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Nanoscale characterization of engineered cementitious composites (ECC)

Aaron Richard Sakulich *, Victor C. Li

Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI, 48109, United States

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ABSTRACT

Engineered cementitious composites (ECC) are ultra-ductile fiber-reinforced cementitious composites. The nanoscale chemical and mechanical properties of three ECC formulae (one standard formula, and two containing nanomaterial additives) were studied using nanoindentation, electron microscopy, and energy dispersive spectroscopy. Nanoindentation results highlight the difference in modulus between bulk matrix (~30 GPa) and matrix/fiber interfacial transition zones as well as between matrix and unreacted fly ash (~20 GPa). The addition of carbon black or carbon nanotubes produced little variation in moduli when compared to standard M45-ECC. The indents were observed by electron microscopy; no trace of the carbon black particles could be found, but nanotubes, including nanotubes bridging cracks, were easily located in ultrafine cracks near PVA fibers. Elemental analysis failed to show a correlation between modulus and chemical composition, implying that factors such as porosity have more of an effect on mechanical properties than elemental composition.

1. Introduction

Engineered cementitious composites (ECC) are ultra-ductile fiber-reinforced ordinary Portland cement (OPC)-based composites. The extreme tensile strain capacity of ECC (>3%) is hundreds of times larger than that of ordinary concrete [1]. This ultra ductility is the product of controlled distributed microcracking under tensile forces caused by a low loading (<2 wt.%) of short polymer fibers. The development of ECC has been aided by micromechanical models that predict the behavior of ECC formulae based on fiber/matrix interactions.

The unique properties of ECC are the result of mechanical properties that have their origin on the nanoscale. The most important of these are the fiber/matrix interface, which dictates the behavior of fibers during loading, and the composition of the calcium silicate hydrates (C–S–H) that make up the main binding phase in OPC, which dictates the initiation and behavior of cracks during loading [1]. C–S–H is not a homogeneous material, and occurs in the form of nanoscale grains mixed with nanoscale porosity [2]. High density 'inner product' C–S–H and low density 'outer product' C–S–H [3–5] exist, and have different mechanical properties. A possible third, ultra-high density phase consisting of C–S–H and portlandite has recently been described [6,7].

In addition to ECC formulae containing large quantities of fly ash [8] or granulated ground blast furnace slag [9] for increased sustainability, several ECC formulae containing nanomaterials have been developed. Carbon buckyballs have been investigated as a replacement for superplasticizers [10] while carbon black and carbon nanotubes are being investigated as methods of altering electrical properties.

Such nanomaterial additives are becoming more and more commonplace in traditional cements. In addition to carbon black and carbon nanotubes [11,12] being used to alter electrical properties, nanoclays have been used in ordinary cement to tailor porosity [2], and titanium dioxide has been used to tailor photocatalytic properties [13]. Other common admixtures, such as superplasticizers and silica fume, have nanoscale attributes.

This study is meant to address three gaps in the current understanding of the behavior of nanomaterial-modified ECC materials: 1) to obtain a more accurate understanding of the mechanical properties of ECC below the microscale; 2) to observe the influence that two nanomaterials (carbon black and single-wall carbon nanotubes) have on these properties, and 3) to attempt to observe the location and disposition of carbon nanotubes, which could theoretically bridge submicron-sized cracks for which micro- or macrofibers are ineffective. Electron microscopy is used here for elemental analysis and to image indentation sites, carbon nanotubes, and general morphology. Microindentation techniques that once made up the bulk of cement indentation research [14,15] have been passed over in favor of nanoindentation techniques that provide information about the nanoscale mechanical properties of cements [3,16–20]. These nanoindentation experiments provide a detailed description of the variation of moduli across the fiber/matrix interface.

2. Materials and methods

2.1. Sample preparation

Three ECC formulae were tested. The first, a basic M45 formula without additives, provided baseline data on the mechanical properties of the various phases in ECC as well as the level of

* Corresponding author. 2350 Hayward St., G.G.Brown Building, Room 1022, Ann Arbor, MI, 48109, United States. Tel.: +1 267 752 8119; fax: +1 734 764 4292.
E-mail address: asakulic@umich.edu (A.R. Sakulich).

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