Carbon Fiber Cement-Matrix Composites

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This is a review of cement-matrix composites containing short carbon fibers. These composites exhibit attractive tensile and flexural properties, low drying shrinkage, high specific heat, low thermal conductivity, high electrical conductivity and high corrosion resistance. Moreover, they facilitate the cathodic protection of steel reinforcement in concrete, and have the ability to sense their own strain, damage and temperature. Fiber surface treatment can improve numerous properties of the composites.

KEYWORDS : *Carbon fiber, Cement, Composite, Mechanical properties, Thermal, Corrosion, Sense, Surface treatment.*

1. Introduction

Carbon fiber cement-matrix composites are structural materials that are gaining in importance quite rapidly due to the decrease in carbon fiber cost[1] and the increasing demand of superior structural and functional properties. These composites contain short carbon fibers, typically 5 mm in length, as the short fibers can be used as an admixture in concrete (whereas continuous fibers cannot be simply added to the concrete mix) and short fibers are less expensive than continuous fibers. However, due to the weak bond between carbon fiber and the cement matrix, continuous fibers[2]-[4] are much more effective than short fibers in reinforcing concrete. Surface treatment of carbon fiber (e.g., by heating[5] or by using ozone[6],[7], silane[8], SiO2 particles[9] or hot NaOH solution[10]) is useful for improving the bond between fiber and matrix, thereby improving the properties of the composite. In the case of surface treatment by ozone or silane, the improved bond is due to the enhanced wettability by water. Admixtures such as latex[6],[11], methylcellulose[6] and silica fume[12] also help the bond.

The effect of carbon fiber addition on the properties of concrete increases with fiber volume fraction[13], unless the fiber volume fraction is so high that the air void content becomes excessively high[14]. (The air void content increases with fiber content and air voids tend to have a negative effect on many properties, such as the compressive strength.) In addition, the workability of the mix decreases with fiber content[13]. Moreover, the cost increases with fiber content. Therefore, a rather low volume fraction of fibers is desirable. A fiber content as low as 0.2 vol. % is effective[15], although fiber contents exceeding 1 vol. % are more common[16],[20]. The required fiber content increases with the particle size of the aggregate, as the flexural strength decreases with increasing particle size[21].

Effective use of the carbon fibers in concrete requires dispersion of the fibers in the mix. The dispersion is enhanced by using

silica fume (a fine particulate) as an admixture[14],[22]-[24]. A typical silica fume content is 15% by weight of cement[14]. The silica fume is typically used along with a small amount (0.4% by weight of cement) of methylcellulose for helping the dispersion of the fibers and the workability of the mix[14]. Latex (typically 15-20% by weight of cement) is much less effective than silica fume for helping the fiber dispersion, but it enhances the workability, flexural strength, flexural toughness, impact resistance, frost resistance and acid resistance[14],[25],[26]. The ease of dispersion increases with decreasing fiber length[24].

The improved structural properties rendered by carbon fiber addition pertain to the increased tensile and flexible strengths, the increased tensile ductility and flexural toughness, the enhanced impact resistance, the reduced drying shrinkage and the improved freeze-thaw durability[13]-[15],[17]-[25],[27]-[38]. The tensile and flexural strengths decrease with increasing specimen size, such that the size effect becomes larger as the fiber length increases[39]. The low drying shrinkage is valuable for large structures and for use in repair[40],[41] and in joining bricks in a brick structure[42],[43]. The functional properties rendered by carbon fiber addition pertain to the strain sensing ability[7],[44]-[57] (for smart structures), the temperature sensing ability[58]-[61], the damage sensing ability[44],[48],[62]-[64], the thermal insulation ability[65]-[67] (to save energy for buildings), the electrical conduction ability[68]-[77] (to facilitate cathodic protection of embedded steel and to provide electrical grounding or connection), and the radio wave reflection/absorption ability[78]-[82] (for electromagnetic interference or EMI shielding, for lateral guidance in automatic highways, and for television image transmission).

In relation to the structural properties, carbon fibers compete with glass, polymer and steel fibers[10],[27]-[29],[32],[36]-[38],[83]. Carbon fibers (isotropic pitch based)[1],[83] are advantageous in their superior ability to increase the tensile strength of concrete, even though the tensile strength, modulus and ductility of the isotropic pitch based carbon fibers are low compared to most other fibers.

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Carbon fibers are also advantageous in the relative chemical inertness[84]. PAN-based carbon fibers are also used[17),19),22),33)], although they are more commonly used as continuous fibers than short fibers. Carbon-coated glass fibers[85),86)] and submicron diameter carbon filaments[76)-78)] are even less commonly used, although the former is attractive for the low cost of glass fibers and the latter is attractive for its high radio wave reflectivity (which results from the skin effect). C-shaped carbon fibers are more effective for strengthening than round carbon fibers[87)], but their relatively large diameter makes them less attractive.

Carbon fibers can be used in concrete together with steel fibers, as the addition of short carbon fibers to steel fiber reinforced mortar increases the fracture toughness of the interfacial zone between steel fiber and the cement matrix[88)]. Carbon fibers can also be used in concrete together with steel bars[89),90)], or together with carbon fiber reinforced polymer rods[91)].

In relation to the functional properties, carbon fibers are exceptionally compared to the other fiber types. Carbon fibers are electrically conducting, in contrast to glass and polymer fibers, which are not conducting. Steel fibers are conducting, but their typical diameter ($\geq 60\,\mu m$) is much larger than the diameter of a typical carbon fiber (15 mm). The combination of electrical conductivity and small diameter makes carbon fibers superior to the other fiber types in the area of strain sensing. Carbon fibers are likely superior for temperature sensing, electrical conduction and radio wave reflection as well, but comparative studies of various fiber types in relation to these properties have not been done.

Although carbon fibers are thermally conducting, addition of carbon fibers to concrete lowers the thermal conductivity[65)], thus allowing applications related to thermal insulation. This effect of carbon fiber addition is due to the increase in air void content. The electrical conductivity of carbon fibers is higher than that of the cement matrix by about 8 orders of magnitude, whereas the thermal conductivity of carbon fibers is higher than that of the cement matrix by only one or two orders of magnitude. As a result, the electrical conductivity is increased upon carbon fiber addition in spite of the increase in air void content, but the thermal conductivity is decreased upon fiber addition.

The use of pressure after casting[92)], and extrusion[93),94)] can result in composites with superior microstructure and properties. Moreover, extrusion improves the shapability[94)].

This paper is a review of short carbon fiber reinforced cement-matrix composites, including concrete (with fine and coarse aggregates), mortar (with fine aggregate and no coarse aggregate) and cement paste. Previous reviews are noted[95)-100)].

Table 1 shows the properties of the isotropic-pitch-based

Table 1   Properties of carbon fibers

Filament diameter	$15 \pm 3\ \mu m$
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	$3.0 \times 10^{-3}\ \Omega.cm$
Specific gravity	$1.6\ g\,cm^{-3}$
Carbon content	98 wt.%

carbon fibers (nominally 5 mm long) used by the author in the cement-matrix composites described below for the purpose of illustration.

