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# Carbon fiber-reinforced cement as a thermistor

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**Abstract**

Carbon fiber (~5 mm long, 0.5% by mass of cement)-reinforced silica fume (15% by mass of cement) cement paste was found to be an effective thermistor. Its electrical resistivity decreased reversibly with increasing temperature (1–45°C), with an activation energy of electrical conduction (electron hopping) of 0.4 eV. This is comparable to those of semiconductors (typical thermistor materials) and higher than that of carbon fiber polymer-matrix composites. Without carbon fibers, or with latex in place of silica fume, the activation energy was much lower and the resistivity was higher. The voltage range for a linear current-voltage characteristic was wider in the absence of fibers. The current-voltage characteristic of carbon fiber-reinforced silica fume cement paste was linear up to 8 V at 20°C. 

*Keywords:* Fiber reinforcement; Cement paste; Electrical properties; Thermal analysis; Thermistor

The temperature affects the performance, operation, and safety of a structure, and the sensing of the temperature allows appropriate measures to be taken in response to temperature changes. A thermistor is a thermometric device consisting of a material (typically a semiconductor) whose electrical resistivity decreases with rise in temperature. Although previous work has been reported on the electrical resistivity of cement pastes, mortars, and concretes, including those containing various volume fractions of electrically conductive short fibers such as carbon fibers [1–5], we have found no previous report on the effect of temperature on the resistivity. The temperature dependence is relevant to the use of the cement-based material (i.e., the structural material itself) as a thermistor, so that no attached or embedded thermometric device is needed and cost saving and durability improvement result. Moreover, the temperature dependence gives fundamental information on the nature of the electrical conduction.

Cement reinforced with short carbon fibers is itself a strain sensor [6–10], due to the effect of strain on its electrical resistivity. As shown in this paper, the temperature also affects the resistivity. Thus, compensation for the effect of temperature is necessary in order for the strain sensor to give accurate strain information. Similarly, compensation for the effect of strain is necessary in order for the thermistor to give accurate temperature information. Therefore, the results of this paper are relevant to the use of carbon fiber-reinforced cement as a strain sensor.

This paper addresses both cement pastes with and without carbon fiber reinforcement in terms of the temperature dependence of the DC electrical resistivity. Carbon fiber-reinforced cement is attractive for its low drying shrinkage and high flexural strength and toughness [11–16], in addition to its strain sensing ability [6–10]. The short carbon fibers are usually used along with silica fume and methylcellulose, which serve to help the fiber dispersion in the mix [17].

## 1. Materials and methods

### *1.1. Materials*

The carbon fibers were isotropic pitch-based, unsized, with lengths ~5 mm, as obtained from Ashland Petroleum Co. (Ashland, Kentucky, USA). The fiber properties are shown in Table 1. No aggregate (fine or coarse) was used.

The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI, USA). The silica fume (Elkem Materials, Inc., Pittsburgh, PA, USA, EMS 965) was used in the amount of 15% by mass of cement. The methylcellulose, used in the amount of 0.4% by mass of cement, was from Dow Chemical Co. (Midland, MI, USA, Methocel A15-LV). The defoamer (Colloids Inc., Marietta, GA, USA, 1010) used whenever methylcellulose was used was in the amount of 0.13 vol%. The latex, used in the amount of 20% by mass of cement, was a styrene butadiene polymer (Dow Chemical Co., 460NA) with the polymer making up about 48% of the dispersion and with the styrene and butadiene having a mass ratio of

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Table 1
Properties of carbon fibers

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

66:34. The latex was used along with an antifoaming agent (Dow Corning Corp., Midland, MI, USA, #2210, 0.5% by mass of latex).

### 1.2. Methods

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Latex (if applicable) was mixed with the antifoam by hand for about 1 min. Then the methylcellulose mixture (if applicable), the latex mixture (if applicable), cement, water, silica fume (if applicable), and fibers (if applicable) were mixed in the mixer for 5 min. After pouring into molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured in air at room temperature and a relative humidity of 100% for 28 days.

