

Performance of carbon nanofiber-cement composites subjected to accelerated decalcification

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Abstract. The effect of decalcification on the chemo-mechanical behavior of carbon nanofiber (CNF)-cement composites was studied. Portland cement pastes with and without 0.2% CNFs were subjected to accelerated decalcification by exposure to ammonium nitrate solutions. The influence of microstructural alterations during decalcification on the physical and mechanical properties of the composites was examined. The presence of CNF agglomerates influenced the chemo-mechanical behavior of the composite during decalcification. Precipitation of secondary hydrates within the agglomerates during decalcification resulted in a decrease in local porosity, which strengthened the composite and slowed the loss of flexural strength.

1 Introduction

Given the growing interests and economic incentives for extending the safe storage period of nuclear wastes beyond 100 years, it is critical to ensure that the structural integrity of the storage systems can be maintained for long periods of time. Fiber reinforced cement composites provide an excellent alternative for amelioration, protection, and deterioration prevention of the containment structure based on a demonstrated resistance to corrosion, control of crack propagation and exceptional strength to weight ratios [1]. Lately, with the recent advances in nanotechnology, the use of carbon nanofibers (CNFs) in cement composites has received increasing attention due to the promising potential for the development of superior structural and multifunctional materials [2]. CNFs possess a number of unique properties, such as high specific strength, chemical resistance, and electrical and thermal conductivity, making them excellent candidates for nanoscale reinforcement in cement composites [3, 4]. While most studies to date have been conducted to examine the direct structural, mechanical, and electrical properties provided by the CNFs [5-7], the long-term chemical and structural stability of these materials in response to severe conditions such as decalcifying environments and the potential impact of the CNF dispersion on the chemo-mechanical behavior of CNF-cement composites has received little attention.

This paper reports on how microstructural alteration of the cement paste due to decalcification affects the nano-scale reinforcement ability of the CNFs, and in turn, the macro-scale properties of the material. Portland cement pastes with and without CNFs (0.2% per weight of cement) were subjected to accelerated decalcification by exposure to ammonium nitrate solutions [8]. Microstructural and morphological changes within the materials were studied as a function of degradation depth and exposure duration. Mechanical testing was performed and reviewed as a function of exposure duration and in relation to the CNF dispersion state.

2 Experimental approach

2.1 Sample 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 high range water reducer (HRWR), Glenium 7500 (BASF, Ludwigshafen, Germany), was used to promote the dispersion of the CNFs in the cement pastes.

Two types of materials were prepared: a plain Portland cement (PC) paste and a Portland cement paste containing 0.2% CNFs per weight of cement (PC-CNF). The HRWR was used at a loading of 1% per weight of cement. A water to cement ratio of 0.28 was used for all mixes. The water, HRWR, and CNFs (where applicable) were combined and sonicated with a bath sonicator (Aquasonic model 250D) for 30 minutes prior to mixing. After mixing, the cement pastes were poured into beam molds and allowed to cure at room temperature under 100% relative humidity for 28 days.

2.2 Accelerated decalcification

After a minimum of 28 days of curing, PC and PC-CNF specimens were sectioned into beams of size 25.4mm x 25.4mm x 114.3mm and exposed to a concentrated solution of ammonium nitrate (NH_4NO_3) to accelerate decalcification. Decalcification of cement paste by NH_4NO_3 has been shown to be similar to decalcification by water [9-11]. Both leaching processes yield the dissolution of calcium hydroxide (CH) followed by the decalcification of the C-S-H phases [9], but the NH_4NO_3 solution provides an accelerated decalcification (by approximately two orders of magnitude [10]) due to the increased equilibrium calcium solubility of the NH_4NO_3 solution over that of pure water [11]. Accelerated decalcification was achieved by immersing each specimen in an enclosed plastic container containing 1 L of non-renewed NH_4NO_3 solution at a concentration of 480g/L (6 M) for 28 or 125 days. Five specimens of each material type were immersed for each exposure period. The pH of the solution was periodically monitored to determine if renewal was needed. At the end of each exposure period, the specimens were stored in Milli-Q water until further testing.

