Crack Free Concrete Made with Nanofiber Reinforcement

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Mechanical Properties and Nanostructure of Cement-Based Materials Reinforced with Carbon Nanofibers and Polyvinyl Alcohol (PVA) Microfibers

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Synopsis: There have been numerous studies that have aimed at improving the low tensile strength, stiffness, and toughness of cementitious materials. This study aims to show that all of these characteristics can be greatly improved by the addition of ladder scale reinforcement at the nano and micro scale. Carbon nanofibers (CNFs) as well as polyvinyl alcohol (PVA) microfibers were used as reinforcement. The mechanical properties of the nanocomposites were investigated by fracture mechanics three-point bending test. The microstructure and the morphology of nanocomposite samples were studied using an ultra high resolution scanning electron microscope (SEM). The results clearly illustrate that the incorporation of nanofibers and microfibers greatly improves the flexural strength, Young's modulus, and toughness of the cement matrix.

Keywords: carbon nanofibers; hybrid composites; mechanical properties; nanofiber reinforcement; polyvinyl alcohol microfibers; scanning electron microscopy.

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INTRODUCTION

Failure in cement based materials is a gradual multi-scale process. When loaded, initially short and discontinuous microcracks are created in a distributed manner. These microcracks coalesce to form large macroscopic cracks, known as macrocracks. Fibers bridge cracks and transfer the load, delaying the coalescence of cracks. Due to the multi-scale nature of fracture, the influence of fibers in reinforcing cement based materials, mainly depends on the scale of reinforcement. Macrofibers (typically defined as fibers with diameters greater than 500 μm [0.02 in]) can improve post-peak toughness by bridging macrocracks. Fine microfibers (typically defined as fibers with diameter less than 50 μm [0.002 in]) on the other hand, bridge the microcracks which delay the process by which the microcracks coalesce to form macrocracks. However, cracks in cement based materials initiate from the nanoscale where micro-fibers are not effective.

The development of fibers at the nanoscale has opened a new field of research within concrete. Previous research by the authors of this work on reinforcing cementitious materials using nanofibers, such us multi wall carbon nanotubes (MWCNTs), has shown that the flexural strength and stiffness of cementitious matrices can be significantly increased by adding very low concentrations of homogenously dispersed carbon nanotubes (as little as 0.025% by weight of cement)[1]. Nanoimaging of the fracture surfaces of cement nanocomposites have shown that MWCNTs reinforce cement paste by bridging nanocracks and pores, indicating that the addition of MWCNTs can enable the control of the matrix cracks at the nanoscale level[2]. The nanoindentation results have indicated that MWCNTs can strongly modify and reinforce the nanostructure of the cementitious matrix by increasing the amount of high stiffness C-S-H and reducing the nanoporosity[3-4]. Besides the benefits of reinforcement, autogenous shrinkage results have shown that MWCNTs can also have beneficial effects on the transport properties of cementitious materials[5].

Recently in the field of fiber reinforced concrete there has been much enthusiasm for the development of hybrid fiber systems where two or more types of fibers are combined. Hybrid fiber systems are a promising approach for making efficient use of fibers with the intent of conferring the best performance characteristics of each of the constituent fiber types to the composite material[6]. Recent work at ACBM has shown that fiber hybridization effectively enhances the material performance. The mechanical properties of cementitious composites were improved by using fibers of varying sizes and moduli. Use of hybridization was also shown to enhance the mechanical performance of extruded high performance fiber reinforced cement composites. Peled et al.[7] as well as Cyr[8] examined the effect of combining low modulus polypropylene microfibers (PP) with high strength and high modulus glass or polyvinyl alcohol (PVA) microfibers in extruded composites. They found that the addition of PVA microfibers to glass/PP hybrid composite significantly increases strength and toughness. Lawler et al.[9-11] reinforced concrete and mortar with steel macrofibers and steel or PVA microfibers. The macrofibers enhanced the post-peak performance, increasing the composite ductility. The microfibers increased the strength of the composite. The hybrid-reinforced composite was stronger and tougher than singly-reinforced composites. To date, all the efforts have been concentrated in combining microfibers with macrofibers. However, current research has shown that the fundamental properties of concrete are affected by the material properties at the nanoscale. With this premise, the main objective of the present study is to examine the effects of nanofibers and microfibers on the mechanical properties and structure of cementitious composites.

