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Toughening cement-based materials through the control of interfacial bonding

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Abstract

Mortars are made from inherently brittle components: sand grains and hardened cement paste. Under normal circumstances, cracks will propagate rapidly through the cement matrix, bypassing the strong sand grains but fracturing some of the weakest. The approach of the work described in this paper was to modify the mortar in order to alter this process. These modifications produced tensile residual stresses between the matrix and the aggregate, which when released by an additional applied tensile stress produced microcracking, debonding of matrix from aggregate, a small expansion and increased toughness. This work demonstrates toughening in sand/Portland cement mortars modified with different expansive admixtures: sodium sulphate or dead-burnt lime. Additionally, mortars of sand/ASTM Type K cement were tested. In order to give additional insight into the toughening mechanism, spherical and angular aggregate have been used to ascertain the consequences of microcracking and aggregate-bridging. The role of aggregate-bridging, especially when related to fracture paths, is also discussed and suggests that the bond between the aggregate and the matrix has been found in some cases to control not only the crack path but consequently the apparent toughness.

Keywords: Cement; Mechanical properties; Microstructure; Fracture toughness

1. Introduction

It has previously been shown that the fracture behaviour of brittle materials, such as ceramics [1] and cements [2], can be altered by manipulation of their microstructures. An important aspect of this behaviour is the resistance to crack growth and how this changes as the crack grows, especially where thermal shock is a consideration [3–5]. In particular, it has been shown that it is better to allow easy propagation when the crack is small and to increase the resistance to crack growth as the crack extends [6]. If this is achieved then a large number of small cracks emerge as an alternative to the propagation of one large crack, a situation which improves the impact and thermal shock resistance of the component [7].

This paper focuses on ways to engineer the toughness of cement systems. In any material this requires recognition of the principal toughening mechanisms and we identify two possible mechanisms applicable to cement-bonded systems:

- aggregate particles acting as bridges across the crack, similar to aggregate-bridging in polycrystalline ceramics [8], and
- closure of the macrocrack as a result of the release of residual stresses and subsequent expansion [9].

These mechanisms are shown schematically (Figs. 1–3) and are discussed in more detail in the following.

1.1. Crack bridging

The incorporation of aggregates into a brittle matrix may have a role in increasing the toughness of the ceramic materials through aggregate-bridging, but only if an aggregate particle can act as a bridge, i.e., having the ability to anchor matrix on both sides of a crack so that crack face separation is inhibited. We believe that the key to toughening lies in understanding how cracks intercept aggregate

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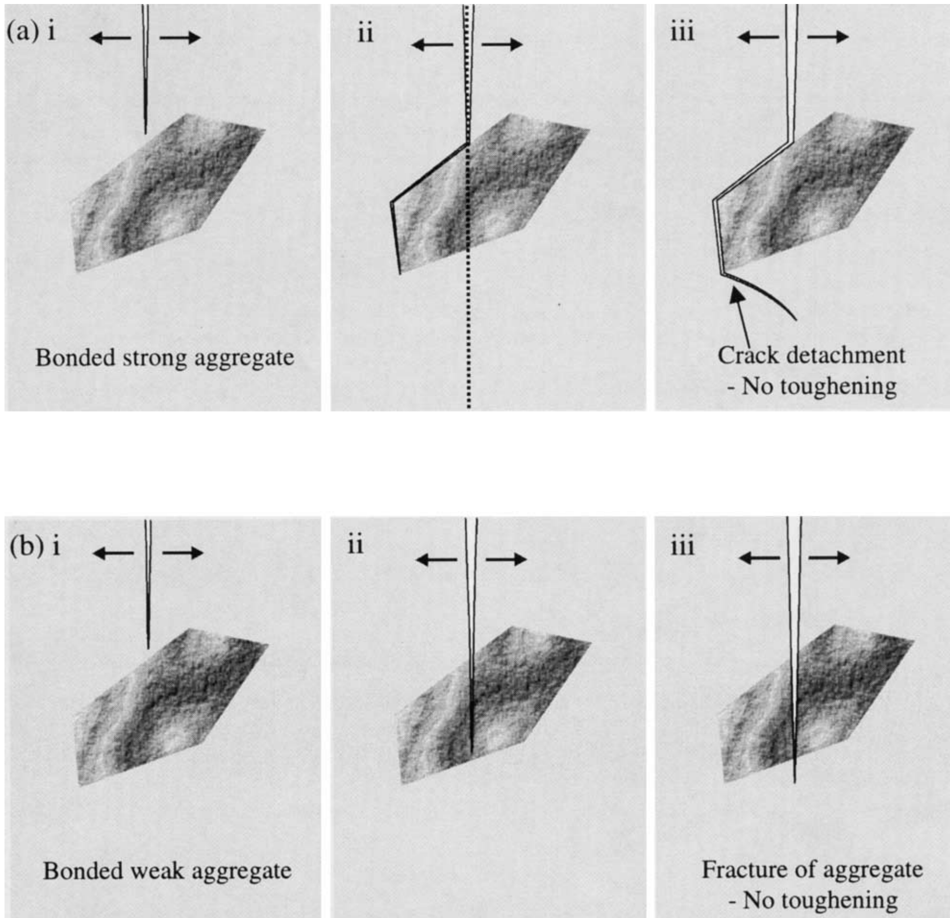