Five types of cement pastes were prepared, namely (a) plain cement paste (consisting of just cement and water), (b) silica fume cement paste (consisting of cement, water, and silica fume), (c) carbon fiber silica fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer, and carbon fibers), (d) latex cement paste (consisting of cement, water, and latex), and (e) carbon fiber latex cement paste (consisting of cement, water, latex, and carbon fibers). The water/cement ratio was 0.45 for pastes (a), (b), and (c), and was 0.25 for pastes (d) and (e).

Electrical resistivity measurements were conducted using the two-probe method, with silver paint in conjunction with copper wires for electrical contacts. The two-probe method gave essentially the same result as the four-probe method, due to the high sample resistance. A Keithley 2001 (Keithley Instruments, Inc., Cleveland, OH, USA) multimeter was used. Samples were in the form of rectangular bars of size 150 × 12 × 11 mm. Each electrical contact was applied around the entire 12 × 11 mm perimeter of the bar. The two contacts were at two parallel cross-sectional planes that were 40 mm apart. The temperature was varied by putting a sample in a steel open box (200 × 200 × 80 mm) that was sandwiched by hot platens (280 × 280 mm) that were resistance heated (Fig. 1). The sample was electrically insulated from the steel box and did not touch either platen. A removable plate (100 × 80 mm) at a side of the steel box allowed electrical leads from the sample to come out. The temperature was raised and then lowered in steps between 20 and 45°C (Fig. 2). Current-voltage characteristic measurements were made at each step. Six samples of each of the five types of paste were tested.

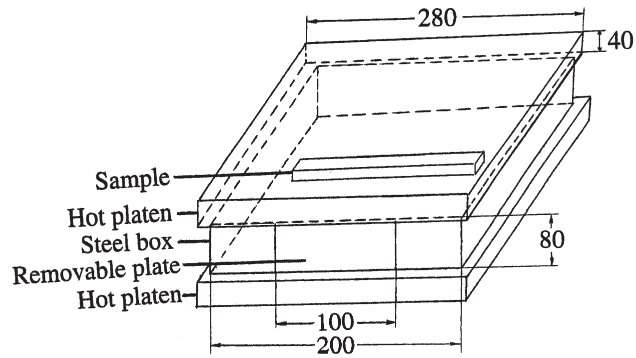


Fig. 1. Experimental setup for measuring the temperature dependence of the electrical resistivity at and above room temperature. Dimensions are in mm.

For paste (c) alone, electrical resistivity measurements were also conducted below room temperature by putting the sample in a freezer with temperature control. The temperature was raised in steps from 1 to 7°C and then to 14°C, and then lowered in steps to 7°C and then to 1°C. The time at each step was 20 min, as in Fig. 2. Six samples of paste (c) were tested.

## 2. Results

Fig. 3 shows the current-voltage characteristic of carbon fiber silica fume cement paste at 38°C 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 hereby referred to as the critical voltage. The shape of the characteristic is similar for all samples at all temperatures, though the values of the resistivity and critical voltage differ, as listed in Table 2.

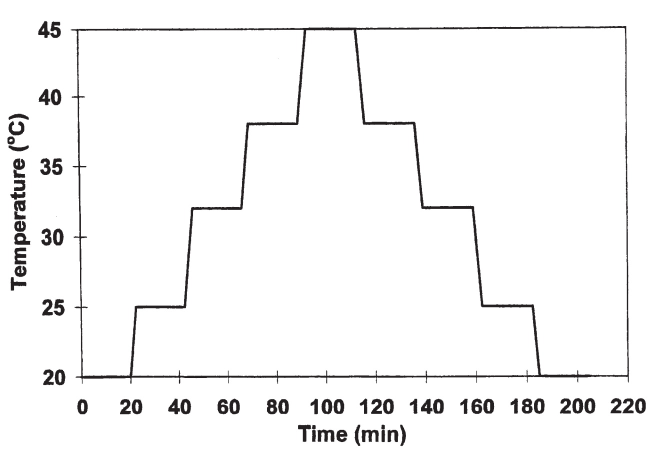


Fig. 2. Temperature vs. time during stepped heating and cooling.

