Cement and Concrete Composites 65 (2016) 101–109

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Influence of carbon nanofiber clustering on the chemo-mechanical behavior of cement pastes

Lesa Brown, Florence Sanchez*

Department of Civil and Environmental Engineering, Vanderbilt University, PMB #351831, 2301 Vanderbilt Place, Nashville, TN, USA

ARTICLE INFO

Article history:
Received 3 January 2015
Received in revised form
26 August 2015
Accepted 7 October 2015
Available online 22 October 2015

Keywords:
Carbon nanofibers
Durability
Decalcification
Cement-based materials
Agglomeration

ABSTRACT

The influence of carbon nanofiber (CNF) clustering on the chemo-mechanical behavior of cement pastes subjected to a decalcifying environment was studied. Portland cement pastes with and without CNFs were exposed to a concentrated solution of ammonium nitrate to accelerate decalcification. Microstructural changes and evolution of the porosity were examined as a function of exposure duration. Changes in the flexural response of the cement paste with CNFs were studied and reviewed in relation to CNF clustering and microstructural evolution. Results showed a strong coupling between decalcification, CNF clustering, microstructural evolution, and the flexural properties of the cement paste. After 7 days of decalcification by NH_4NO_3, the CNF clusters acted as weak zones that reduced the flexural strength retention of the cement paste. However, after 125 days of decalcification by NH_4NO_3, a dissolution-filling mechanism within the clusters created a better bond with the surrounding cement paste, slowing down the loss of flexural strength and providing added ductility to the cement paste.

1. Introduction

Carbon nanotubes/nanofibers (CNTs/CNFs) possess a number of unique properties, including exceptional mechanical properties and high aspect ratios, that make them attractive for reinforcement of cement-based materials at the nano-level [1–3]. The contribution of CNTs/CNFs to the reinforcement is strongly dependent upon their distribution and arrangement in the cement matrix – CNT/CNF clustering has proven to be a critical factor in influencing the material mechanical and electrical properties [4]. Despite much effort to homogeneously disperse CNTs/CNFs in the cement matrix [5–7], there is still evidence of the presence of localized sub-micro and micro-scale clusters and inhomogeneous distribution of CNTs/CNFs [5,7–12]. While the occurrence of CNT/CNF clustering may constitute a defect causing a loss of mechanical properties, it may not always be undesirable. For example, it has been shown for polymer composites to enhance certain mechanical properties [13] and to favor the formation of a percolating network for electrical conductivity [14–16]. During their service life, cement-based materials are subjected to a wide variety of weathering induced degradation. Given that perfect dispersion at the individual fiber level may not be achievable and that controlled clustering may even be desirable for certain applications, it is therefore critical to understand the effect of CNT/CNF clustering on the durability of cement-based materials exposed to aggressive environments.

Decalcification is closely associated with various types of concrete degradation [17], including during sulfate attack and leaching by exposure to neutral or acidic waters. It is a complex dissolution-diffusion process that involves the removal of calcium from the cement paste and results in both chemical and physical degradation. A loss of cohesion of the cement paste, an increase in porosity, and a decrease in the mechanical properties are all common manifestations of decalcification [17,18]. While the addition of CNFs is anticipated to improve the cement paste durability through pore refinement [19,20] and by increasing the cohesion of the paste, the influence of a non-uniform dispersion of the CNFs, specifically CNF clustering on the cement paste during exposure to a decalcifying environment, is unclear. Yet, CNF clustering is expected to introduce a secondary porosity into the cement paste, which could significantly impact the chemical and mechanical property evolution during decalcification. This paper focuses on CNFs in Portland cement paste and reports on the effects of CNF clustering on the chemo-mechanical behavior of cement pastes subjected to a decalcifying environment. Portland cement pastes with and without CNFs were exposed to a concentrated solution of ammonium nitrate to accelerate decalcification. Microstructural changes

* Corresponding author.
E-mail address: florence.sanchez@vanderbilt.edu (F. Sanchez).

http://dx.doi.org/10.1016/j.cemconcomp.2015.10.008
0958-9465/

and evolution of the porosity were examined as a function of exposure duration. Changes in the flexural response of the paste with CNFs were studied and reviewed in relation to CNF clustering and microstructural evolution.

2. Materials and methods

2.1. Cement paste preparation

Commercially available, vapor grown, Pyrograf® –III PR-19-LHT CNFs (Applied Sciences, Inc., Cedarville, Ohio) were used as received from the manufacturer. Type I/II Portland cement (Lafarge, Nashville, Tennessee) was used as the cementitious material, and a polycarboxylate-based high range water reducer (HRWR), Glenium 7500 (BASF, Ludwigshafen, Germany), was used to promote the dispersion of the CNFs in the cement paste [5,7,21]. Two types of paste were prepared: a plain Portland cement paste (reference cement paste) and a Portland cement paste containing 0.2% CNFs per mass of cement (cement paste with CNFs). The HRWR was used at a loading of 1% per mass of cement, and a water to cement ratio of 0.28 was used for all mixes. The same amount of HRWR was used for both the reference cement paste and the cement paste with CNFs so that any differences seen between the two cement pastes during decalcification could be attributed solely to the addition of the CNFs. The water, HRWR, and CNFs (where applicable) were combined and sonicated with a bath sonicator (Aquasonic model 250D) for 30 min before mixing with the cement powder. After mixing, the pastes were poured into 2.54 cm × 2.54 cm × 69 cm (height × width × length) beam molds and compacted by hand. The beams were allowed to cure at room temperature under 100% relative humidity for a minimum of 28 days and sectioned into shorter beams with a length of 11.5 cm prior to decalcification.

