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Double percolation in the electrical conduction in carbon fiber reinforced cement-based materials

Sihai Wen, D.D.L. Chung *

Composite Materials Research Laboratory, University at Buffalo, State University of New York, Buffalo, NY 14260-4400, USA

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Abstract

Electrically conductive cement-based materials are important as multifunctional structural materials. Double percolation has been observed for the first time in the electrical conduction in carbon fiber cement-based materials. It involves fiber percolation and cement paste percolation. The fiber percolation threshold increases with increasing sand/cement ratio and ranges from 0.30 to 0.80 vol.% fibers in the paste portion. The cement paste percolation threshold is between 70 and 76 vol.% carbon fiber cement paste in the mortar. A sand volume fraction of 24% or less (i.e., a sand/cement ratio of 0.75 or less) and a fiber content of 0.80 vol.% (or more) of the paste portion are recommended for attaining high conductivity. The use of a higher sand/cement ratio requires a higher fiber content to attain the same level of conductivity. For a compromise between cost and conductivity, a sand/cement ratio of 0.75 and a fiber content of 0.80 vol.% of the paste portion (corresponding to 0.59 vol.% of the mortar) is attractive. At a fixed fiber volume fraction in the paste portion, the conductivity of the mortar decreases with increasing sand/cement ratio.

1. Introduction

Cement-based materials reinforced by discontinuous carbon fibers that are dispersed in the cement are of technological importance, due to their combination of good structural properties and exceptional functional properties [1,2]. The good structural properties pertain to the high flexural toughness and strength, high tensile ductility and strength, and low drying shrinkage. The exceptional functional properties pertain to the high electrical conductivity and the associated high effectiveness for electromagnetic interference shielding [3], in addition to the piezoresistivity (change of the electrical resistivity with strain), which results in the ability to sense strain [4]. The high conductivity is attractive for applications including electrical grounding and resistance heating (as for deicing).

The attainment of a high electrical conductivity in carbon fiber cement-based materials requires percolation, i.e., the structure in which the adjacent fibers touch one another, thereby resulting in a continuous electrically conductive path. The fiber volume fraction above which percolation occurs is known as the percolation threshold. The electrical conductivity increases abruptly at the percolation threshold as the fiber volume fraction is increased. As a consequence, the curve of conductivity versus fiber volume fraction is S-shaped, i.e., the conductivity varies only slightly with the fiber volume fraction in the regimes below and above the threshold, but increases abruptly at the threshold. The observation of percolation in carbon fiber reinforced cement has been made by Chen and Chung [5] and confirmed by a number of other researchers [6–9].

A cement-based structural material such as concrete contains aggregates. The fibers are located in the cement (i.e., cement paste) part of the composite material. The change of the conductivity with fiber volume fraction in the vicinity of the fiber percolation threshold is more

* Corresponding author. Tel.: +1 716 645 2593x2243; fax: +1 716 645 3875.
E-mail address: ddlchung@buffalo.edu (D.D.L. Chung).
URL: http://alum.mit.edu/www/ddlchung (D.D.L. Chung).

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gradual when an aggregate is present [5]. The higher is the aggregate proportion (e.g., the sand/cement ratio), the lower is the conductivity for the same fiber volume fraction [6,8,9], as expected due to the non-conductive nature of the aggregates. However, no S-shaped curve corresponding to cement percolation (to be distinguished from fiber percolation) in the presence of an aggregate has been reported.

Double percolation refers to the structure in which there are two types of percolation in the same composite material. For the case of fibers in cement paste (without aggregate), there is only one type of percolation, which is associated with the electrical continuity of the fibers. For the case of fibers in cement mortar (which contains sand as the aggregate), there can be two types of percolation – one associated with the electrical continuity of the fibers in the cement (Fig. 1) and the other associated with the electrical continuity of the cement (Fig. 2). The second type of percolation is characterized by the conductivity decreasing abruptly as the sand volume fraction is increased beyond a threshold value, at which the cement starts to fail to attain continuity. The attainment of high electrical conductivity in a cement-based material that contains an aggregate, both types of percolation are required. Thus, the characterization of the double percolation behavior is important for the development of electrically conductive mortar or concrete. Double percolation has been reported in numerous polymer–matrix composites, particularly those involving polymer blends [10–13]. This paper provides the first report of double percolation in cement-based materials.

