the composite.
5. The formation of the 'petrified' fibre morphology after natural ageing and accelerated ageing in a CO₂ rich environment, is suggested to be the result of deposition of hydration products within the core of the cellulose fibre. This process takes place more readily under carbonating conditions, probably due to the lower pH and greater solubility of the hydration products.
6. During all of the ageing treatments a mild reduction in the degree of polymerisation could be observed. The possible reduction in strength, expected from this change, is more than compensated for by the petrification effect which takes place in natural ageing and accelerated ageing in CO₂ environment.
7. Accelerated ageing in CO₂ reproduces the ageing processes occurring in nature, whereas accelerated ageing in a normal environment fails to simulate it.

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