Discussion

Comments on "The mechanical properties and tensile failure mechanism of a high strength polymer modified Portland cement"

A recent paper by Eden and Bailey [1] concerning the mechanical properties of polymer-modified Portland Cement (often known as MDF cement) explains the tensile strength with the aid of a model in which failure occurs by the pulling apart of hydrate fibrils. This promotes us to make two points.

1. A fibrillar hydrate morphology does not appear by transmission electron microscopy to be a prominent feature of OPC-based MDF cement pastes and furthermore, fibrils are not observed to protrude from the fracture surfaces of such pastes, an example of which is shown in Fig. 1.

2. Elevated mechanical properties are obtained in cements other than OPC (such as calcium aluminate cements and glass-ionomer cements) in which the mechanism of setting is totally different from that in OPC and in which fibrillar morphology does not occur at all [2]. Fig. 2 shows the micro-

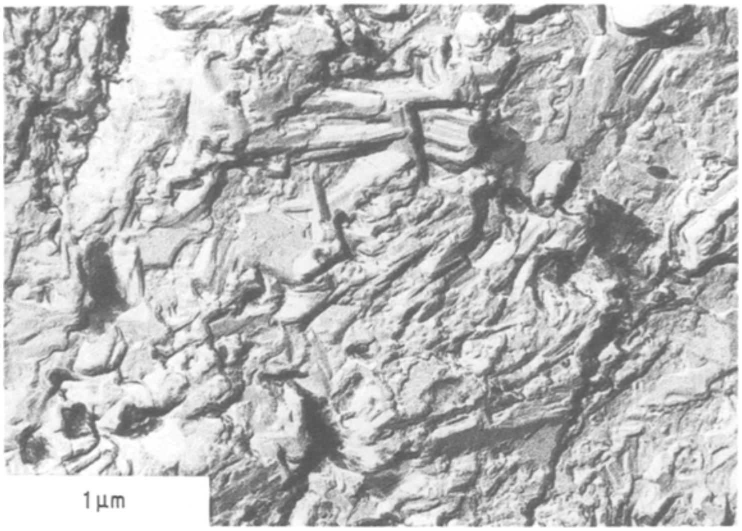

Figure 1 Carbon replica of a fracture surface of OPC macro-defect-free (MDF) cement. A dense gel structure is shown with no evidence of fibrillar morphology. Note that Eden and Bailey conjecture 10^{12} fibrils m^{-2} having dimensions $l =$ 0.5 to 1.0 μm and $d =$ about 0.3 μm.

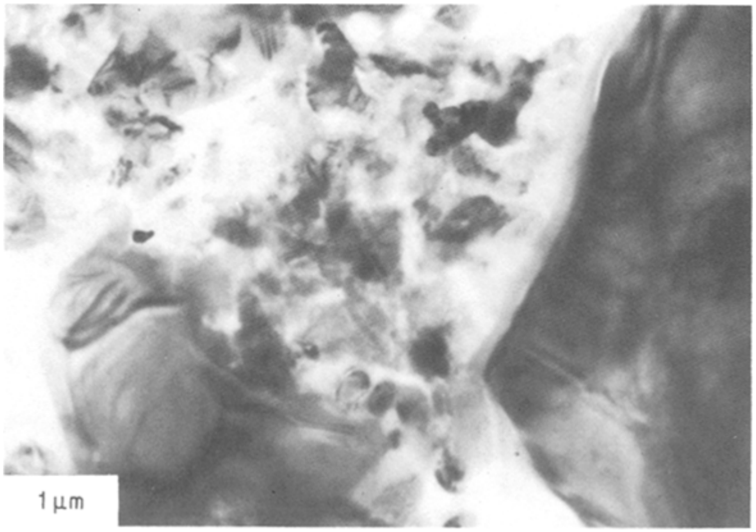

Figure 2 Transmission electron micrograph of aluminate cement (Secar 71, Lafarge). Non-fibrillar hydrated material is shown (centre) between two clinker grains.

0022–2461/85 $03.00 + .12

structure of a calcium aluminate-based MDF cement paste consisting of crystalline particles together with a dense amorphous phase.

We prefer to explain high mechanical properties in terms of the porosity characteristics of these materials [3–5].

