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On the fracture toughness of calcium aluminate cement–phenol resin composites

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Abstract

Macro-defect-free (MDF) cement with high flexure strength has been an active research area over several decades. To study the tensile properties of these materials, it is essential to understand the mode I crack propagation. In this article, cleavage cracking in calcium aluminate cement (CAC)–phenol resin composites is analyzed based on an energy method. The crack-trapping effect of the cement particles is found to be significant. The fracture toughness rises with the particle size and is independent of the spacing between the particles. When the cement volume fraction is higher than a critical value the effective work of separation of the phenol resin decreases with the particle content with a coefficient of -1.88.

Keywords: Fracture toughness; Tensile properties

1. Introduction

Macro-defect-free (MDF) cements have received great attention since early 1980s due to the excellent mechanical properties [1–3]. Associated with the decreasing of the porosity and the chemical reactions in the polymer phase involving ions released from cement particles [4], the flexural strength of MDF cements can be as high as that of structural steels [5,6]. Calcium aluminate cement (CAC) was found to be one of the best host cements. To produce the MDF cement, cement particles, plastisizers, polymers, such as poly(vinyl alcohol), phenol–formaldehyde resin, or nylon, as well as a small amount of solvent, such as water or methanol, should be combined in a low-shear planetary mixer and then roll-milled. Then the material is calendared into sheet and heat-treated to complete the polymerization process [3]. The MDF cement consists of the cement phase, the polymer phase, and the interphase. The interphase is formed through the reactions of the polymers and the hydration products. In the cement phase, the bulk material is partially anhydrous and could be partially replaced by other fillers [7,8].

MDF cements potentially have great applicability in structures where tensile stresses are significant. However, to implement these materials in engineering practice, the fracture behavior must be understood adequately. In an experimental study on CAC–phenol resin composites [9], it was found that, due to the strong CAC–phenol resin bonding, the fracture mostly occurred through the phenol resin matrix and the cement phase acted as reinforcing particles, as shown in Fig. 1 [9]. Although the phenol resin matrix was greatly toughened by the high-degree cross-linking through calcium and aluminum ions, the fracture mode was pure cleavage, resulting in the brittle behavior of the composites that fit well into the Griffith curve.

In a brittle matrix reinforced by well-bonded, tough particles, the crack-trapping effect of the particles causes additional resistance to cleavage cracking and the overall fracture toughness should increase with the particle content. However, experimental data [9] showed that in CAC–phenol resin composites, once the volume fraction of the cement particles, c, exceeds 60–70%, the flexural strength decreases significantly, which was attributed to that with high cement content the particles could not be fully lubricated.

To obtain the optimum mechanical properties and cost–performance balance, the cement content in MDF cements should be maximized. Understanding the cleavage-cracking

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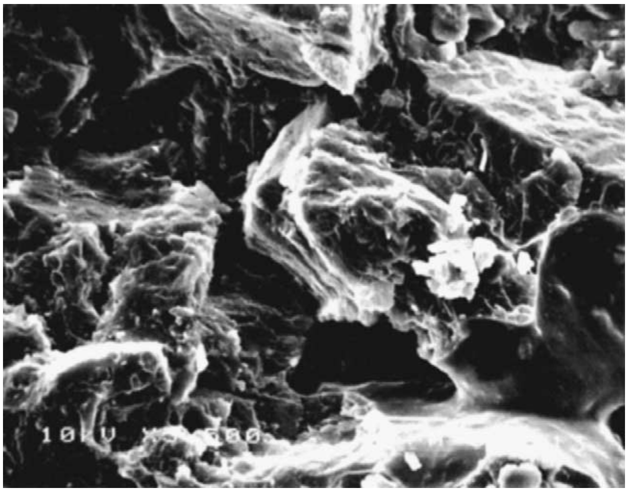

Fig. 1. SEM micrography of the fracture surface in a CAC–phenol resin composite [9].

behavior of these materials is of both basic scientific interest and immense technological importance. Currently, there is still no satisfactory model for the complicated crack-trapping effect of close packed hard particles. In this article, this phenomenon will be studied based on an energy method and the relationship between the fracture toughness and the cement content will be quantified.