Fig. 1. Interaction of a crack with bonded aggregates in a brittle matrix. (a) Strong aggregate where the crack has detached early. Note that the path of a flat fracture is indicated in (a-ii) and that detachment means that the crack does not follow the flat fracture path (a-iii). (b) Weak aggregate fractured by the crack, i.e., no crack-bridging.

zones and this in turn is influenced by the nature of the interfacial bond between the aggregate and the matrix. If the particle is fully bonded to the matrix there is no guarantee that the toughness is increased, as seen when coarse magnesia grains are added to a fine magnesia matrix [9]. This may be due to the crack detaching from the aggregate early and not allowing the formation of a bridge (Fig. 1a). If the aggregate is relatively weak, crack propagation may occur through the aggregate particle (Fig. 1b) and no bridging occurs. There is also no basis for toughening when the aggregate is spherical, whether bonded or unbonded to the matrix (Fig. 2a), because there is no irregularity in shape and consequently no pinning points. However, where no appreciable bond between the matrix and the aggregate exists, the mechanism for crack propagation is different. Here, the crack interacts with what appears to be an inclusion-shaped hole. Just as the crack would be undeviated by an empty hole (referred to here as a flat fracture path [see Fig. 2]), the crack attempts to pass undeviated through the region of the inclusion. Now, there are opportunities for crack bridging.

Fig. 2b shows the path of an undeviated crack being bridged by an irregularly shaped aggregate. Further separation of the crack faces (i.e., continuing propagation of the crack) depends on the aggregate or crack bridge breaking through the obstructing portion of matrix and this additional energy requirement dissipates crack energy and slows it down. The weak bonding between cement paste and glass [10] provides an example of a system where the conditions in Fig. 2b would be satisfied.

1.2. Release of residual stress

Prevention of matrix–aggregate bonding in mortars utilising conventional aggregates may be difficult to achieve in practise. However, it is possible to manipulate deliberately generated residual stresses to provide the necessary conditions for ‘active’ debonding and increased toughening. In a system containing dimensionally stable aggregates bonded to an expansive matrix, expansion of the matrix is restrained by the interfacial bond between the matrix and aggregates. The aggregate is therefore in tension and the matrix is in hoop compression around the aggregate. These residual stresses lead to metastability such that an approaching macrocrack may release these stresses resulting in an ‘active’ debonding of the