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Reply to 'Comments on "The mechanical properties and tensile failure mechanism of a high strength polymer modified Portland cement"'

We thank Alford, Birchall, Groves and Kendall for raising some issues regarding our recent paper. We are aware that microstructural evidence for the model is lacking; however, it is the only model published so far which adequately explains the changes in mechanical properties on drying polymer-modified Portland cement, and the effect of polymer content on the magnitude of these changes. This latter is not explicable in terms of porosity characteristics alone. The model is based primarily upon fracture mechanics studies and optical microscopy of conventional Portland cement paste, and its usefulness in explaining the mechanical properties of the materials studied was considered sufficient reason for proposing it.

There seems no doubt that fibrillar, foil-like and platelet morphologies are found in Portland cements of conventional water/cement ratios, i.e. above 0.3 [1], and that cementing of neighbouring grains occurs by interaction of these outgrowing hydrates. Furthermore, in the absence of clear evidence to the contrary, it is reasonable to extrapolate these findings to higher-density polymer-modified cement.

Two points must be raised here with regard to the visibility of microstructural evidence of fibrillar pull-out. Firstly, it is not immediately obvious what morphology will appear on the fracture "surface" after pull-out. A picture of a plane surface with well-spaced and easily definable fibrils jutting out is unlikely, because we might expect the surface to have a mottled appearance as the ratio of "holes" to "fibrils" should be close to unity. Secondly, it must be emphasized that the development of the "tied-crack" process zone occurs prior to peak load, and as such is related to failure origin, and not necessarily to rapid crack propagation after the peak load has been attained. In a flexural test specimen, we would expect this area to be at most a semi-circle with a diameter of the order of the zone length in conventional hardened cement paste, i.e. 1 mm [2], most likely on the tensile face of the specimen, and as such will occupy only a small fraction of the total fracture surface. For instance, even on a small specimen of cross-sectional dimensions 12 mm × 6 mm, this would constitute no more than about 0.5% of the total projected fracture surface area. Examination of the fracture surface by random sampling would be unlikely to pick this up.

Further work is required to examine the possibility of changes in the growth pattern of calcium silicate hydrate brought about by the

0022–2461/85 $03.00 + .12

polymer; our model presumes only a purely physical interaction between hydrates and polymer.

The second point by Alford *et al.* involves the use of hydraulic cements other than Portland, and also that of glass-ionomer cements where a chemical reaction between the glass and polymeric acid is the mechanism of setting and hardening, rather than reaction of the solid material with water. We are aware of the published data on polymer-modified calcium aluminate cements, though at present no detailed study of the fracture mechanics of both unmodified and modified calcium aluminate cement pastes, upon which to base a model of failure, has been published. There is no reason to presume that the fracture mechanics will be the same as those of Portland cement, as the hydration mechanism is so different.

Preliminary results of our investigations of polymer-modified calcium aluminate cements indicate that the development of mechanical properties is very different to that in the Portland cement detailed in our paper, and is very likely due to differences in the mechanism of hydration. Although direct comparisons are difficult because of this very reason, we have found that after curing, mixtures of calcium aluminate cement (Secar 71, Lafarge) and polyvinyl acetate/alcohol (Gohsenol KH 17S, Nippon Gohsei) designed to give strengths in excess of 150 MPa (e.g. 10 to 12% polymer by volume) do not possess the properties found after curing Portland cements, i.e. rigidity and moderate strength (e.g. 30 MPa) but are distinctly flexible and rubbery. On drying at ambient humidity, a flexural strength of about 100 to 120 MPa is rapidly attained, whilst the Young's modulus remains relatively low, generally under 30 GPa. On warm drying at 80° C both flexural strength and modulus increase markedly, to about 150–170 MPa and 45–50 GPa respectively. Both of these drying stages are accompanied by significant volume shrinkage. Birchall [3] has recorded a net volumetric drying shrinkage of about 10%, together with a shrinkage during curing.

These volume changes were not found by us to occur in polymer-modified Portland cement, and we consider that this is because of the nature of Portland cement hydration. Hydrates grow out from the surface of grains and interlock, forming a rigid network which is able to resist the forces of contraction exerted by the dehydrating polymer gel. Cements such as calcium aluminates, which do not hydrate by this mechanism, have the potential of forming an intimate mixture of hydrates and polymer molecules with fewer solid–solid contacts, hence producing the initial rubberiness and relatively low ambient modulus. Such a mixture would much more readily pack together as the polymer dehydrates, to form a non-porous finished product. The morphology of the calcium aluminate hydrates, many of which are platey [4], may affect the properties of such a material.

In conclusion, we would agree that clear microstructural evidence of the failure mechanism in Portland cement is still lacking, but would be cautious in drawing comparisons between different types of hydraulic cements which have different hydration mechanisms and are known to behave differently when modified by the addition of polymers.

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