Effects of silica additives on fracture properties of carbon nanotube and carbon fiber reinforced Portland cement mortar

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ABSTRACT

Fiber reinforcements provide many benefits to cementitious composites, including reduction of crack widths and increases in ductility. However, the interfacial transition zone between fibers and hydrated cement can contain a high proportion of calcium hydroxide and porosity. With their high moduli of elasticity, carbon nanotubes and carbon fibers could provide substantial mechanical reinforcement at multiple length scales, but only if their bond to the matrix can be controlled. Surface treatments of fibers and addition of supplemental materials in the matrix can influence both the mechanical interaction at the interface and the dispersion of these relatively small reinforcements. We performed a broad study of Portland cement mortar mixtures containing silica fume, plain or silica-functionalized carbon nanotubes, and carbon fibers to characterize changes in fracture properties. The early age hydration kinetics of cement pastes containing carbon nanotubes were compared using isothermal calorimetry. Early age fracture surfaces of cement pastes containing carbon fibers were observed using a scanning electron microscope. The notched beam test method of the Two Parameter Fracture Model was used to determine the fracture properties of each mix. We observed that silica fume and silica functional groups improved the fracture performance of mixtures containing carbon nanotubes and carbon fibers. Further optimization of dosage, size, and interface strength is required to fully utilize carbon nanotubes in cementitious composites.

1. Introduction

For many years, concrete engineers have reinforced cementitious composites with micro- and macro-fibers made of various materials to control plastic shrinkage cracking [1], improve abrasion resistance [2], maintain small crack sizes to enhance durability [3], and impart a strain hardening characteristic to a traditionally brittle composite [4]. The mechanism of failure of fiber-reinforced concrete (FRC) is well described in the literature, perhaps best by the Aveston, Cooper, and Kelly (ACK) model of multiple cracking [5]. Fibers are loaded by longitudinal elastic shear until either the fiber fractures or the shear strength between the fiber and matrix is reached, at which point a frictional pull-out failure mode is observed. Therefore, one should focus separately on the elastic and frictional components of fiber contributions to mechanical properties. Fibers exhibiting a greater modulus than cement paste, such as those made from steel or carbon, can carry a significant portion of a load placed on the composite, but only if the elastic bond is strong. On the other hand, the friction during pull-out increases the work required to fracture the composite, thereby raising its fracture toughness. When properly tuned, fiber pull-out also provides a closing stress across cracks, which encourages stable crack growth and multiple cracking in the matrix [6].

Carbon fiber (CF) was first suggested for use in concrete due to its chemical stability and high specific strength and elastic modulus, which typically ranges between 200 and 350 GPa [7]. The properties of carbon nanotubes (CNTs) are even more impressive, with elastic moduli on the order of 1 TPa and aspect ratios of up to 10,000 [8]. Recently, scientists have developed hybrid mixtures of CF/CNT FRC to take advantage of the remarkable properties of graphitic structures at multiple length scales. Azhari and Banthia utilized the piezoresistive property of CF and CNT to sense compressive loads and found that the hybrid composite produced the best, most consistent results [9]. Hunashyal and his co-authors

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found that the flexural strength and ductility index of a hybrid CF/CNT FRC exceeded those of their control mixture by an order of magnitude [10]. While these results are promising, there remains a need for characterization and optimization in the area of hybrid CF/CNT FRC.

The interfacial transition zone (ITZ) between the hydrated cement matrix and fiber reinforcements is known to contain high levels of calcium hydroxide and porosity [11]. Densification of this region increases its elastic shear strength, raises the frictional shear stress during fiber pull-out, and discourages crack growth along the length of the fiber. The bond between a cementitious matrix and fiber reinforcement may be improved either by employing additional materials in the matrix, such as fine filler and silica fume, or by chemical or mechanical fiber surface treatments. Some fiber types may take advantage of mechanical anchorage via deformations or fibrillations that reach out into the matrix, but carbon fibers are limited in this regard by their ordered structure and brittle nature, which can contribute to an undesirable fiber rupture failure mechanism [12]. Therefore, it is important to concentrate on the strength of the ITZ between carbon fibers and the matrix in order to enhance the overall reinforcement capacity [13].