2.3 Characterization

A FEI Quanta FEG 650 high resolution environmental scanning electron microscope (ESEM) equipped with a Schottky field emission gun, digital imaging, and an energy dispersive X-ray spectrometer (EDS) was used to examine the dispersion of the CNFs within the cement paste and changes in porosity due to decalcification. A scanning electron microscope (SEM) counting technique was utilized to evaluate the changes in porosity. This method involved systematically (in a grid-like fashion) collecting backscatter electron images from the polished cross-section of a specimen and analyzing the gray-scale histogram of each image to determine the porosity. At least 200 images were collected from each specimen cross-section. Porosity measurements from SEM counting techniques provide only a partial porosity measurement due to the fact that fine pores typically cannot be resolved due to the pixel resolution limitation of the image collected [12]. It is possible, however, to compare the porosity values between samples using this technique as long as it is understood that these values are not indicative of total porosity. A Tinius Olsen Super L 60K (300kN) universal testing machine was used to perform flexural testing of the materials at 28 days of curing and after exposure to the NH_4NO_3 solution for 28 and 125 days. A standard 3-point bending set-up and a load rate of 0.1mm/min were utilized for all flexural tests. A minimum of five specimens of each material were used for each test. All specimens were tested in a saturated-surface-dried condition.

3 Results and discussion

3.1 CNF dispersion state

SEM studies of the PC-CNF composite prior to exposure to NH_4NO_3 indicated the presence of CNF agglomerates throughout the cement paste, with an increasing gradient in size and number of agglomerates towards the top surface (as poured in the beam molds) (Figure 1). The CNFs were thought to agglomerate during the mixing and curing process, most likely migrating with the bleed water towards the top surface of the specimens during the first 24 hours of curing [13]. Individually embedded fibers were also found throughout the PC-CNF composite, but the primary dispersion state of the CNFs was in agglomerate form.

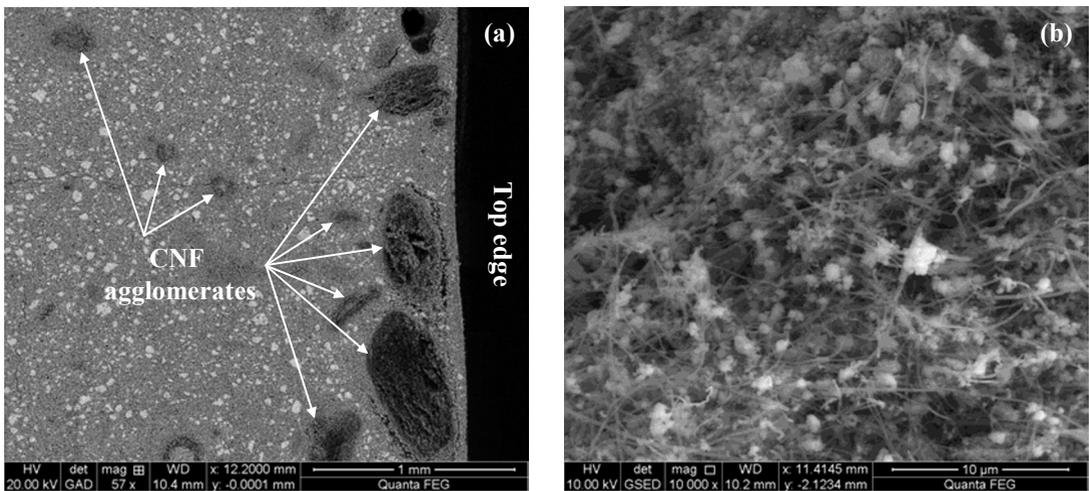


Fig. 1. SEM images of the PC-CNF composite showing (a) the presence of CNF agglomerates and a gradient towards the top edge and (b) the density of CNFs within an agglomerate near the top edge.