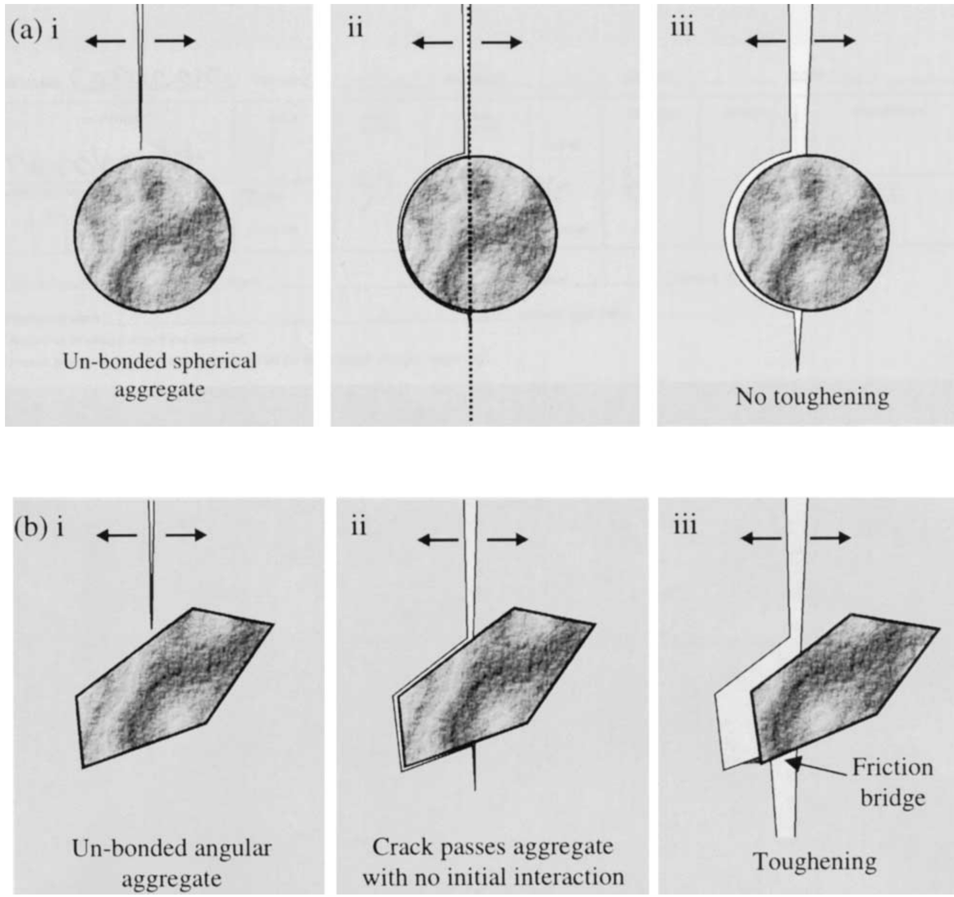

Fig. 2. Interaction of a crack with aggregates which are *not* bonded to the matrix. (a) Spherical aggregate. Note that although the crack follows a flat fracture path (broken line (a-ii)) there is no toughening because the aggregate is unable to form a bridge. (b) Angular aggregate. Able to act as a bridge *because* the crack follows the flat fracture path *and* irregular shape leads to pinning (see (b-iii)). In all cases, lack of interfacial bond is indicated by the line surrounding the grains.

matrix from the aggregate (Fig. 3). Two scenarios are now possible:

(i) the crack is attracted towards the aggregate as above and toughening is improved by aggregate-bridging (Fig. 3), and

(ii) the resulting relaxation of the expansive matrix causes a net compression from the bulk material towards the main crack faces causing crack closure.

Expanding the matrix of cement-based systems can be achieved using chemical admixtures, e.g., sodium sulphate

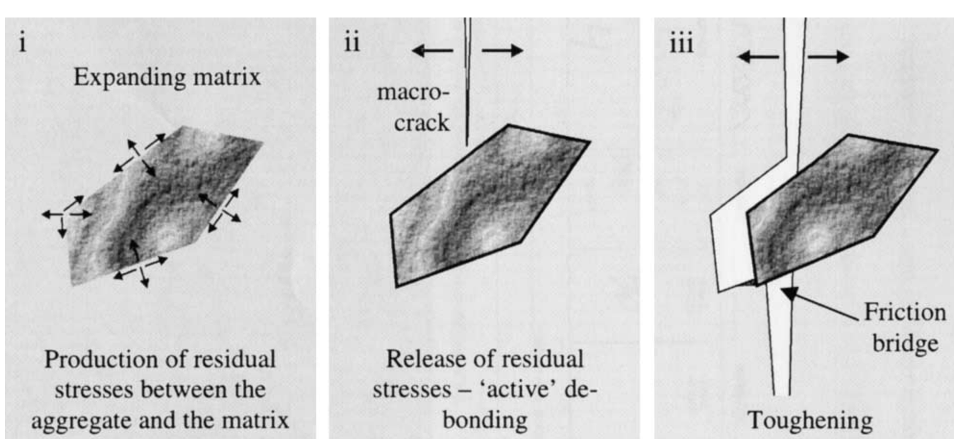

Fig. 3. Interaction of a crack with bonded aggregates in an expansive ceramic matrix. The figure shows 'active' debonding after the release of residual tensile stresses (3-ii) and subsequent toughening. Note: The line surrounding the grains indicates debonding.