2. Structural behavior

The properties relevant to the structural behavior of cement-matrix composites containing short carbon fibers are given in this section.

Table 2 and **Table 3** show the tensile strength and modulus respectively of twelve types of cement pastes. The strength is slightly increased by the addition of methylcellulose and defoamer, but the modulus is slightly decreased by the addition of methylcellulose and defoamer. However, both strength and modulus are increased by the addition of fibers. The effectiveness of the fibers in increasing strength and modulus increases in the following order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives substantially higher strength and modulus than as-received silica fume. The highest tensile strength and modulus are exhibited by cement paste with silane-treated silica fume and silane-treated fibers. The strength is 56% higher and the modulus is 39% higher than those of the cement paste with as-received silica fume and as-received fibers. The strength is 26% higher and the modulus is 14% higher than those of the cement paste with as-received silica fume and silane-treated fibers. Hence, silane treatments of silica fume and of

Table 2   Tensile strength (MPa) of cement pastes with and without fibers.

Formulation	As-received silica fume	Silane-treated silica fume
A	1.53 ± 0.06	2.04 ± 0.06
A^+	1.66 ± 0.07	2.25 ± 0.09
A^+F	2.00 ± 0.09	2.50 ± 0.11
A^+O	2.25 ± 0.07	2.67 ± 0.09
A^+K	2.32 ± 0.08	2.85 ± 0.11
A^+S	2.47 ± 0.11	3.12 ± 0.12

A   : cement + water + water reducing agent + silica fume
A^+ : A + methylcellulose + defoamer
A^+F : A^+ + as-received fibers
A^+O : A^+ + O_3-treated fibers
A^+K : A^+ + dichromate-treated fibers
A^+S : A^+ + silane-treated fibers

Table 3   Tensile modulus (GPa) of cement pastes with and without fibers.

Formulation	As-received silica fume	Silane-treated silica fume
A	10.2 ± 0.7	11.5 ± 0.6
A^+	9.3 ± 0.5	10.7 ± 0.4
A^+F	10.9 ± 0.3	12.9 ± 0.7
A^+O	11.9 ± 0.3	13.1 ± 0.6
A^+K	12.7 ± 0.4	14.3 ± 0.4
A^+S	13.3 ± 0.5	15.2 ± 0.8

A   : cement + water + water reducing agent + silica fume
A^+ : A + methylcellulose + defoamer
A^+F : A^+ + as-received fibers
A^+O : A^+ + O_3-treated fibers
A^+K : A^+ + dichromate-treated fibers
A^+S : A^+ + silane-treated fibers

fibers are about equally valuable in providing strengthening.

Table 4 shows the tensile ductility. It is slightly increased by the addition of methylcellulose and defoamer, and is further increased by the further addition of fibers. The effectiveness of the fibers in increasing the ductility also increases in the above order. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations involving surface treated fibers, silane-treated silica fume gives higher ductility than as-received silica fume. The highest ductility is exhibited by cement paste with silane-treated silica fume and silane-treated fibers. The ductility is 39% higher than that of the cement paste

with as-received silica fume and as-received fibers. It is 14% higher than that of the cement paste with as-received silica fume and silane-treated fibers.

Table 5 shows the air void content. It is decreased by the addition of methylcellulose and defoamer, but is increased by the further addition of fibers, whether the fibers have been surface treated or not. Among the formulations with fibers, the air void content decreases in the following order: as-received fibers, O_3-treated fibers, dichromate-treated fibers and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations (including those without fibers), silane-treated silica fume gives lower air void content than as-received silica fume.

Table 6-Table 8 give the dynamic flexural properties of twelve types of cement pastes. Six of the types have as-received silica fume; the other six have silane-treated silica fume.

The loss tangent (**Table 6**) is increased slightly by the addition of methylcellulose. Further addition of carbon fibers decreases the loss tangent. The loss tangent decreases in the following order: as-received fibers, ozone-treated fibers, dichromate-treated fibers and silane-treated fibers, at least for the case of as-received silica fume at 0.2 Hz.

The storage modulus (**Table 7**) is decreased by the addition of methylcellulose. Further addition of carbon fibers increases the storage modulus, such that the modulus increases in the order: as-received fibers, ozone-treated fibers, dichromate-treated fibers and silane-treated fibers. These trends apply whether the silica fume is as-received or silane-treated, and whether the frequency is 0.2, 1.0 or 2.0 Hz.

The loss modulus (**Table 8**, product of loss tangent and storage modulus) is increased by the addition of methylcellulose, except for the case of the paste with silane-treated silica fume at 0.2 Hz. Further addition of carbon fibers increases the loss modulus very slightly, if at all.

Table 9 gives the drying shrinkage strain of ten types of cement paste as a function of curing age. The drying shrinkage is decreased by the addition of carbon fibers, such that it decreases in the following order: as-received fibers, ozone-treated fibers, dichromate-treated fibers and silane-treated fibers. This trend applies for any curing age, whether the silica fume is as-received

Table 4 Tensile ductility (%) of cement pastes with and without fibers.

Formulation	As-received silica fume	Silane-treated silica fume
A	0.020 ± 0.0004	0.020 ± 0.0004
A$^+$	0.023 ± 0.0004	0.021 ± 0.0004
A$^+$F	0.025 ± 0.0003	0.024 ± 0.0004
A$^+$O	0.026 ± 0.0003	0.027 ± 0.0004
A$^+$K	0.028 ± 0.0003	0.030 ± 0.0004
A$^+$S	0.031 ± 0.0004	0.034 ± 0.0004

A　：cement＋water＋water reducing agent＋silica fume
A$^+$　：A＋methylcellulose＋defoamer
A$^+$F：A$^+$＋as-received fibers
A$^+$O：A$^+$＋O$_3$-treated fibers
A$^+$K：A$^+$＋dichromate-treated fibers
A$^+$S：A$^+$＋silane-treated fibers

Table 5 Air void content (%, ±0.12) of cement pastes with and without fibers.