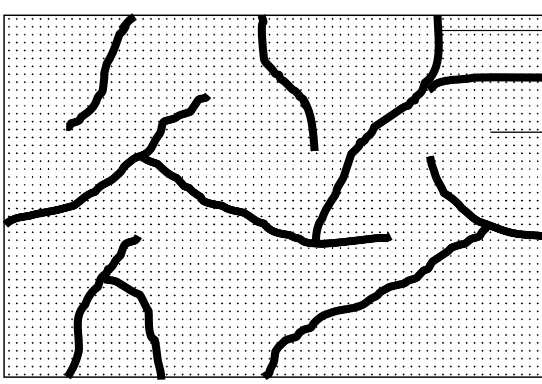

Fig. 1. Fiber percolation attained in cement.

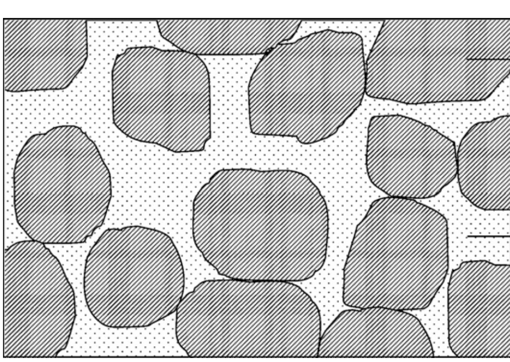

Fig. 2. Cement percolation attained in the presence of an aggregate.

The main objective of this paper is to observe and characterize the double percolation behavior of carbon fiber cement mortar. A related objective is to determine the appropriate proportions of carbon fiber and sand for attaining high electrical conductivity in carbon fiber cement mortar.

2. Experimental methods

The carbon fiber is isotropic pitch based, unsized and of diameter 15 μm and nominal length 5 mm, as obtained from Ashland Petroleum Co. (Ashland, Kentucky). The fiber properties are shown in Table 1 of Ref. [14].

Ozone treatment of the fiber, as conducted prior to incorporating the fibers in the cement mix, involves drying the fibers at 110 °C in air for 1 h and then surface treating with ozone by exposure to ozone gas (0.6 vol.% in oxygen) at 160 °C for 10 min [15]. This surface treatment of the fiber is for improving the wettability by water, thereby enhancing the fiber dispersion in the mix [16].

The cement is Portland cement (Type I) form Lafarge Corp. (Southfield, MI). The water-cement ratio is 0.40. A high-range water-reducing admixture (Glenium 3000 NS, Degussa Admixtures, Cleveland, OH) that is based on polycarboxylate chemistry is used in the amount of 1.0% by mass of cement.

Silica fume (Elkem Materials Inc., Pittsburgh, PA, Microsilica, EMS 965) is used in the amount of 15% by mass of cement for helping the dispersion of the fibers in the mix [16]. Methylcellulose (Dow Chemical Corp., Midland, MI, Methocel A15-LV) in the amount of 0.4% by mass of cement is used along with the silica fume. A defoamer (Colloids Inc., Marietta, GA, 1010) in the amount of 0.13 vol.% (% of specimen volume) is used along with the methylcellulose.

The sand is natural sand (100% passing 2.36 mm sieve, 99.9% SiO_2), with the particle size distribution shown in Fig. 1 of Ref. 17. The sand/cement ratio is 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00. For each of these seven values of the sand/cement ratio, up to 10 carbon fiber contents in the range from 0% to 3.00% by mass of cement are used.

A rotary mixer with a flat beater is used for mixing. Methylcellulose is dissolved in water and then the defoamer is added and stirred by hand for about 2 min. Then the methylcellulose solution, cement, water, silica fume and fibers are mixed in the mixer for 5 min. After pouring into steel molds of size 160 × 40 × 40 mm, an external vibrator is used to facilitate compaction and decrease the amount of air bubbles. The specimens are demolded after 24 h and then cured in air at room temperature and a relative humidity of 100% for 28 days.

DC electrical resistivity measurement is conducted by using the four-probe method, with electrical contacts in the form of silver paint in conjunction with copper wire. Each electrical contact is applied around the whole perimeter of the specimen in a plane that is perpendicular to the length of the specimen, which is the direction of resistance measurement. The outer two contacts (120 mm apart) are for passing current. The inner two contacts (80 mm apart) are for voltage measurement. A multimeter (Model 2002, Keithley Inc., Cleveland, OH) is used for the resistance measurement. Three specimens of each composition are tested.