Table 1
Batch details of mortars with various admixtures

Batch	Cement[a] (wt.%)	Aggregate (wt.%)	Admixtures Na_2SO_4 (wt.%)	Admixtures Lime (wt.%)
OPC	100	0	0	0
CON — Chelford 30	50	50	0	0
NS — Chelford 30	50	50	7.5	0
C — Chelford 30	50	50	0	10
K — Chelford 30	50	50	0	0
AG — angular glass	50	50	0	0
SG — spherical glass	50	50	0	0
SS — spherical steel	50	50	0	0
SSS — spherical steel	50	50	7.5	0

[a] OPC was used except for Batch K where ASTM Type K cement was used.

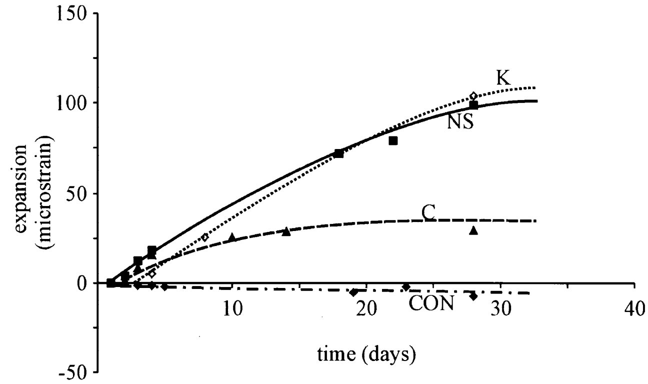

Fig. 4. Change in length of mortar bars made from sand, OPC with added sodium sulphate (NS; ■) or dead-burnt lime (C; ▲) or from sand and Type K cement (K; ✧) compared with sand/OPC mortar as control (CON; ◆). All samples were cured at 25°C at 100% RH.

(Na_2SO_4) or dead-burned lime, CaO. Alternatively, expansive cement such as ASTM Type K may be used. The expansion must be controlled so that it is capable of filling available porosity (passive) and loading the matrix during the (active) phase [11] just sufficiently to allow a build up of residual stress without expansive failure. This paper reports on the toughening effect produced by these various admixtures and tests the relative importance of the scenarios described above.

2. Experimental details

2.1. Sample preparation

Cement-bonded mortars were made from ordinary Portland cement (OPC),[1] Chelford 30 sand[2] and different admixtures[3] (see Table 1). In Batch K the OPC was substituted by Type K cement.[1] The mortars were mixed in a domestic food mixer and cast on a vibrating table into steel moulds to produce bars (25 × 25 × 150 mm) and notched plates (76 × 150 × 25 mm). The specimens were kept at 25°C in a 100% relative humidity (RH) environment prior to mechanical testing at 28 days. The change in length of the bars was measured over the 28 days and the results are shown in Fig. 4.

Cement-bonded specimens were also prepared using steel and glass aggregates (see Table 1). Steel balls[4] and glass spheres,[5] 3 mm in diameter, were used so that the potential for aggregate-bridging was eliminated and the effect of a strong bond (between matrix and steel) and a weak bond (with glass) could be observed. The incorporation of an expansive additive to a matrix containing steel aggregate provides an opportunity to investigate the relationship between nonlinear mechanical behaviour and toughness characteristics. The dimensional properties of these composites are illustrated in Fig. 5. Broken glass pieces[6] with a grain diameter of approximately 5.0 mm were used to provide a comparison between unbonded angular and near spherical aggregate (see Fig. 2a and b).

2.2. Mechanical testing

Four-point flexure-bend tests were carried out using a Hounsfield H10KS testing machine. The strain was measured by attaching a strain gauge to the tensile face. Cyclic load tests (increasing the load on a bar and then relaxing it back to zero load) were carried out on the mortar batches at a displacement rate of 0.25 mm/min and the stress estimated using linear elasticity. Toughness measurements were carried out on the plate specimens. The test geometry consisted of a double cantilever and the crack was propagated by the application of two compressive loads onto the end of the specimen.[7] These loads were parallel to the crack direction, thus providing a bending moment in the cantilevers. Crack growth was measured visually using a travelling microscope as a load was applied by an Instron 1185 test machine. Toughness (K_{app}) was expressed as follows:

$$K_{app} = \frac{F}{\sqrt{w}}\left(\frac{x}{w}-\frac{1}{4}\right)\sqrt{2}\sqrt{\left(\frac{12}{1-\nu^2}\right)}\frac{1}{B}$$

where F is applied load, w is specimen width, B is specimen depth, x is half the distance between the loading points and

[1] Donated by Blue Circle Industries, Dunbar Works, East Lothian, Scotland.