Formulation	As-received silica fume	Silane-treated silica fume
A	3.73	3.26
A$^+$	3.42	3.01
A$^+$F	5.32	4.89
A$^+$O	5.07	4.65
A$^+$K	5.01	4.49
A$^+$S	4.85	4.16

A　：cement＋water＋water reducing agent＋silica fume
A$^+$　：A＋methylcellulose＋defoamer
A$^+$F：A$^+$＋as-received fibers
A$^+$O：A$^+$＋O$_3$-treated fibers
A$^+$K：A$^+$＋dichromate-treated fibers
A$^+$S：A$^+$＋silane-treated fibers

Table 6 Loss tangent (tan δ, ±0.002) of cement pastes

Formulation	With as-received silica fume			With silane-treated silica fume		
	0.2 Hz	1.0 Hz	2.0 Hz	0.2 Hz	1.0 Hz	2.0 Hz
A	0.082	0.030	$<10^{-4}$	0.087	0.032	$<10^{-4}$
A$^+$	0.102	0.045	$<10^{-4}$	0.093	0.040	$<10^{-4}$
A$^+$F	0.089	0.053	$<10^{-4}$	0.084	0.034	$<10^{-4}$
A$^+$O	0.085	0.043	$<10^{-4}$	0.084	0.032	$<10^{-4}$
A$^+$K	0.079	0.039	$<10^{-4}$	0.086	0.035	$<10^{-4}$
A$^+$S	0.076	0.036	$<10^{-4}$	0.083	0.033	$<10^{-4}$

A　：cement＋water＋water reducing agent＋silica fume
A$^+$　：A＋methylcellulose＋defoamer
A$^+$F：A$^+$＋as-received fibers
A$^+$O：A$^+$＋O$_3$-treated fibers
A$^+$K：A$^+$＋dichromate-treated fibers
A$^+$S：A$^+$＋silane-treated fibers

Table 7 Storage modulus (GPa, ±0.03) of cement pastes

Formulation	With as-received silica fume			With silane-treated silica fume		
	0.2 Hz	1.0 Hz	2.0 Hz	0.2 Hz	1.0 Hz	2.0 Hz
A	12.71	12.14	11.93	16.75	16.21	15.95
A$^+$	11.52	10.61	10.27	15.11	14.73	14.24
A$^+$F	13.26	13.75	13.83	17.44	17.92	18.23
A$^+$O	14.14	14.46	14.72	18.92	19.36	19.57
A$^+$K	15.42	16.15	16.53	19.33	19.85	20.23
A$^+$S	17.24	17.67	15.95	21.34	21.65	21.97

A   : cement + water + water reducing agent + silica fume
A$^+$: A + methylcellulose + defoamer
A$^+$F : A$^+$ + as-received fibers
A$^+$O : A$^+$ + O$_3$-treated fibers
A$^+$K : A$^+$ + dichromate-treated fibers
A$^+$S : A$^+$ + silane-treated fibers

Table 8 Loss modulus (GPa, ±0.03) of cement pastes

Formulation	With as-received silica fume			With silane-treated silica fume		
	0.2 Hz	1.0 Hz	2.0 Hz	0.2 Hz	1.0 Hz	2.0 Hz
A	1.04	0.39	$<10^{-3}$	1.46	0.52	$<10^{-3}$
A$^+$	1.18	0.48	$<10^{-3}$	1.41	0.59	$<10^{-3}$
A$^+$F	1.18	0.45	$<10^{-3}$	1.47	0.61	$<10^{-3}$
A$^+$O	1.20	0.62	$<10^{-3}$	1.59	0.62	$<10^{-3}$
A$^+$K	1.22	0.63	$<10^{-3}$	1.66	0.70	$<10^{-3}$
A$^+$S	1.31	0.63	$<10^{-3}$	1.77	0.71	$<10^{-3}$

A   : cement + water + water reducing agent + silica fume
A$^+$: A + methylcellulose + defoamer
A$^+$F : A$^+$ + as-received fibers
A$^+$O : A$^+$ + O$_3$-treated fibers
A$^+$K : A$^+$ + dichromate-treated fibers
A$^+$S : A$^+$ + silane-treated fibers

Table 9 Drying shrinkage strain (10^{-4}, ±0.015) different curing ages

Formulation	With as-received silica fume				With silane-treated silica fume			
	1 day	4 days	8 days	19 days	1 day	4 days	8 days	19 days
B	1.128	3.021	3.722	4.365	1.013	2.879	3.623	4.146
BF	0.832	2.417	3.045	3.412	0.775	2.246	2.810	3.113
BO	0.825	2.355	3.022	3.373	0.764	2.235	2.793	3.014
BK	0.819	2.321	3.019	3.372	0.763	2.232	2.790	3.010
BS	0.812	2.316	2.976	3.220	0.752	2.118	2.724	2.954

B   : cement + water + water reducing agent + silica fume + methylcellulose + defoamer
BF : B + as-received fibers
BO : B + O$_3$-treated fibers
BK : B + dichromate-treated fibers
BS : B + silane-treated fibers

or silane-treated. The drying shrinkage is decreased by the use of silane-treated silica fume in place of as-received silica fume, whether fibers are present or not. The drying shrinkage strain at 28 days is decreased by 5% when fibers are absent and silane-treated silica fume is used in place of as-received silica fume. When silane-treated fibers are present, it is decreased by 10% when silane-treated silica fume is used in place of as-received silica fume. By adding silane-treated fibers to the paste with as-received silica fume, the shrinkage at 28 days is decreased by 25%. By adding silane-treated fibers to the paste with silane-treated silica fume, the shrinkage at 28 days is decreased by

28%. By adding silane-treated fibers and replacing as-received silica fume by silane-treated silica fume, the shrinkage at 28 days is decreased by 32%.

3. Non-structural behavior

3.1 Thermal behavior

Table 10 shows the specific heat of cement pastes. The specific heat is significantly increased by the addition of silica fume. It is further increased by the further addition of methylcellulose and defoamer. It is still further increased by the still further addition of carbon fibers. The effectiveness of the fibers in

Table 10 Specific heat（J/g.K, ±0.001）of cement pastes. The value for plain cement paste（with cement and water only）is 0.736 J/g.K

Formulation	As-received silica fume	Silane-treated silica fume
A	0.782	0.788
A$^+$	0.793	0.803
A$^+$F	0.804	0.807
A$^+$O	0.809	0.813
A$^+$K	0.812	0.816
A$^+$S	0.819	0.823

A 　: cement＋water＋water reducing agent＋silica fume
A$^+$ 　: A＋methylcellulose＋defoamer
A$^+$F : A$^+$＋as-received fibers
A$^+$O : A$^+$＋O$_3$-treated fibers
A$^+$K : A$^+$＋dichromate-treated fibers
A$^+$S : A$^+$＋silane-treated fibers

Table 11 Thermal diffusivitiy（mm²/s, ±0.03）of cement pastes. The value for plain cement paste（with cement and water only）is 0.36 mm²/s.

Formulation	As-received silica fume	Silane-treated silica fume
A	0.26	0.24
A$^+$	0.25	0.22
A$^+$F	0.27	0.26
A$^+$O	0.29	0.27
A$^+$K	0.29	0.27
A$^+$S	0.25	0.23

A 　: cement＋water＋water reducing agent＋silica fume
A$^+$ 　: A＋methylcellulose＋defoamer
A$^+$F : A$^+$＋as-received fibers
A$^+$O : A$^+$＋O$_3$-treated fibers
A$^+$K : A$^+$＋dichromate-treated fibers
A$^+$S : A$^+$＋silane-treated fibers

increasing the specific heat increases in the following order: as-received fibers, O$_3$-treated fibers, dichromate-treated fibers and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives higher specific heat than as-received silica fume. The highest specific heat is exhibited by the cement paste with silane-treated silica fume and silane-treated fibers. The specific heat is 12% higher than that of plain cement paste, 5% higher than that of the cement paste with as-received silica fume and as-received fibers, and 0.5% higher than that of the cement paste with as-received silica fume and silane-treated fibers. Hence, silane treatment of fibers is more valuable than that of silica fume for increasing the specific heat.

