

Age effect on the characteristics of fibre/cement interfacial properties

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The experimental findings of an investigation on the age development of interfacial properties of polyethylene fibers in a cementitious matrix are reported. It was found that the interfacial bond strength matures much faster, in less than 7 days, in comparison with bulk property development, which typically takes 14–28 days. A parallel ESEM study of the microstructure development in the interfacial transition zone supported the fact that the rapid early age saturation of the interfacial adhesive bond strength is associated with the growth of a CH rim around the fibre periphery. The formation of the CH layer appears to be completed much earlier than the hydration process of the bulk material. The slip-dependent friction after initial debonding was found to develop with age up to 28 days, gradually converting from a slip-weakening to a slip-hardening behaviour. These findings should be useful in interpreting early age fibre-reinforced cementitious composite properties.

1. Introduction

The mechanical properties of cement-based materials are time-dependent due to the prolonged cement hydration process. For a fibre-reinforced cementitious composite (FRCC), mechanical behaviour may also be time-dependent due to the ageing effect not only on the matrix properties, such as strength, stiffness, fracture toughness, etc., but also on the fibre/matrix bond property. It is known that the interfacial transition zone between fibre and matrix is different from the bulk matrix in the microstructure and the fibre/matrix bond properties are critical in determining the composite properties. In general, compared to the bulk matrix, the transition zone has a higher porosity because of bleeding and inefficient packing of cement particles in the fresh state. As a consequence there is preferential growth of CH crystals in this zone which remains more porous than the bulk paste. Owing to the distinctions in microstructure, the time-dependency of fibre/matrix bond strength is expected to be different from that of the mechanical properties of the matrix. The contrast in the rate of development between interfacial bonds and various matrix properties could result in much more complicated composite age-dependent behaviour compared with ordinary cement materials, especially at the early age.

Dimensional stability under desiccated conditions has been an important issue for concrete structure. While cementitious materials usually suffer from cracking due to restrained crack shrinkage, fibre reinforcements have been found to be an efficient method of shrinkage crack control. Obviously, the required fibre content for shrinkage crack control depends mostly on the fibre-bridging efficiency. Although a cementitious material is subjected to different ex-

tents of shrinkage at different ages, the influence of shrinkage on cement materials is more significant at an early age. Therefore, to apply fibre reinforcement for shrinkage crack resistance, it would be necessary to understand the age effect on the behaviour of fibre/matrix interfacial bond strength, which is one of the main parameters of fibre-bridging efficiency. This serves as an example of why the time-dependency of fibre/cement bond strength deserves careful investigation.

This paper reports the findings of an investigation on the development of interfacial bond strength and transition zone microstructure as a function of hydration age. The microstructure of the transition zone near the fibre surface can be very different from that of the bulk matrix and the interfacial bond properties are closely related to the characteristics of this unique material structure. It is therefore necessary to study the formation of this transition zone with age to identify the mechanisms of bond formation.

In this study, fibre pull-out tests were conducted to measure the early bond strength development in polyethylene fibre/cement matrix. Observation of microstructural development of the transition zone material was carried out by means of an ESEM. It was found that the rate of increase in fibre/cement bond strength with age is different from the hardened cement paste. In fact, the fibre/cement bond strength achieved a steady state magnitude at a very early age with no substantial increase thereafter. Evidence from microstructural observation indicates that the development of the CH layer at the fibre/cement interface is mostly responsible for the bond property for the material systems tested and provides an explanation of the mechanism of early bond strength development.

2. Age-dependency of the mechanical properties of FRCC

The constitutive properties of cement-based materials are time-dependent due to the hydration reaction that progressively densifies the structure of hardened cement paste (hcp). Generally, the increase in the degree of hydration results in a decrease in the porosity of hcp, whereas porosity is mostly responsible for the mechanical properties of cement-based materials. A number of material structural models have been proposed to relate porosity to mechanical properties of hcp. For instance, the strength and stiffness have been expressed as a function of porosity of hcp [1–4]. Models that relate the degree of hydration and the age of hcp have also been proposed [5]. Therefore, for the normal range of water/cement (w/c) ratio and curing conditions, the mechanical properties of hcp can be determined by the porosity and are obviously functions of age. The similarity among the relationships between various constitutive properties of hcp, such as strength and stiffness, and the porosity may lead to the conclusion that the rates of increase in various mechanical properties of hcp with age, are comparable.