3. Results and discussion

Fig. 3 shows the dependence of the electrical conductivity with the fiber volume fraction in the paste portion of the mortar for each value of the sand/cement ratio. The percolation threshold in relation to Fig. 1 increases with increas-

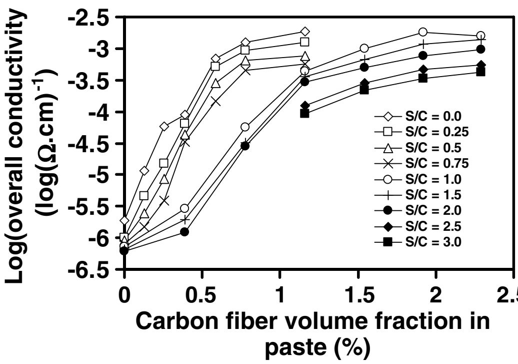

Fig. 3. Electrical conductivity (log scale) of the mortar versus the fiber volume fraction in the paste portion for various values of the sand/cement ratio (S/C).

ing sand/cement ratio. It ranges from 0.30 to 0.80 vol.% fiber in the paste. At a fixed fiber volume fraction, the conductivity decreases with increasing sand/cement ratio, such that the decrease is most significant between sand/cement ratios of 0.75 and 1.00.

The conductivity of the cement paste portion is calculated from the measured conductivity of the mortar by using the Rule of Mixtures, assuming that the sand is not conductive. Fig. 4 shows the variation of the paste conductivity with the fiber volume fraction in the paste portion. At a fixed fiber content, the paste conductivity decreases slightly with increasing sand/cement ratio. This means that a decrease in distance between adjacent sand particles essentially does not increase the preferred orientation of the fibers in the paste. An increase in fiber preferred orientation in the direction of the percolating path would have caused the paste conductivity to increase.

Fig. 5 shows the dependence of the electrical conductivity on the sand/cement ratio for each value of the fiber content. For a fixed fiber content, the conductivity decreases monotonically with increasing sand content, as expected. The percolation threshold in relation to Fig. 2 occurs at sand contents between 24 and 30 vol.% (corresponding to cement paste contents between 70 and 76 vol.%), as shown

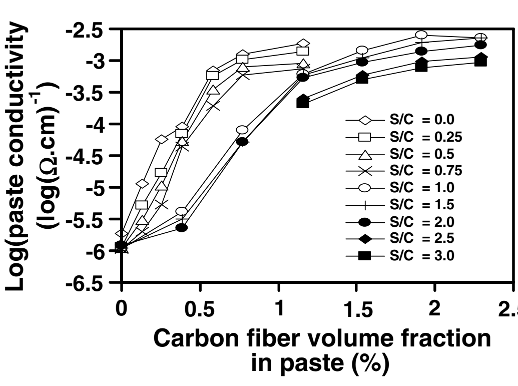

Fig. 4. Electrical conductivity (log scale) of the paste portion versus the fiber volume fraction in the paste portion for various values of the sand/cement ratio (S/C).

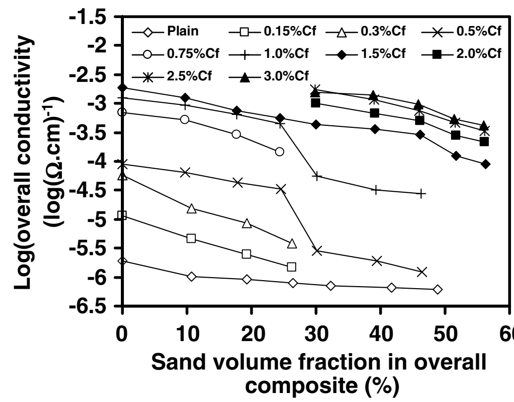

Fig. 5. Electrical conductivity (log scale) versus the sand volume fraction for various values of the fiber content (% by mass of cement). Cf = carbon fiber.

for fiber contents of 0.5% and 1.0% by mass of cement. At fiber contents of 0.3% by mass of cement and below, a percolation threshold is not observed, because of the low conductivity associated with the low fiber content, which is below the percolation threshold in relation to Fig. 1. At fiber contents of 1.5% by mass of cement and above, a percolation threshold is also not observed, because of the high conductivity associated with the high fiber content, which is above the percolation threshold in relation to Fig. 1. At a fixed sand volume fraction, the conductivity increases monotonically with increasing fiber content (% by mass of cement), as expected.