[2] Purchased from Hepworth Minerals and Chemicals, Sandbach, Cheshire, England.

[3] BDH 'AnalaR' Na_2SO_4 and CaO fired from BDH 'AnalaR' $CaCO_3$ at 1400°C for 10 h.

[4] Purchased from Gamebore Cartridge, Hull, England.

[5] Purchased from Potters-Ballotini, Barnsley, England.

[6] Donated by Adshel, Aberdeen, Scotland.

[7] Testing configuration is illustrated in Fig. 7.

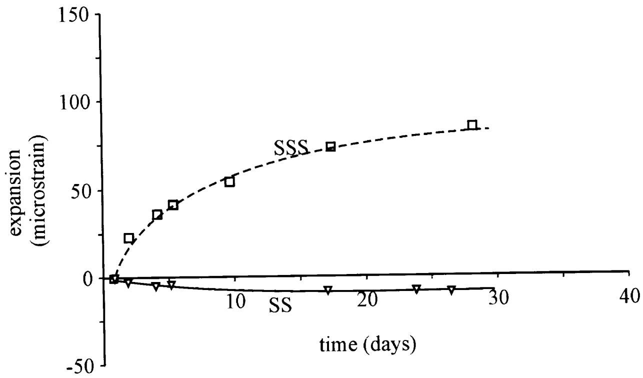

Fig. 5. Change in length of mortar bars containing steel balls with (SSS; □) and without (SS; ▽) a sodium sulphate addition. Samples were cured at 25°C at 100% RH.

ν is the Poisson's ratio [12]. The cross-head displacement rate was 0.2 mm/min.

3. Results and discussion

3.1. Toughening admixtures

The stress–strain relationships of the mortars with different admixtures can be seen in Fig. 6. The expanding matrices produced radically different stress–strain behaviour to the standard cement-bonded mortar. The amount of permanent deformation in Batch NS, with a 7.5% addition of Na_2SO_4, was nearly 250 μstrain. The stress–strain relationship in Batch C, with a 10% addition of lime, did not show as much nonlinearity as seen with the sulphate addition, but was still noticeable. The substitution of the OPC by Type K cement, Batch K, induced a small permanent deformation, greater than OPC but less than burned lime and sodium sulphate.

Toughness curves (Fig. 7) indicate that the initial toughness of a cement mortar is higher than that of a cement paste, indicating the toughening role that aggregate inclusions have in the matrix, but importantly, does not lead to rising toughness in relation to crack extension. However, additions of sulphate, lime and substitution of Type K cement for OPC in the matrix do lead to rising toughness as the crack extends through the test specimens (Fig. 8). While only moderate improvements are seen in Type K cement mortars, lime-modified mortars showed a particularly steep toughness curve (i.e., greater loads were required to propagate the crack, even after it had started to grow).

3.2. Toughening mechanism

It appeared that nonlinear stress–strain curves and increasing toughness with crack growth were correlated. However, further experiments showed that this is not always true. A nonlinear response is observed in the stress–strain