Table 11 shows the thermal diffusivity of cement pastes. The thermal diffusivity is significantly decreased by the addition of silica fume. The further addition of methylcellulose and defoamer or the still further addition of fibers has relatively little effect on the thermal diffusivity. Surface treatment of the fibers by ozone or dichromate slightly increases the thermal diffusivity, whereas surface treatment of the fibers by silane slightly decreases the thermal diffusivity. These trends apply whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly lower（or essentially the same）thermal diffusivity than as-received silica fume. Silane treatments of silica fume and of fibers are about equally effective for lowering the thermal diffusivity.

Table 12 shows the density of cement pastes. The density is significantly decreased by the addition of silica fume. It is further decreased slightly by the further addition of methylcellulose and defoamer. It is still further decreased by the still further addition of fibers. The effectiveness of the fibers in decreasing the density decreases in the following order: as-received fibers, O$_3$-treated fibers, dichromate-treated fibers and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly higher（or essentially the same）density than as-received silica fume. Silane treatment of fibers is more valuable than that of silica fume for increasing the density.

Table 13 shows the thermal conductivity. It is significantly decreased by the addition of silica fume. The further addition

Table 12 Density（g/cm³, ±0.02）of cement pastes. The value for plain cement paste（with cement and water only）is 2.01 g/cm³.

Formulation	As-received silica fume	Silane-treated silica fume
A	1.72	1.73
A$^+$	1.69	1.70
A$^+$F	1.62	1.64
A$^+$O	1.64	1.65
A$^+$K	1.65	1.66
A$^+$S	1.66	1.68

A 　: cement＋water＋water reducing agent＋silica fume
A$^+$ 　: A＋methylcellulose＋defoamer
A$^+$F : A$^+$＋as-received fibers
A$^+$O : A$^+$＋O$_3$-treated fibers
A$^+$K : A$^+$＋dichromate-treated fibers
A$^+$S : A$^+$＋silane-treated fibers

Table 13 Thermal conductivity（W/m.K, ±0.03）of cement pastes. The value for plain cement paste（with cement and water only）is 0.53 W/m.K.

Formulation	As-received silica fume	Silane-treated silica fume
A	0.35	0.33
A$^+$	0.34	0.30
A$^+$F	0.35	0.34
A$^+$O	0.38	0.36
A$^+$K	0.39	0.37
A$^+$S	0.34	0.32

A 　: cement＋water＋water reducing agent＋silica fume
A$^+$ 　: A＋methylcellulose＋defoamer
A$^+$F : A$^+$＋as-received fibers
A$^+$O : A$^+$＋O$_3$-treated fibers
A$^+$K : A$^+$＋dichromate-treated fibers
A$^+$S : A$^+$＋silane-treated fibers

of methylcellulose and defoamer or the still further addition of fibers has little effect on the density. Surface treatment of the fibers by ozone or dichromate slightly increases the thermal conductivity, whereas surface treatment of the fibers by silane has negligible effect. These trends apply whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly lower（or essentially the same）thermal conductivity as as-received silica fume. Silane treatments of silica fume and of fibers contribute comparably

to reducing the thermal conductivity.

3.2 Electrical behavior

Fig.1 gives the volume electrical resistivity of composites at 7 days of curing. The resistivity decreases much with increasing fiber volume fraction, whether a second filler (silica fume or sand) is present or not. When sand is absent, the addition of silica fume decreases the resistivity at all carbon fiber volume fractions except the highest volume fraction of 4.24%; the decrease is most significant at the lowest fiber volume fraction of 0.53%. When sand is present, the addition of silica fume similarly decreases the resistivity, such that the decrease is most significant at fiber volume fractions below 1%. When silica fume is absent, the addition of sand decreases the resistivity only when the fiber volume fraction is below about 0.5%; at high fiber volume fractions, the addition of sand even increases the resistivity due to the porosity induced by the sand. Thus, the addition of a second filler (silica fume or sand) that is essentially non-conducting decreases the resistivity of the composite only at low volume fractions of the carbon fibers and the maximum fiber volume fraction for the resistivity to decrease is larger when the particle size of the filler is smaller. The resistivity decrease is attributed to the improved fiber dispersion due to the presence of the second filler. Consistent with the improved fiber dispersion is the increased flexural toughness and strength due to the presence of the second filler.

Fig.2 shows the fractional increase in conductivity (reciprocal of resistivity) due to the fibers alone. At a given fiber volume fraction, the fractional increase is higher when silica fume is present, whether sand is present or not. At fiber volume fractions above 1%, the use of silica fume but no sand gives the highest fracitonal increase, while the use of sand but no silica fume gives the lowest fractional increase. At fiber volume fractions below 1%, the use of both sand and silica fume gives the highest fractional increase, while the use of no sand nor silica fume gives the lowest fractional increase.
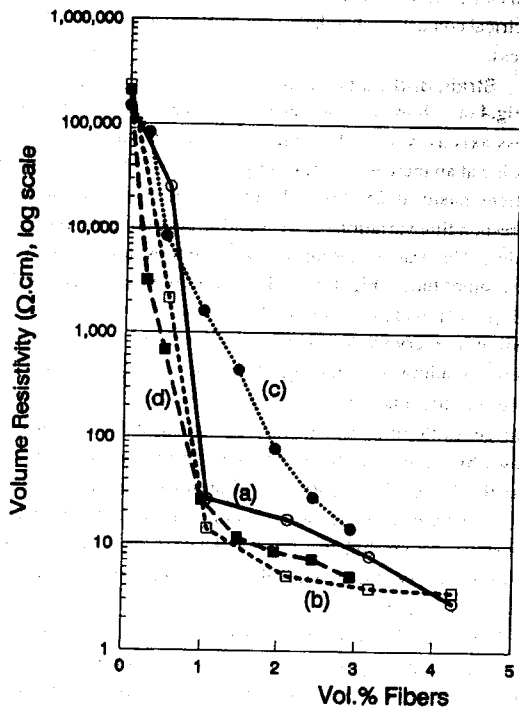
Fig.3 shows the measured conductivity as a fraction of the calculated value obtained from the Rule of Mixtures by assuming that the fibers were continuous and parallel along the axis of the conductivity measurement. This fraction provides an indication of the degree of fiber dispersion. At a given fiber volume fraction, it is higher when silica fume is present, whether sand is present or not. When sand is absent, the use of silica fume does not affect the percolation threshold volume fraction (1%), but increases the fibers' effectiveness. When sand is present, the use of silica fume greatly diminishes the percolation threshold volume fraction. On the other hand, the addition of sand without silica fume greatly increases the threshold.