Researchers have observed significant improvements in fiber dispersion [14], mixture workability [15], and composite toughness [8,16–18] when using fibers and silica fume together in concrete and mortar. While silica fume traditionally causes concrete to fail in a more brittle manner, densification of the ITZ by the pozzolanic reaction actually increases the toughness of FRC by improving the frictional bond between the matrix and fiber [13,16,18]. Sanchez and Ince applied this concept to carbon nanofiber reinforced cement paste using nano-silica as the supplementary material [19]. They observed considerable pore refinement as did Katz and Bentur [12], but found little change in compressive and splitting tensile strengths. Surface functionalization of CNTs could provide similar benefits by offering chemical bond sites to hydration products and providing steric stabilization or a hydrophilic surface to improve dispersion, but progress in this area is mixed. One study confirmed chemical interactions between cement hydration products and CNT surface functional groups, resulting in modest increases in compressive and flexural strengths over a plain composite [20]. Unfortunately, this experiment lacked a control group containing plain CNTs. On the other hand, when carbon nanofilaments were surface-treated with hydroxyl and carboxyl groups, Abu Al-Rub and his co-authors observed a degradation of the mechanical property improvements brought by the nanofilaments [21]. They attributed the reduced efficacy of treated nanofilaments to decalcification and ettringite formation within the cementitious matrix. We have shown previously that silica functional groups on CNTs improve their dispersion and suspension stability in water [22], but have not presented the mechanical benefits of this treatment in cementitious composites until now. To our knowledge, this article is the first to study the fracture properties of a cementitious composite containing silica-functionalized CNTs as well as those of a CF/CNT hybrid cementitious composite.

2. Materials/methods

2.1. Raw materials

Type I Portland Cement used throughout this study was sourced from Continental Cement Company, Hannibal, MO. Microsilica Grade 965 having loss on ignition of 2.88% and 0.01% water content, with less than 1.5% of particles over 45 μm in diameter, was obtained from Elkem Materials, Inc., Charleston, WV. Natural river sand from Prairie Material, Champaign, IL, was sieved from a stockpile and graded to ASTM C778 specifications. ADVA Cast 575 HRWR was procured from Grace Construction Products, Cambridge, MA. Panex 35 dried (Type-01), chopped CF in 6 mm length, having a tensile modulus of 242 GPa, was obtained from Zoltek Corporation, St. Louis, MO. The CF was ordered without sizing to avoid adding incompatible compounds to the mortar mixture. Multiple-walled plain CNTs (herein designated as pCNTs) with diameters of 20–40 nm and lengths of 0.5–40 μm were obtained from Helix Material Solutions, Richardson, TX. Silica-functionalized CNTs (denoted as sCNTs) were prepared according to a procedure reported previously by the authors [22].

2.2. Isothermal calorimetry

The rate of heat evolution during early age cement hydration indicates the hydration rate, so we can determine the effects of CNTs and silica functional groups on cement hydration using a calorimeter. A TAM Air eight channel isothermal calorimeter (TA Instruments, New Castle, DE) measured heat flow from cement paste samples having a water-to-cement ratio of 0.485. During each test, four channels measured plain cement paste specimens while the remaining four channels measured cement paste containing CNTs. Dispersions of 51.5 mg of either pCNTs or sCNTs in 10 mL of water were prepared separately before mixing in order to provide a 0.25 wt% ratio of CNTs to cement. A higher dosage was used for calorimetry than for mechanical testing in order to amplify differences in the heat of hydration. The dispersions were sonicated for 3 min using a 3 mm probe at the 30% amplitude setting (EW-04714-52, Cole-Parmer, Vernon Hills, IL). Approximately 540 J of energy was input to the system during sonication. After equilibrating all materials to 22 ± 1 °C, mixing was performed manually for 90 s before sealing the ampoules and loading them into the calorimeter, which was set to 22 ± 0.1 °C. A calculated mass of reference quartz sand balanced the heat capacity between the sample and reference ampoules. Results were normalized to the mass of cement within each sample.

2.3. Preparation of mortar beams

Dispersion is an important discussion point when using strongly hydrophobic CNTs in water-based materials like cementitious composites. Yazdanbakhsh and his co-authors have modeled the maximum achievable dispersion of CNTs in cement paste and discussed the challenges of CNT movement in the plastic state, among other issues [8,23]. A state of truly monodisperse CNTs is difficult to achieve and even more difficult to characterize [24]. Many researchers have incorporated surfactants, including commercially available water reducing admixtures, to solve the problem of agglomeration of CNTs, but they often affect mixture workability or cement hydration [25]. Surface functionalization of CNTs improves their dispersibility in water, but can also affect workability [22,26]. Unfortunately, due to the nature of dispersing agents and surface treatments, it is difficult to control separately the dispersion of CNTs and the workability of the overall mixture. During preliminary work, we identified a strong dependence of fracture parameters on the workability of mortar mixtures as measured by the standard flow test. Stiff mixtures were difficult to compact into the thin beam molds and wet mixtures suffered from segregation, resulting in large differences in the cast unit weight between stiff and wet mixtures. Therefore, for this study, we chose to control the flow across mixtures using high range water reducing admixture (HRWR).

Table 1 indicates the four variable constituent proportions for the ten mortar mixtures studied here. The ratio of water to cementitious material to sand in all mixtures was maintained at 0.485:1:2.75 as recommended by ASTM C109 and ASTM C348.