In the work presented here, the characteristics of cement paste containing ladder scale reinforcement using carbon nanofibers (CNFs) and PVA microfibers were investigated. Scanning electron microscopy (SEM) was employed to investigate the nanostructure of the nanocomposites. Fracture mechanics three-point bending tests were performed to determine the effect of CNFs and PVA microfibers on the flexural strength, Young's modulus and toughness of the cementitious matrix.

RESEARCH SIGNIFICANCE

Cement based materials are complex materials consisting of several phases. In order to effectively reinforce and improve the response of cementitious materials to loading, crack growth must be abated at the macro, micro, and nano level. This research investigates the reinforcing efficiency of nanofibers, microfibers and the combination of both. The goal of this research is to evaluate the effect of ladder scale reinforcement in cement based materials using low concentrations of well dispersed carbon nanofibers and PVA microfibers. It also provides insight into the nanostructure of the nanocomposites. The hybridization was found to enhance the flexural strength, Young's modulus and toughness of the cementitious matrix.

EXPERIMENTAL PROCEDURE

Materials

The cement used was Type I ordinary portland cement (OPC). The nanocomposites were prepared using commercially available as received CNFs. In general, CNFs are described as an ultrahigh-strength material characterized by a high tensile modulus, tensile strength, electrical and thermal conductivity and corrosion resistance. The properties of the nanofibers are presented in Table 1. Typically, nanofibers exhibit different morphologies. The CNFs used in this study exhibit a cylindrical nanostructure with graphite planes which extend beyond the diameter of the nanofiber. The morphology of the nanofibers with the graphite planes are presented in Fig. 1. The graphite edges which exhibit along the circumference of the fiber can be used to effectively embed the nanofibers in the cement matrix, improving the interfacial bond and enabling more sufficient load transfer across nanocracks and pores. For reinforcement at the micro scale, polyvinylalcohol (PVA) microfibers were used. The mechanical and geometrical properties of the micro PVA fibers used are shown in Table 1. Micro PVA fibers were chosen because they develop a very strong bond to the cement paste[12] and they are known to reduce the widening of coalesced micro-cracks, and induce multiple cracks before the peak load[10].

Preparation of specimens

In addition to the ladder reinforced cement nanocomposites, control mixes of unreinforced cement paste, nanofiber reinforced cement paste and microfiber reinforced cement paste composites were cast. The fiber mix proportions examined appear in Table 2. To develop high performance nanofiber/cement nanocomposites, homogeneous dispersion of the nanofibers in the cementitious matrix must be accomplished[13]. Good dispersion leads to the reduction of the fiber free area in the material and improves the efficiency of the CNFs in the matrix. In this study, the method described in Reference 5 was used to disperse the CNFs in the mixing water. Based on this method, CNFs were dispersed in an aqueous surfactant solution by applying ultrasonic energy using a 500 W cup-horn high intensity ultrasonic processor. After dispersion, OPC was added to the CNF suspensions at a water-cement ratio (w/c) of 0.5. The materials were mixed using a standard mixer, following the procedure outlined by ASTM 305. After mixing, the material was cast in 20 × 20 × 80 mm (0.79 × 0.79 × 3.15 in) molds and cured in water with lime until testing.

Scanning electron microscopy

The effect of the fibers on the structure of the composites was examined using an ultra-high resolution field emission scanning electron microscope operated at 5 kV. The fracture surfaces of the composites were imaged using secondary electron (SE) imaging at medium to high magnifications (10,000× to 150,000×). Specimens of 25.4 × 6.35 × 6.35 mm (0.79 × 0.79 × 3.15 in) were prepared for each mixture and cured sealed for 18 hours. After curing, specimens were demolded and kept in acetone for at least 1 week to stop hydration. Prior to their observation, the samples were coated with a 20 nm (7.87×10^{-7} in) thick layer of gold-palladium (Au/Pd).

Flexural testing

The mechanical performance of the composites was evaluated by fracture mechanics tests which provide more consistent results compared to the results of the bending test. Beam specimens of 20 × 20 × 80 mm (0.79 × 0.79 × 3.15 in) with a 6 mm (0.24 in) notch cut at the midspan were tested by three-point bending at the age of 3, 7, and 28 days. The dimensions of the three-point bent beams and the notch were defined according to the Rilem method of Jenq and Shah[14]. An average value of three specimens was used for each curing age, based on ASTM C 348, which assures that the variations of the test results are not significant and do not affect the conclusions. The tests were performed with a closed-loop MTS servo-hydraulic testing machine with an 89 kN (20,000 lb) capacity. The crack mouth opening displacement (CMOD), measured at the notch, was used to control the test and was advanced at a rate of 0.012 mm/min (4.72×10^{-4} in/min). The load versus CMOD graphs were created from the test results. Young's modulus was then calculated from these graphs using the two-parameter fracture model by Jenq and Shah[14]. Strength was calculated using the net specimen depth. The area under the load-CMOD curve was used as an indicator of the amount of energy required for the material to fail and it was considered as a measurement of toughness.