The use of both silica fume and sand results in an electrical resistivity of 3.19×10^3 Ω.cm at a carbon fiber volume fraction of just 0.24 vol.%. This is an outstandingly low resistivity value compared to those of polymer-matrix composites with
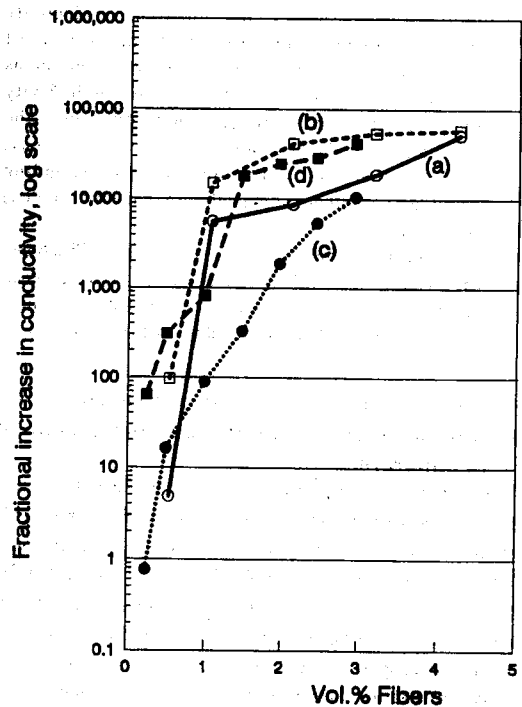
Fig.1 Variation of the volume electrical resistivity with carbon fiber volume fraction.
(a) Without sand, with methylcellulose, without silica fume,
(b) Without sand, with methylcellulose, with silica fume,
(c) With sand, with methylcellulose, without silica fume,
(d) With sand, with methylcellulose, with silica fume.

Fig.2 Variation with the carbon fiber volume fraction of the fractional increase in volume electrical conductivity due to the carbon fibers alone.
(a) Without sand, with methylcellulose, without silica fume,
(b) Without sand, with methylcellulose, with silica fume,
(c) With sand, with methylcellulose, without silica fume,
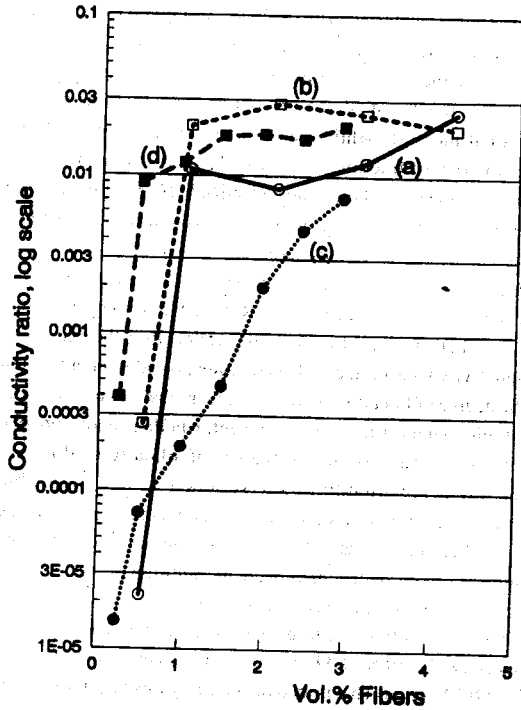(d) With sand, with methylcellulose, with silica fume.

Fig.3 Variation with the carbon fiber volume fraction of the ratio of the measured volume electrical conductivity to the calculated value obtained from the Rule of Mixtures by assuming that the fibers were continuous and unidirectional along the axis of conductivity measurement. The matrix conductivity used in the calculation was the measured conductivity for the case without fibers but containing the corresponding additives, i.e., either methylcellulose or methylcellulose +silica fume.

(a) Without sand, with methylcellulose, without silica fume,
(b) Without sand, with methylcellulose, with silica fume,
(c) With sand, with methylcellulose, without silica fume,
(d) With sand, with methylcellulose, with silica fume.

discontinuous conducting fillers at similar volume fractions.

3.3 Cathodic protection of steel reinforcement in concrete

Cathodic protection is one of the most common and effective methods for corrosion control of steel reinforced concrete. This method involves the application of a voltage so as to force electrons to go to the steel reinforcing bar (rebar), thereby making the steel a cathode. As the steel rebar is embedded in concrete, the electrons need to go through the concrete in order to reach the rebar. However, concrete is not very conducting electrically. The use of carbon fiber reinforced concrete for embedding the rebar to be cathodically protected facilitates cathodic protection, as the short carbon fibers enhance the conductivity of the concrete.

For directing electrons to the steel reinforced concrete to be cathodically protected, an electrical contact is needed on the concrete. The electrical contact is electrically connected to the voltage supply. One of the choices of an electrical contact

material is zinc, which is a coating deposited on the concrete by thermal spraying. It has a very low volume resistivity (thus requiring no metal mesh embedment), but it suffers from poor wear and corrosion resistance, the tendency to oxidize, high thermal expansion coefficient, and high material and processing costs. Another choice is a conductor filled polymer[101], which can be applied as a coating without heating, but it suffers from poor wear resistance, high thermal expansion coefficient and high material cost. Yet another choice is a metal (e.g., titanium) strip or wire embedded at one end in cement mortar, which is in the form of a coating on the steel reinforced concrete. The use of carbon fiber reinforced mortar for this coating facilitates cathodic protection, as it is advantageous to enhance the conductivity of this coating.

Due to the decrease in volume electrical resistivity associated with carbon fiber addition (0.35 vol.%) to concrete (embedding steel rebar), concrete containing carbon fibers and silica fume reduces by 18% the driving voltage required for cathodic protection compared to plain concrete, and by 28% compared to concrete with silica fume. Due to the decrease in resistivity associated with carbon fiber addition (1.1 vol.%) to mortar, overlay (embedding titanium wires for electrical contacts to steel reinforced concrete) in the form of mortar containing carbon fibers and latex reduces by 10% the driving voltage required for cathodic protection, compared to plain mortar overlay. In spite of the low resistivity of mortar overlay with carbon fibers, cathodic protection requires multiple metal electrical contacts embedded in the mortar at a spacing of 11 cm or less.

3.4 Strain and damage sensing

Fig.4 (a) shows the fractional change in resistivity along the stress axis as well as the strain during repeated compressive loading at an increasing stress amplitude for carbon-fiber latex cement paste at 28 days of curing. Fig.4 (a) shows the corresponding variation of stress and strain during the repeated loading. The strain varies linearly with the stress up to the highest stress amplitude (**Fig.4** (b)). The strain returns to zero at the end of each cycle of loading. The resistivity decreases upon loading in every cycle (due to fiber push-in) and increases upon unloading in every cycle (due to fiber pull-out). The resistivity has a net increase after the first cycle, due to minor damage. Little further damage occurs in subsequent cycles, as shown by the resistivity after unloading not increasing much after the first cycle. The greater the strain amplitude, the more is the resistivity decrease during loading, although the resistivity and strain are not linearly related. The effects of Fig.4 were similarly observed in carbon-fiber silica-fume cement paste at 28 days of curing.