3.2 Degradation state of the materials

Visible degradation of the materials was marked by the presence of layers surrounding a dark core, indicating a series of degradation fronts corresponding to changes in local chemistry within the materials (Figure 2). After 28 days of exposure to NH_4NO_3 , both materials exhibited similar degradation layers and depths. After 125 days of exposure, visible degradation of the PC-CNF composite was less than that of the PC paste as seen from the circular shape of the PC paste core compared to the square shape of the PC-CNF composite core. The rounded core for the PC paste compared to the original square shape of the specimen indicated that the diffusion fronts had penetrated more deeply in the PC paste than in the PC-CNF composite. Both materials experienced a mass loss during decalcification as a result of the dissolution of calcium hydroxide and calcium-silicate-hydrate phases. At all stages of decalcification, the PC-CNF composite experienced a mass loss that was statistically lower than the mass loss of the PC paste (Student's *t*-test, $\alpha = 0.5$) (Figure 3). After 125 days of exposure, the PC paste and PC-CNF composite showed average mass losses that were statistically different from each other with an average mass loss of $15.7 \pm 0.1\%$ for the PC paste vs. a $15.3 \pm 0.2\%$ mass loss for the PC-CNF composite (based on 5 replicates for each material).

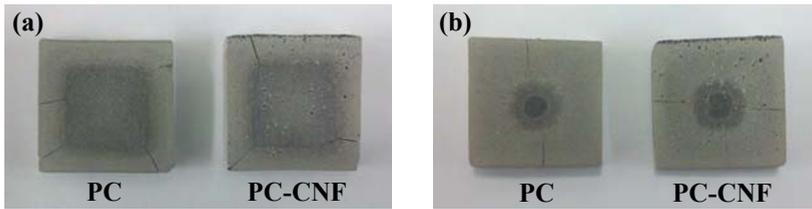


Fig. 2. Visible degradation of the PC paste and PC-CNF composite after (a) 28 days and (b) 125 days of exposure to ammonium nitrate solution.

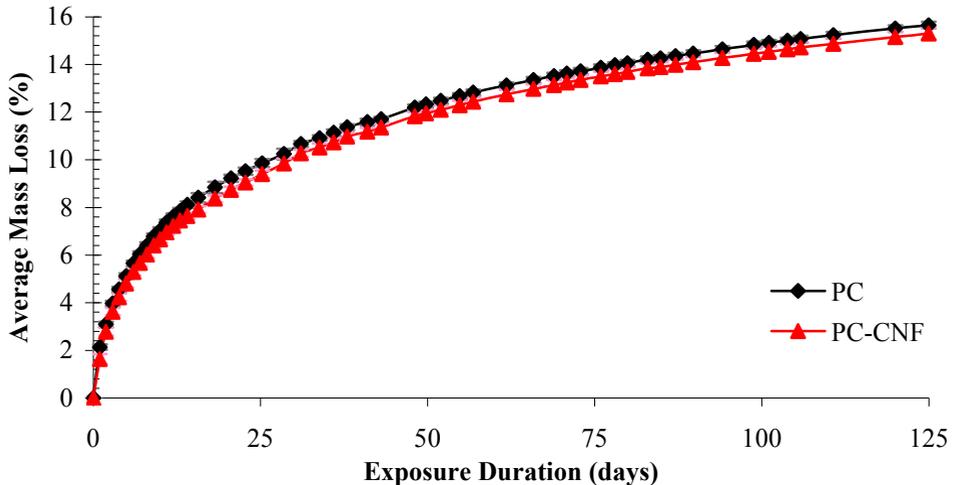


Fig. 3. Mass loss of the PC paste and PC-CNF composite during exposure to ammonium nitrate solution.