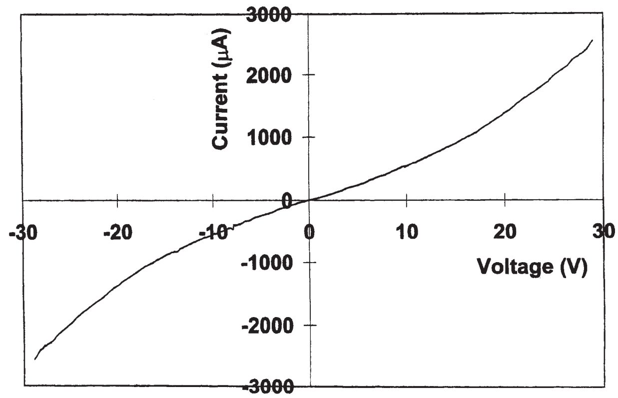


Fig. 3. Current-voltage characteristic of carbon fiber silica fume cement paste at 38°C during stepped heating.

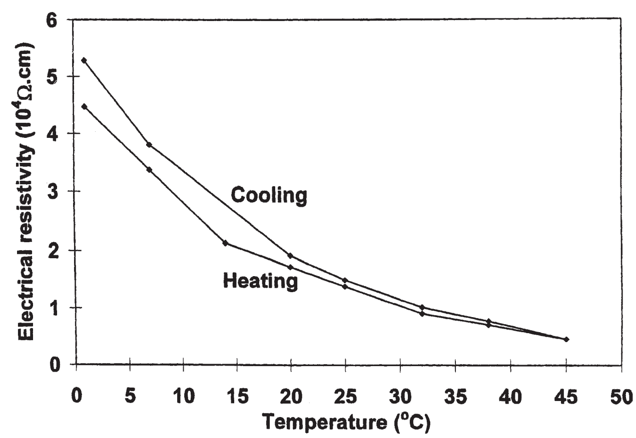


Fig. 4. Plot of electrical resistivity vs. temperature during heating and cooling for carbon fiber silica fume cement paste.

Fig. 4 shows a plot of the resistivity vs. temperature during heating and cooling for carbon fiber silica fume cement paste. The resistivity decreased upon heating and the effect was quite reversible upon cooling. That the resistivity was slightly increased after a heating-cooling cycle is probably due to thermal degradation of the material. Fig. 5 shows the Arrhenius plot of 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. Fig. 6 shows a plot of the critical voltage vs. temperature during heating and cooling. The critical voltage decreased upon heating and the effect was reversible upon cooling. That the critical voltage was slightly increased after a heating-cooling cycle is probably due to thermal degradation of the material.

Results similar to those of carbon fiber silica fume cement paste were obtained with the remaining types of cement paste (i.e., carbon fiber latex cement paste, silica fume cement paste, latex cement paste, and plain cement paste). However, for all the remaining four types of cement paste, the resistivity was higher by about an order of magnitude, and the activation energy was lower by about an order of magnitude, as shown in Table 3. The critical voltage was higher when fibers were absent (Table 3).

Table 2
Resistivity and critical voltage of carbon fiber silica fume cement paste