RESULTS AND DISCUSSION

Composites reinforced with CNFs

Table 3 presents the results of all mixtures tested at the age of 3, 7, and 28 days. Comparing the results of plain OPC with nanocomposites reinforced with CNFs, it is observed, that at all ages an increase in flexural strength, Young's modulus and toughness up to 40%, 75% and 35%, respectively, is achieved with the incorporation of CNFs. Typical load-CMOD curves of the 28 days response of plain cement paste and cement paste with CNFs are presented in Fig. 2. It is impressive that a concentration as low as 0.048wt% of cement CNFs can impose such a high increase in the Young's modulus. During the early stages of loading, nanofibers provide the material with the ability to carry higher load at the same CMOD. To better understand the effect of CNFs on the nanostructure of cement paste SEM was employed. Figure 3 shows SEM images of the fracture surface of the nanocomposites at a scale of 500 nm (0.02×10^{-3} in). Initially, it is observed that mostly individual CNFs can be identified on the fracture surface. This indicates that good dispersion was achieved. It can also be seen that CNFs appear to be embedded into the hydration products, showing that good bonding between the nanofibers and the matrix was also achieved. Good bonding enables the load transfer between the matrix and the nanofibers which results to the improvement of the overall strength of the nanocomposite. A good illustration of CNFs acting as bridges between nanocracks and pores is also shown.

Composites reinforced with PVA microfibers

The results of composites incorporating PVA microfibers are shown in Table 3. Compared to OPC, the samples reinforced with microfibers exhibit slightly higher flexural strength and Young's modulus (less than 10% increase at all ages). As expected, the addition of microfibers has caused a tremendous increase on the fracture toughness of the matrix. Figure 4 illustrates the 28 days load-CMOD response of plain cement paste and cement paste with PVA microfibers. It is observed that, while plain OPC fails at a CMOD of 0.04 mm (0.0015 in), the composites retain load for ten times higher CMOD (higher than 0.5 mm [0.0196 in]). The results indicate that after fracture the microfibers provide the material with the capacity to carry higher loads, improving the post-peak behavior of cement paste, which results in a highly ductile behavior.

Composites reinforced with CNFs and PVA microfibers

Similar to the specimens reinforced with CNFs, the nanocomposites with ladder scale reinforcement exhibit higher strength, Young's modulus and toughness than plain cement paste (Table 3). It is observed that the hybrid composites exhibit higher strength, Young's modulus and slightly higher toughness than the composites reinforced with PVA microfibers. It is also noticed that specimens with ladder reinforcement show higher strength and Young's modulus than the specimens reinforced only with CNFs. Looking at the 28 days load-CMOD graphs (Fig. 5 and 6) it is observed that the pre-peak mechanical behavior of the ladder reinforced mixes is mainly controlled by the CNFs, while the post-peak response is controlled by the microfibers. Figure 7 shows an SEM image of cement matrix reinforced with PVA microfibers and CNFs. Due to the low magnification of the image, only the PVA microfiber can be viewed and not the CNFs. As can be seen, both ends of the microfiber are embedded in the cement matrix bridging a large pore. Additionally, parts of the cement matrix are attached to the microfiber, which indicates a good level of bonding between the fiber and the matrix was achieved. Furthermore, fiber delamination is observed. A close view of the fiber surface is shown in Fig. 8. Fibrils of PVA material are peeled from the fiber surface. Similar observations have been reported by Reference 12, where PVA microfibers were found to have strong chemical and frictional bonding in cementitious matrix. Images of the fracture surface of the hybrid nanocomposites at higher magnification (scale of 500 nm [0.02×10^{-3} in]) are illustrated in Fig. 9. In both images, the cement matrix and a part of a PVA microfiber are shown. Individual CNFs can also be identified in the cementitious matrix bridging nanopores. From the SEM observations, it can be clearly seen that the CNFs are effectively reinforcing the matrix at the nanoscale level, while the PVA microfibers, due to their larger diameter can bridge efficiently the larger scale pores and cracks.