Fig.5 gives the corresponding plots for carbon-fiber latex cement paste at 7 days of curing. Comparison of **Fig.4** and **Fig.5** shows that (i) the resistivity increases upon loading at 7 days (**Fig.5**), but decreases upon loading at 28 days (**Fig.4**), (ii) the resistivity increase upon loading at 7 days is not totally reversible, whereas the resistivity decrease upon loading at 28 days is totally reversible, and (iii) the fractional increase in resistivity upon loading is up to 10% at 7 days, but the fractional decrease in resistivity upon loading is only up to 2% at 28 days,
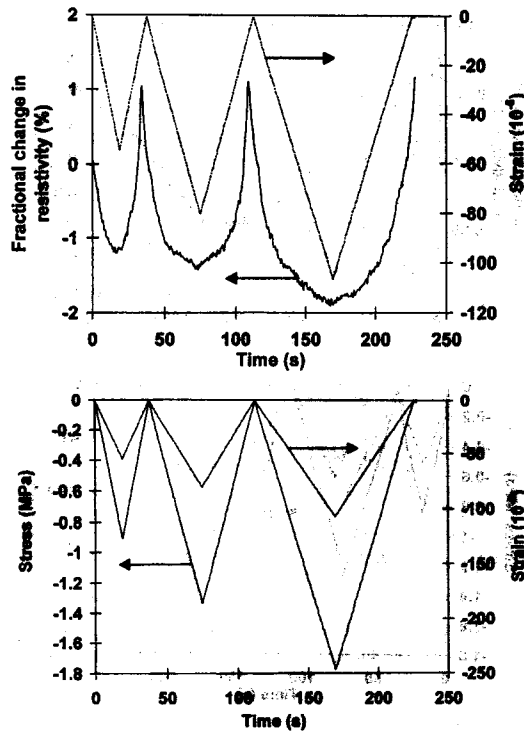
Fig.4 Variation of the fractional change in volume electrical resistivity with time (a), of the stress with time (b), and of the strain (negative for compressive strain) with time (a,b) during dynamic compressive loading at increasing stress amplitudes within the elastic regime for carbon-fiber latex cement paste at 28 days of curing.
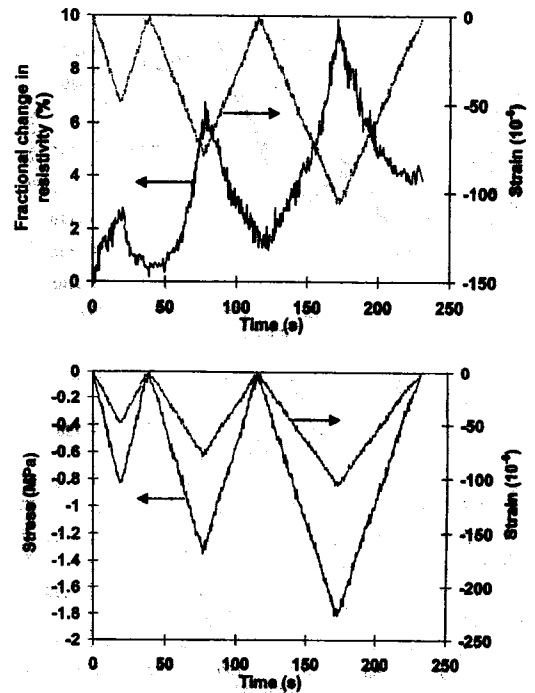
Fig.5 Variation of the fractional change in volume electrical resistivity with time (a), of the stress with time (b), and of the strain (negative for compressive strain) with time (a,b) during dynamic compressive loading at increasing stress amplitudes within the elastic regime for carbon-fiber latex cement paste at 7 days of curing.

though R_0 is similar at 7 and 28 days. The effects in **Fig.5** were similarly observed in carbon-fiber silica-fume cement paste at 7 days. The changeover from the 7-day behavior to the 28-day behavior occurs between 7 and 14 days.

Although the fractional change in resistivity upon loading is larger at 7 days (**Fig.5**) than at 28 days (**Fig.4**) for carbon-fiber latex cement paste, the greater reversibility upon unloading and the less noise in the resistivity variation at 28 days makes the behavior at 28 days more attractive than that at 7 days for use in resistance-based strain sensing. In practice, concrete is used in a fully cured state (exceeding 28 days of curing). Therefore, the behavior at 28 days is practically more important than that at 7 days. Nevertheless, the behavior at 7 days is of fundamental interest.

Comparison of **Fig.6** and **Fig.5** (both at 7 days) shows that the effects are qualitatively similar with fibers (**Fig.5**) and without fibers (**Fig.6**), though (i) the fractional change in resistivity is larger in the presence of fibers, and (ii) the resistivity increase upon loading is more reversible in the presence of fibers. Thus, the origins of the effects in **Fig.6** and **Fig.5** are basically similar, though the presence of fibers, which are electrically conductive, in **Fig.5** adds to the types of defects that are generated upon loading and the fiber-related defects make the resistivity changes more pronounced and more reversible. Comparison of **Fig.7** and **Fig.4** (both at 28 days) shows that

the effects are qualitatively and quantitatively different between latex cement paste (**Fig.7**) and carbon-fiber latex cement paste (**Fig.4**). In the presence of carbon fibers, the resistivity decreases reversibly upon loading; in the absence of fibers, the resistivity mainly increases upon unloading.

Fig.4-**Fig.7** show that the effect of carbon fibers on the variation of the resistivity with strain is more drastic at 28 days than at 7 days.

3.5 Temperature sensing through the thermistor effect

A thermistor is a thermometric device consisting of a material (typically a simiconductor, but in this case a cement paste) whose electrical resistivity decreases with rise in temperature.

Fig.8 shows the current-voltage characteristic of carbon-fiber (0.5% by weight of cement) silica-fume (15% by weight of cement) cement paste at 38℃ during stepped heating. The characteristic is linear below 5 V and deviates positively from linearity beyond 5 V. The resistivity is obtained from the slope of the linear portion. The voltage at which the characteristic starts to deviate from linearity is referred to as the critical voltage.