However, the fibre/matrix bond is related to the microstructure of the interfacial transition zone. The bond strength is generally determined by the adhesion (adhesion failure) between the fibre and adjacent cement materials, as well as strength (cohesion failure) of the transition zone material. For fibre-reinforced cementitious composites, a unique layer of transition zone material is typically observed [6, 7]. The transition zone is considerably weaker than the bulk matrix due to large CH crystals and higher porosity as reflected in microhardness tests, which show that the weakest point in the interfacial zone is about 30 μm away from the fibre surface (the typical thickness of the transition zone is approximately 50 μm) [8]. This weak phase may be diminished or even removed by control of packing density and hydration around the fibre surface. Silica fume and superplasticizer have been found to be very effective (e.g. [9]). Depending on fibre types and matrix constituents, either adhesive or cohesive type of bond failure can occur [10]. Hence, proper strategy should be employed towards enhancing interfacial bonds or strengthening the transition zone. Densification of the transition zone may not necessarily increase the bond strength effectively in material systems governed by adhesive bond failure. In such cases, although the ageing effect may essentially reduce the porosity in the transition zone, the interfacial bond strength may not be necessarily increased accordingly. Therefore, the time-dependency of the fibre/cement bond strength can be very different from those of the mechanical properties of hcp. A microscopic investigation would be necessary to resolve the time-dependent characteristics of fibre/matrix bond properties.

3. Experimental procedure

3.1. Materials

The fibres used were Spectra fibre (38 μm diameter) and Snia fibre (20 μm diameter). Both are high-

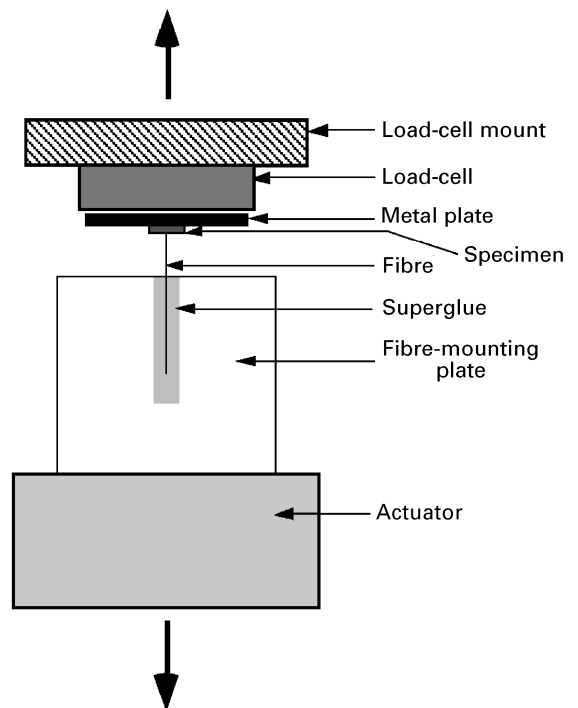


Figure 1 Miniature pull-out test apparatus.

modulus polyethylene fibres probably with different surface finishes, supplied by different manufacturers. The matrices were a plain matrix (w/c = 0.5 and no admixture) and an SF matrix (silica fume/c = 0.20, w/c = 0.27, superplasticizer/c = 0.05). Specimens were moisture-cured until the date of testing, at ages of 0.5, 1, 1.5, 2, 7, 14, 21, 28 days. For each material system, at least three specimens were tested at each age.

3.2. Test apparatus

The miniature pull-out test apparatus (Fig. 1) was employed in this study. The specimen was linked to a small load cell (2.2 N capacity) via a base plate using superglue. However, the penetration of superglue into the embedment end of the fibre must be avoided. After properly adjusting the appropriate position of a metal plate held by the lower hydraulic grip, the protruded fibre is then attached by superglue to the metal plate that provides pull-out load. Details of this test apparatus can be found in Katz and Li [11].