3.3 Porosity evolution of the materials during decalcification

Using the SEM counting technique, an average porosity was calculated for each material from the porosity values collected from images of the specimen cross-section (*ca.* 200 images per cross-section). This average porosity represents only a percentage of the total porosity. Prior to decalcification, the PC-CNF composite had a higher average porosity (6.1%) than the PC paste (5.1%). Both materials exhibited slightly higher porosities near the edges, but the PC-CNF composite also had zones of higher porosity spread throughout the cross-section (Figure 4). These zones typically corresponded to the presence of CNF agglomerates, which most likely increased the local porosity due to the different packing density of the CNFs within the agglomerates compared to the surrounding cement matrix. After 28 days of exposure, both materials showed similar average porosities (5.6% for the PC paste vs. 5.4% for the PC-CNF composite). Contour plots (Figure 4) of the PC paste and PC-CNF composite after 28 days of exposure exhibited higher porosities along the outer 3-4mm of the sample, indicative of a degradation front corresponding to the layers seen in Figure 2. The interior ‘cores’ of the materials appeared to be approximately equal in size after 28 days of exposure, although the PC-CNF composite did have a more pronounced gradient of porosity in the outer 3-4mm of the composite. After 125 days of exposure, the average porosity of the PC paste (6.6%) was clearly higher than that of the PC-CNF composite (5.2%). The contour plots of porosity indicated that the PC paste had a smaller interior core compared to the PC-CNF composite and a higher porosity in the outer degraded zone. It is interesting to note that the PC-CNF composite experienced a decrease in porosity as the exposure duration increased (from 6.1% prior to exposure to 5.2% after 125 days of exposure), while the PC paste experienced the opposite trend (increase in porosity from 5.1% to 6.6%). The greater local porosity initially caused by the CNF agglomerates

decreased during decalcification due to a filling effect of the CNF agglomerates as a result of the precipitation of secondary hydration within the agglomerates.