CONCLUSIONS

The reinforcing efficiency of carbon nanofibers, PVA microfibers and the combination of both in cementitious matrix, with a w/c of 0.5, was investigated. Three-point bending tests have shown that CNFs at a concentration as low as 0.048wt% can be used, under the test conditions employed in the research reported here, to increase the flexural strength and the Young's modulus of cement matrix up to 40% and 75%, respectively. These improvements on the mechanical properties of the matrix can be attributed to good bonding between the CNFs and the cement hydration products as well as the ability of the CNFs to control cracking at the nanoscale by bridging nanocracks and pores. On the other hand, the incorporation of PVA microfibers improved only the post-peak behavior of cement paste resulting in a highly ductile behavior. SEM images have shown that PVA microfibers have a very good bonding with cement matrix. The ladder scale reinforcement was found to improve the flexural strength up to 50%, Young's modulus up to 84% and toughness up to 33 times (3,351%) of the cementitious matrix. Over all the incorporation of CNFs and PVA microfibers have resulted into a stronger and tougher composite compared to the singly-reinforced composites or plain cement paste.

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Table 1–Fiber properties

	Diameter, nm (in×10^{-6})	Length, μm (in)	Tensile strength, GPa (ksi)	Modulus, GPa (ksi)	Aspect ratio
Carbon nanofibers (CNFs)	60-150 (2.4-5.9)	30 to 100 (0.001 to 0.004)	7.0 (1015)	600 (87023)	650
PVA microfibers	14,000 (55.1)	4,000 (0.16)	1.9 (276)	41 (5950)	650

Table 2–Mixture proportions of fibers by weight of cement

Mixture	CNFs	Micro PVA
Plain OPC	—	—
Cement paste + CNFs	0.048	—
Cement paste + micro PVA	—	0.54
Cement paste + CNFs + micro PVA	0.048	0.54

Table 3–Flexural strength, Young's modulus, and toughness of cement paste at 3, 7, and 28 days of hydration

	3 days			7 days			28 days		
Mixture	MOR, MPa (ksi)	E, GPa (ksi)	T, N × mm (lb×in×10^2)	MOR, MPa (ksi)	E, GPa (ksi)	T, N×mm (lb×in×10^2)	MOR, MPa (ksi)	E, GPa (ksi)	T, N×mm (lb×in×10^2)
Plain OPC (CP)	3.9 (566)	5.6 (812)	1.8 (1.6)	4.9 (711)	7.4 (1073)	2.1 (1.9)	5.5 (798)	8.8 (1276)	2.3 (2.0)
CP + CNFs	5.6 (812)	9.9 (1436)	2.5 (2.2)	6.5 (943)	11.9 (1726)	2.7 (2.4)	7.2 (1044)	13.2 (1914)	2.8 (2.5)
CP + micro PVA	4.1 (595)	6.5 (943)	61.5 (54.4)	5.4 (783)	8.1 (1175)	66.2 (58.6)	5.8 (841)	8.9 (1291)	68.2 (60.4)
CP + CNFs + micro PVA	5.8 (841)	10.4 (1508)	61.8 (54.7)	6.6 (957)	12.7 (1842)	67.7 (59.9)	7.3 (1059)	14.6 (2118)	72.7 (64.3)

Note: MOR = flexural strength; E = Young's modulus; and T = toughness.

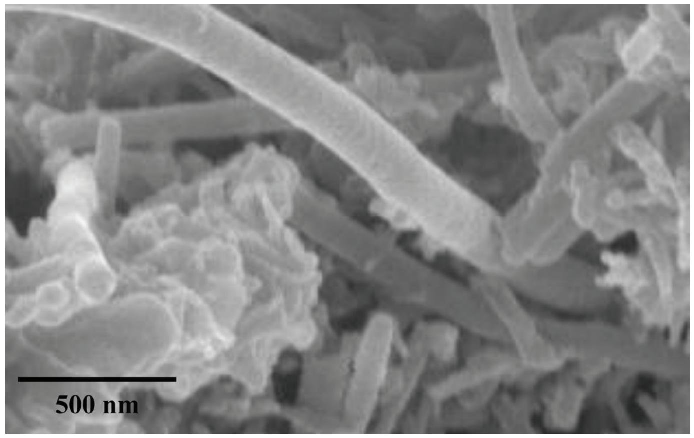


Fig. 1—SEM image of CNF in cement matrix showing morphology of nanofiber.