4. Results and discussion

4.1. Age-dependence of fibre/matrix bond strength

The interpreted data of fibre/matrix bond strength are summarized in Figs 2 and 3 for Spectra and Snia fibres in different cement matrices. The data are plotted with respect to age on a log-scale to demonstrate the age effect. As indicated by Fig. 2a and b for plain and SF matrices, respectively, Spectra fibre/cement bond strength increases rapidly within the first 2 days. The early bond strength is of the order of 0.4 MPa after 12 h hydration. In two days, the bond strength is able to build up to the level of 0.6 MPa and does not have a substantial increase thereafter. In general, the bond strength of the Spectra fibre/cement matrix matures in

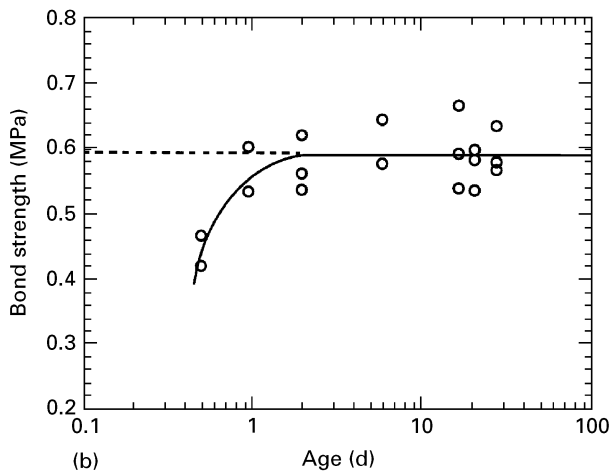
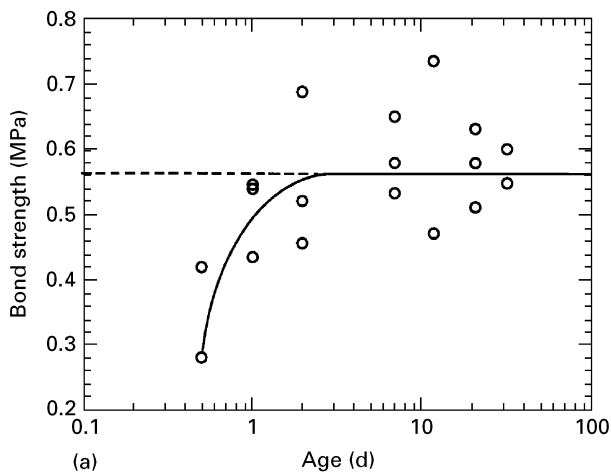


Figure 2 Age effect on bond strength of Spectra fibre in (a) plain matrix, and (b) silica fume matrix.

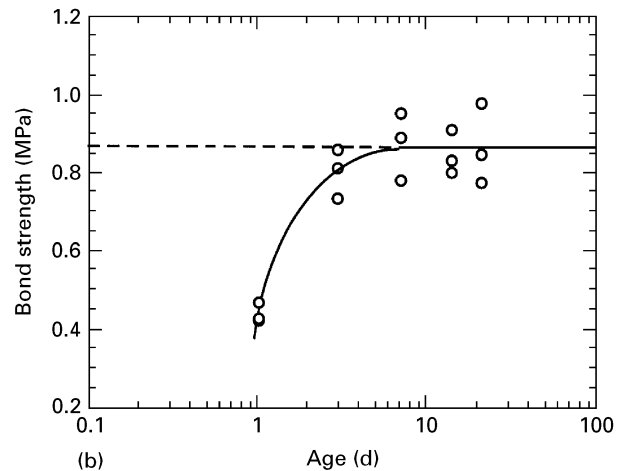
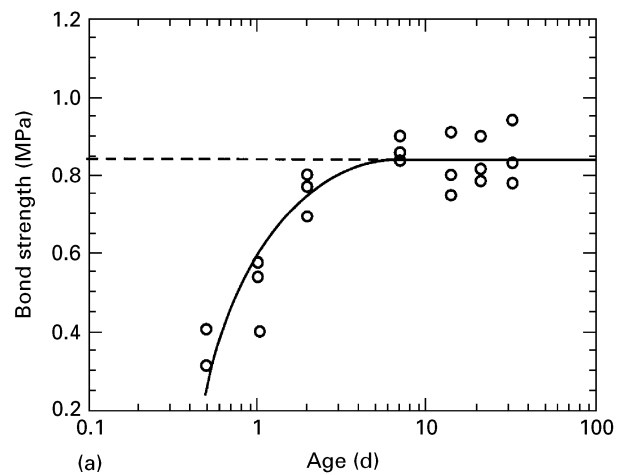