2. Toughening effect of cement particles

In the brittle phenol resin matrix, the toughening effect of the cement particles is associated with both the additional work of separation and the crack-trapping effect. The cleavage front will be trapped locally when it encounters an array of cement particles. When the critical energy release rate G_{IC} is reached, the front will overcome the resistance offered by the particles and keep propagating unstably until it is arrested by the next array. If the cement content is relatively high, the particles are separated from the matrix before the front fully bypasses them, i.e., the separation occurs simultaneously with the onset of the unstable crack advance. Under this condition, the breakthrough processes at different particle arrays should be independent of each other. Neither the absence of the particles that the crack has already exposed nor the presence of the particles ahead of the crack front to be broken through has influence on the value of G_{IC}. Thus, in the following discussion, we will consider only one array of cement particles in the phenol resin matrix as depicted in Fig. 2.

To take account for the fact that the crack plane does not pass the main circle of each particle, the effective radius of particles exposed on the fracture surface, r, should be modified as [10]:

$$r = \sqrt{2/3}r_0 \approx 0.82r_0 \tag{1}$$

where r_0 is the actual particle radius. The volume fraction of the cement particles, c, is

$$c = \alpha\frac{(4/3)\pi r_0^3}{D^3} = \alpha\frac{4}{3}\left(\frac{3}{2}\right)^{3/2}\frac{\pi r^3}{D^3} \approx 7.69\alpha\frac{r^3}{D^3} \tag{2}$$

where α is a coefficient in the range of 1.0–1.91 related to the particle shape and D is the center-to-center distance of the cement particles.

With the increasing of the nominal stress intensity at the crack tip, the crack front stably penetrates between the cement particles. When the critical penetration depth associated with G_{IC} is reached, the particles will be separated from the matrix and, since for reasons that will become clear G_{IC} is larger than the fracture resistance G_{pr} of the phenol resin matrix, the front will jump forward by a distance Δa, until the energy release rate decreases to G_{pr0}, the critical value for the matrix to arrest the propagating crack. Note that according to the experimental observations of dynamic crack advance [11], if the crack jump length Δa is smaller than the initial crack length a_0, the dynamic fracture resistance is about the same as the resistance to a stationary crack, i.e., $G_{pr0} \approx G_{pr}$. The validity of this assumption will be discussed shortly. During the breakthrough process, in addition to the work required to produce the fracture surfaces, significant work needs to be done to overcome the crack-trapping effect. Although this phenomenon has been studied intensively for low volume-fraction particles through the calculation of the sigmoidal crack front profile [12–16], there is still no satisfactory model that can be utilized to predict the front behavior across close-packed particles. It will be shown below that the critical stress intensity factor for the cleavage front to overcome a regular array of tough particles can be calculated through relatively simple energy analysis without simulating the detailed penetration process.

To calculate G_{IC}, consider the double cantilever beam (DCB) specimen depicted in Fig. 3. The major part of the specimen is homogenous phenol resin except for point "A" where the crack tip is trapped by a regular array of cement particles. With the increasing of the crack opening displacement, the energy release rate G_I rises. When $G_I = G_{IC}$, the

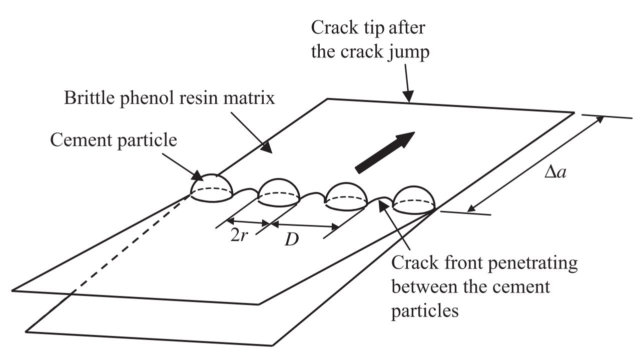

Fig. 2. A schematic diagram of the cleavage front overcoming the crack-trapping effect of a regular array of cement particles.