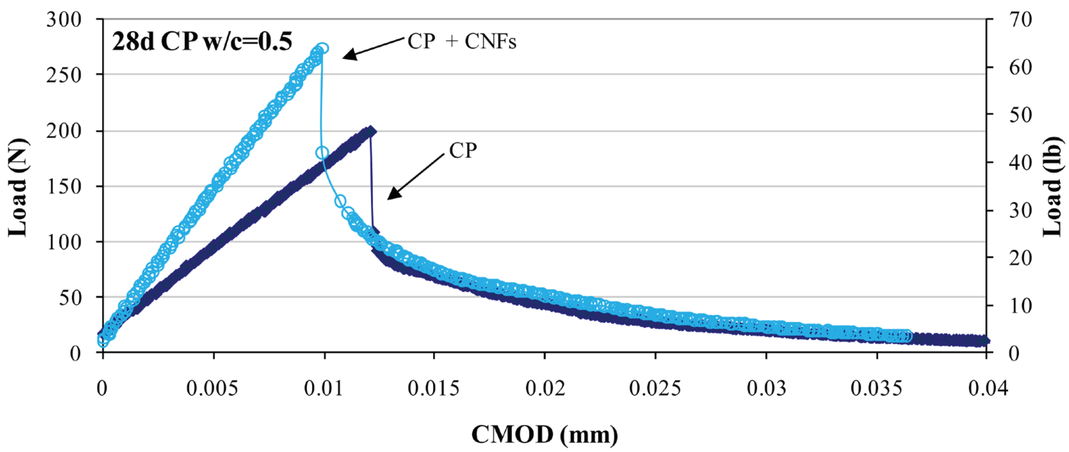


Fig. 2—Typical load-CMOD curves of 28 days plain cement paste and cement paste reinforced with CNFs. (Note: 1 mm = 0.0394 in.)

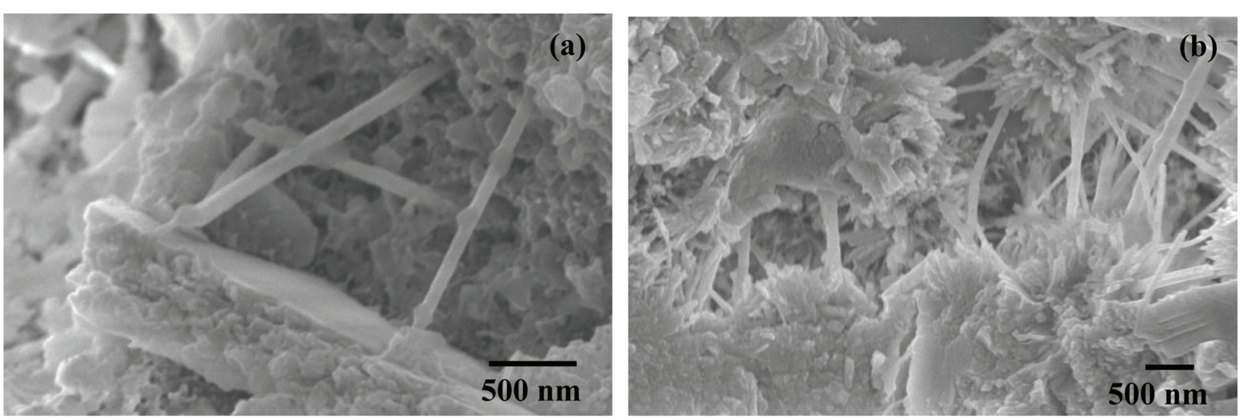


Fig. 3—SEM images of fracture surface of cement nanocomposites reinforced with CNFs.