Figure 3 Ageing effect on bond strength of Snia fibre in (a) plain matrix, and (b) silica fume matrix.

approximately 2 days after casting and the ultimate magnitude is of the order of 0.6 MPa.

The development of the bond strength between Snia fibre and the cement matrix is similar to the case of Spectra fibre except that Snia fibre takes longer to saturate its bond strength. As shown in Fig. 3a and b for plain and SF matrices, respectively, the bond strength between Snia fibre and the cement matrix at the age of 1 day is of the order of 0.4 MPa, similar to Spectra fibre. However, it takes approximately 7 days to achieve the ultimate bond strength, approximately 0.85 MPa for both plain matrix and SF matrix. After 7 days, no significant gain in bond strength was found.

From the results shown in Figs 2 and 3, it is clear that the bond strength between Spectra or Snia fibres and the cement matrix develops and matures rapidly. The maturation rates of 2 and 7 days (for Spectra and Snia fibres, respectively), appear much faster than the typical 28 days maturation rate expected of most cement property development.

There is supporting literature available on the ageing effect on adhesion. In a study of the microstructural features of the steel/mortar interface by Page *et al.* [12] and Khalaf and Page [13], the adhesion between steel and cement paste or mortar was measured. Generally, it takes approximately 7 days for the adhesion between steel and various cement pastes or mortar to achieve the ultimate magnitude, although the ultimate bond strength varies with steel substrates

with different surface treatments. Page *et al.* [12] suggested that separation between steel and cement paste or mortar tends to take place along the “grain boundary”. This “grain boundary” presumably corresponds to the contact surface between steel substrate and cement materials.

4.2. Effect of matrix compactness

It was found that for both plain matrix and SF matrix, the long-term bond strengths are very close in magnitude, 0.6 MPa for Spectra fibre and 0.85 MPa for Snia fibre. The bond strength-age development curves are also similar (compare Fig. 2a with 2b and Fig. 3a with 3b). While the SF matrix is expected to have a much higher compactness than the plain matrix at the interfacial transition zone, the effect of matrix type on bond strength is found to be negligible. This implies that the bond strength is probably dominated by adhesion, mainly the weak van der Waal force, between the fibre surface and the immediate adjacent CH layer in the hcp (see further discussion on microstructural observations below). Modification of the microstructure of the interface transition zone via microfilling by silica fume does not alter the bond strength.

4.3. The post-peak pull-out behaviour

Although the bond strength seems to mature rapidly, the fibre/matrix interaction in the post-peak pull-out

behaviour does continue to vary substantially with age. Fig. 4 shows the entire pull-out curves of Spectra fibre in two different matrix types at various ages. At an early age of 1 day, the pull-out load, which is mainly contributed by the interfacial frictional resistance, decays rapidly with increase in pull-out distance. Basically, there are two mechanisms responsible for this non-linear decreasing behaviour of pull-out curves. First, the decrease in pull-out load can be attributed to the reduction in contact area as the fibre is gradually withdrawn from the matrix. However, the non-linear relation between pull-out load and the pull-out distance can be mostly due to the breakdown in the matrix in contact with the fibre, caused by abrasion. The frictional stress between the fibre and matrix is thus deteriorated accordingly, resulting in a concave (upwards) pull-out curve. This phenomenon, however, vanishes as the age increases such as the almost linear pull-out curves of 7 days. Furthermore, the pull-out load may even increase with the pull-out distance at longer ages, e.g. the cases of 28 days.