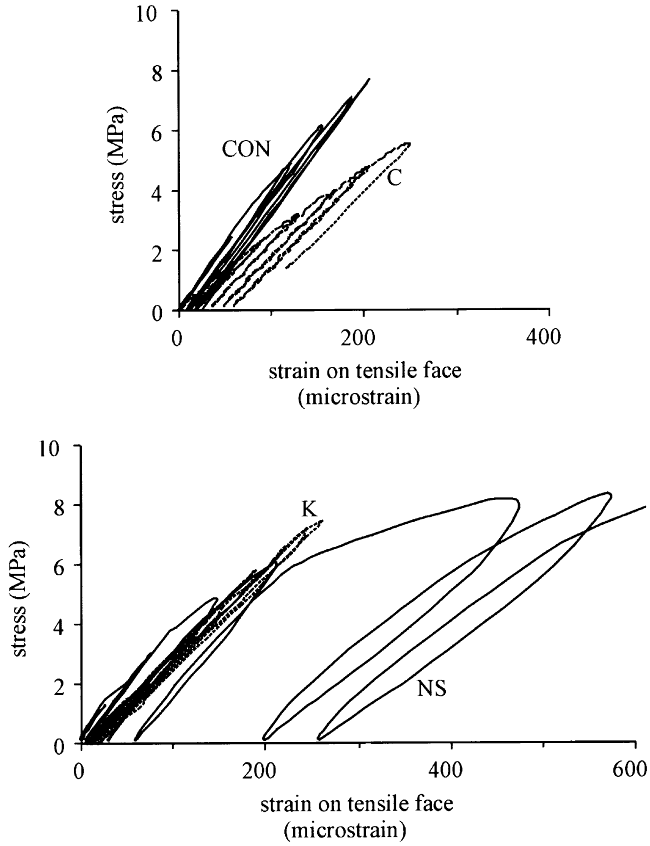

Fig. 6. Stress–strain behaviour of the mortar bars during four-point flexure-bend tests. Samples were made from sand, OPC and sodium sulphate (NS), dead-burned lime (C) or from sand and Type K cement (K) compared with sand/OPC mortar as control (CON). All samples were cured at 25°C at 100% RH.

relationship for batches containing spherical steel aggregates and sulphate additions (Fig. 9). This is thought to reflect the production of microcracks as residual stresses are

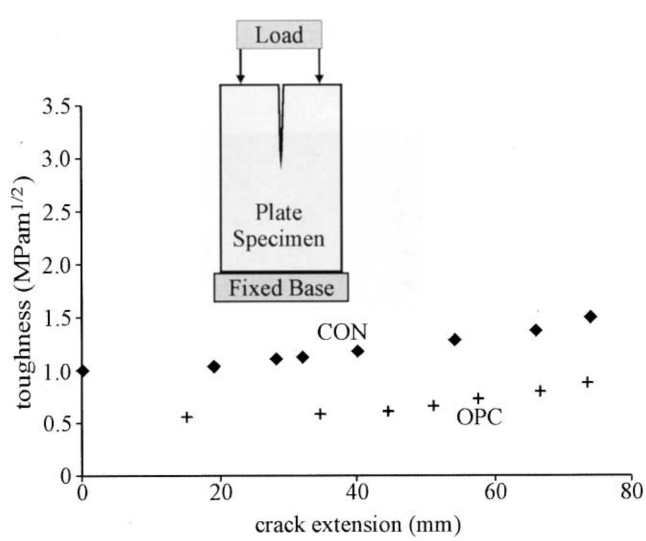

Fig. 7. Toughness curves for plates made with OPC (+) compared with sand/OPC mortar as control (CON; ◆). All samples were cured at 25°C at 100% RH. Insert shows testing configuration.

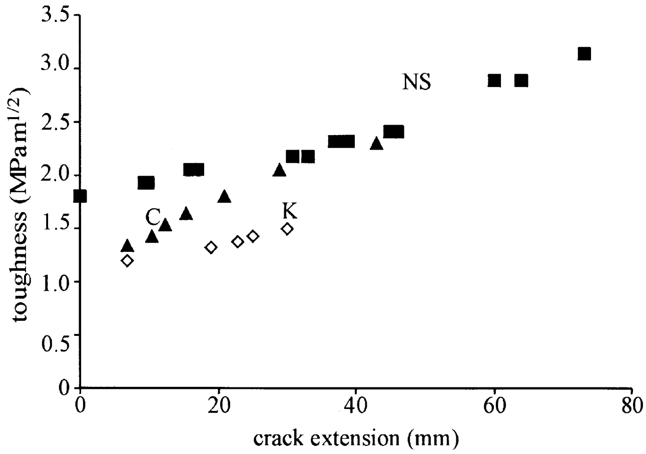

Fig. 8. Toughness curves for mortar plates made with sand, OPC and sodium sulphate (NS; ■) and dead-burned lime (C; ▲) or from sand and Type K cement (K; ✧). All samples were cured at 25°C at 100% RH.