2.2. Accelerated decalcification

After curing, some cement pastes were exposed to a concentrated solution of ammonium nitrate (NH_4NO_3). NH_4NO_3 accelerates decalcification by increasing the solubility of calcium [17]. Decalcification of cement paste by NH_4NO_3 has been shown to be similar to decalcification by water [17,18,22,23]: both yield preferential dissolution of calcium hydroxide (CH) followed by progressive decalcification of the calcium-silicate-hydrate (C–S–H) phases [22]. Each specimen was immersed in an enclosed plastic container containing 1 L of NH_4NO_3 solution at a concentration of 480 g/L (6 M) for 7, 14, 28, and 125 days. Five specimens of each cement paste (with and without CNFs) were immersed for each exposure period. The pH of the solution was periodically monitored to ensure that no renewal of the solution was needed. At the end of each exposure period, the specimens were stored in Milli-Q water until further testing.

2.3. Characterization

2.3.1. CNF cluster and interphase region analysis

The 3D internal physical structure of the cement paste with CNFs was examined using x-ray micro-computed tomography (micro-CT). The micro-CT projection images were acquired using a Scanco Medical μCT50. Each sample was scanned using a voxel size of 20 μm with x-ray source settings of 90 kVp and 200 μA, 1000 projections per 360°, and an integration time of 1000 μs. The Scanco μCT Evaluation Program V6.5-1 and the μCT Ray V4.0-1 3D software were utilized for 2D and 3D image reconstructions. The air voids and CNF clusters were segmented from the cement paste using a threshold of 250 per thousand, a Gaussian noise filter of 1.2, and a Gauss support of 3. Scanning electron microscopy (SEM) analysis was used to confirm the presence of air voids and CNF clusters seen in the micro-CT images. In addition, the 2D spatial and size distributions of the CNF clusters were characterized using the image mapping system of a New Wave UP-213 Laser Ablation System. A total of 1350 images (27.6 × 20.6 pixels each) were collected and assembled into a single image, which represented the entire cross-section of the paste. The CNF clusters were then analyzed by subjecting the image to thresholding techniques and particle analysis using ImageJ, a Java-based open source digital image processing software (National Institute of Health, Bethesda, Maryland, USA). Due to resolution limitations with the image mapping system, only CNF clusters larger than 0.007 mm^2 were included in the analysis.

Microstructural analysis of the CNF clusters and interphase regions before and after decalcification by NH_4NO_3 was conducted using an environmental FEI Quanta FEG 650 high resolution scanning electron microscope (ESEM) equipped with a Schottky field emission gun, digital imaging, and an energy dispersive X-ray spectrometer (EDS). Fracture surfaces and polished surfaces were mounted on an aluminum stage using double-sided carbon tape. Samples were polished using a series of polishing cloths of increasingly finer grit (240, 400, 600, 1200, and 2500). An accelerating voltage of 20 kV, a working distance of 10.5 mm, and a spot size of 3.5 were used for digital imaging and EDS studies. Copper was used as a quantifying element for EDS semi-quantitative work. A pressure of 130Pa was maintained when working in ESEM mode.

2.3.2. Elemental depth profile analysis

Elemental depth profiles of the cement pastes before and after decalcification were obtained by profile grinding and x-ray fluorescence (XRF) measurement of the powder samples using a Thermoscientific Niton XL3 Portable XRF Analyzer. Each exposed paste cross-section was segmented at 2.5 mm increments to obtain XRF samples that corresponded to a depth profile. Each sample was then pulverized into a fine powder and manually compacted into a sample cup for XRF measurements. Relative intensity values obtained from micro-CT projection images were used to calibrate the XRF measurements to account for changes in cross-section density occurring in the cement pastes as a result of decalcification. The relative intensity values of the non-decalcified pastes were used to create a unitless calibration factor (i.e., a ratio of the decalcified paste intensity value at a given location to that of the non-decalcified paste intensity value).

2.3.3. 2D porosity mapping and distribution

A SEM counting technique modified from Ref. [24] was utilized to determine the 2D porosity (areal porosity) distribution of the cement pastes as a function of exposure duration. SEM porosity mapping allows for the examination of porosity changes as a function of location and therefore can capture the degradation-induced porosity gradient occurring during decalcification. The technique involved collecting backscattered electron images from the polished surface of a cement paste cross-section in a grid-like fashion (a minimum of 200 images was collected from each cement paste cross-section). Each image was then processed using MATLAB to yield a gray-scale histogram. The areal porosity of each image was calculated by fitting the primary peak of the histogram with a Gaussian curve. The inflection point in the ascending region of the Gaussian curve was calculated, and the tangent line was computed for that point by taking the analytical first derivative of the Gaussian curve. The threshold value for the areal porosity was then defined as the intersection of the tangent and the abscissa. Once an areal porosity value was calculated for each image, a 3D surface contour plot of the cross-section areal porosity was created utilizing built-in functions in MATLAB. The median areal porosity of the various zones of degradation found throughout the cross-