A linear post-peak branch in a pull-out curve would be expected in a pull-out process, if the frictional stress between fibre and matrix has been constant. However, due to the abrasion during fibre pull-out, damage may occur to different extents on fibre or matrix and result in either slip-weakening or slip-

hardening. At early age the cement matrix is not fully hydrated. The abrasion due to fibre slip may cause damage on the matrix and result in poor contact between fibre and hcp. Hence slip-weakening is observed. On the other hand, a fully hydrated hcp might have a higher hardness than the polymeric fibres which are usually weaker in the lateral direction due to molecular structure. As a result, fibre pull-out causes damage on the fibre surface and the peeled-off tiny fibrils could increase the resistance to further slip by jamming the fibre. The slip-weakening behaviour has also been observed by Naaman and Shah [14] in the case of steel fibre which is much harder than the cement matrix. The mechanism of slip-hardening in the polymeric fibre pull-out was first proposed by Wang *et al.* [15] on the pull-out testing of polypropylene and nylon fibres. However, the observation of both slip-weakening and slip-hardening of the present study in the same material system due to the ageing effect, has not been reported previously. This characteristic on this slip-dependent interfacial friction suggests the importance of the transition in mechanical properties of fibre-reinforced cementitious composites with age.

4.4. Microstructural observation

Fig. 5 indicates the microstructure of the transition zone in Spectra fibre/plain matrix at ages 1, 7, and 28 days. At an age as early as 1 day, a rim formed by CH crystals has already been well developed and can be clearly identified on the fibre side of the transition zone (Fig. 5a). Between the CH layer and the bulk matrix, partially hydrated C-S-H gels and unhydrated cement particles are found in this porous region. At longer age, not much change in the CH layer can be observed. However, the microstructure in the initially porous region was substantially densified. As in Fig. 5b, at the age of 7 days, unhydrated cement particles can hardly be found. Instead, massive C-S-H gels and needle-like ettringite are the main hydration products at this stage. As the age increases even further, the transition zone becomes amorphous in microstructure and the porosity has been greatly reduced (Fig. 5c).

These observations indicate that the CH rim in the transition zone is the first material structure to develop due to its crystallization process and more open space available at the early age, while the main hydration product in the matrix, C-S-H gels, develops gradually with age. As suggested by Diamond [16], larger vacancy and higher w/c ratio are favourable for the crystallization process of CH. The groove surface, after the removal of Spectra fibre, was also examined. As shown in Fig. 6, the surface directly in contact with fibres is very smooth as expected because this surface is mainly constructed by the dense CH layer. Fig. 7 shows the peeled-off Spectra fibre. After easily peeling off the Spectra fibres, the surface originally in contact with hcp is clean and is free from cement remnant. The fibre surface retains its virgin texture.

This microscopic evidence suggests that the adhesive bond between Spectra fibre and hcp is relatively weak and is probably contributed by the van der Waal