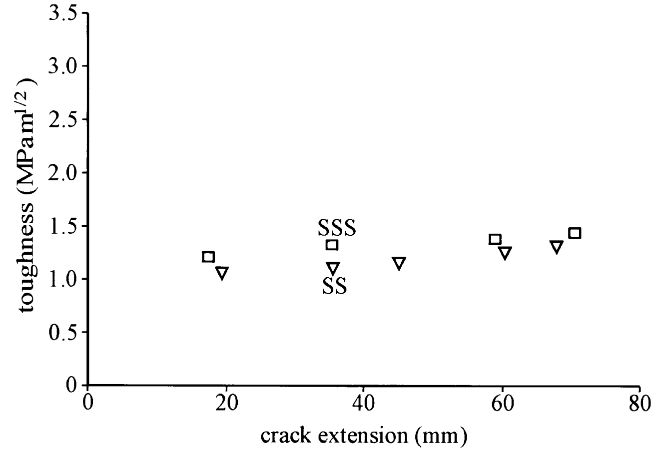

Fig. 10. Toughness curves for mortar plates containing steel balls with (SSS; □) and without (SS; ▽) a sodium sulphate addition. Samples were cured at 25°C at 100% RH.

released and the expanding matrix breaks away from the steel aggregates. However, it is shown that the toughness in this system does not increase as the crack grows (Fig. 10). This is the first indication that the net compression from the bulk material towards the main crack due to the release of residual stress is not a significant mechanism responsible for the enhancement of toughness in cement-bonded mortars. Instead, the alternative mechanism, involving aggregate-bridging, is more consistent with the observed performance because the spherical aggregate is unable to form a bridge between the crack faces.

On the other hand, angular grains in themselves do not necessarily produce rising toughness as the crack extends [9] although they may produce a higher initial toughness, as is the case when angular sand is added to the cement matrix (CON). However, once the crack has begun to propagate through the cement matrix there is no further resistance to crack growth and the result is a flat toughness curve. This situation is most likely to be similar to the example of a bonded aggregate within the brittle matrix, illustrated in Fig. 1a, where early detachment of the crack from the aggregate does not allow any bridging to take place.

The use of glass aggregates in the cement matrix enables the importance of aggregate–matrix debonding to be highlighted. Fig. 11 shows, again, that spherical aggregates (SG) do not produce a rising toughness curve mainly because their regular shapes are unable to bridge the crack surfaces. However, with angular glass (AG) rising toughness curves are produced even when there is no expansive agent in the matrix. Where the interfacial bond is weak, or there is no bond at all, the crack is attracted to the 'pore' where, as the crack faces open, friction between the angular bridging aggregate and the cement matrix pins the crack faces and toughens the matrix (as shown in Fig. 2b). Without an irregular shape, spherical aggregates are not able to prevent crack face separation (Fig. 2a).

As in a previous study using similar systems [13], examination of crack faces show a higher incidence of

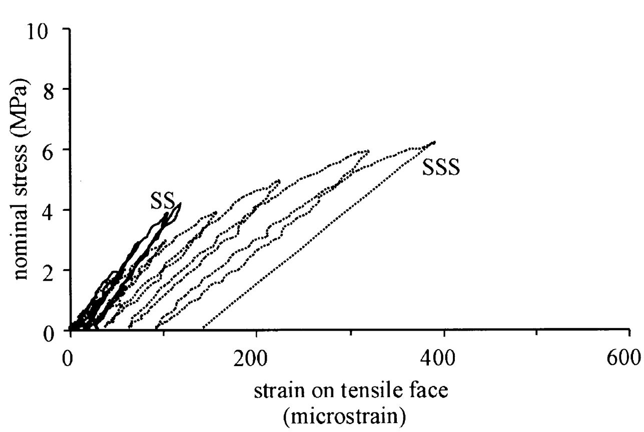

Fig. 9. Stress–strain curves for mortar bars containing steel balls with (SSS) and without (SS) a sodium sulphate addition. Samples were cured at 25°C at 100% RH.

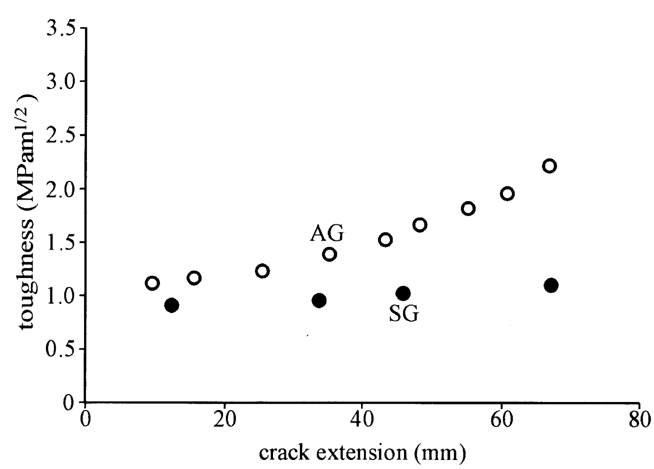

Fig. 11. Toughness curves for plates made with OPC and spherical glass (SG; ●) and angular glass (AG; ○). Samples were cured at 25°C at 100% RH.