The percolation threshold in relation to Fig. 1 is much lower than that in relation to Fig. 2. The low percolation threshold in relation to Fig. 1 is consistent with prior work [5–9] and reflects the high aspect ratio of the fibers, which govern the percolation in relation to Fig. 1.

The high percolation threshold in relation to Fig. 2 reflects the limited workability of the cement paste and the small distance between the adjacent sand particles. The paste must spread between adjacent sand particles and form a continuous path in order for the percolation of Fig. 2 to occur.

The workability of cement paste decreases with increasing fiber content. However, the absence of a drop in conductivity as the fiber content increases to its maximum in this work (Fig. 3) means that the reduction in paste workability at a high value of the fiber content is not serious.

The higher is the sand content, the smaller is the distance between adjacent sand particles and the greater is the demand on the workability of the paste. Thus, the paste workability is particularly challenging when both the sand and fiber contents are high. The limited workability probably causes the slight decrease in conductivity observed at a sand content of 48 vol.% (between sand/cement ratios of 2.00 and 2.50) and a fiber content of 1.50%, 2.00% and 3.00% by mass of cement (Fig. 3).

Both fiber percolation (that of Fig. 1) and cement percolation (that of Fig. 2) are necessary for the attainment of

Table 1
Electrical resistivity of mortars with various sand/cement ratios and carbon fiber volume fraction in the mortar

Sand to cement ratio	Fiber content (vol.%)	Resistivity (Ω cm)
0.0	0	$(5.30 \pm 0.71) \times 10^5$
	0.129	$(8.71 \pm 1.13) \times 10^4$
	0.257	$(1.74 \pm 0.26) \times 10^4$
	0.390	$(1.12 \pm 0.15) \times 10^4$
	0.583	$(1.45 \pm 0.21) \times 10^3$
	0.776	$(8.06 \pm 0.90) \times 10^2$
	1.160	$(5.41 \pm 0.58) \times 10^2$
0.25	0	$(9.80 \pm 1.20) \times 10^5$
	0.106	$(2.19 \pm 0.29) \times 10^5$
	0.211	$(6.61 \pm 0.83) \times 10^4$
	0.352	$(1.57 \pm 0.18) \times 10^4$
	0.526	$(1.95 \pm 0.31) \times 10^3$
	0.701	$(1.08 \pm 0.12) \times 10^3$
	1.047	$(8.03 \pm 1.07) \times 10^2$
0.50	0	$(1.11 \pm 0.15) \times 10^6$
	0.096	$(4.07 \pm 0.59) \times 10^5$
	0.192	$(1.15 \pm 0.16) \times 10^5$
	0.320	$(2.29 \pm 0.28) \times 10^4$
	0.480	$(3.47 \pm 0.44) \times 10^3$
	0.639	$(1.52 \pm 0.18) \times 10^3$
	0.955	$(1.32 \pm 0.17) \times 10^3$
0.75	0	$(1.26 \pm 0.17) \times 10^6$
	0.088	$(6.76 \pm 0.81) \times 10^5$
	0.177	$(2.57 \pm 0.33) \times 10^5$
	0.294	$(3.02 \pm 0.42) \times 10^4$
	0.441	$(6.92 \pm 0.91) \times 10^3$
	0.587	$(2.24 \pm 0.33) \times 10^3$
	0.877	$(1.77 \pm 0.24) \times 10^3$
1.0	0	$(1.39 \pm 0.15) \times 10^6$
	0.272	$(3.45 \pm 0.42) \times 10^5$
	0.542	$(1.80 \pm 0.23) \times 10^4$
	0.811	$(2.31 \pm 0.29) \times 10^3$
	1.079	$(1.00 \pm 0.13) \times 10^3$
	1.345	$(5.62 \pm 0.63) \times 10^2$
	1.610	$(6.31 \pm 0.74) \times 10^2$
1.5	0	$(1.54 \pm 0.18) \times 10^6$
	0.236	$(5.16 \pm 0.60) \times 10^5$
	0.471	$(3.14 \pm 0.37) \times 10^4$
	0.705	$(2.80 \pm 0.31) \times 10^3$
	0.938	$(1.48 \pm 0.19) \times 10^3$
	1.170	$(8.51 \pm 0.11) \times 10^2$
	1.401	$(7.24 \pm 0.97) \times 10^2$
2.0	0	$(1.63 \pm 0.21) \times 10^6$
	0.209	$(8.09 \pm 1.08) \times 10^5$
	0.417	$(3.58 \pm 0.44) \times 10^4$
	0.624	$(3.43 \pm 0.41) \times 10^3$
	0.830	$(2.00 \pm 0.28) \times 10^3$
	1.035	$(1.32 \pm 0.21) \times 10^3$
	1.240	$(1.05 \pm 0.17) \times 10^3$
2.5	0.559	$(8.13 \pm 1.08) \times 10^3$
	0.744	$(3.55 \pm 0.53) \times 10^3$
	0.929	$(2.14 \pm 0.29) \times 10^3$
	1.112	$(1.82 \pm 0.31) \times 10^3$
3.0	0.507	$(1.10 \pm 0.15) \times 10^4$
	0.675	$(4.57 \pm 0.72) \times 10^3$
	0.842	$(2.95 \pm 0.47) \times 10^3$
	1.008	$(2.40 \pm 0.30) \times 10^3$