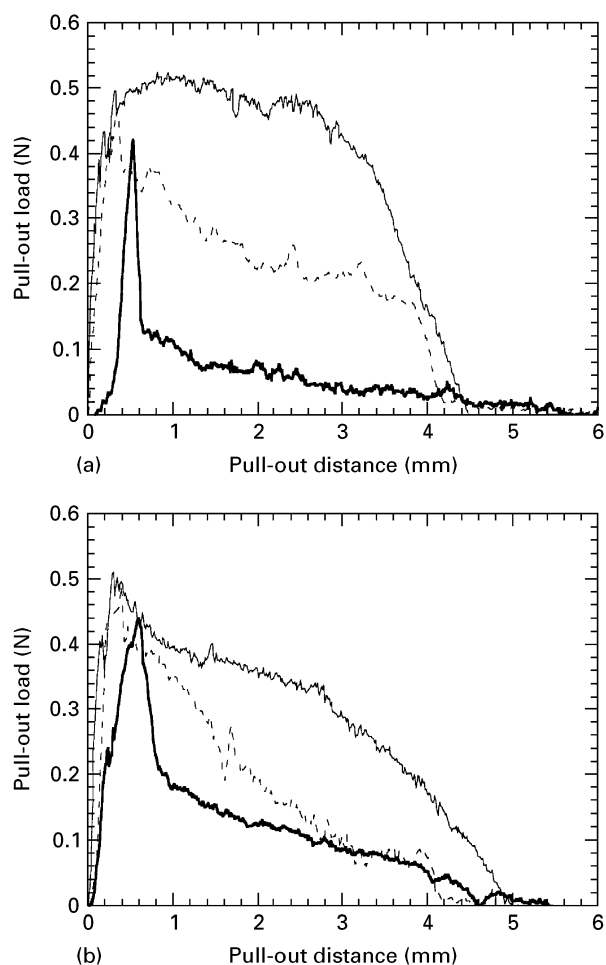


Figure 4 Ageing effect on pull-out behaviour of Spectra fibre in (a) plain matrix, and (b) silica fume matrix. (—) 1day, (---) 7days, (- · -) 28 days.

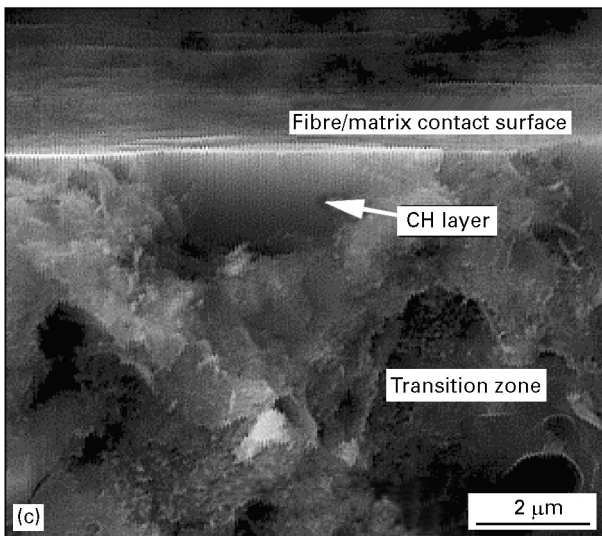
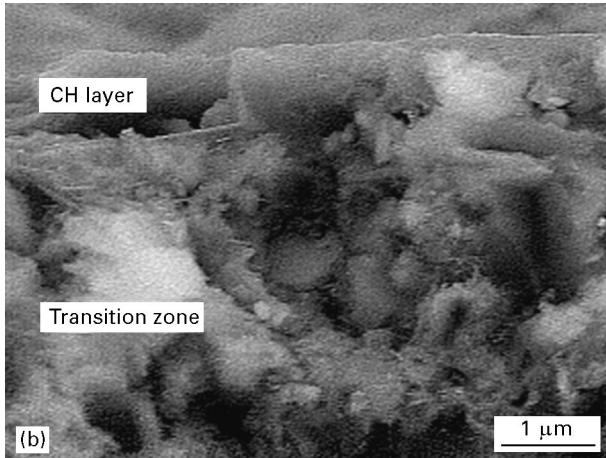
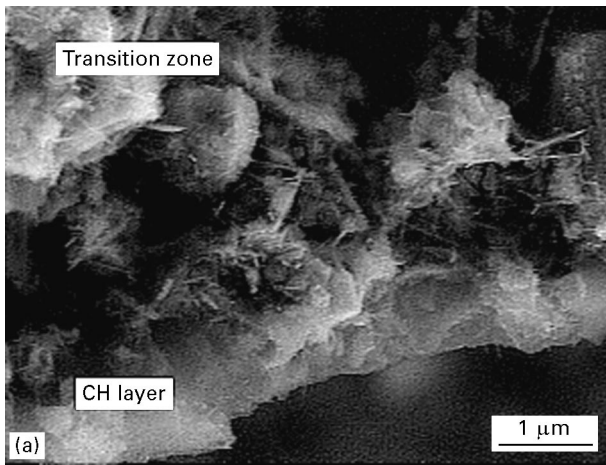


Figure 5 Spectra fibre/plain matrix transition zone microstructure at ages of (a) 1 day, (b) 14 days, and (c) 28 days.

force. Hence the hcp directly in contact with Spectra fibre, which is the early developed CH layer in this case, is responsible for the fibre/cement bond strength. The early age bond property of Spectra fibre shown in Fig. 2 can be explained by the weak adhesive force with hcp. Although further increase in age (beyond 2 days) significantly reduces the porosity and strengthens the transition zone, the bond strength is not much influenced by the ageing effect because it is mostly governed by the fibre/matrix adhesion.