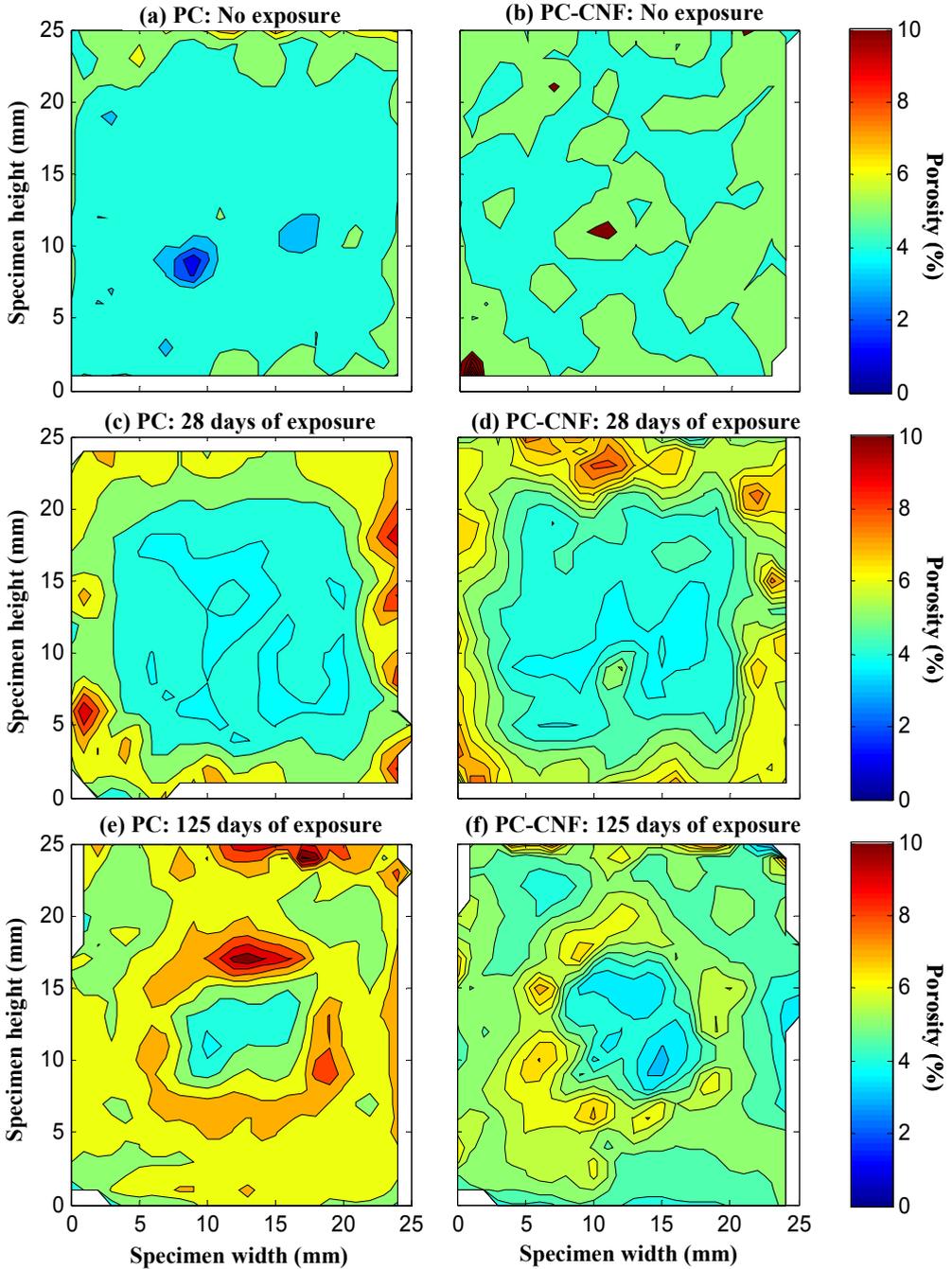


Fig. 4. Porosity contour plots for PC paste and PC-CNF composite, respectively. (a) and (b) before exposure to ammonium nitrate solution, (c) and (d) after 28 days of exposure, and (e) and (f) after 125 days of exposure.

3.4 Mechanical performance of the materials

Flexural strengths of the PC paste and PC-CNF composite before and after immersion in the NH_4NO_3 solution are shown in Figure 5. Both materials experienced a steady decrease in flexural strength as the exposure duration increased. After 28 days of exposure to decalcification, the PC-CNF composite experienced a stronger reduction (41% of the original strength) in flexural strength compared to the PC paste (34%). The initial greater porosity of the PC-CNF composite due to the presence of the CNF agglomerates may have influenced the mechanical behavior of the composite at early stages of exposure. However, after 125 days of exposure, the PC-CNF composite experienced a smaller reduction in strength (58%) compared to the PC paste (65%). The decrease in porosity seen in the PC-CNF composite after 125 days of exposure provided a better interaction of the CNFs with the surrounding cement paste which strengthened the PC-CNF composite and slowed the flexural strength loss.

As decalcification progressed, the flexural failure behavior of both materials evolved to a more ductile behavior as shown by the decrease in flexural modulus throughout all exposure durations (Figure 6). The flexural modulus of the PC-CNF composite was lower than that of the PC paste both before and after exposure to NH_4NO_3 solution. The fracture toughness of the materials was also affected by decalcification, with a decrease seen for both materials (Figure 6). After 125 days of decalcification, the PC-CNF composite had a better retention of fracture toughness (41%) compared to the PC paste (31%). The ability of the PC-CNF composite to maintain a lower flexural modulus during decalcification and a higher fracture toughness indicated that the CNFs provided the composite with a more pronounced ductility during flexural failure.