Fig.9 shows a plot of the resistivity vs. temperature during heating and cooling for carbon-fiber silica-fume cement paste. The resistivity decreases upon heating and the effect is quite reversible upon cooling. That the resistivity is slightly increased after a heating-cooling cycle is probably due to thermal degradation of the material. **Fig.10** shows the Arrhenius plot of
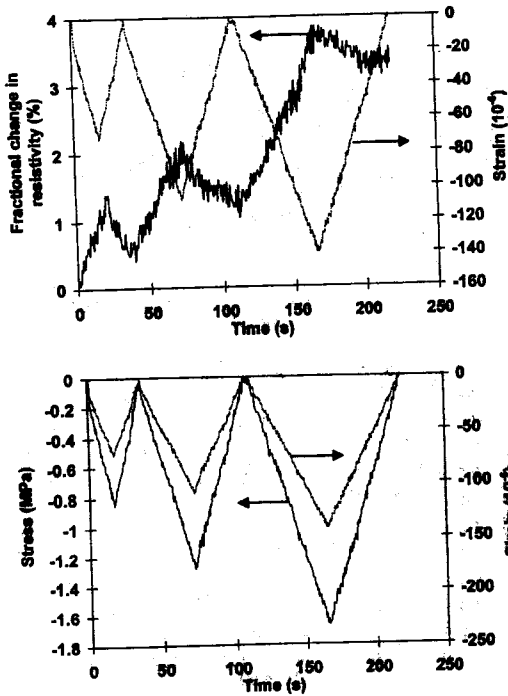
Fig.6 Variation of the fractional change in volume electrical resistivity with time (a), of the stress with time (b), and of the strain (negative for compressive strain) with time (a,b) during dynamic compressive loading at increasing stress amplitudes within the elastic regime for latex cement paste at 7 days of curing.
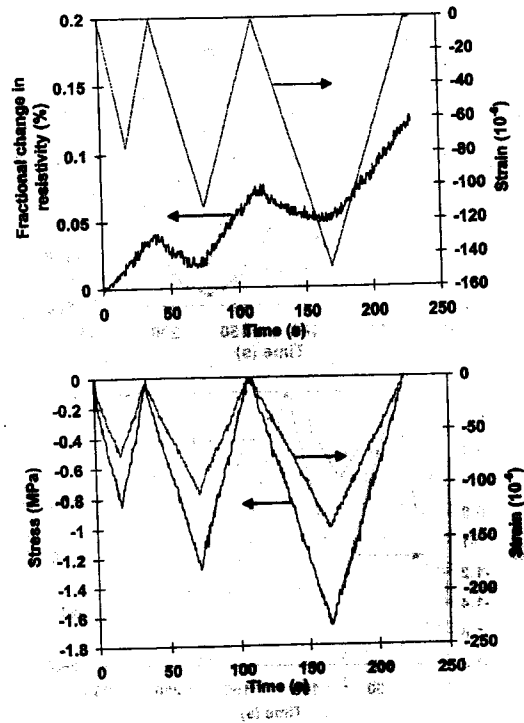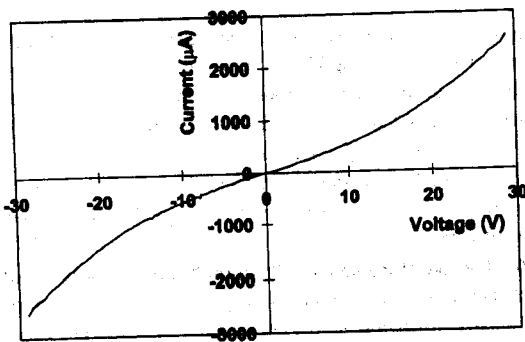

Fig.7 Variation of the fractional change in volume electrical resistivity with time (a), of the stress with time (b), and of the strain (negative for compressive strain) with time (a,b) during dynamic compressive loading at increasing stress amplitudes within the elastic regime for latex cement paste at 28 days of curing.

Fig.8 Current-voltage characteristic of carbon-fiber silica-fume cement paste at 38℃ during stepped heating.
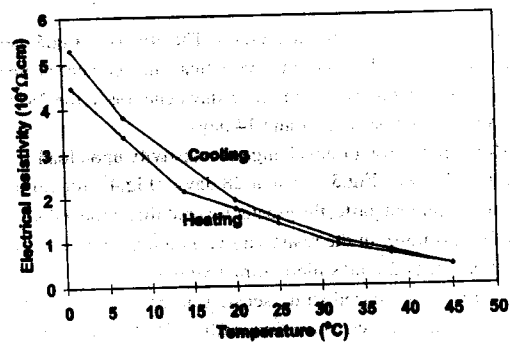

Fig.9 Plot of volume electrical resistivity vs. temperature during heating and cooling for carbon-fiber silica-fume cement paste.

log conductivity (conductivity=1/resistivity) vs. reciprocal absolute temperature. The slope of the plot gives the activation energy, which is 0.390±0.014 and 0.412±0.017 eV during heating and cooling respectively.

Results similar to those of carbon-fiber silica-fume cement paste were obtained with carbon-fiber (0.5% by weight of cement) latex (20% by weight of cement) cement paste, silica-fume cement paste, latex cement paste and plain cement paste. However, for all these four types of cement paste, (i) the

resistivity is higher by about an order of magnitude, and (ii) the activation energy is lower by about an order of magnitude, as shown in **Table 14**. The critical voltage is higher when fibers are absent (**Table 14**).

3.5　Temperature sensing through the Seebeck effect

The Seebeck effect is a thermoelectric effect which is the basis for thermocouples for temperature measurement. This effect involves charge carriers moving from a hot point to a cold point within a material, thereby resulting in a voltage difference

between the two points. The Seebeck coefficient is the voltage difference per unit temperature difference between the two points. Negative carriers (electrons) make it more positive and positive carriers (holes) make it more negative.

Eight types of cement paste were studied, namely (i) plain cement paste (consisting of just cement and water), (ii) silica-fume cement paste (consisting of cement, water and silica
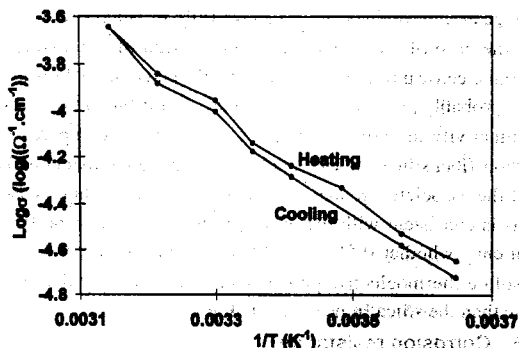

Fig.10 Arrhenius plot of log electrical conductivity vs. reciprocal absolute temperature for carbon-fiber silica-fume cement paste.

fume), (iii) carbon-fiber silica-fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer and carbon fibers in the amount of 0.5% by weight of cement), (iv) carbon-fiber silica-fume cement paste (same as (iii) except for having carbon fibers in the amount of 1.0% by weight of cement), (v) carbon-fiber silica-fume cement paste (same as (iii) except for having carbon fibers in the amount of 1.5% by weight of cement), (vi) latex cement paste (consisting of cement, water, latex and antifoam), (vii) carbon-fiber latex cement paste (consisting of cement, water, latex, antifoam and carbon fibers in the amount of 0.5% by weight of cement, and (viii) carbon-fiber latex cement paste (same as (vii) except for having carbon fibers in the amount of 1.0% by weight of cement).

Table 15 shows the Seebeck coefficient (with copper as the reference) and the absolute thermoelectric power. A negative value of the absolute thermoelectric power indicates p-type (hole) behavior; a positive value indicates n-type (electron) behavior. All types of cement paste studied are n-type except pastes (iv) and (v), which were p-type. The higher the fiber content, the less n-type (the more p-type) is the paste, whether silica fume or latex is present. Without fibers, the absolute thermoelectric power is 2 μV/℃, whether silica fume and latex are present or not. This is consistent with the similar values of

Table 14 Resistivity, critical voltage and activation energy of five types of cement paste.