| Temperature (°C) during stepped heating and cooling | Resistivity ($10^4$ Ω · cm) | Critical voltage (V) |
|---|---|---|
| 20 | 1.73 ± 0.08 | 8.15 ± 0.34 |
| 25 | 1.38 ± 0.12 | 6.82 ± 0.47 |
| 32 | 0.90 ± 0.14 | 5.76 ± 0.52 |
| 38 | 0.69 ± 0.09 | 5.07 ± 0.39 |
| 45 | 0.44 ± 0.09 | 4.24 ± 0.43 |
| 38 | 0.76 ± 0.13 | 5.15 ± 0.38 |
| 32 | 1.01 ± 0.09 | 6.44 ± 0.56 |
| 25 | 1.50 ± 0.16 | 7.41 ± 0.49 |
| 20 | 1.92 ± 0.18 | 9.05 ± 0.66 |
| 1 | 4.47 ± 0.24 | 10.30 ± 0.21 |
| 7 | 3.36 ± 0.31 | 9.76 ± 0.30 |
| 14 | 2.13 ± 0.15 | 9.14 ± 0.32 |
| 7 | 3.80 ± 0.19 | 10.10 ± 0.36 |
| 1 | 5.28 ± 0.36 | 10.70 ± 0.27 |

## 3. Discussion

Comparison between carbon fiber silica fume cement paste and silica fume cement paste shows that the presence of carbon fibers decreases the electrical resistivity and causes the resistivity to decrease with increasing temperature more significantly. This is indicated by a higher activation energy, which is desirable for thermistors. The low resistivity when fibers are present is due to the high conductivity of the fibers compared to the cement matrix. The high activation energy when fibers are present is due to the hopping conduction between cement matrix and fiber. Note that the fiber volume fraction is below the percolation threshold [1], so that direct hopping from fiber to fiber is relatively insignificant. In the absence of fibers, the activation energy is low, because the interfaces in silica fume cement paste are relatively diffuse and hopping across them does not require much energy.

Comparison of latex cement paste and carbon fiber latex cement paste shows that the resistivity is decreased by the fiber addition, but the extent of the decrease is much less than that in the case of adding fibers to silica fume cement paste. Moreover, adding fibers to latex cement paste does not affect the activation energy, in contrast to the large increase in activation energy upon adding fibers to silica fume cement paste. Comparison of carbon fiber silica fume cement paste and carbon fiber latex cement paste shows that the replacement of silica fume with latex increases the resistivity and decreases the activation energy to values below those of plain cement paste. These characteristics are attributed to the lower ability of latex compared to silica fume for dispersing the fibers [17] and the electrical insulation ability of latex, which resides at the fiber-matrix interface [18].

Table 3
Resistivity, critical voltage, and activation energy of five types of cement paste

| Formulation | Resistivity at 20°C (Ω · cm) | Critical voltage at 20°C (V) | Activation energy (eV) | |
|---|---|---|---|---|
| | | | Heating | Cooling |
| Plain | $(4.87 \pm 0.37) \times 10^5$ | $10.80 \pm 0.45$ | $0.040 \pm 0.006$ | $0.122 \pm 0.006$ |
| Silica fume | $(6.12 \pm 0.15) \times 10^5$ | $11.60 \pm 0.37$ | $0.035 \pm 0.003$ | $0.084 \pm 0.004$ |
| Carbon fibers + silica fume | $(1.73 \pm 0.08) \times 10^4$ | $8.15 \pm 0.34$ | $0.390 \pm 0.014$ | $0.412 \pm 0.017$ |
| Latex | $(6.99 \pm 0.12) \times 10^5$ | $11.80 \pm 0.31$ | $0.017 \pm 0.001$ | $0.025 \pm 0.002$ |
| Carbon fibers + latex | $(9.64 \pm 0.08) \times 10^4$ | $8.76 \pm 0.35$ | $0.018 \pm 0.001$ | $0.027 \pm 0.002$ |

Hence, like cement pastes without carbon fibers, carbon fiber latex cement paste is not attractive for use as thermistors.

The activation energy for hopping from carbon fiber to carbon fiber in a polymer-matrix composite ranges from 0.01 to 0.1 eV [19]. The polymer matrix is not conducive, so hopping from fiber to fiber is necessary. However, the cement matrix is conducive, so hopping between fiber and cement paste is sufficient for conduction. It appears that hopping between fiber and cement matrix (without latex but with silica fume) requires more energy than hopping from fiber to fiber. This is reasonable due to the weak bond between carbon fiber and the cement matrix [20,21]. Hence, carbon fiber silica fume cement-matrix composites are more attractive than carbon fiber polymer-matrix composites for use as thermistors. The cement-matrix composites are not as attractive as silicon (a semiconductor), which has an activation energy of 0.56 eV (half of the energy band gap), but are more attractive than germanium (a semiconductor), which has an activation energy of 0.34 eV. On the other hand, cement-matrix composites are much less expensive than the semiconductors.