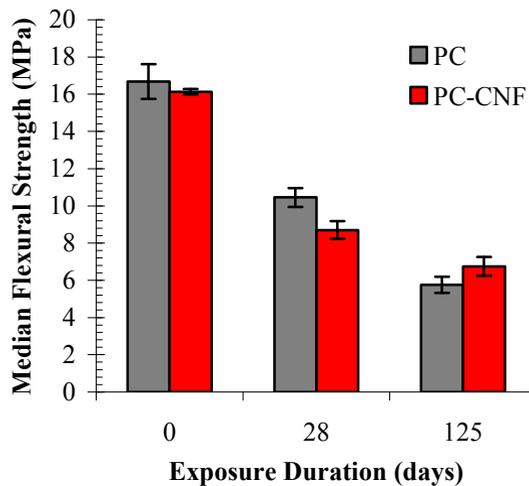


Fig. 5. Flexural strength of the PC paste and PC-CNF composite before and after exposure to ammonium nitrate solution.

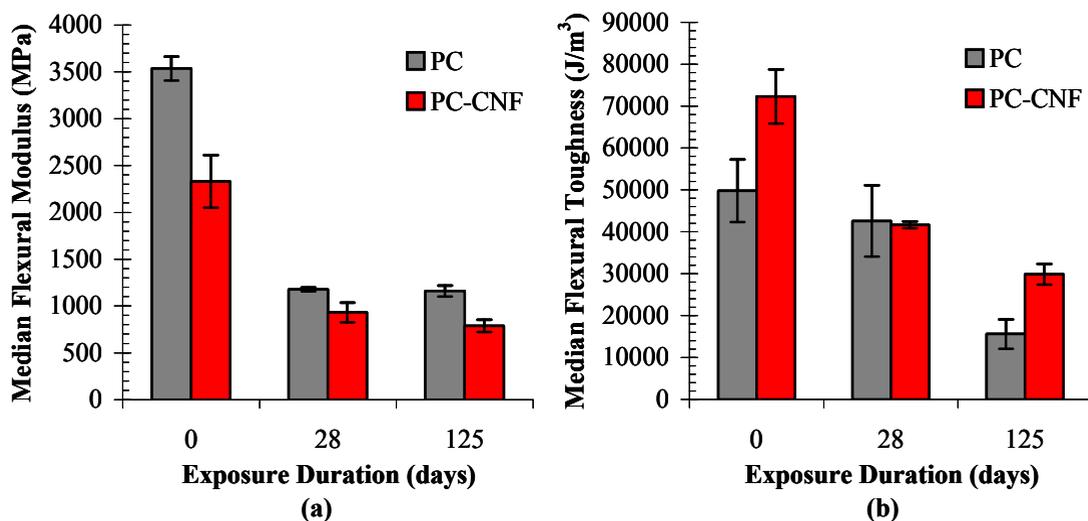


Fig. 6. (a) Flexural modulus and (b) flexural toughness of the PC paste and PC-CNF composite before and after exposure to ammonium nitrate solution.

4 Conclusions

The effect of decalcification on the chemo-mechanical behavior of cement pastes with and without CNFs was investigated. The CNF dispersion state was primarily in agglomerate form, although individual fibers were also found throughout the PC-CNF composite. The visible degradation and mass loss of the PC-CNF composite due to exposure to ammonium nitrate solutions were generally less than that of the PC paste. The greater initial porosity due to the presence of CNF agglomerates influenced the mechanical performance of the composite at early stages of degradation by allowing the aggressive solution to penetrate more rapidly, resulting in a lower flexural strength retention (i.e. greater loss of flexural strength). However, at late stages of degradation, a decrease in local porosity indicated a filling effect of the agglomerates, most likely due to precipitation of secondary hydrates within the CNF agglomerates. This provided a better interaction of the CNFs with the surrounding cement matrix and slowed the loss of flexural strength. At all stages of decalcification, the PC-CNF composite showed a more ductile flexural failure compared to the PC paste.

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