Formulation	Resistivity at 20℃ (Ω cm)	Critical voltage at 20℃ (V)	Activation energy (eV)	
			Heating	Cooling
Plain	$(4.87\pm0.37)\times10^5$	10.80 ± 0.45	0.040 ± 0.006	0.122 ± 0.006
Silica fume	$(6.12\pm0.15)\times10^5$	11.60 ± 0.37	0.035 ± 0.003	0.084 ± 0.004
Carbon fibers +silica fume	$(1.73\pm0.08)\times10^4$	8.15 ± 0.34	0.390 ± 0.014	0.412 ± 0.017
Latex	$(6.99\pm0.12)\times10^5$	11.80 ± 0.31	0.017 ± 0.001	0.025 ± 0.002
Carbon fibers +latex	$(9.64\pm0.08)\times10^4$	8.76 ± 0.35	0.018 ± 0.001	0.027 ± 0.002

Table 15 Seebeck coefficient (mV/℃) and absolute thermoelectric power (mV/℃) of eight types of cement paste.

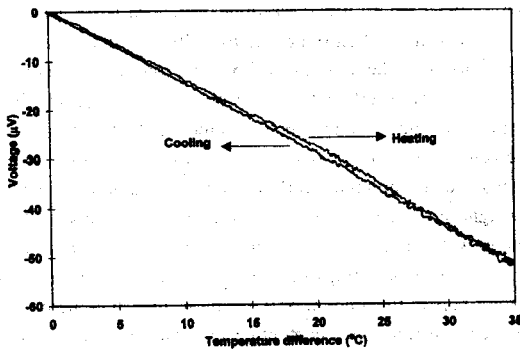| Cement paste	Heating		Cooling	
	Seebeck coefficient*	Absolute thermoelectric power	Seebeck coefficient*	Absolute thermoelectric power
(i) Plain	$-(0.35\pm0.03)$	1.99 ± 0.03	$-(0.38\pm0.05)$	1.96 ± 0.05
(ii) Silica fume	$-(0.31\pm0.02)$	2.03 ± 0.02	$-(0.36\pm0.03)$	1.98 ± 0.03
(iii) 0.5% fibers+silica fume	$-(1.45\pm0.09)$	0.89 ± 0.09	$-(1.45\pm0.09)$	0.89 ± 0.09
(iv) 1.0% fibers+silica fume	$-(2.82\pm0.11)$	-0.48 ± 0.11	$-(2.82\pm0.11)$	-0.48 ± 0.11
(v) 1.5% fibers+silica fume	$-(3.10\pm0.14)$	-0.76 ± 0.14	$-(3.10\pm0.14)$	-0.76 ± 0.14
(vi) Latex	$-(0.28\pm0.02)$	2.06 ± 0.02	$-(0.30\pm0.02)$	2.04 ± 0.02
(vii) 0.5% fibers+latex	$-(1.20\pm0.05)$	1.14 ± 0.05	$-(1.20\pm0.05)$	1.14 ± 0.05
(viii) 1.0% fibers+latex	$-(2.10\pm0.08)$	0.24 ± 0.08	$-(2.10\pm0.08)$	0.24 ± 0.08

* With copper as the reference

Fig.11 Variation of the Seebeck voltage (with copper as the reference) vs. the temperature difference during heating and cooling for cement paste (iii), i.e., carbon-fiber silica-fume cement paste.

the electrical conductivity for cement pastes with silica fume and with latex, but without fibers. Thus, silica fume or latex addition does not have much influence on the thermoelectric power when fibers are absent, but carbon fiber addition does by enhancing the hole conduction.

As shown in **Table 15**, the thermopower results obtained during heating and cooling are very close. **Fig.11** shows the variation of the Seebeck voltage vs. the temperature difference during heating and cooling for paste (iii). With fibers present, the variation is linear and essentially identical during heating and cooling. Without fibers, the variation is non-linear and hysteretic (i.e., not totally reversible upon cooling subsequent to heating)

Thus, although the fiber addition does not increase the magnitude of the absolute thermoelectric power, it enhances the linearity and reversibility of the Seebeck effect. This enhancement is attributed to the increase in the contribution of holes to the electrical conduction and the association of hole conduction to conduction through the fibers.

The absolute thermoelectric power monotonically becomes less positive (more negative) as the fiber content increases through the percolation threshold, which is at a fiber content between 0.5% and 1.0% by weight of cement. The change of the absolute thermoelectric power from positive to negative values occurs at a fiber content between 0.5% and 1.0% by weight of cement when silica fume is present. This means that at this fiber content, which happens to be the percolation threshold, compensation takes place between the electron contribution from the cement matrix and the hole contribution from the fibers. It should be noted that, at any fiber content, electrons and holes contribute additively to the electrical conductivity, but subtractively to the thermopower. The correlation between the percolation threshold and change in sign of the absolute thermoelectric power is reasonable since the fibers dominate the conduction by means of holes above the percolation threshold and the cement matrix dominates the conduction by means of electrons below the percolation threshold. In the presence of latex instead of silica fume, the highest fiber content investigated was 1.0% by weight of cement and a change in sign of the absolute thermoelectric power was not observed,

even though the percolation threshold is also between fiber contents of 0.5% and 1.0% by weight of cement for the case of latex. Although a change in sign of the absolute thermoelectric power was not observed for the case of latex, the absolute thermoelectric power is a very small positive value at a fiber content of 1.0% by weight of cement and the absolute thermoelectric power decreases monotonically with increasing fiber content. Based on this trend, it is highly probable that a change in sign would occur just above 1.0% by weight of cement for the case of latex. That a change in sign of the absolute thermoelectric power does not occur at the percolation threshold (but probably just above the threshold) is attributed to the low conductivity of carbon-fiber latex cement paste compared to carbon-fiber silica-fume cement paste at the same fiber content and the associated weaker hole conduction in the latex case. This is consistent with the observation that, at the same fiber content (whether 0.5% or 1.0% by weight of cement), the absolute thermoelectric power is more positive for the latex case than the silica fume case (**Table 15**).

3.6 Corrosion resistance

Carbon fibers decrease the corrosion resistance of steel rebar in concrete, mainly due to the decrease in the volume electrical resistivity of concrete. However, the negative effect can be compensated by adding either silica fume or latex. Silica fume is more effective than latex for improving the corrosion resistance of carbon fiber concrete. This is mainly because silica fume reduces the water absorptivity. The small increases in electrical resistivity of carbon fiber concrete after adding either silica fume or latex contribute only slightly to the effect on corrosion. Corrosion of rebar in concrete with silica fume and carbon fibers is inactive in $Ca(OH)_2$ solution, but active in NaCl solution. However, the corrosion resistance in NaCl is better than rebar in plain concrete and similar to that of rebar in latex concrete without fibers[102].

4. Conclusion

Short carbon fiber cement-matrix composites exhibit attractive tensile and flexural properties, low drying shrinkage, high specific heat, low thermal conductivity, high electrical conductivity and high corrosion resistance. Moreover, they facilitate the cathodic protection of steel reinforcement in concrete, and have the ability to sense their own strain, damage and temperature.

Acknowledgement

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