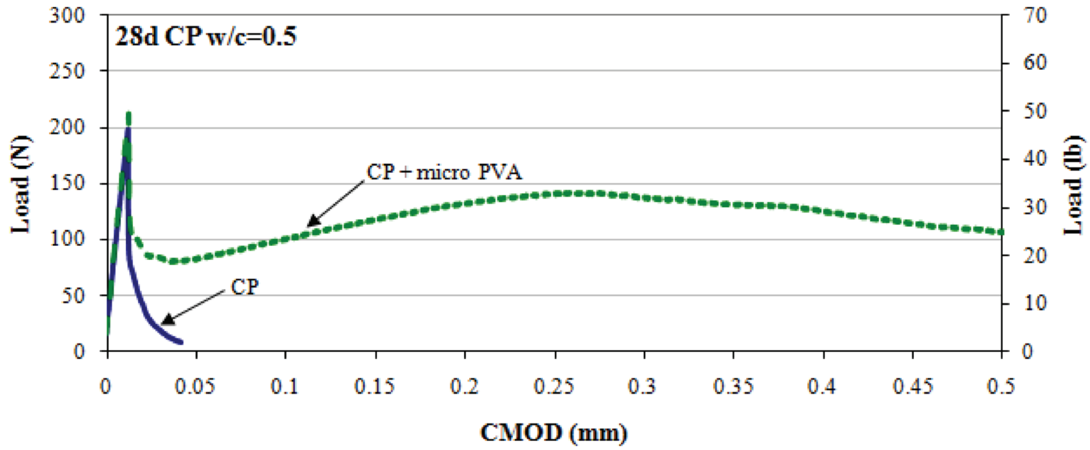


Fig. 4—Typical load-CMOD curves of 28 days plain cement paste and cement paste reinforced with PVA microfibers. (Note: 1 mm = 0.0394 in.)

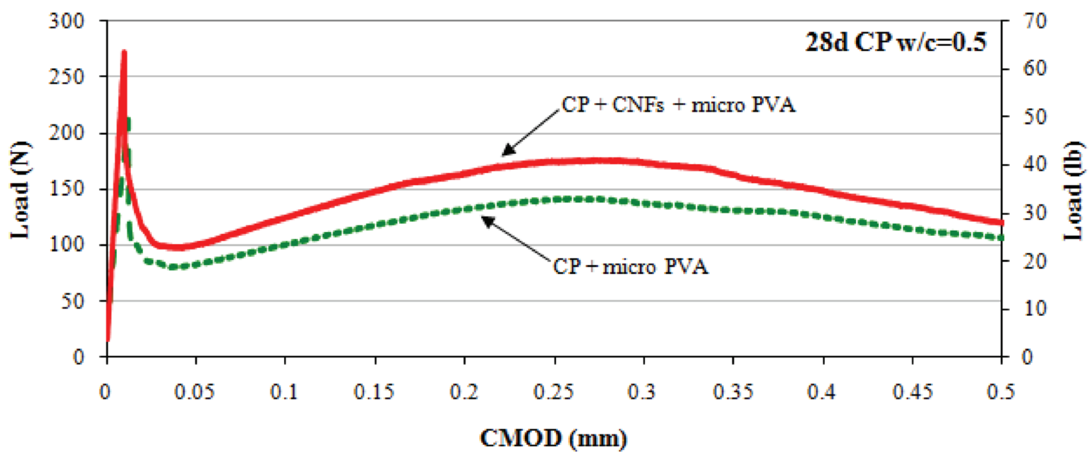


Fig. 5—Typical load-CMOD curves of 28 days cement paste with PVA microfibers and hybrid cement paste. (Note: 1 mm = 0.0394 in.)

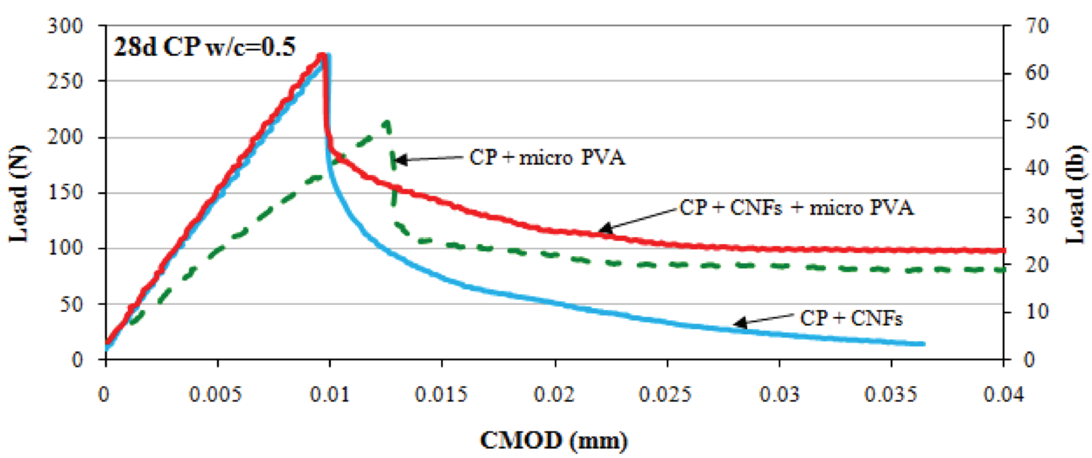


Fig. 6—Typical load-CMOD curves of 28 days cement paste with CNTs, cement paste with PVA microfibers and hybrid cement paste for CMOD values less than 0.04 mm (0.002 in). (Note: 1 mm = 0.0394 in.)