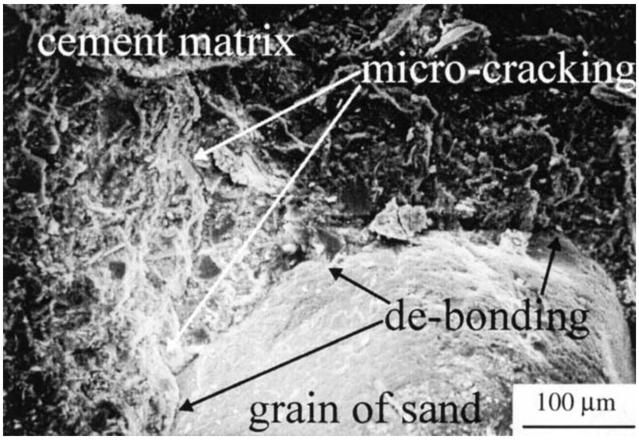

Fig. 12. Scanning electron image of fracture surface of mortar made with OPC, sand and sodium sulphate (NS). Evidence of 'active' debonding due to release of residual stresses. A gap is apparent between the grain and the matrix, and the surface of the grain is smooth — both probable indications of debonding.

exposed aggregate when unbonded aggregates are used, in this case glass. This is a significant observation because again this indicates that propagating cracks are attracted to regions in which aggregates have been debonded from the matrix.

A scanning electron image of a typical fracture surface of a mortar made from OPC, sand and sodium sulphate (NS) is shown in Fig. 12. A large portion of aggregate is clearly visible, a gap surrounding the grain indicating debonding from the matrix. Here, the opportunity for a flat fracture path and crack bridging by the sand grain is provided. The adjacent microcracking may be attributed either to the release of the residual stresses or fracture of the matrix pinned by the grain but further analysis would be required to establish the exact cause.

The roles of aggregate shape, bonding strength and residual stress now become clearer. The rising toughness comes from aggregate-bridging, but in order to bridge a crack an aggregate needs to be nonspherical and be unbonded from the matrix. This can be achieved by either poor bonding in the first place or by the release of residual stresses that induce 'active' debonding in the crack process zone.

We recognise certain limitations of the residual stress mechanism for toughening. Ideally, debonding by this mechanism is desired just prior to arrival of the crack. Premature debonding could lead to deposition of hydration products in the debonded region and mechanical recovery of an interfacial bond. Also, even in systems that remain bonded and retain tensile loads across aggregate–matrix interfaces, the importance of visco-elastic relaxation (creep), which would dissipate the residual stress, must be considered. Both processes could effectively eliminate long-term toughening of mortars and measures to address these issues are currently being developed.

4. Conclusions

The results obtained to date highlight the importance of weak or nonbonded interfaces in the toughening of cement-based mortars. This work has demonstrated that:

- Rising toughness, as opposed to improved toughness, can be achieved by maximising the interaction between cracks and crack-bridging aggregates. This has been achieved by creating aggregate-filled 'holes' (regions in which aggregates have been debonded from the matrix) which attract the crack by appearing to be an easy propagation path.
- The use of expansive additives appears to promote 'active' debonding and enhanced toughness. This is associated with the release of residual stresses, an important toughening mechanism.
- The addition of soluble sulphate produced the best combination of stress–strain and toughness results but the addition of lime showed a steeper toughness curve. This, coupled with the reduced levels of expansion over 28 days, confirmed that the lime admixture has provided the best conditions for improving toughness in the present study.
- Toughness was improved by substitution of OPC by ASTM Type K cement. However, the enhancement was small in comparison with mortars made with sulphate or lime additions to the OPC mortar.
- The use of glass aggregates requires no expansive admixtures to improve toughness. This is due to the poor chemical bond between glass and cement.
- The dependence of the aggregate shape on toughening is critical. The results have confirmed that angular grains are needed to produce effective aggregate-bridging.

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