The mechanism described above may also explain the similar bond property in the SF matrix. For the SF

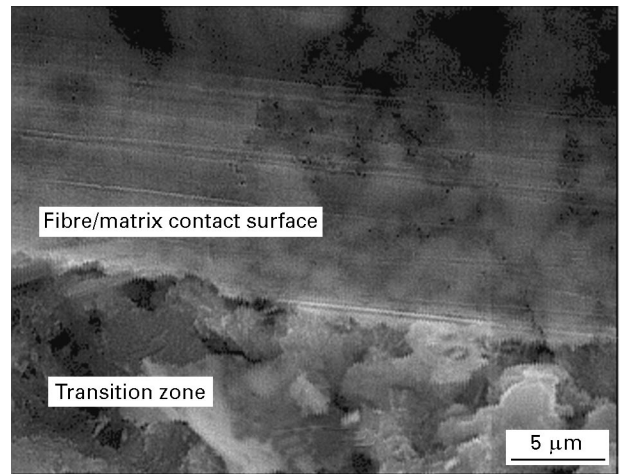


Figure 6 Fibre/plain matrix contact surface (age = 2 days).

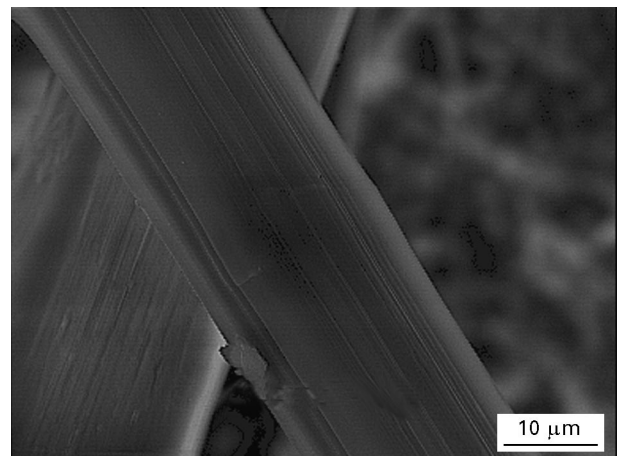


Figure 7 Surface texture of a Spectra fibre peeled from plain cement matrix.

matrix, the transition zone is less distinctive than that of the plain matrix as shown in Fig. 8 due to the microfiller effect of the small silica particles. However, similarly dense hcp, as in the case of plain matrix, is also observed. Fig. 9a and b indicate that the dense and smooth matrix surface in contact with Spectra fibre has already formed at the early age. Fig. 9 also suggests the adhesion to be the dominant factor of bond strength. Therefore, it is expected that the Spectra/matrix bond strength is not influenced by the ageing of the cement matrix and the bond property does not seem to benefit from the dense SF matrix.

In the matrix with or without silica fume, the CH layer was found to develop at a very early age. However, it is not clear whether the structure of the CH layer has been changed due to pozzolanic reaction or fine particle sizes of silica fume. The incorporation of silica fume did not lead to substantial increase in bond strength (Figs 2 and 3). This suggests that silica fume does not affect the adhesion between the fibre and the contact layer, at least in this particular material system.

5. Conclusion

The material systems tested in this study indicate that the fibre/matrix bond strength can develop rapidly,

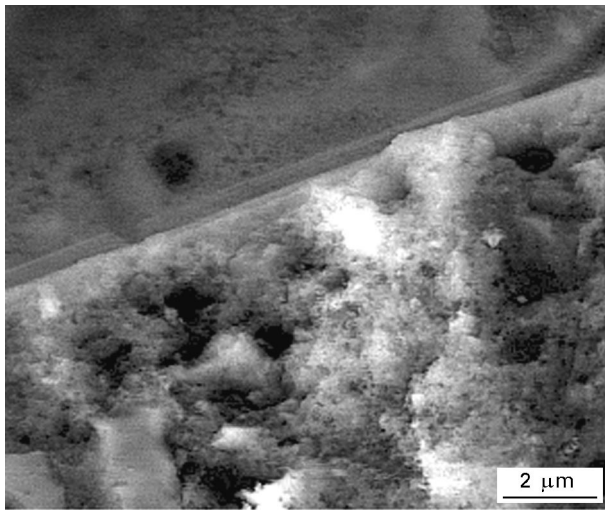


Figure 8 Spectra/SF matrix transition zone (age = 1 day).