high electrical conductivity in a cement-based material that contains an aggregate. Thus, a sand volume fraction of 24% or less (i.e., a sand/cement ratio of 0.75 or less) and a fiber content of 0.8 vol.% (or more) of the paste portion are recommended. The use of a higher sand/cement ratio requires a higher fiber content to attain the same level of conductivity. For the purpose of cost reduction, a low value of the fiber content is preferred.

For a compromise between cost and conductivity, a sand/cement ratio of 0.75 and a fiber content of 0.80 vol.% of the paste portion (corresponding to 0.59 vol.% of the mortar) are recommended, yielding a resistivity of $(2.24 \pm 0.33) \times 10^3\ \Omega$ cm (Table 1). This value is lower by three orders of magnitude than the value of $(1.26 \pm 0.17) \times 10^6\ \Omega$ cm for the same mortar without fiber (Table 1). However, this value is higher than the lowest value of $(5.41 \pm 0.58) \times 10^2\ \Omega$ cm for the case of no sand, as attained at a fiber content of 1.20 vol.%.

For a sand/cement ratio of 1.00, which is quite common, a fiber content of 2.50% by mass of cement (corresponding to 1.90 vol.% of the paste portion and 1.34 vol.% of the mortar) is recommended (Fig. 3). The associated resistivity is $(5.62 \pm 0.63) \times 10^2\ \Omega$ cm, which is higher than the value of $(2.24 \pm 0.33) \times 10^3\ \Omega$ cm for the best case when sand/cement ratio is 0.75, and is almost four orders of magnitude lower than the corresponding value without fiber, i.e., $(1.39 \pm 0.15) \times 10^6\ \Omega$ cm (Table 1).

Fig. 6 shows the width of the cement paste between adjacent sand particles in mortar without fiber (but with silica fume) for various values of the sand/cement ratio. The width is determined experimentally by optical microscopic examination of mechanically polished sections and averaging the width measured at 20 or more points for each specimen. The width is also calculated by geometry by considering the distance of closest approach between adjacent sand particles and assuming that each sand particle is a sphere of diameter 459.1 μm (calculated according to the measured particle size distribution [17]) and that the sand particles are uniformly distributed according to a cubic grid. The measured and calculated values of the cement paste width are in close agreement. The measured width decreases from 27 to 1 μm as the sand/cement ratio increases from 0.25 to 2.00. Microscopic observation also

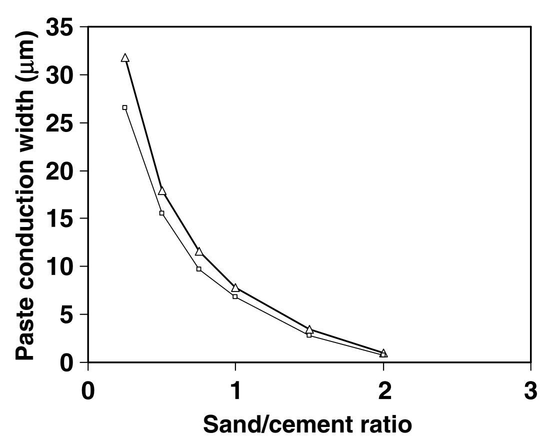

Fig. 6. Variation of the width of the cement paste (without fiber) between adjacent sand particles with the sand/cement ratio. Thin curve: measured width. Thick curve: calculated width.

shows that the paste forms a continuous network for all of these values of the sand/cement ratio.