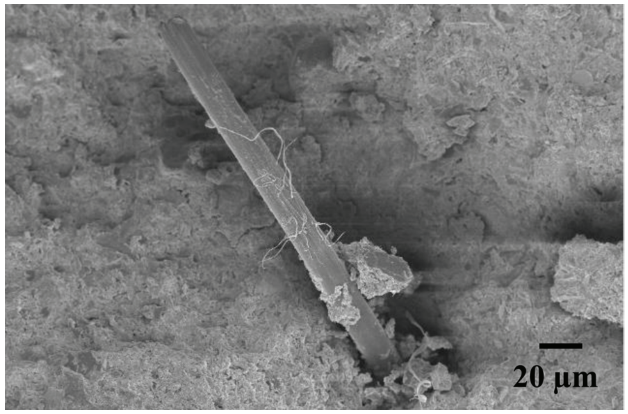


Fig. 7—SEM image of cement matrix reinforced with CNFs and PVA microfibers.

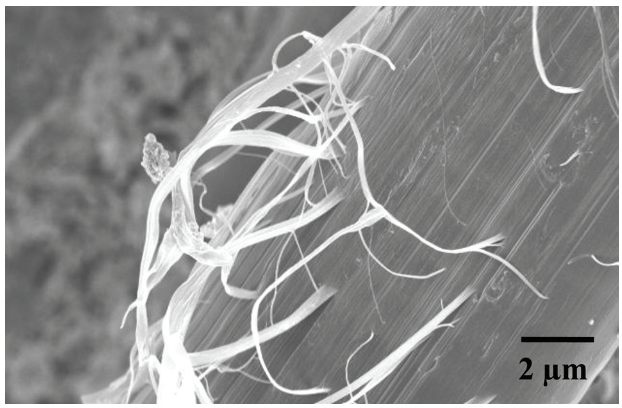
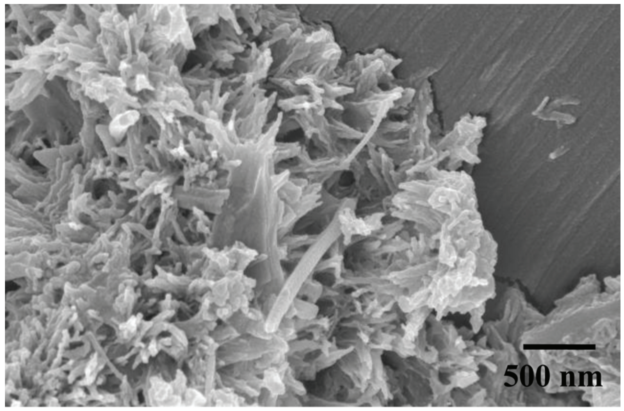
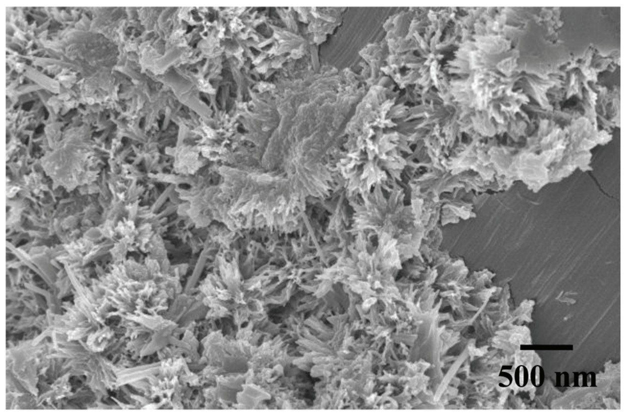


Fig. 8—SEM image of PVA microfiber surface in a failed specimen.



(a)



(b)

Fig. 9—SEM images cement matrix reinforced with CNFs and PVA microfibers at high magnification.