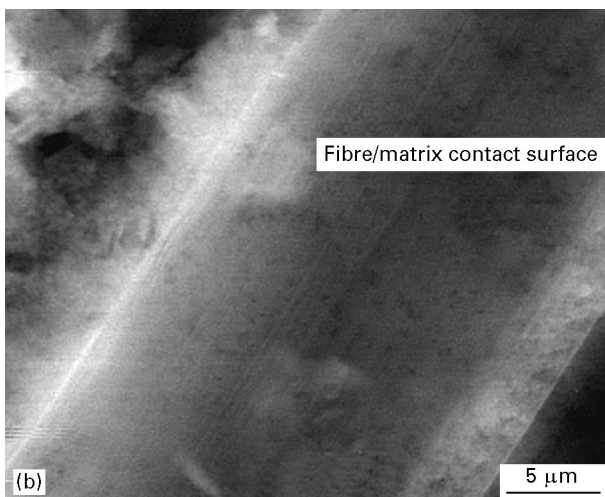
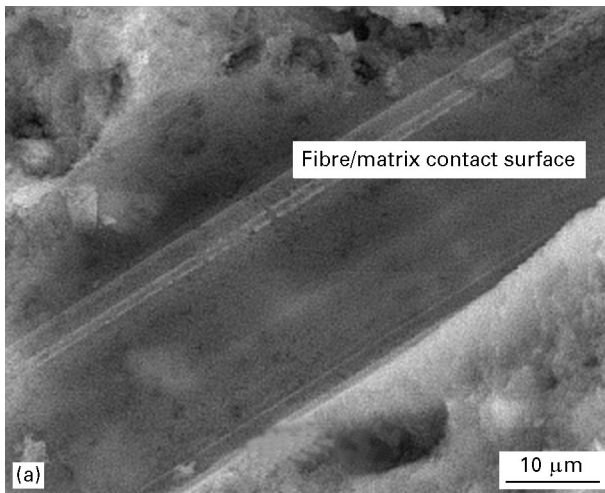


Figure 9 Spectra/SF matrix contact surface at age (a) 2 days, and (b) 28 days.

maturing much earlier than matrix properties in a cementitious composite. For example, the ultimate bond strength can be achieved as fast as 2 days for Spectra/cement system and 7 days for Snia fibre/cement case. The age effect also causes a change in the fibre post-peak pull-out behaviour from slip-weakening to slip-hardening in the material system studied.

According to the microstructure study, the adhesion between polyethylene fibre and adjacent

hardened cement paste is found to be responsible for the fibre/matrix bond. In addition, the CH layer in contact with the fibre grows much faster than the rest of the material structure in the transition zone because more nucleation sites and open space are available in the annular region of the fibre. Although further hydration results in a decrease in porosity of the transition zone, no further increase in this initial (at zero slip) bond strength occurs because the structure of the transition zone does not contribute directly to the fibre/matrix bond. Therefore, the fibre/matrix bond strength can saturate in a much shorter period as compared to 14–28 days typical for matrix strength.

The conclusions stated above should be valid for fibre/matrix systems in which debonding is governed by fibre/matrix adhesive strength. For material systems of cohesive bond failure, the characteristics of bond formation and the interfacial bond strength maturation rate may not be the same as found in this study.

In contrast to the initial bond strength, the slip-dependent friction does develop with age up to 28 days, the maximum age in this study. This slower development is associated with the hydration process in the interface transition zone, which interacts mechanically with the fibre during the post-peak pull-out process. The fibre pull-out test indicates a gradual conversion of slip-weakening at early age (less than 7 days) to a slip-hardening behaviour in the fibre/matrix system examined.

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