4. Conclusion

Double percolation has been observed in carbon fiber cement-based materials. The fiber percolation threshold increases with increasing sand/cement ratio up to 3.00 and ranges from 0.30 to 0.80 vol.% fibers in the paste portion. The cement paste percolation threshold is between 70 and 76 vol.% carbon fiber cement paste in the mortar, as observed at fiber contents from 0.50% to 1.00% by mass of cement. A sand volume fraction of 24% or less (i.e., a sand/cement ratio of 0.75 or less) and a fiber content of 0.80 vol.% (or more) of the paste portion are recommended for attaining high conductivity. The use of a higher sand/cement ratio requires a higher fiber content to attain the same level of conductivity. For a compromise between cost and conductivity, a sand/cement ratio of 0.75 and a fiber content of 0.80 vol.% of the paste portion (corresponding to 0.59 vol.% of the mortar) is attractive. At a fixed fiber volume fraction in the paste portion, the conductivity of the mortar decreases with increasing sand/cement ratio.

References

[1] Chung DDL. Electrical conduction behavior of cement–matrix composites. J Mater Eng Perform 2002;11(2):194–204.
[2] Chung DDL. Multifunctional cement-based materials. New York (NY): Marcel Dekker; 2003.
[3] Chung DDL. Electromagnetic interference shielding effectiveness of carbon materials. Carbon 2001;39(2):279–85.
[4] Wen S, Chung DDL. Strain sensing characteristics of carbon fiber cement. ACI Mater J 2005;102(4):244–8.
[5] Chen P-W, Chung DDL. Improving the electrical conductivity of composites comprised of short conducting fibers in a non-conducting matrix: the addition of a non-conducting particulate filler. J Electron Mater 1995;24(1):47–51.
[6] Chen B, Wu K, Yao W. Conductivity of carbon fiber reinforced cement-based composites. Cem Concr Compos 2004;26:291–7.
[7] Wang X, Wang Y, Jin Z. Electrical conductivity characterization and variation of carbon fiber reinforced cement composite. J Mater Sci 2002;37(1):223–7.
[8] Reza F, Batson GB, Yamamuro JA, Lee JS. Volume electrical resistivity of carbon fiber cement composites. ACI Mater J 2001;98(1):25–35.
[9] Chiarello M, Zinno R. Electrical conductivity of self-monitoring CFRC. Cem Concr Compos 2005;27:463–9.
[10] Potschke P, Bhattacharyya AR, Janke A. Carbon nanotube-filled polycarbonate composites produced by melt mixing and their use in blends with polyethylene. Carbon 2004;42(5–6):965–9.
[11] Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H. Polymer 2004;45(3):739–48.
[12] Ibarra-gomez R, Marquez A, Ramos-de Valle LF, Rodriguez-fernandez OS. Influence of the blend viscosity and interface energies on the preferential location of CB and conductivity of BR/EPDM blends. Rubber Chem Technol 2003;76(4):969–78.
[13] Thongruang W, Spontak RJ, Balik CM. Bridged double percolation in conductive polymer composites: an electrical conductivity, morphology and mechanical property study. Polymer 2002; 43(13):3717–25.
[14] Wen S, Chung DDL. Carbon fiber-reinforced cement as a thermistor. Cem Concr Res 1999;29(6):961–5.
[15] Fu X, Lu W, Chung DDL. Ozone treatment of carbon fiber for reinforcing cement. Carbon 1998;36(9):1337–45.
[16] Chung DDL. Dispersion of short fibers in cement. J Mater Civil Eng 2005;17(4):379–83.
[17] Chen P, Chung DDL. Carbon fiber reinforced concrete as an intrinsically smart concrete for damage assessment during static and dynamic loading. ACI Mater J 1996;93(4):341–50.