Presumably due to thermal degradation, the resistivity of cement-matrix composites is higher during cooling than during the initial heating. As a result, the activation energy is higher during cooling than during heating. For thermistor applications, the behavior during cooling is more relevant, due to its relative stability.

The deviation from linearity of the current-voltage characteristic corresponds to the resistivity decreasing with increasing electric field. This effect is attributed to Joule heating and the decrease of the resistivity with increasing temperature. The critical voltage is lower for cement pastes containing carbon fibers than those without fibers, probably because of the lower resistivity when fibers are present. Carbon fiber silica fume cement paste has lower resistivity and lower critical voltage than carbon fiber latex cement paste.

## 4. Conclusions

Carbon fiber silica fume cement paste was found to be an effective thermistor. The electrical resistivity decreased with increasing temperature (1–45°C), with an activation energy of electrical conduction (electron hopping) of 0.4 eV, which is comparable to those of semiconductors (typical thermistor materials) and higher than that of carbon fiber polymer-matrix composites. Without carbon fibers, or with latex in place of silica fume, the activation energy is much lower and the resistivity is higher. The voltage range for linear current-voltage characteristic is narrower when fibers are present than when fibers are absent. Linearity occurred up to 8 V for carbon fiber silica fume cement paste at 20°C.

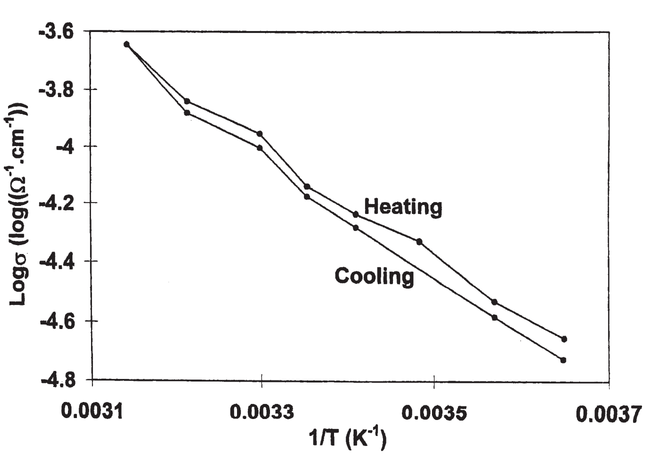


Fig. 5. Arrhenius plot of log electrical conductivity vs. reciprocal absolute temperature for carbon fiber silica fume cement paste.

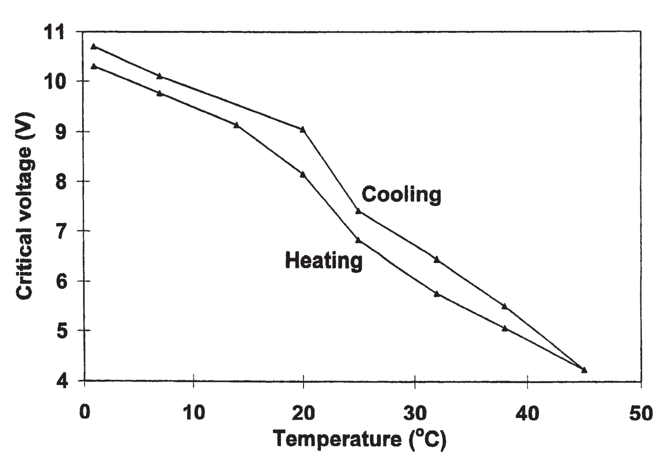


Fig. 6. Plot of the critical voltage vs. temperature during heating and cooling for carbon fiber silica fume cement paste.

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